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INORGANIC CHEMISTRY DIVISION
WORKING PARTY ON IUPAC GLOSSARY OF TERMS USED IN
BIOINORGANIC CHEMISTRY*

GLOSSARY OF TERMS USED IN BIOINORGANIC CHEMISTRY

(IUPAC Recommendations 1997)

Prepared for publication by

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Glossary of terms used in bioinorganic chemistry (IUPAC Recommendations 1997)

Abstract: The glossary contains definitions and (where needed) explanatory notes for about 400 terms used in the multidisciplinary field of bioinorganic chemistry. A need has been recognized for globally acceptable definitions of terms in this field and this glossary was compiled with the objective of fulfilling this need. It is by no means a comprehensive dictionary. The terms selected were those considered essential and/or widely used. The definitions given reflect current usage and complement IUPAC guidelines. Abbreviations and acronyms, frequently used in bioinorganic chemistry, are included.

PREFACE

The project of compiling a glossary of Terms in Bioinorganic Chemistry was started in 1991 on request of the Inorganic Chemistry Division of the International Union of Pure and Applied Chemistry. It was felt that in such a rapidly-growing, interdisciplinary field, communication would be greatly facilitated by standardization of terminology. The glossary is intended to provide a basic vocabulary of bioinorganic chemistry.

In compiling the approximately 400 entries, we have attempted to select terms which are directly relevant to bioinorganic chemistry, but which either a biochemist or an inorganic chemist might have difficulty to understand or define. This is particularly important where a term has different meanings in the two fields. To avoid repetition, the entries are extensively cross-referenced. We have omitted terms which are self-explanatory; terms occurring in standard English dictionaries; terms which are of minor interest, and terms for which the current definition is ambiguous or controversial. Where appropriate, the definitions have been extracted from other IUPAC glossaries and publications. Other descriptions given are believed to reflect current usage and no attempt has been made to introduce new nomenclature. Most of the entries are necessarily brief but should put the reader in a better position to seek further information.

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The Working Party on IUPAC Glossary of Terms in Bioinorganic Chemistry,

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NOTES FOR THE USER OF THIS GLOSSARY

Terms are arranged alphabetically, starting with a capital letter and printed in bold face. Extensive cross-referencing has been included, and italicized terms in bold face within individual definitions refer to other entries where relevant information is available. No distinction is made between singular, plural, etc. in

cross-referencing. The appearance of a term in quotation marks in the body of a definition indicates that no further information will be found under that heading. Related terms are cited in the 'see also' form.

Abbreviations and acronyms used in the field are included in the glossary; their definitions are presented in the 'see' form. Nevertheless, abbreviations and acronyms should only be used after a full explanation of their meaning has been given.

Terms starting with a Greek letter are spelt out and placed alphabetically in the document. A compilation of these terms can be found under the entry 'Greek letters' and at the beginning of the document, directly after the terms that start with an (Arabic) numeral.

SOURCES

K.J. Laidler, A Glossary of Terms Used in Chemical Kinetics, Including Reaction Dynamics, IUPAC Physical Chemistry Division, Pure Appl. Chem., **68**, 149–192 (1996).

G.P. Moss, P.A.S. Smith and D. Tavernier, Glossary of Class Names of Organic Compounds and Reactive Intermediates Based on Structure, IUPAC Organic Chemistry Division, Pure Appl. Chem., **67**, 1307–1375 (1995).

P. Müller, Glossary of Terms Used in Physical Organic Chemistry, IUPAC Organic Chemistry Division, Pure Appl. Chem., **66**, 1077–1184 (1994).

I. Mills, T. Cvitas, K. Homann, N. Kallay and K. Kuchitsu, Quantities, Units and Symbols in Physical Chemistry, IUPAC Physical Chemistry Division, Blackwell Scientific Publications, Oxford, 1993.

R. Panico, W.H. Powell and J.-C. Richer, A Guide to IUPAC Nomenclature of Organic Compounds, IUPAC Organic Chemistry Division, Blackwell Scientific Publications, Oxford, 1993.

IUPAC Organic Chemistry Division, Basic Terminology of Stereochemistry, 1993 (Draft).

J.H. Duffus, Glossary for Chemists of Terms Used in Toxicology, IUPAC Clinical Chemistry Division, Pure Appl. Chem., **65**, 2003–2122 (1993).

B. Nagel, H. Dellweg and L.M. Gierasch, Glossary for Chemists of Terms Used in Biotechnology, IUPAC Applied Chemistry Division, Pure Appl. Chem., **64**, 143–168 (1992).

C. Liébecq, Biochemical Nomenclature and Related Documents (A Compendium), International Union of Biochemistry and Molecular Biology, Second Edition, Portland Press, London, 1992.

E.C. Webb, Enzyme Nomenclature, International Union of Biochemistry and Molecular Biology, Academic Press, New York, 1992.

J.F.J. Todd, Recommendations for Nomenclature and Symbolism for Mass Spectroscopy, IUPAC Physical Chemistry Division, Pure Appl. Chem., **63**, 1541–1566 (1991).

N. Sheppard, English-Derived Abbreviations for Experimental Techniques in Surface Science and Chemical Spectroscopy, IUPAC Physical Chemistry Division, Pure Appl. Chem., **63**, 887–893 (1991).

D.A.W. Wendisch, Acronyms and Abbreviations in Molecular Spectroscopy (An Encyclopedic Dictionary), Springer-Verlag, Berlin, 1990.

J.G. Calvert, Glossary of Atmospheric Chemistry Terms, IUPAC Applied Chemistry Division, Pure Appl. Chem., **62**, 2167–2219 (1990).

G.J. Leigh, Nomenclature of Inorganic Chemistry, IUPAC Inorganic Chemistry Division, Blackwell Scientific Publications, Oxford, 1990.

H. Kon, Recommendations for EPR/ESR Nomenclature and Conventions for Presenting Experimental Data in Publications, IUPAC Physical Chemistry Division, Pure Appl. Chem., **61**, 2195–2200 (1989).

D.E. Braslavsky and K.N. Houk, Glossary of Terms Used in Photochemistry, IUPAC Organic Chemistry Division, Pure Appl. Chem., **60**, 1055–1106 (1988).

H. Freiser and G.H. Nancollas, Compendium of Analytical Nomenclature, IUPAC Analytical Chemistry Division, Second Edition, Blackwell Scientific Publications, Oxford, 1987.

H.Q. Porter and D.W. Turner, A Descriptive Classification of the Electron Spectroscopies, IUPAC Physical Chemistry Division, Pure Appl. Chem., **59**, 1343–1406 (1987).

V. Gold, K.L. Loening, A.D. McNaught and P. Sehmi, Compendium of Chemical Terminology, International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, Oxford, 1987.

M. Orchin, F. Kaplan, R.S. Macomber, R.M. Wilson and H. Zimmer, The Vocabulary of Organic Chemistry, Wiley, New York, 1980.

TERMS STARTING WITH AN (ARABIC) NUMERAL :

[2Fe-2S]

Designation of a two-iron, two-labile-sulfur ***cluster*** in a protein, comprising two sulfido-bridged iron atoms. The oxidation levels of the clusters are indicated by adding the charges on the iron and sulfide atoms, i.e. $[2Fe\text{-}2S]^{2+}$;$[2Fe\text{-}2S]^{+}$. The alternative designation, which conforms to inorganic chemical convention is to include the charges on the ***ligands***; this is more appropriate where the ligands are other than the usual cysteine sulfurs, such as in the ***Rieske*** proteins. See also ***ferredoxin***.

[4Fe-4S]

Designation of a four-iron, four-labile-sulfur ***cluster*** in a protein. (See ***[2Fe-2S]***). Possible oxidation levels of the clusters are $[4Fe\text{-}4S]^{3+}$;$[4Fe\text{-}4S]^{2+}$;$[4Fe\text{-}4S]^{+}$. See also ***ferredoxin***, ***HiPIP***.

TERMS STARTING WITH A GREEK LETTER :

Greek letters used as entry in this glossary

α See ***helix*** (for alpha helix)
β See ***beta sheet***, ***beta strand*** and ***beta turn***
γ See ***Soret band*** (for gamma band)
η See ***hapto***
κ See ***donor atom symbol*** (for kappa-convention)
μ See ***bridging ligand*** (for mu-symbol)

ALPHABETICALLY ARRANGED TERMS:

Absolute configuration

The spatial arrangement of the atoms of a ***chiral*** molecular entity (or group) and its ***stereochemical*** description.

Abzyme

See ***catalytic antibody***.

Achiral

See ***chirality***.

Acid

See ***Brønsted acid***, ***Lewis acid***, ***hard acid***, ***soft acid.***

Acidity constant

The equilibrium constant for splitting off a ***hydron*** from a ***Brønsted acid***.

Acid-labile sulfide

Refers to sulfido ***ligands***, e.g. the ***bridging ligands*** in ***iron-sulfur proteins***, which are released as H_2S at acid pH. See also ***ferredoxin***.

Aconitase

Trivial name for citrate (isocitrate) hydro-***lyase*** (aconitate hydratase), ***EC*** 4.2.1.3, which catalyzes the interconversion of citrate, *cis*-aconitate ((*Z*)-prop-1-ene-1,2,3-tricarboxylate) and isocitrate. The active ***enzyme*** contains a catalytic ***[4Fe-4S] cluster***.

Active center

The location in an ***enzyme*** where the specific reaction takes place.

Active site

See ***active center***.

Adenosine 5′-triphosphate (ATP)

Key ***nucleotide*** in energy-dependent cellular reactions, in combination with Mg(II). The reaction: ATP + water → ADP + phosphate is used to supply the necessary energy.

Adrenodoxin

A ***[2Fe-2S] ferredoxin*** involved in electron transfer from ***NADPH***$^+$ (via a ***reductase***) to ***cytochrome P-450*** in the adrenal gland.

Aerobe

An organism that needs dioxygen for respiration and thus for growth.

Albumin

A type of protein, especially a protein of blood ***plasma*** which transports various substances, including metal ions, drugs and ***xenobiotics***.

Allosteric effector

Specific small molecules that bind to a protein at a site other than a catalytic site and modulate (by activation or ***inhibition***) the biological activity.

Allosteric enzyme

An ***enzyme*** that contains a region, separate from the region that binds the ***substrate*** for catalysis, where a small, ***regulatory*** molecule binds and affects that catalytic activity. This effector molecule may be structurally unrelated to the substrate, or may be a second molecule of substrate. If the catalytic activity is enhanced by binding, the effector is called an activator; if it is diminished, the effector is called an ***inhibitor***.

Alpha(α) helix

See ***helix***.

Ambidentate

Ligands, such as $(NCS)^-$, that can bind to a ***central atom*** through either of two or more donor atoms are termed ambidentate.

Amicyanin

An ***electron transfer protein*** containing a ***type 1 copper*** site, isolated from certain bacteria.

Amino-acid residue (in a polypeptide)

When two or more amino acids combine to form a peptide, the elements of water are removed, and what remains of each amino acid is called an amino-acid residue. Amino-acid residues are therefore structures that lack a hydrogen atom of the amino group (-NH-CHR-COOH), or the hydroxy moiety of the carboxy group (NH_2-CHR-CO-), or both (-NH-CHR-CO-); all units of a peptide chain are therefore amino-acid residues. (Residues of amino acids that contain two amino groups or two carboxy groups may be joined by isopeptide bonds, and so may not have the formulas shown). The residue in a peptide that has an amino group that is free, or at least not acylated by another amino-acid residue (it may, for example, be acylated or formylated), is called N-terminal; it is the N-terminus. The residue that has a free carboxy group, or at least does not acylate another amino-acid residue, (it may, for example, acylate ammonia to give -NH-CHR-CO-NH_2), is called C-terminal.

Symbols for amino acids (use of the one-letter symbols should be restricted to the comparison of long sequences) :

A	Ala	Alanine
B	Asx	Asparagine or aspartic acid
C	Cys	Cysteine
D	Asp	Aspartic acid
E	Glu	Glutamic acid
F	Phe	Phenylalanine
G	Gly	Glycine
H	His	Histidine
I	Ile	Isoleucine
K	Lys	Lysine
L	Leu	Leucine
M	Met	Methionine
N	Asn	Asparagine
P	Pro	Proline
Q	Gln	Glutamine
R	Arg	Arginine
S	Ser	Serine
T	Thr	Threonine
V	Val	Valine
W	Trp	Tryptophan
Y	Tyr	Tyrosine
Z	Glx	Glutamine or glutamic acid

Anabolism

The processes of ***metabolism*** that result in the synthesis of cellular components from precursors of low molecular weight.

Anemia

Condition in which there is a reduction in the number of red blood cells or amount of ***hemoglobin*** per unit volume of blood below the reference interval for a similar individual of the species under consideration, often causing pallor and fatigue.

Anaerobe

An organism that does not need dioxygen for growth. Many anaerobes are even sensitive to dioxygen. Obligate (strict) anaerobes grow only in the absence of dioxygen. Facultative anaerobes can grow either in the presence or in the absence of dioxygen.

Anation

Replacement of the ***ligand*** water by an anion in a ***coordination*** entity.

Anisotropy

The property of molecules and materials to exhibit variations in physical properties along different molecular axes of the substance.

Anti

In the representation of ***stereochemical*** relationships "anti" means "on opposite sides" of a reference plane, in contrast to "syn" which means "on the same side".

Antibody

A protein, belonging to the class of immunoglobulins, designed to bind a specific ***antigen*** in order to remove it from the body. They are synthesized exclusively by B-lymphocytes, in millions of forms, each with a different amino acid sequence and a specific ***binding site*** for a specific antigen (antigenic determinant or epitope). Presently a world-wide interest exists in ***catalytic antibodies*** (abzymes), elicited against transition-state analogues of chemical reactions. Such an approach has permitted the design of immunoglobulins with ***enzymatic*** activity.

Antiferromagnetic

See ***ferromagnetic***.

Antigen

A compound (protein, polysaccharide, microorganism, virus) foreign to the body that induces the production of specific ***antibodies***.

Apoprotein

A protein without its characteristic ***prosthetic group*** or metal.

Aquation

The incorporation of one or more integral molecules of water into another chemical species with or without displacement of one or more other atoms or groups. See also ***hydration***.

Archaea

A group of ***prokaryotes***, which can be subdivided into three groups (***methanogenic***, halophilic, thermoacidophilic), that are characterized by special constituents such as ether-bonded lipids and special ***coenzymes***. The archaea are members of a separate kingdom that falls in between eubacterial and ***eukaryotic*** organisms.

Assimilation

To change food and other nutrients into a part of the living organism.

Assimilative

See ***assimilation***.

Assimilator

See ***assimilation***.

Asymmetric synthesis

A traditional term for stereoselective synthesis. A chemical reaction (or reaction sequence) in which one or more new elements of ***chirality*** are formed in a ***substrate*** molecule and which produces the ***stereoisomeric (enantiomeric*** or ***diastereoisomeric)*** products in unequal amounts.

Asymmetry parameter

In nuclear quadrupole resonance spectroscopy this parameter, η, is used for describing non-symmetric fields. It is defined as $\eta = (q_{xx} - q_{yy})/q_{zz}$ in which q_{xx}, q_{yy} and q_{zz} are the components of the field gradient q (which is the second derivative of the time-averaged electric potential) along the x-, y- and z-axes. By convention q_{zz} refers to the largest field gradient, q_{yy} to the next largest and q_{xx} to the smallest when all three values are different.

ATP

See ***adenosine 5′-triphosphate***.

Auranofin

See ***gold drugs***.

Autotrophic organisms

Organisms that are capable of using carbon dioxide as the sole carbon source for growth and product formation. Organisms that use light as a source of energy are said to be photoautotrophs, those that use the energy from chemical reactions are chemoautotrophs.

Auxotroph

An organism which requires a particular organic compound for growth.

Azurin

An ***electron transfer protein*** containing a ***type 1 copper*** site, isolated from certain bacteria.

Bacteriochlorin

7,8,17,18-tetrahydroporphyrin. A reduced ***porphyrin*** with two pairs of non-fused saturated carbon atoms (C7 – C8 and C17 – C18) in two of the pyrrole rings. See also ***isobacteriochlorin***.

Bacteriochlorophyll

See ***chlorophyll***.

Base

See ***Brønsted base***, ***Lewis base***, ***hard base***, ***soft base***.

Base pairing

The specific association between two complementary strands of ***nucleic acids*** that results from the formation of hydrogen bonds between the base components of the ***nucleotides*** of each strand: A=T and G≡C in ***DNA***, A=U and G≡C (and in some cases G≡U) in ***RNA*** (the lines indicate the number of hydrogen bonds). Single-stranded nucleic acid molecules can adopt a partially double-stranded structure through intrastrand base pairing. See also ***nucleosides***.

Basicity constant

See ***acidity constant***.

Beta(β) sheet

Preferentially called a beta pleated sheet; a regular structure in an extended polypeptide chain, stabilized in the form of a sheet by hydrogen bonds between CO and NH groups of adjacent (parallel or antiparallel) chains.

Beta(β) strand

Element of a ***beta sheet***. One of the strands that is hydrogen bonded to a parallel or antiparallel strand to form a beta sheet.

Beta(β) turn

A hairpin structure in a polypeptide chain reversing its direction by forming a hydrogen bond between the CO group of ***amino-acid residue*** *n* with the NH group of residue (*n*+3). See also ***helix***.

Bifunctional ligand

A ***ligand*** that is capable of simultaneous use of two of its donor atoms to bind to one or more ***central atoms*** (see also ***ambidentate***).

Binding constant

See ***stability constant***.

Binding site

A specific region (or atom) in a molecular entity that is capable of entering into a stabilizing interaction with another molecular entity. An example of such an interaction is that of an ***active site*** in an ***enzyme*** with its ***substrate***. Typical forms of interaction are by hydrogen bonding, ***coordination***, and ion pair formation. Two binding sites in different molecular entities are said to be complementary if their interaction is stabilizing.

Binuclear

Less-frequently used term for the IUPAC recommended: dinuclear. See ***nuclearity***.

Bioassay

A procedure for determining the concentration or biological activity of a substance (e.g. vitamin, hormone, plant growth factor, antibiotic, ***enzyme***) by measuring its effect on an organism or tissue compared with a standard preparation.

Bioavailability

The availability of a food component or a ***xenobiotic*** to an organ or organism.

Biocatalyst

A catalyst of biological origin, typically an ***enzyme***.

Bioconjugate

A molecular species produced by living systems of biological origin when it is composed of two parts of different origins, e.g. a conjugate of a ***xenobiotic*** with some groups, e.g. glutathione, sulfate or glucuronic acid, to make it soluble in water or compartmentalized within the cell.

Bioconversion

The conversion of one substance to another by biological means. The fermentation of sugars to alcohols, catalyzed by yeasts, is an example of bioconversion. See also ***biotransformation***.

Bioleaching

Extraction of metals from ores or soil by biological processes, mostly by microorganisms.

Biological half life

The time at which the amount of a biomolecule in a living organism has been reduced by one half. See also ***half life***.

Biomass

Material produced by the growth of micro-organisms, plants or animals.

Biomembrane

Organized sheet-like assemblies consisting mainly of proteins and lipids (bilayers), acting as highly selective permeability barriers, containing specific molecular pumps and gates, receptors and ***enzymes***.

Biomimetic

Refers to a laboratory procedure designed to imitate a natural chemical process. Also refers to a compound that mimics a biological material in its structure or function.

Biomineralization

The synthesis of inorganic crystalline or amorphous mineral-like materials by living organisms. Among the minerals synthesized biologically in various forms of life are: fluoroapatite, hydroxyapatite ($Ca_5(PO_4)_3(F, OH)$), magnetite (Fe_3O_4) and calcium carbonate ($CaCO_3$).

Biopolymers

Macromolecules (including proteins, ***nucleic acids*** and polysaccharides) formed by living organisms.

Biosensor

A device that uses specific biochemical reactions mediated by isolated ***enzymes***, immunosystems, tissues, organelles or whole cells to detect chemical compounds, usually by electrical, thermal or optical signals.

Biotransformation

A chemical transformation mediated by living organisms or ***enzyme*** preparations. See also ***bioconversion***.

Bleomycin (BLM)

A glycopeptide molecule that can serve as a metal ***chelating ligand***. The Fe(III) complex of bleomycin is an antitumor agent and its activity is associated with ***DNA*** cleavage.

BLM

See ***bleomycin***.

Blotting

A technique used for transferring ***DNA***, ***RNA*** or protein from gels to a suitable binding matrix, such as nitrocellulose or nylon paper, while maintaining the same physical separation.

Blue copper protein

An ***electron transfer protein*** containing a ***type 1 copper*** site. Characterized by a strong absorption in the visible region, and an ***EPR*** signal with an unusually small ***hyperfine*** coupling to the copper nucleus.

Bone imaging

The construction of bone tissue images from the radiation emitted by ***radionuclides*** that have been absorbed by the bone. Radionuclides such as ^{18}F, ^{85}Sr and ^{99m}Tc are introduced as complexes with specific ***ligands*** (very often phosphonate ligands) and are absorbed in the bones by metabolic activity. See also ***imaging***.

Brain imaging

In addition to ***magnetic resonance imaging*** that is based on the absorption by the brain of electromagnetic radiation, brain images can be acquired by scintillation counting (scintigraphy) of radiation emitted from radioactive nuclei that have crossed the blood-brain barrier. The introduction of ***radionuclides*** into brain tissue is accomplished with the use of specific $^{99m}Tc(V)$ complexes with lipophilic ligands. See also ***imaging***.

Bridging ligand

A bridging ***ligand*** binds to two or more ***central atoms***, usually metals, thereby linking them together to produce poly***nuclear coordination*** entities . Bridging is indicated by the Greek letter μ appearing before the ligand name and separated by a hyphen. For an example, see ***FeMo-cofactor***.

Brønsted acid

A molecular entity capable of donating a ***hydron*** to a base (i.e., a "hydron donor") or the corresponding chemical species.

Brønsted base

A molecular entity capable of accepting a ***hydron*** from an acid (i.e., a "hydron acceptor") or the corresponding chemical species.

Cage

An aggregate of molecules, generally in the condensed phase, that surround the fragments formed by thermal or photochemical dissociation of a species.

Calmodulin

A Ca^{2+} binding protein involved in intracellular ***metabolic regulation***.

Calpain

A calcium-activated neutral protease, ***EC*** 3.4.22.17.

Carbonic anhydrase

A zinc-containing ***enzyme*** (carbonate hydro-lyase, carbonate dehydratase, ***EC*** 4.2.1.1) that catalyzes the reversible decomposition of carbonic acid to carbon dioxide and water.

Carbon monoxide dehydrogenases

Enzymes that catalyze the oxidation of carbon monoxide to carbon dioxide. They contain ***iron-sulfur clusters*** and either nickel and zinc, or ***molybdopterin***. Some nickel-containing enzymes are also involved in the synthesis of acetyl coenzyme A from CO_2 and H_2.

Carboplatin

A "second generation" platinum drug effective in cancer chemotherapy named: *cis*-diammine(cyclobutane-1,1-dicarboxylato)platinum(II). Carboplatin is less toxic than the "first generation" antitumor drug, ***cisplatin***.

Cardiotech

A species radiolabeled with ^{99m}Tc with formula $[Tc(CNR)_6]^+$ (R = *tert*-butyl) known for ***imaging*** the heart after a heart attack.

Catabolism

Reactions involving the breaking down of organic ***substrates***, typically by oxidative breakdown, to provide chemically available energy (e.g. ***ATP***) and/or to generate ***metabolic*** intermediates used in subsequent ***anabolic*** reactions.

Catalase

A ***hemeprotein*** (***EC*** 1.11.1.6), which catalyzes the ***disproportionation*** of dihydrogen peroxide to O_2 and water ; it also catalyzes the oxidation of other compounds, such as ethanol, by dihydrogen peroxide. A non-

heme protein containing a dinuclear manganese ***cluster*** with catalase activity is often called pseudocatalase.

Catalytic antibody

An ***antibody*** which catalyzes a chemical reaction analogous to an ***enzymatic*** reaction, such as an ester hydrolysis. It is obtained by using a ***hapten*** which mimics the transition state of the reaction. Also known as an abzyme.

CBS

Acronym for colloidal bismuth subcitrate. See ***De-Nol***.

CD

See ***circular dichroism***.

Central atom

The atom in a ***coordination*** entity that binds other atoms or group of atoms (***ligands***) to itself, thereby occupying a central position in the coordination entity.

Ceruloplasmin

A copper protein present in blood ***plasma***, containing ***type 1, type 2*** and ***type 3 copper*** centers, where the type 2 and type 3 are close together, forming a tri***nuclear*** copper ***cluster.*** See also ***multicopper oxidases***.

Charge-transfer complex

An aggregate of two or more molecules in which charge is transferred from a donor to an acceptor.

Charge-transfer transition

An electronic transition in which a large fraction of an electronic charge is transferred from one region of a molecular entity, called the electron donor, to another, called the electron acceptor (intramolecular charge-transfer) or from one molecular entity to another (intermolecular charge-transfer).

Chaperonin

Member of the set of molecular chaperones, located in different organelles of the cell and involved either in transport of proteins through ***biomembranes*** by unfolding and refolding the proteins or in assembling newly formed polypeptides.

Chelation

Chelation involves ***coordination*** of more than one sigma-electron pair donor group from the same ***ligand*** to the same ***central atom***. The number of coordinating groups in a single chelating ligand is indicated by the adjectives didentate, tridentate, tetradentate, etc.

Chelation therapy

The judicious use of ***chelating*** (metal binding) agents for the removal of toxic amounts of metal ions from living organisms. The metal ions are sequestered by the chelating agents and are rendered harmless or excreted. Chelating agents such as 2,3-dimercaptopropan-1-ol, ethylene- diaminetetraacetic acid,

desferrioxamine and D-penicillamine have been used effectively in chelation therapy for arsenic, lead, iron and copper, respectively.

Chemical shift

See ***nuclear magnetic resonance spectroscopy***.

Chirality

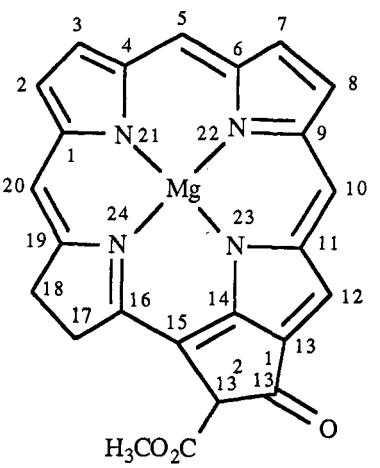
A term describing the geometric property of a rigid object (or spatial arrangement of points or atoms) that is non-superimposable on its mirror image; such an object has no symmetry elements of the second kind (a mirror plane, a centre of inversion, a rotation reflection axis). If the object is superimposable on its mirror image the object is described as being achiral.

Chlorin

2,3-dihydroporphyrin. An unsubstituted, reduced ***porphyrin*** with two non-fused saturated carbon atoms (C-2, C-3) in one of the pyrrole rings.

Chlorophyll

Part of the ***photosynthetic*** systems in green plants. Generally speaking, it can be considered as a magnesium complex of a ***porphyrin*** in which a double bond in one of the pyrrole rings (17-18) has been reduced. A fused cyclopentanone ring is also present (positions 13-14-15). In the case of chlorophyll *a*, the substituted porphyrin ligand further contains four methyl groups in positions 2, 7, 12 and 18, a vinyl group in position 3, an ethyl group in position 8 and a $-(CH_2)_2CO_2R$ group (R = phytyl, (2*E*)-(7*R*, 11*R*)-3,7,11,15-tetramethylhexadec-2-en-1-yl) in position 17. In chlorophyll *b*, the group in position 7 is a -CHO group. In bacteriochlorophyll *a* the porphyrin ring is further reduced (7-8), and the group in position 3 is now a $-COCH_3$ group. In addition, in bacteriochlorophyll *b*, the group in position 8 is a $=CHCH_3$ group.



Chloroplast

The organelle of ***eukaryotic photosynthesis***. See also ***thylakoids***.

Chromophore

That part of a molecular entity consisting of an atom or group of atoms in which the electronic transition responsible for a given spectral band is approximately localized.

Circular dichroism (CD)

A spectroscopic method which measures the difference in absorbance of left- and right-handed circularly polarized light by a material, as a function of the wavelength. Most biological molecules, including proteins and ***nucleic acids***, are ***chiral*** and show circular dichroism in their ultraviolet absorption bands, which may be used as an indication of ***secondary structure***. Metal centers that are bound to such molecules, even if they have no inherent chirality, usually exhibit CD in absorption bands associated with ***ligand***-based or ligand-metal ***charge-transfer transitions***. CD is frequently used in combination with absorption and ***MCD*** studies to assign electronic transitions.

cis

In inorganic nomenclature a structural prefix designating two groups occupying adjacent positions (not generally recommended for precise nomenclature purposes of complicated systems). See also ***trans***.

Cisplatin

cis-diamminedichloroplatinum(II). An antitumor drug highly effective in the chemotherapy of many forms of cancer. Of major importance in the antitumor activity of this drug is its interaction with the ***nucleic acid*** bases of ***DNA***.

Clone

(1) A population of genetically identical cells produced from a common ancestor.

(2) Sometimes, "clone" is also used for a number of recombinant ***DNA*** molecules all carrying the same inserted ***sequence***.

Cluster

A number of metal centers grouped close together which can have direct metal bonding interactions or interactions through a ***bridging ligand***, but are not necessarily held together by these interactions. Examples can be found under the entries ***[2Fe-2S]***, ***[4Fe-4S]***, ***ferredoxin***, ***HiPIP***, ***iron-sulfur cluster***, ***FeMo-cofactor***, ***ferritin***, ***metallo- thionein***, ***nitrogenase***, and ***Rieske iron-sulfur protein***.

Cobalamin

Vitamin B-12 or B_{12}. A vitamin synthesized by microorganisms and conserved in animals in the liver. Deficiency or collective uptake of vitamin B-12 leads to pernicious ***anemia***. Cobalamin is a substituted ***corrin***-Co(III) complex in which the cobalt atom is bound to the four nitrogen atoms of the corrin ring, an axial group R and 5,6-dimethylbenzimidazole. The latter is linked to the cobalt by the N-3 nitrogen atom and is bound to the C-1 carbon of a ribose molecule by the N-1 nitrogen atom. Various forms of the vitamin are known with different R groups such as R = CN, cyanocobalamin; R = OH, hydroxocobalamin; R = CH_3, methylcobalamin; R = 5′-deoxyadenosyl, ***coenzyme*** B-12.

Codon

A sequence of three consecutive ***nucleotides*** that occurs in ***mRNA*** and directs the incorporation of a specific amino acid into a protein, or represents the starting or termination signal of protein synthesis.

Coenzyme

A low-molecular-weight, non-protein organic compound (often a ***nucleotide***) participating in ***enzymatic*** reactions as dissociable acceptor or donor of chemical groups or electrons.

Cofactor

An organic molecule or ion (usually a metal ion) that is required by an ***enzyme*** for its activity. It may be attached either loosely (***coenzyme***) or tightly (***prosthetic*** group).

Colloidal bismuth subcitrate (CBS)

See ***De-Nol***.

Comproportionation

The reverse of ***disproportionation***.

Concanavalin A

A protein from jack beans, containing calcium and manganese, which agglutinates red blood cells and stimulates T lymphocytes to undergo mitosis.

Configuration

In the context of stereochemistry, the term is restricted to the arrangements of atoms of a molecular entity in space that distinguishes ***stereoisomers***, the isomerism between which is not due to ***conformational*** differences.

Conformation

The spacial arrangements of atoms affording distinction between ***stereoisomers*** which can be interconverted by rotations about formally single bonds.

Consensus sequence

A ***sequence*** of ***DNA***, ***RNA***, protein or carbohydrate derived from a number of similar molecules, which comprises the essential features for a particular function.

Contrast agent

Paramagnetic (or ***ferromagnetic***) metal complex or particle causing a decrease in the relaxation times (increase in relaxivity) of nuclei detected in an ***image***, usually of water.

Cooperativity

The phenomenon that binding of an effector molecule to a biological system either enhances or diminishes the binding of a successive molecule, of the same or different kind, to the same system. The system may be an ***enzyme***, or a protein that specifically binds another molecule such as oxygen or ***DNA***. The effector molecule may be an enzyme ***substrate*** or an ***allosteric effector***. The enzyme or protein exists in different ***conformations***, with different catalytic rates or binding affinities, and binding of the effector molecule changes the proportion of these conformations. Enhanced binding is named positive cooperativity; diminished binding is named negative cooperativity. A well-known example of positive cooperativity is in ***hemoglobin***. In ***biocatalysis*** it was originally proposed that only multi-***subunit*** enzymes could respond in this way. However single-subunit enzymes may give such a response (so-called mnemonic enzymes).

Coordination

A coordination entity is composed of a ***central atom***, usually that of a metal, to which is attached a surrounding array of other atoms or group of atoms, each of which is called a ***ligand***. A coordination entity may be a neutral molecule, a cation or an anion. The ligands may be viewed as neutral or ionic entities that

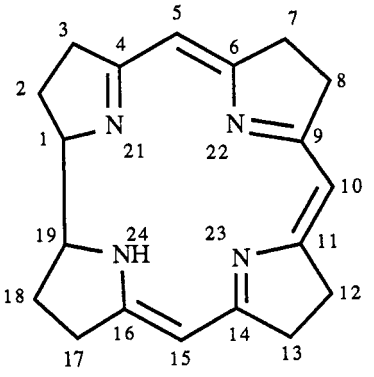
are bonded to an appropriately charged central atom. It is standard practice to think of the ligand atoms that are directly attached to the central atom as defining a coordination polyhedron (tetrahedron, square plane, octahedron, etc.) about the central atom. The coordination number is defined as being equal to the number of sigma-bonds between ligands and the central atom; this definition is not necessarily appropriate in all areas of (coordination) chemistry. In a coordination formula, the central atom is listed first. The formally anionic ligands appear next and they are listed in alphabetic order according to the first symbols of their formula. The neutral ligands follow, also in alphabetical order, according to the same principle. The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. In a coordination name, the ligands are listed in alphabetical order, without regard to charge, before the name of the central atom. Numerical prefixes indicating the number of ligands are not considered in determining that order. All anionic coordination entities take the ending -ate, whereas no distinguishing termination is used for cationic or neutral coordination entities.

Corphin

Corphin is the ***F-430*** cofactor found in methyl-coenzyme M ***reductase***, a nickel containing ***enzyme*** that catalyzes one step in the conversion of CO_2 to methane in ***methanogenic*** bacteria. The Ni ion in F-430 is ***coordinated*** by the tetrahydrocorphin ***ligand***. This ligand combines the structural elements of both ***porphyrins*** and ***corrins***.

Corrin

A ring-contracted ***porphyrin*** derivative that is missing a carbon from one of the meso positions (C-20). It constitutes the skeleton $C_{19}H_{22}N_4$ upon which various B-12 vitamins, ***cofactors*** and derivatives are based.



Crystal field

Crystal field theory is the theory which interprets the properties of ***coordination*** entities on the basis that the interaction of the ***ligands*** and the ***central atom*** is a strictly ionic or ion-dipole interaction resulting from electrostatic attractions between the central atom and the ligands. The ligands are regarded as point negative (or partially negative) charges surrounding a central atom; covalent bonding is completely neglected. The splitting or separation of energy levels of the five degenerate **d** orbitals in a transition metal, when the metal is surrounded by ligands arranged in a particular geometry with respect to the metal center, is called the crystal field splitting. See also ***ligand field***.

C-terminal amino-acid residue

See ***amino-acid residue***.

Curie relation

See ***magnetic susceptibility***.

Cytochrome

A heme protein that transfers electrons, and exhibits intense absorption bands (the α and β bands, the α band having the longer wavelength) between 510 and 615 nm in the reduced form. Cytochromes are designated types *a, b, c* or *d*, depending on the position of the α band, which depends on the type of ***heme***. The iron undergoes oxidation-reduction between oxidation states Fe(II) and Fe(III). Most cytochromes are hemochromes, in which the fifth and sixth ***coordination*** sites in the iron are occupied by strong field ***ligands***, regardless of the oxidation state of iron. Cytochromes may be distinguished by the wavelength of the α band, such as cytochrome *c*-550. Certain specific cytochromes with particular functions, are designated with suffixes, such as cytochrome a_1, b_2, etc., but this practice is discouraged.

Cytochrome-c oxidase

An ***enzyme***, ferrocytochrome-c:dioxygen ***oxidoreductase***, ***EC*** 1.9.3.1, ***cytochrome*** aa_3. The major respiratory protein of animal and plant ***mitochondria***, it catalyzes the oxidation of Fe(II)-cytochrome c, and the reduction of dioxygen to water. Contains two ***hemes*** and three copper atoms, arranged in three centers. Heme a_3 and copper-B form a center that reacts with dioxygen; the second heme is cytochrome *a*; the third site, copper-A, is a ***dinuclear*** center.

Cytochrome P-450

General term for a group of ***heme***-containing ***monooxygenases*** (***EC*** 1.4.14.1). Named from the prominent absorption band of the Fe(II)-carbonyl complex. The heme comprises ***protophorphyrin IX***, and the proximal ***ligand*** to iron is a cysteine sulfur. Cytochromes P-450 of microsomes in tissues such as liver are responsible for ***metabolism*** of many ***xenobiotics***, including drugs. Others, such as the ***mitochondrial enzymes*** from adrenal glands, are involved in biosynthetic pathways such as those of steroids. The reaction with dioxygen appears to involve higher oxidation states of iron, such as Fe(IV)=O.

Cytoplasm

The part of protoplasm in a cell outside of and surrounding the nucleus.

Dehydrogenase

An ***oxidoreductase*** which catalyzes the removal of hydrogen atoms from a ***substrate***.

Denitrification

The reduction of nitrates to nitrites, nitrogen monoxide (nitric oxide), dinitrogen oxide (nitrous oxide) and ultimately dinitrogen catalyzed by microorganisms, e.g. facultative ***aerobic*** soil bacteria under ***anaerobic*** conditions.

De-Nol

Common name for the potassium mixed ammonium potassium salt of a bismuth citrate complex, used in the treatment of ulcers.

Denticity

The number of donor groups from a given ***ligand*** attached to the same ***central atom***.

Deoxyribonucleic acid (DNA)

A high-molecular-mass linear polymer, composed of ***nucleotides*** containing 2-deoxyribose and linked between positions 3′ and 5′ by phosphodiester groups; DNA contains the ***genetic*** information of organisms. The double-stranded form consists of a ***double helix*** of two complementary chains that run in opposite

directions and are held together by hydrogen bonds between pairs of the complementary ***nucleotides***. The way the helices are constructed may differ and is usually designated as A, B, Z, etc.. Occasionally, alternative structures are found, such as those with Hoogsteen ***base pairing***.

Desferal

See ***desferrioxamine***.

Desferrioxamine (dfo)

Chelating agent used world-wide in the treatment of iron overload conditions, such as ***hemochromatosis*** and ***thalassemia***.

dfo

See ***desferrioxamine***.

Diamagnetic

Substances having a negative ***magnetic susceptibility*** are diamagnetic. They are repelled by a magnetic field.

Diastereoisomers

Diastereoisomers are ***stereoisomers*** not related as mirror images.

Dihydrofolate

An oxidation product of ***tetrahydrofolate*** that appears during ***DNA*** synthesis and other reactions. It must be reduced to tetrahydrofolate to be of further use. See also ***folate coenzymes***.

Dinuclear

See ***nuclearity***.

Dioxygenase

An ***enzyme*** that catalyzes the ***insertion*** of two oxygen atoms into a ***substrate***, both oxygens being derived from O_2.

Dismutase

An ***enzyme*** that catalyzes a ***disproportionation*** reaction.

Dismutation

See ***disproportionation***.

Disproportionation

Any chemical reaction of the type $A + A \rightarrow A' + A''$ where A, A′ and A″ are different chemical species. The reverse of disproportionation (or dismutation) is called comproportionation.

Dissimilatory

Related to the conversion of food or other nutrients into products plus energy-containing compounds.

Dissociation constant

See ***stability constant***.

DNA

See ***deoxyribonucleic acid***.

Domain

An independently folded unit within a protein, often joined by a flexible segment of the polypeptide chain.

Donor atom symbol

A polydentate ***ligand*** possesses more than one donor site, some or all of which may be involved in ***coordination***. To indicate the points of ligation, a system is needed. The general and systematic system for doing this is called the kappa convention: single ligating atom attachments of a polyatomic ligand to a coordination centre are indicated by the italic element symbol preceded by a Greek kappa, κ. In earlier practice, the different donors of the ligand were denoted by adding to the end of the name of the ligand the italicized symbol(s) for the atom or atoms through which attachment to the metal occurs.

Double helix

Two strands of ***DNA*** coiled about a central axis, usually a right-handed ***helix***. The two sugar phosphate backbones wind around the outside of the bases (A = adenine, G = guanine, T = thymine, C = cytosine) and are exposed to the solvent. The strands are antiparallel, thus the phosphodiester bonds run in opposite directions. As a result the structure has major and minor grooves at the surface. Each adenine in one strand of DNA is hydrogen bonded to a thymine in the second strand; each guanine is hydrogen bonded to a cytosine.

EC nomenclature for enzymes

A classification of ***enzymes*** according to the Enzyme Commission of the International Union of Biochemistry and Molecular Biology. Enzymes are allocated four numbers, the first of which defines the type of reaction catalyzed, the next two define the ***substrates***, and the fourth is a catalogue number. Categories of enzymes are EC 1, ***Oxidoreductases***; EC 2, ***Transferases***; EC 3, ***Hydrolases***; EC 4, ***Lyases***; EC 5, ***Isomerases***; EC 6, ***Ligases*** (Synthetases).

EDRF

See ***endothelium-derived relaxing factor***.

EF-Hand

A common structure to bind Ca^{2+} in ***calmodulin*** and other Ca^{2+} binding proteins consisting of a ***helix*** (E), a loop and another helix (F).

Electrode potential

The so-called electrode potential of an electrode is defined as the electromotive force (emf) of a cell in which the electrode on the left is a standard hydrogen electrode and the electrode on the right is the electrode in question. See also ***redox potential***.

Electron magnetic resonance (EMR) spectroscopy.

See ***electron paramagnetic resonance spectroscopy.***

Electron-nuclear double resonance (ENDOR)

A magnetic resonance spectroscopic technique for the determination of ***hyperfine*** interactions between electrons and nuclear spins. There are two principal techniques. In continuous-wave ENDOR the intensity of an ***electron paramagnetic resonance*** signal, partially saturated with microwave power, is measured as radiofrequency is applied. In pulsed ENDOR the radiofrequency is applied as pulses and the EPR signal is detected as a spin-echo. In each case an enhancement of the EPR signal is observed when the radiofrequency is in resonance with the coupled nuclei.

Electron paramagnetic resonance (EPR) spectroscopy

The form of spectroscopy concerned with microwave-induced transitions between magnetic energy levels of electrons having a net spin and orbital angular momentum. The spectrum is normally obtained by magnetic field scanning. Also known as electron spin resonance (ESR) spectroscopy or electron magnetic resonance (EMR) spectroscopy. The frequency (υ) of the oscillating magnetic field to induce transitions between the magnetic energy levels of electrons is measured in gigahertz (GHz) or megahertz (MHz). The following band designations are used: L(1.1 GHz), S(3.0 GHz), X(9.5 GHz), K(22.0 GHz) and Q(35.0 GHz). The static magnetic field at which the EPR spectrometer operates is measured by the magnetic flux density (B) and its recommended unit is the tesla (T). In the absence of nuclear hyperfine interactions, B and ν are related by : $h\nu = g\ \mu_B B$ where h is the Planck constant, μ_B is the Bohr magneton, and the dimensionless scalar g is called the g-factor. When the ***paramagnetic*** species exhibits an ***anisotropy***, the spatial dependency of the g-factor is represented by a 3×3 matrix. The interaction energy between the electron spin and a magnetic nucleus is characterized by the hyperfine coupling constant A. When the paramagnetic species has anisotropy, the hyperfine coupling is expressed by a 3×3 matrix called a hyperfine coupling matrix. Hyperfine interaction usually results in splitting of lines in an EPR spectrum. The nuclear species giving rise to the hyperfine interaction should be explicitly stated, e.g. "the hyperfine splitting due to ^{65}Cu". When additional hyperfine splittings due to other nuclear species are resolved ("superhyperfine"), the nomenclature should include the designation of the nucleus, and the isotopic number.

Electron spin-echo envelope modulation (ESEEM)

See ***electron spin-echo spectroscopy.***

Electron spin-echo (ESE) spectroscopy

A pulsed technique in ***electron paramagnetic resonance***, in some ways analogous to pulsed techniques in ***NMR***. ESE may be used for measurements of electron spin relaxation times as they are influenced by neighbouring ***paramagnets*** or molecular motion. It may also be used to measure ***anisotropic*** nuclear ***hyperfine*** couplings. The effect is known as electron spin-echo envelope modulation (ESEEM). The intensity of the electron spin-echo resulting from the application of two or more microwave pulses is measured as a function of the temporal spacing between the pulses. The echo intensity is modulated as a result of interactions with the nuclear spins. The frequency-domain spectrum corresponds to hyperfine transition frequencies.

Electron spin resonance (ESR) spectroscopy

See ***electron paramagnetic resonance spectroscopy.***

Electron transfer protein

A protein, often containing a metal ion, that oxidizes and reduces other molecules by means of electron transfer.

EMR

Acronym for electron magnetic resonance. See ***electron paramagnetic resonance spectroscopy***.

Enantiomer

One of a pair of molecular entities that are mirror images of each other and non-superimposable.

Endogenous

Originating internally. In the description of metal ion ***coordination*** in metalloproteins, endogenous refers to internal, or protein-derived, ***ligands***.

ENDOR

Acronym for ***electron-nuclear double resonance***.

Endothelium-derived relaxing factor (EDRF)

The factor originally described as EDRF is NO', produced by a specific P-450-type of ***enzyme*** from arginine upon response of a cell to a biological signal (molecule). Different types of cells respond differently to the presence of NO'. See also ***cytochrome P-450***.

Entatic state

A state of an atom or group which due to its binding in a protein, has its geometric or electronic condition adapted for function. Derived from entasis (Greek) meaning tension.

Enterobactin

A ***siderophore*** found in enteric bacteria such as *Escherichia coli*; sometimes called enterochelin.

Enterochelin

See ***enterobactin***.

Enzyme

A macromolecule that functions as a ***biocatalyst*** by increasing the reaction rate, frequently containing or requiring one or more metal ions. In general, an enzyme catalyzes only one reaction type (reaction specificity) and operates on only a narrow range of ***substrates*** (substrate specificity). Substrate molecules are attacked at the same site (regiospecificity) and only one or preferentially one of the ***enantiomers*** of ***chiral*** substrate or of ***racemic*** mixtures is attacked (enantiospecificity).

EPR

See ***electron paramagnetic resonance spectroscopy***.

Equilibrium constant

See ***acidity constant*** and ***stability constant***.

ESE

See ***electron spin-echo spectroscopy***.

ESEEM

Acronym for electron spin-echo envelope modulation. See ***electron spin-echo spectroscopy***.

ESR

Acronym for electron spin resonance. See ***electron paramagnetic resonance spectroscopy***.

Eukaryotes

Organisms whose cells have their ***genetic*** material packed in a membrane-surrounded, structurally discrete nucleus, and that have well-developed cell organelles. Eukaryotes include all organisms except ***archaea*** and eubacteria. See also ***prokaryote.***

Ewens–Bassett number

See ***oxidation number***.

EXAFS

Acronym for ***extended X-ray absorption fine structure***.

Exogenous

Originating externally. In the context of metalloprotein ***ligands***, exogenous describes ligands added from an external source, such as CO or O_2.

Exon

A section of ***DNA*** which carries the coding ***sequence*** for a protein or part of it. Exons are separated by intervening, non-coding sequences (called ***introns***). In ***eukaryotes*** most ***genes*** consist of a number of exons.

Expression

The cellular production of the protein encoded by a particular ***gene***. The process includes ***transcription*** of ***DNA***, processing of the resulting ***mRNA*** product and its ***translation*** into an active protein.

N.B. A recombinant gene inserted into a host cell by means of a vector is said to be expressed if the synthesis of the encoded polypeptide can be demonstrated. For the expression of metalloproteins usually other gene products will be required.

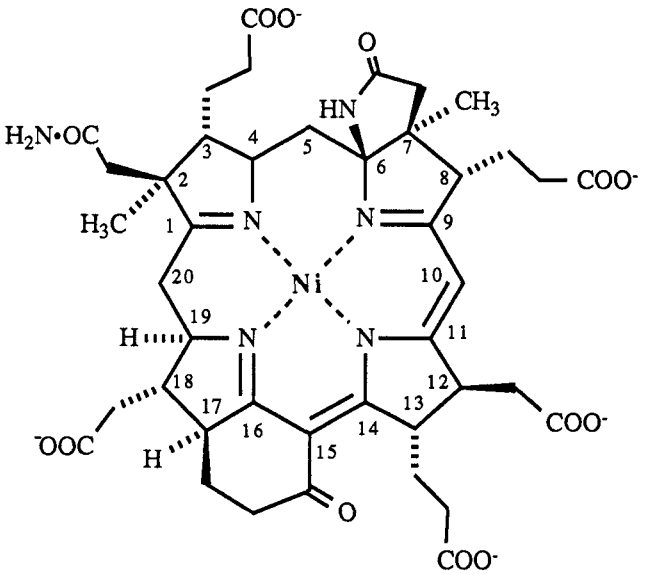
Extended X-ray absorption fine structure (EXAFS)

EXAFS effects arise because of electron scattering by atoms surrounding a particular atom of interest as that special atom absorbs X-rays and emits electrons. The atom of interest absorbs photons at a characteristic wavelength and the emitted electrons, undergoing constructive or destructive interference as they are scattered by the surrounding atoms, modulate the absorption spectrum. The modulation frequency corresponds directly to the distance of the surrounding atoms while the amplitude is related to the type and number of atoms. EXAFS studies are a probe of the local structure. EXAFS can be applied to systems which have local structure, but not necessarily long-range structure, such as non-crystalline materials. In particular, bond lengths and local symmetry (***coordination*** numbers) may be derived. The X-ray absorption

spectrum may also show detailed structure below the absorption edge. This X-ray absorption near edge structure (XANES) arises from excitation of core electrons to high level vacant orbitals.

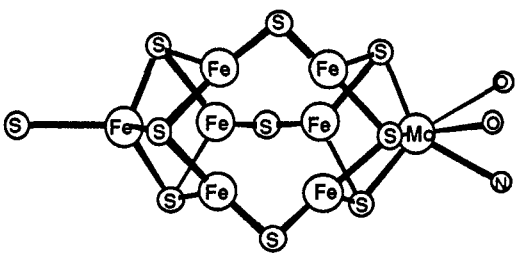
F-430

A tetrapyrrole structure containing nickel, a component of the ***enzyme*** methyl-coenzyme M ***reductase***, which is involved in the formation of methane in ***methanogenic*** bacteria. The highly reduced macrocyclic structure, related to ***porphyrins*** and ***corrins***, is termed a ***corphin***.



FeMo-cofactor

An inorganic ***cluster*** that is found in the FeMo protein of the molybdenum-***nitrogenase*** and is essential for the catalytic reduction of N_2 to ammonia. This cluster contains Fe, Mo and S in a 7:1:9 ratio. The structure of the ***cofactor*** within the FeMo protein can be described in terms of two cuboidal ***subunits***, Fe_4S_3 and $MoFe_3S_3$ bridged by three S^{2-} ions and "anchored" to the protein by a histidine bound via an imidazole group to the Mo atom and by a cysteine bound via a deprotonated SH group to an Fe atom of the Fe_4S_3 subunit. The Mo atom at the periphery of the molecule is six-***coordinate*** and in addition to the three sulfido ***ligands*** and the histidine imidazole is also bound to two oxygen atoms from an *(R)*-homocitrate molecule.



Fenton reaction

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^-$. This is the iron-salt-dependent decomposition of dihydrogen peroxide, generating the highly reactive hydroxyl radical, possibly via an oxoiron(IV) intermediate. Addition of a reducing agent such as ascorbate leads to a cycle which increases the damage to biological molecules. See also ***Haber–Weiss reaction***.

Ferredoxin

A protein containing more than one iron and ***acid-labile sulfur***, that displays electron-transfer activity but not classical ***enzyme*** function. See also ***HiPIP***.

Ferriheme

An iron(III) ***porphyrin coordination*** complex.

Ferritin

An iron storage protein consisting of a shell of 24 protein ***subunits***, encapsulating up to 4500 iron atoms in the form of a hydrated iron(III) oxide.

Ferrochelatase

An ***enzyme*** which catalyzes the insertion of iron into ***protoporphyrin IX*** to form ***heme***. The mammalian enzyme contains an ***iron-sulfur cluster***.

Ferroheme

An iron(II) ***porphyrin coordination*** complex.

Ferromagnetic

If there is coupling between the individual magnetic dipole moments of a ***paramagnetic*** sample, spontaneous ordering of the moments will occur at low temperatures. If this ordering results in an electronic ground state in which the moments are aligned in the same direction (parallel), the substance is said to be "ferromagnetic". If the ordering results in an electronic ground state in which the moments are aligned in opposite directions, the substance is said to be "antiferromagnetic".

[2Fe-2S]

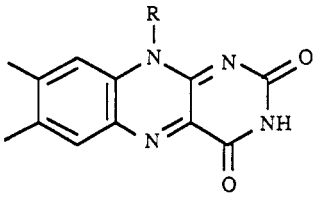
Designation of a two-iron, two-labile-sulfur ***cluster*** in a protein, comprising two sulfido-bridged iron atoms. The oxidation levels of the clusters are indicated by adding the charges on the iron and sulfide atoms, i.e. $[2Fe\text{-}2S]^{2+}$;$[2Fe\text{-}2S]^{+}$. The alternative designation, which conforms to inorganic chemical convention is to include the charges on the ***ligands***; this is more appropriate where the ligands are other than the usual cysteine sulfurs, such as in the ***Rieske*** proteins. See also ***ferredoxin***.

[4Fe-4S]

Designation of a four-iron, four-labile-sulfur ***cluster*** in a protein. (See ***[2Fe-2S]***). Possible oxidation levels of the clusters are $[4Fe\text{-}4S]^{3+}$;$[4Fe\text{-}4S]^{2+}$;$[4Fe\text{-}4S]^{+}$. See also ***ferredoxin***, ***HiPIP***.

Flavin

A ***prosthetic group*** found in flavoproteins and involved in biological oxidation and reduction. The oxidized flavin can be reduced stepwise by two electrons with the concomitant stepwise acceptance of two ***hydrons*** to give flavin semiquinone and flavin hydroquinone.

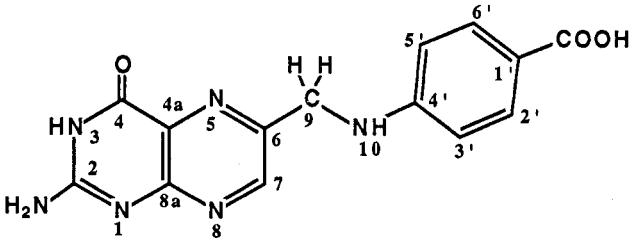


Fluxional

In inorganic chemistry this term is used to designate positional changes among ***ligands***. A fluxional chemical species undergoes rapid (degenerate) rearrangements, generally detectable by methods that observe the behaviour of individual nuclei in a rearranged chemical species.

Folate coenzymes

A group of heterocyclic compounds that are based on the [4-(pteridin-6-ylmethyl)amino] benzoic acid (pteroic acid) and conjugated with one or more L-glutamate units. Folate derivatives are important in ***DNA*** synthesis and erythrocyte formation. Folate deficiency leads to ***anemia***.



Formation constant

See ***stability constant***.

Fur

The iron uptake regulating protein present in ***prokaryotes***, which binds simultaneously Fe and ***DNA*** thereby preventing the biosynthesis of ***enzymes*** for the production of ***scavenger chelates*** (***siderophores***).

Gamma(γ) band

Identical to ***Soret band***.

Gene

Structurally, a basic unit of hereditary material; an ordered ***sequence*** of ***nucleotide*** bases that encodes one polypeptide chain (via ***mRNA***). The gene includes, however, regions preceding and following the coding region (leader and trailer) as well as (in ***eukaryotes***) intervening sequences (***introns***) between individual coding segments (***exons***). Functionally, the gene is defined by the cis-trans test that determines whether independent ***mutations*** of the same phenotype occur within a single gene or in several genes involved in the same function.

g-factor

See ***electron paramagnetic resonance spectroscopy***.

Gold drugs

Gold ***coordination*** compounds used in the treatment of rheumatoid arthritis, examples being auranofin, (tetraacetylthioglucosato-*S*)(triethylphosphane)gold(I), and myocrysin, disodium thiomalatogold(I).

Greek letters used as entry in this glossary

α See ***helix*** (for alpha helix)

β See ***beta sheet***, ***beta strand*** and ***beta turn***

γ See ***Soret band*** (for gamma band)

η See ***hapto***

κ See ***donor atom symbol*** (for kappa-convention)

μ See ***bridging ligand*** (for mu-symbol)

Guanylate cyclase

An ***enzyme*** catalyzing the conversion of guanosine 5′-triphosphate to cyclic guanosine 3′,5′-monophosphate, which is involved in cellular ***regulation*** processes. One member of this class is a ***heme***-containing enzyme involved in processes regulated by nitrogen monoxide.

Haber–Weiss reaction

The Haber–Weiss cycle consists of the following two reactions :

$H_2O_2 + OH^{\cdot} \rightarrow H_2O + O_2^{-} + H^{+}$ and

$H_2O_2 + O_2\text{-} \rightarrow O_2 + OH^{-} + OH^{\cdot}$

The second reaction achieved notoriety as a possible source of hydroxyl radicals. However, it has a negligible rate constant. It is believed that iron(III) complexes can catalyze this reaction: first Fe(III) is reduced by superoxide, followed by oxidation by dihydrogen peroxide. See also ***Fenton reaction***.

Half life

For a given reaction the half life $t_{½}$ of a reactant is the time required for its concentration to reach a value that is the arithmetic mean of its initial and final (equilibrium) value. For a reactant that is entirely consumed it is the time taken for the reactant concentration to fall to one half of its initial value. For a first-order reaction, the half life of the reactant may be called the half life of the reaction. In nuclear chemistry, (radioactive) half life is defined, for a simple radioactive decay process, as the time required for the activity to decrease to half its value by that process. See also ***biological half life***.

Haloperoxidase

A ***peroxidase*** which catalyzes the oxidative transformation of halides to XO^{-} (X being Cl, Br or I), or organic halogen compounds. Most are ***heme***proteins, but some bromoperoxidases from algae are vanadium-containing ***enzymes*** .

Hapten

A molecule (usually a small organic molecule) which can be bound to an ***antigenic*** determinant/epitope. Usually they are too small to give a response of their own. They become antigenic if they are coupled to a suitable macromolecule, such as a protein.

Hapto

The hapto symbol, η (Greek eta), with numerical superscript, provides a topological description for the bonding of hydrocarbons or other π-electron systems to metals, by indicating the connectivity between the ***ligand*** and the ***central atom***. The symbol is prefixed to the ligand name, or to that portion of the ligand name most appropriate. The right superscript numerical index indicates the number of ***coordinating*** atoms in the ligand which bind to the metal. Examples :

$[PtCl_2(C_2H_4)(NH_3)]$	amminedichloro(η^2-ethene)platinum
$[Fe(\eta^5\text{-}C_5H_5)_2]$	bis(η5cyclopentadienyl)iron or ferrocene

Hard acid

A ***Lewis acid*** with an acceptor centre of low polarizability. It preferentially associates with ***hard bases*** rather than with soft bases, in a qualitative sense (sometimes called "HSAB rule"). Conversely a soft acid

possesses an acceptor centre of high polarizability and exhibits the reverse preference for a partner for ***coordination***.

Hard base

A ***Lewis base*** with a donor centre of low polarizability; the converse applies to soft bases. See also ***hard acid***.

Helix

A particular rigid left- or right-handed arrangement of a polymeric chain, characterised by the number of strands, the number (n) of units per turn and its pitch (p), the distance the helix rises along its axis per full turn. Examples of single-stranded helices are the protein helices : α-helix: $n = 3.6$, $p = 540$ pm; 3_{10}-helix: $n = 3.0$, $p = 600$ pm; π-helix: $n = 4.4$, $p = 520$ pm. See also ***double helix***.

Heme

A near-planar ***coordination*** complex obtained from iron and the dianionic form of ***porphyrin***. Derivatives are known with substituents at various positions on the ring named a, b, c, d, etc. Heme b, derived from ***protoporphyrin IX***, is the most frequently occurring heme.

Hemerythrin

A dioxygen-carrying protein from marine invertebrates, containing an oxo-bridged ***dinuclear*** iron center.

Hemochromatosis

A genetic condition of massive iron overload leading to cirrhosis and/or other tissue damage, attributable to iron.

Hemocyanin

A dioxygen-carrying protein (from invertebrates, e.g. arthropods and molluscs), containing ***dinuclear type 3 copper*** sites.

Hemoglobin

A dioxygen-carrying heme protein of red blood cells, generally consisting of two alpha and two beta ***subunits***, each containing one molecule of ***protoporphyrin IX***.

Heterolysis

The cleavage of a bond (heterolytic cleavage or heterolytic fission) so that both bonding electrons remain with one of the two fragments between which the bond is broken.

Heterotrophic organisms

Organisms that are not able to synthesize cell components from carbon dioxide as sole carbon source. Heterotrophic organisms use preformed oxidizable organic ***substrates*** such as glucose as carbon and energy sources, while energy is gained through chemical processes (chemoheterotrophy) or through light sources (photoheterotrophy).

High-spin

See ***low-spin***.

HiPIP

Formerly-used abbreviation for High-Potential ***Iron-sulfur Protein***, now classed as a ***ferredoxin***. An ***electron transfer protein*** from ***photosynthetic*** and other bacteria, containing a ***[4Fe-4S] cluster*** which undergoes oxidation-reduction between the $[4Fe\text{-}4S]^{2+}$ and $[4Fe\text{-}4S]^{3+}$ states.

Holoenzyme

An ***enzyme*** containing its characteristic ***prosthetic group(s)*** and/or metal(s).

Homolysis

The cleavage of a bond (homolytic cleavage or homolytic fission) so that each of the molecular fragments between which the bond is broken retains one of the bonding electrons.

Hydration

Addition of water or the elements of water (i.e. H and OH) to a molecular entity. The term is also used in a more restricted sense for the process : A (gas) ® A (aqueous solution); cf. the use of the term in inorganic and physical chemistry to describe the state of ions of an aqueous electrolyte solution. See also ***aquation*** and ***solvation***.

Hydrogenase

An ***enzyme***, dihydrogen:acceptor ***oxidoreductase***, that catalyzes the formation or oxidation of H_2. Hydrogenases are of various types. One class ([Fe]-hydrogenases) contains only ***iron-sulfur clusters***. The other major class ([NiFe]-hydrogenases) has a nickel-containing center and iron-sulfur clusters; a variation of the latter type ([NiFeSe]-hydrogenases) contains selenocysteine.

Hydrolase

An ***enzyme*** of ***EC*** class 3, also known as a hydro-***lyase***, that catalyzes the ***hydrolysis*** of a ***substrate***.

Hydrolysis

Solvolysis by water.

Hydron

General name for the ion H^+ either in natural abundance, or where it is not desired to distinguish between the isotopes, as opposed to proton for $1H^+$, deuteron for $2H^+$ and triton for $3H^+$.

Hydrophilic

The term is used to mean "water preferring". May also be used to describe the character of interaction of a particular atomic group with the medium.

Hydrophobic interaction

The tendency of hydrocarbons (or of lipophilic hydrocarbon-like groups in solutes) to form intermolecular aggregates in an aqueous medium, and analogous intramolecular interactions. The name arises from the attribution of the phenomenon to the apparent repulsion between water and hydrocarbons. Use of the misleading alternative term hydrophobic bond is discouraged.

Hyperfine

See ***electron paramagnetic resonance spectroscopy***.

Imaging

A medical diagnostic technique by which useful organ images are obtained from the radiation emitted by ***radionuclides*** that are introduced into organs, or from radiation absorbed by atomic nuclei within the organs. Typical examples are imaging obtained by recording the radiation emitted by a radionuclide such as ^{99m}Tc, and the ^{1}H-NMR imaging obtained by whole body ***nuclear magnetic resonance*** measurements. See also ***bone imaging***, ***brain imaging***, and ***magnetic resonance imaging***.

Immunogold

A method for visualizing proteins in electron microscopy within a cell using gold particles attached to an ***antibody*** that binds specifically to that protein.

Inert

Stable and unreactive under specified conditions. See also ***labile***.

Inhibition

The decrease in the rate of a reaction brought about by the addition of a substance (***inhibitor***).

Inhibitor

A substance that decreases the rate of an ***enzyme*** catalyzed or other chemical reaction.

Insertion reaction

A chemical reaction or transformation of the general type X-Z + Y → X-Y-Z in which the connecting atom or group Y replaces the bond joining the parts X and Z of the reactant XZ.

Intercalation compounds

Compounds resulting from inclusion, usually without covalent bonding, of one kind of molecule (the guest molecule) in a matrix of another compound (the host compound), which has a layered structure. The host compound, with a rather rigid structure, may be macromolecular, crystalline, or amorphous.

Intron

An intervening section of ***DNA*** which occurs almost exclusively within a ***eukaryotic gene***, but which is not ***translated*** to amino-acid ***sequences*** in the gene product. The introns are removed from the pre-mature ***mRNA*** through a process called splicing, which leaves the ***exons*** untouched, to form an active ***mRNA***.

Ion channel

Ion channels enable ions to flow rapidly through membranes in a thermodynamically downhill direction after an electrical or chemical impulse. Their structures usually consist of 4–6 membrane-spanning ***domains***. This number determines the size of the pore and thus the size of the ion to be transported. See also ***ion pumps***.

Ionophore

A compound which can carry specific ions through membranes of cells or organelles.

Ion pumps

Ion pumps enable ions to flow through membranes in a thermodynamically uphill direction by the use of an energy source such as ***ATP*** or light. They consist of sugar-containing hetero-peptide assemblies, which open and close upon the binding and subsequent ***hydrolysis*** of ATP, usually transporting more than one ion towards the outside or the inside of the membrane. See also ***ion channel***.

Iron-responsive element

A specific base ***sequence*** in certain messenger ***RNAs*** that code for various proteins of iron ***metabolism***, which allows ***regulation*** at ***translational*** level by the ***iron-reponsive protein***.

Iron-responsive protein (IRP)

A protein that responds to the level of iron in the cell, and ***regulates*** the biosynthesis of proteins of iron ***metabolism***, by binding to the ***iron-responsive element*** on messenger ***RNA***.

Iron-sulfur cluster

A unit comprising two or more iron atoms and ***bridging*** sulfide ***ligands*** in an ***iron-sulfur protein***. The recommended designation of a ***cluster*** consists of the iron and sulfide content, in square brackets, for example ***[2Fe-2S]***, [3Fe-4S]. The possible oxidation levels are indicated by the net charge excluding the ligands, for example a ***[4Fe-4S]***$^{2+}$; [4Fe-4S]$^{+}$ (or [4Fe-4S]$^{2+;1+}$) cluster.

Iron-sulfur proteins

Proteins in which non-heme iron is ***coordinated*** with cysteine sulfur and usually also with inorganic sulfur. Divided into three major categories: ***rubredoxins***; "simple iron-sulfur proteins", containing only ***iron-sulfur clusters***, and "complex iron-sulfur proteins", containing additional active redox centers such as ***flavin***, molybdenum or ***heme***. In most iron-sulfur proteins the clusters function as electron transfer groups, but in others they have other functions such as catalysis of hydratase/dehydratase reactions, maintenance of protein structure, or ***regulation*** of activity.

IRP

See ***iron-responsive protein***.

Ischemia

Local deficiency of blood supply and hence dioxygen to an organ or tissue owing to constriction of the blood vessels or to obstruction.

Isobacteriochlorin

2,3,7,8-tetrahydroporphryin. A reduced ***porphyrin*** with two pairs of non-fused saturated carbon atoms (C2 – C3 and C7 – C8) in two of the pyrrole rings. See also ***bacteriochlorin***.

Isoenzymes

Multiple forms of ***enzymes*** arising from genetically determined differences in ***primary structure***. The term does not apply to those derived by modification of the same primary ***sequence***.

Isomerase

An ***enzyme*** of ***EC*** class 5, which catalyzes the isomerization of a ***substrate***.

Isotropy

Lack of ***anisotropy*** ; the property of molecules and materials of having identical physical properties in all directions.

Kappa(κ)-convention

See ***donor atom symbol.***

Labile

The term has loosely been used to describe either a relatively unstable and transient chemical species or a relatively ***stable*** but reactive species. See also ***inert.***

Laccase

A copper-containing ***enzyme***, benzene-1,4-diol oxidase (***EC*** 1.10.3.2), found in higher plants and microorganisms. Laccases are ***multicopper oxidases*** of wide specificity that carry out one-electron oxidation of phenolic and related compounds, and reduce O_2 to water. The enzymes are polymeric and generally contain one each of *type 1*, *type 2*, and *type 3 copper* centers per *subunit*, where the type 2 and type 3 are close together forming a tri*nuclear* copper *cluster*.

Lactoferrin

An iron-binding protein from milk, structurally similar to the ***transferrins***.

Leghemoglobin

A monomeric ***hemoglobin*** synthesized in the root nodules of leguminous plants that are host to ***nitrogen-fixing*** bacteria. Has a high affinity for dioxygen and serves as an oxygen supply for the bacteria.

Lewis acid

A molecular entity that is an electron pair acceptor and therefore able to react with a ***Lewis base*** to form a ***Lewis adduct***, by sharing the electron pair furnished by the Lewis base.

Lewis adduct

The adduct formed between a ***Lewis acid*** and a ***Lewis base.***

Lewis base

A molecular entity able to provide a pair of electrons and thus capable of ***coordination*** to a ***Lewis acid***, thereby producing a ***Lewis adduct.***

Ligand

In inorganic chemistry the ligands are the atoms or groups of atoms bound to the ***central atom*** (see also ***coordination***). The root of the word is sometimes converted into the verb to ligate, meaning to coordinate as a ligand, and the derived participles, ligating and ligated. This use should not be confused with its use to describe the action of ***ligases*** (a class of ***enzymes***). The names for anionic ligands, whether inorganic or organic, end in -o. In general, if the anion name ends in -ide, or -ate, the final -e is replaced by -o, giving -ido, and -ato, respectively. Neutral and cationic ligand names are used without modification. Ligands bonded by a single carbon atom to metals are regarded as radical substituents, their names being derived from the parent hydrocarbon, from which one hydrogen atom has been removed. In general, the final letter -e of the name is replaced by -yl.

In biochemistry the term ligand has been used more widely: if it is possible or convenient to regard part of a polyatomic molecular entity as central, then the atoms or groups or molecules bound to that part may be called ligands.

Ligand field

Ligand field theory is a modified ***crystal field*** theory that assigns certain parameters as variables rather than taking them as equal to the values found for free ions, thereby taking into account the potential covalent character of the metal-***ligand*** bond.

Ligase

An ***enzyme*** of ***EC*** class 6, also known as a synthetase, which catalyzes the formation of a bond between two ***substrate*** molecules coupled with the ***hydrolysis*** of a diphosphate bond of a ***nucleoside*** triphosphate or similar co-substrate.

Ligating

See ***ligand***.

Lipoxygenase

A non-heme iron ***enzyme*** (***EC*** 1.13.11.12) which catalyzes the ***insertion*** of O_2 into polyunsaturated fatty acids to form hydroperoxy derivatives.

Low-spin

In any ***coordination*** entity with a particular $\mathbf{d}^{\mathbf{n}}$ ($1 < \mathbf{n} < 9$) configuration and a particular geometry, if the **n** electrons are distributed so that they occupy the lowest possible energy levels, the entity is a low-spin complex. If some of the higher energy **d** orbitals are occupied before all the lower energy ones are completely filled, then the entity is a high-spin complex.

Lyase

An ***enzyme*** of ***EC*** class 4, which catalyzes the separation of a bond in a ***substrate*** molecule.

Macrophages

Blood cells which are able to ingest a wide variety of particulate materials. They are a type of ***phagocyte***.

Magnetic circular dichroism (MCD)

A measurement of ***circular dichroism*** of a material which is induced by a magnetic field applied parallel to the direction of the measuring light beam. Materials which are achiral still exhibit MCD (the Faraday effect), since the magnetic field leads to the lifting of the degeneracy of electronic orbital and spin states and to the mixing of electronic states. MCD is frequently used in combination with absorption and CD studies to effect electronic assignments. The three contributions to the MCD spectrum are the A-term, due to Zeeman splitting of the ground and/or excited degenerate states, the B-term, due to field-induced mixing of states, and the C-term, due to a change in the population of molecules over the Zeeman sublevels of a ***paramagnetic*** ground state. The C-term is observed only for molecules with ground-state paramagnetism, and becomes intense at low temperatures; its variation with field and temperature can be analyzed to provid magnetic parameters of the ground state, such as spin, *g*-factor, and zero-field splitting. Variable-temperature MCD is particularly effective in identifying and assigning electronic transitions originating from paramagnetic ***chromophores***.

Magnetic resonance imaging (MRI)

The visualization of the distribution of nuclear spins (usually water) in a body by using a magnetic field gradient (***NMR imaging***). A similar technique, but less widely used, is to visualize the distribution of ***paramagnetic*** centres (***EPR*** imaging).

Magnetic susceptibility

For ***paramagnetic*** materials the magnetic susceptibility may be measured experimentally and used to give information on the molecular magnetic dipole moment, and hence on the electronic structure of the molecules in the material. The paramagnetic contribution to the molar magnetic susceptibility of a material, χ, is related to the molecular magnetic dipole moment m by the Curie relation : $\chi = \text{constant} \times m^2/T$.

Magnetotactic

Able to orient in a magnetic field.

MCD

See ***magnetic circular dichroism***.

Menkes' disease

A sex-linked inherited disorder, causing defective gastrointestinal absorption of copper and resulting in copper deficiency early in infancy.

Met

A qualifying prefix indicating the oxidized form of the parent protein, e.g. methemoglobin.

Metabolism

The entire physical and chemical processes involved in the maintenance and reproduction of life in which nutrients are broken down to generate energy and to give simpler molecules (***catabolism***) which by themselves may be used to form more complex molecules (***anabolism***).

Metalloenzyme

An ***enzyme*** that, in the active state, contains one or more metal ions which are essential for its biological function.

Metallo-immunoassay

A technique in which ***antigen-antibody*** recognition is used, with attachment of a metal ion or metal complex to the antibody. The specific absorption or (radioactive) emission of the metal is then used as a probe for the location of the recognition sites. See also ***imaging***, ***radionuclide***.

Metallothionein

A small, cysteine-rich protein that binds heavy metal ions, such as zinc, cadmium and copper in the form of ***clusters***.

Metastable

See ***stable***.

Methane mono-oxygenase

A ***metalloenzyme*** that converts methane and dioxygen to methanol using ***NADH*** as co-***substrate***. Two types are known, one containing a ***dinuclear*** oxo-bridged iron center, the other is a copper protein.

Methanogens

Strictly ***anaerobic archaea***, able to use a variety of ***substrates*** (e.g., dihydrogen, formate, methanol, methylamine, carbon monoxide or acetate) as electron donors for the reduction of carbon dioxide to methane.

Michaelis–Menten kinetics

The dependence of the initial rate of conversion of a ***substrate*** (S), of the product (P) by an ***enzyme*** or other catalyst (E). The simplest mechanism:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P$$

yields, under initial *steady state* conditions, and [P] = 0, the Michaelis–Menten equation,

$$v = \frac{V[S]}{K_m + [S]}$$

where v is the rate of conversion (Ms^{-1}), $V = k_2[E]$ is the maximum rate at [S] = ∞ for a particular enzyme/catalyst concentration, k_2 is the turnover number (s^{-1}), and $K_m = (k_{-1} + k_2)/k_1$ is the Michaelis constant under the conditions used. In the case of an impure enzyme or catalyst, [E] is given as gl^{-1} instead of M. This equation leads to a hyperbolic dependence of v upon [S], which is frequently observed in practice even when [S] is not in great excess over [E].

Micronutrient

A compound essential for cellular growth, being present in concentrations less than about 1 mM in the growth medium (see also ***trace elements***).

Mitochondria

Cytoplasmic organelles of most ***eukaryotic*** cells, they are surrounded by a double membrane and produce ***adenosine 5′-triphosphate*** as useful energy for the cell by oxidative ***phosphorylation***. The proteins for the ***ATP***-generating electron transport of the respiration chain are located in the inner mitochondrial membrane. Mitochondria contain many ***enzymes*** of the citric acid cycle and for fatty acid β-oxidation.They also contain ***DNA*** which encodes some of their proteins, the remainder being encoded by nuclear DNA.

Mixed valency

This is one of several names, such as 'mixed oxidation state' or 'non-integral oxidation state' used to describe ***coordination*** compounds and ***clusters*** in which a metal is present in more than one level of oxidation. The importance in biology is due to the often complete delocalization of the valence electrons over the cluster, allowing efficient electron-transfer processes. See also ***oxidation number***.

Moco

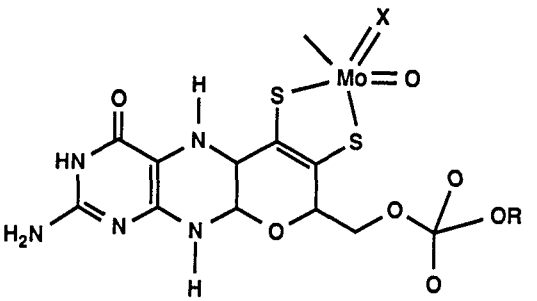
See ***molybdenum cofactor***.

Model

A synthetic ***coordination*** entity that closely approaches the properties of a metal ion in a protein and yields useful information concerning biological structure and function. Given the fact that the term is also loosely used to describe various types of molecular structures, constructed, for example, in the computer, the term ***biomimetic*** is more appropriate.

Molybdenum cofactor (Moco)

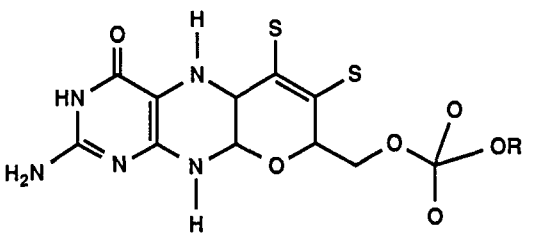
The molybdenum complex of the ***molybdopterin prosthetic group (ligand)***. In the molybdenum ***cofactor*** the minimal ***coordination*** of the Mo atom is thought to be provided by the ***chelating*** dithiolenato group of the molybdopterin and either two oxo or one oxo and one sulfido ligands.



X = O or S

Molybdopterin

The ***prosthetic group*** associated with the Mo atom of the ***molybdenum cofactor*** found in the oxo-***transferase enzymes***. The enzymes catalyze two-electron redox reactions that involve the net exchange of an oxygen atom between ***substrate*** and water. In enzymes from ***eukaryotic*** sources R = H. In bacterial enzymes R = ***nucleotide***. See also ***pterin***.



Monooxygenase

An ***enzyme*** that catalyzes the ***insertion*** of one atom of oxygen, derived from O_2, into an aromatic or aliphatic compound. The reaction is coupled to the oxidation of a co-***substrate*** such as ***NAD(P)H*** or 2-oxoglutarate.

Mössbauer effect

Resonance absorption of gamma radiation by specific nuclei arranged in a crystal lattice in such a way that the recoil momentum is shared by many atoms. It is the basis of a form of spectroscopy used for studying ***coordinated*** metal ions. The principal application in bioinorganic chemistry is ^{57}Fe. The parameters derived from the Mössbauer spectrum (isomer shift, quadrupole splitting, and the ***hyperfine*** coupling) provide information about the oxidation, spin and ***coordination*** state of the iron.

Motif

A pattern of amino acids in a protein ***sequence*** which has a specific function, e.g. metal binding. See also ***consensus sequence***.

MRI

See ***magnetic resonance imaging***.

Multicopper oxidases

A group of ***enzymes*** that oxidize organic ***substrates*** and reduce dioxygen to water. These contain a combination of copper ions with different spectral features, called ***type 1*** centers, ***type 2*** centers, and ***type 3*** centers, where the type 2 and type 3 sites are ***clustered*** together as a tri***nuclear*** unit. Well-known examples are: ***laccase***, ascorbate oxidase and ***ceruloplasmin***.

Multienzyme

A protein possessing more than one catalytic function contributed by distinct parts of a polypeptide chain (***domains***), or by distinct ***subunits***, or both.

Multiheme

Refers to a protein containing two or more ***heme*** groups.

Mu(μ)-symbol

See ***bridging ligand***.

Mutagenesis

The introduction of permanent heritable changes, i.e. ***mutations*** into the ***DNA*** of an organism. In case of site-directed mutagenesis the substitution or modification of a single amino acid at a defined location in a protein is performed by changing one or more ***base pairs*** in the DNA using recombinant DNA technology.

Mutation

A heritable change in the ***nucleotide sequence*** of genomic ***DNA*** (or ***RNA*** in RNA viruses), or in the number of ***genes*** or chromosomes in a cell, which may occur spontaneously or be brought about by chemical mutagens or by radiation (induced mutation).

Myocrysin

See ***gold drugs***.

Myoglobin

A monomeric dioxygen-binding heme protein of muscle tissue, structurally similar to a ***subunit*** of ***hemoglobin***.

NAD^+

Oxidized form of nicotinamide adenine dinucleotide. Note that despite the plus sign in the symbol, the ***coenzyme*** is anionic under normal physiological conditions.

NADH

Reduced form of nicotinamide adenine dinucleotide.

$NADP^+$

Oxidized form of nicotinamide adenine dinucleotide phosphate. Note that despite the plus sign in the symbol, the ***coenzyme*** is anionic under normal physiological conditions.

NADPH

Reduced form of nicotinamide adenine dinucleotide phosphate.

nif

A set of about 20 ***genes*** required for the assembly of the ***nitrogenase enzyme*** complex.

Nitrate reductase

A ***metalloenzyme***, containing molybdenum, that reduces nitrate to nitrite.

Nitrite reductase

A ***metalloenzyme*** that reduces nitrite. ***Dissimilatory*** nitrite reductases contain copper and reduce nitrite to nitrogen monoxide. ***Assimilatory*** nitrite reductases contain ***siroheme*** and ***iron-sulfur clusters*** and reduce nitrite to ammonia.

Nitrogenase

An ***enzyme*** complex (***EC*** 1.18.6.1) from bacteria that catalyzes the reduction of dinitrogen to ammonia: $N_2 + 8e^- + 10H^+ \rightarrow 2NH_4^+ + H_2$ with the simultaneous ***hydrolysis*** of at least 16 ***ATP*** molecules. The electron donor is reduced ***ferredoxin*** or flavodoxin. Dihydrogen is always a co-product of the reaction. Ethyne (acetylene) can also be reduced to ethene (ethylene) and in some cases ethane. All nitrogenases are ***iron-sulfur proteins***. Three different types which differ in the type of ***cofactor*** present, have been identified: molybdenum-nitrogenase (the most common, which contains the iron-molybdenum ***cofactor***), vanadium-nitrogenase, and iron-only nitrogenase. See also ***FeMo-cofactor***.

Nitrogen fixation

The ***assimilation*** of dinitrogen by microbial reduction to ammonia and conversion into organonitrogen compounds such as amino acids. Only a limited number of microorganisms are able to fix nitrogen. See also ***nitrogenase***.

NMR

See ***nuclear magnetic resonance spectroscopy***.

N-terminal amino-acid residue

See ***amino-acid residue***.

Nuclearity

The number of ***central atoms*** joined in a single ***coordination*** entity by ***bridging ligands*** or metal-metal bonds is indicated by dinuclear, trinuclear, tetranuclear, polynuclear, etc.

Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy makes it possible to discriminate nuclei, typically protons, in different chemical environments. The electron distribution gives rise to a chemical shift of the resonance frequency. The

chemical shift, δ, of a nucleus is expressed in parts per million (ppm) by its frequency, ν_n, relative to a standard, ν_{ref}, and defined as $\delta = 106\ (\nu_n - \nu_{ref})/\nu_o$, where ν_o is the operating frequency of the spectrometer. It is an indication of the chemical state of the group containing the nucleus. More information is derived from the ***spin-spin couplings*** between nuclei, which give rise to multiplet patterns. Greater detail may be derived from two- or three-dimensional techniques. These use pulses of radiation at different nuclear frequencies, after which the response of the spin system is recorded as a free-induction decay (FID). Multi-dimensional techniques, such as COSY and NOESY, make it possible to deduce the structure of a relatively complex molecule such as a small protein (molecular weight up to 25 000). In proteins containing ***paramagnetic*** centres, nuclear ***hyperfine*** interactions can give rise to relatively large shifts of resonance frequencies known as contact and pseudo-contact (dipolar) shifts, and considerable increases in the nuclear spin relaxation rates. From this type of measurement, structural information can be obtained about the paramagnetic site.

Nucleation

The process by which nuclei are formed, usually in solution. The term "nucleus" as used here is defined as the smallest solid phase aggregate of atoms, molecules or ions which is formed during a precipitation and which is capable of spontaneous growth.

Nucleic acids

Macromolecules composed of ***sequences*** of ***nucleotides*** that perform several functions in living cells, e.g. the storage of ***genetic*** information and its transfer from one generation to the next (***DNA***), and the ***expression*** of this information in protein synthesis (***mRNA, tRNA***), and may act as functional components of subcellular units such as ***ribosomes*** (***rRNA***). ***RNA*** contains D-ribose, DNA contains 2-deoxy-D-ribose as the sugar component. Currently, synthetic nucleic acids can be made consisting of hundreds of ***nucleotides***. See also ***oligonucleotide***.

Nucleobases

See ***nucleosides***.

Nucleosides

Compounds in which a purine or pyrimidine base is β-*N*-glycosidically bound to C-1 of either 2-deoxy-D-ribose or of D-ribose, but without any phosphate groups. The common nucleosides in biological systems are adenosine, guanosine, cytidine, and uridine (which contain ribose) and deoxyadenosine, deoxyguanosine, deoxycytidine and thymidine (which contain deoxyribose).

Nucleotides

Nucleosides with one or more phosphate groups esterified mainly to the 3′- or the 5′- position of the sugar moiety. Nucleotides found in cells are adenylic acid, guanylic acid, uridylic acid, cytidylic acid, deoxyadenylic acid, deoxyguanylic acid, deoxycytidylic acid and thymidylic acid. See also ***adenosine 5′-triphosphate***, ***NAD$^+$***, ***NADP$^+$***.

Octahedron

See ***coordination***.

ODMR

See ***optically detected magnetic resonance***.

OEC

See ***oxygen-evolving complex***.

Oligonucleotide

Macromolecules composed of short ***sequences*** of ***nucleotides*** that are usually synthetically prepared and used e.g. in ***site-directed mutagenesis***.

Operon

A functional unit consisting of a ***promoter***, an operator and a number of structural ***genes***, found mainly in ***prokaryotes***. An example is the operon ***nif***. The structural genes commonly code for several functionally related ***enzymes***, and although they are ***transcribed*** as one (polycistronic) ***mRNA***, each has its separate ***translation*** initiation site. In the typical operon, the operator region acts as a controlling element in switching on or off the synthesis of mRNA.

Optically detected magnetic resonance (ODMR)

A double resonance technique in which transitions between spin sublevels are detected by optical means. Usually these are sublevels of a triplet, and the transitions are induced by microwaves.

Ovotransferrin

An iron-binding protein from eggs, structurally similar to the ***transferrins***.

Oxidase

An ***enzyme*** which catalyzes the oxidation of ***substrates*** by O_2.

Oxidation number

The oxidation number of an element in any chemical entity is the number of charges which would remain on a given atom if the pairs of electrons in each bond to that atom were assigned to the more electronegative member of the bond pair. The oxidation (Stock) number of an element is indicated by a roman numeral placed in parentheses immediately following the name (modified if necessary by an appropriate ending) of the element to which it refers. The oxidation number may be positive, negative or zero. Zero, not a roman numeral, is represented by the usual cipher, 0. The positive sign is never used. An oxidation number is always positive unless the minus sign is explicitly used. Note that it cannot be non-integral (see also ***mixed valency***). Non-integral numbers may seem appropriate in some cases where a charge is spread over more than one atom, but such a use is not encouraged. In such ambiguous cases, the charge number, which designates ionic charge, can be used. A charge (Ewens–Bassett) number is a number in parentheses written without a space immediately after the name of an ion, and whose magnitude is the ionic charge. Thus the number may refer to cations or anions, but never to neutral species. The charge is written in arabic numerals and followed by the sign of the charge. In a ***coordination*** entity, the oxidation number of the ***central atom*** is defined as the charge it would bear if all the ***ligands*** were removed along with the electron pairs that were shared with the central atom. Neutral ligands are formally removed in their closed-shell configurations. Where it is not feasible or reasonable to define an oxidation state for each individual member of a group or ***cluster***, it is again recommended that the overall oxidation level of the group be defined by a formal ionic charge, the net charge on the coordination entity.

Oxidative addition

The ***insertion*** of a metal of a ***coordination*** entity into a covalent bond involving formally an overall two-electron loss on one metal or a one-electron loss on each of two metals.

Oxidoreductase

An ***enzyme*** of ***EC*** class 1, which catalyzes an oxidation-reduction reaction.

Oxygen-evolving complex (OEC)

The ***enzyme*** which catalyzes the formation of O_2 in ***photosynthesis***. Contains a ***cluster*** of probably four manganese ions.

Paramagnetic

Substances having a positive ***magnetic susceptibility*** are paramagnetic. They are attracted by a magnetic field.

PCR

See ***polymerase chain reaction***.

Periplasm

The fluid occupying the space between the inside and outside cellular membranes of bacteria.

Peroxidase

A heme protein (donor:hydrogen peroxide ***oxidoreductase, EC*** class 1.11.1) which catalyzes the one-electron oxidation of a ***substrate*** by dihydrogen peroxide. Substrates for different peroxidases include various organic compounds, ***cytochrome*** *c*, halides, and Mn^{2+}.

Phagocyte

A cell which is able to ingest, and often to digest, large particles such as bacteria and dead tissue cells.

Phosphatase

An ***enzyme*** that catalyzes the hydrolysis of orthophosphoric monoesters. Alkaline phosphatases (***EC*** 3.1.3.1) have an optimum pH above 7 and are zinc-containing proteins. Acid phosphatases (***EC*** 3.1.3.2) have an optimum pH below 7 and some of these contain a ***dinuclear*** center of iron, or iron and zinc.

Phosphorylation

A process involving the transfer of a phosphate group (catalyzed by ***enzymes***) from a donor to a suitable acceptor; in general an ester linkage is formed, for example :

ATP + alcohol → ADP + phosphate ester

Photolysis

A light-induced bond cleavage. The term is often used incorrectly to describe irradiation of a sample.

Photosynthesis

A ***metabolic*** process in plants and certain bacteria, using light energy absorbed by ***chlorophyll*** and other photosynthetic pigments for the reduction of CO_2, followed by the formation of organic compounds. See also ***photosystem***.

Photosystem

A membrane-bound protein complex in plants and ***photosynthetic*** bacteria, responsible for light harvesting and primary electron transfer. Comprises light-harvesting pigments such as ***chlorophyll***; a primary electron-transfer center, and secondary electron carriers. In green plant photosynthesis, Photosystem I transfers electrons from ***plastocyanin*** to a ***[2Fe-2S] ferredoxin***, and contains ***iron-sulfur proteins***. Photosystem II transfers electrons from the ***oxygen-evolving complex*** to plastoquinone, and contains an iron center.

Phytochelatin

A peptide of higher plants, consisting of polymers of 2-11 glutathione (γ-glutamyl-cysteinyl-glycine) groups, which binds heavy metals.

Picket-fence porphyrin

A ***porphyrin*** with a protective enclosure for binding oxygen at one side of the ring that is used to mimic the dioxygen-carrying properties of the ***heme*** group. See also ***biomimetic***.

Plasma

In biology this term has the following three meanings :

(1) Fluid component of blood in which the blood cells and platelets are suspended ('blood plasma'). N.B. Note the distinction between plasma, which describes a part of the blood (the fluid part of blood, outside the blood cells) and serum, which describes a fraction derived from blood by a manipulation (the fluid which separates when blood coagulates).

(2) Fluid component of semen produced by the accessory glands, the seminal vesicles, the prostate, and the bulbo-urethal glands.

(3) Cell substance outside the nucleus (***cytoplasm***).

Plasmid

An extrachromosomal ***genetic*** element consisting generally of circular double-stranded ***DNA***, which can replicate independently of chromosomal DNA. R-plasmids are responsible for the mutual transfer of antibiotic resistance among microbes. Plasmids are used as vectors for ***cloning*** DNA in bacteria or yeast host cells.

Plastocyanin

An ***electron transfer protein***, containing a ***type 1 copper*** site, involved in plant and cyanobacterial ***photosynthesis***, which transfers electrons to ***Photosystem I***.

Polydentate

See ***chelation***, ***donor atom symbol***.

Polyhedral symbol

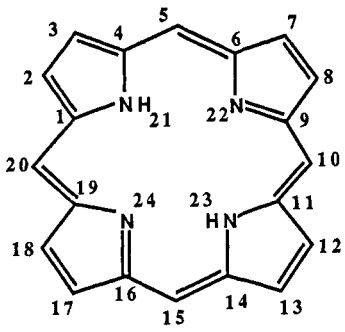
The polyhedral symbol indicates the geometrical arrangements of the coordinating atoms about the ***central atom***. It consists of one or more capital italic letters derived from common geometric terms (tetrahedron, square plane, octahedron, etc.) which denote the idealized geometry of the ***ligands*** around the ***coordination*** center, and an arabic numeral that is the coordination number of the central atom. The polyhedral symbol is used as an affix, enclosed in parentheses, and separated from the name by a hyphen. Examples are *T*-4, *SP*-4, *TBPY*-5, *SPY*-5, *OC*-6, and *CU*-8.

Polymerase chain reaction (*PCR*)

A laboratory technique, to rapidly amplify pre-determined regions of double stranded ***DNA***. Generally involves the use of a heat-stable DNA polymerase.

Porphyrin

A macrocyclic molecule that contains four pyrrole rings linked together by single carbon atom bridges between the alpha positions of the pyrrole rings. Porphyrins usually occur in their dianionic form ***coordinated*** to a metal ion.



Power saturation

A phenomenon used in ***electron paramagnetic resonance spectroscopy*** to estimate the electron-spin relaxation times, providing information about distances between ***paramagnetic*** centers.

Primary structure

The amino-acid ***sequence*** of a protein or ***nucleotide*** sequence of ***DNA*** or ***RNA***.

Prokaryote

A unicellular organism characterized by the absence of a membrane-bound nucleus. See also ***eukaryotes***.

Promoter

The ***DNA*** region, usually upstream to the coding ***sequence*** of a ***gene*** or ***operon***, which binds and directs ***RNA*** polymerase to the correct transcriptional start site and thus permits ***transcription*** at a specific initiation site.

N.B. In catalysis a promoter is used differently: a co-catalyst usually present in much smaller amounts than the catalyst.

Prosthetic group

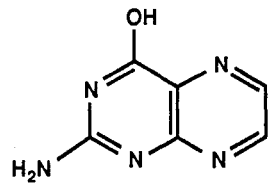
A tightly bound, specific nonpolypeptide unit in a protein determining and involved in its biological activity. See also ***cofactor***.

Protoporphyrin IX

The ***porphyrin ligand*** of ***heme*** b. Heme b is a Fe(II) porphyrin complex readily isolated from the hemoglobin of beef blood, but also found in other proteins including other ***hemoglobins, myoglobins, cytochromes P-450, catalases, peroxidases*** as well as b type ***cytochromes***. Protoporphyrin IX contains four methyl groups in positions 2, 7, 12 and 18, two vinyl groups in positions 3 and 8 and two propionic acid groups in positions 13 and 17.

Pterin

2-Amino-4-hydroxypteridine. See also **molybdopterin**.



Quaternary structure

The level of structural organization in oligomeric proteins (i.e., those composed of more than one ***subunit***) represented by the number and arrangement of the subunits and the interactions between them .

Racemic

Pertaining to a racemate, an equimolar mixture of a pair of ***enantiomers***. It does not exhibit optical activity.

Radical

A molecular entity possessing one or more unpaired electrons, formerly often called "free radical". A radical may be charged, positively (radical cation) or negatively (radical anion). ***Paramagnetic*** metal ions are not normally regarded as radicals.

Radionuclide

A radioactive nuclide. The term nuclide implies an atom of specified atomic number and mass number. In the study of biochemical processes, radioactive isotopes are used for labelling compounds that subsequently are used to investigate various aspects of the reactivity or ***metabolism*** of proteins, carbohydrates and lipids or as sources of radiation in ***imaging***. The fate of the radionuclide in reactive products or metabolites is determined by following (counting) the emitted radiation. Prominent among the radionuclides used in biochemical research are: ^{3}H, ^{14}C, ^{32}P, ^{35}Ca, ^{99m}Tc, ^{125}I and ^{131}I. See also ***imaging***.

Rate-controlling step

A rate-controlling (rate-determining or rate-limiting) step in a reaction occurring by a composite mechanism is an elementary reaction, the rate constant for which exerts a dominant effect—stronger than that of any other rate constant—on the overall rate.

Redox potential

Any oxidation-reduction (redox) reaction can be divided into two half reactions: one in which a chemical species undergoes oxidation and one in which another chemical species undergoes reduction. If a half-reaction is written as a reduction, the driving force is the reduction potential. If the half-reaction is written as oxidation, the driving force is the oxidation potential related to the reduction potential by a sign change. So the redox potential is the reduction/oxidation potential of a compound measured under standard conditions against a standard reference half-cell. In biological systems the standard redox potential is defined at pH = 7.0 versus the hydrogen electrode and partial pressure of hydrogen = 1 bar. See also ***electrode potential***.

Reductase

See ***oxidoreductase***.

Reductive elimination

The reverse of ***oxidative addition***.

Regulation

Refers to control of activity of an ***enzyme*** (system) or ***gene expression***.

Relative configuration

The ***configuration*** of any stereogenic (asymmetric) centre with respect to any other stereogenic center contained within the same molecular entity. A stereogenic unit is a grouping within a molecular entity that may be considered a focus of ***stereoisomerism***.

Relaxation

If a system is disturbed from its state of equilibrium it relaxes to that state, and the process is referred to as relaxation.

Resonance Raman spectroscopy

A spectroscopic technique increasingly used in bioinorganic chemistry for characterization and assignment of vibrations directly connected with a ***chromophore***, as well for the assignment of the chromophore. The excitation frequency is applied close to the absorption maximum of the chromophore. Particularly useful for deeply coloured species.

Ribonucleic acids (RNA)

Linear polymer molecules composed of a chain of ribose units linked between positions 3 and 5 by phosphodiester groups. The bases adenine or guanine (via atom N-9) or uracil or cytosine (via atom N-1), respectively, are attached to ribose at its atom C-1 by β-*N*-glycosidic bonds (see ***nucleotides***). The three most important types of RNAs in the cell are: messenger RNA (mRNA), transfer RNA (tRNA), ribosomal RNA (rRNA).

Ribonucleotide reductases

Enzymes (***EC*** 1.17.4.1-2), which catalyze the reduction of ribonucleotide diphosphates or triphosphates to the corresponding deoxyribonucleotides by a ***radical***-dependent reaction. The enzyme of animal, yeast and ***aerobic*** *E.coli* cells contains an oxo-bridged ***dinuclear*** iron center and a tyrosyl radical cation, and uses thioredoxin, a thiol-containing protein, as reductant. At least three other ribonucleotide reductases are known from bacteria, containing, respectively, an ***iron-sulfur cluster*** with a glycyl radical, adenosyl***cobalamin***, and a dinuclear manganese ***cluster***.

Ribosomes

A subcellular unit composed of specific ***rRNA*** and proteins that are responsible for the ***translation*** of ***mRNA*** into protein synthesis.

Ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco)

A magnesium-dependent ***enzyme*** (***EC*** 4.1.1.39), the primary enzyme of carbon dioxide fixation in plants and ***autotrophic*** bacteria. It catalyzes the synthesis of 3-phospho-D-glycerate from ribulose bisphosphate and also the oxidation of ribulose bisphosphate by O_2 to 3-phospho-D-glycerate and 2-phosphoglycolate.

Rieske iron-sulfur protein

An ***iron-sulfur protein*** of the ***mitochondrial*** respiratory chain, in which the ***[2Fe-2S] cluster*** is ***coordinated*** to two sulfur ***ligands*** from cysteine and two imidazole ligands from histidine. The term is also applied to similar proteins isolated from ***photosynthetic*** organisms and microorganisms, and other proteins containing [2Fe-2S] clusters with similar coordination.

RNA

See ***ribonucleic acids***.

Rubisco

See ***ribulose-1,5-bisphosphate carboxylase/oxygenase***.

Rubredoxin

An ***iron-sulfur protein*** without ***acid-labile sulfur***, in which an iron center is ***coordinated*** by four sulfur-containing ***ligands***, usually cysteine. The function, where known, is as an electron carrier.

Rubrerythrin

A protein assumed to contain both a ***rubredoxin***-like iron center and a ***hemerythin***-like ***dinuclear*** iron center.

Rusticyanin

An ***electron transfer protein***, containing a ***type 1 copper*** site, from the ***periplasm*** of the iron-oxidizing bacterium *Thiobacillus ferrooxidans*.

Scavenger

A substance that reacts with (or otherwise removes) a trace component or ***traps*** a reactive reaction intermediate (as in the scavenging of ***radicals*** or free electrons in radiation chemistry).

Schiff bases

Imines bearing a hydrocarbyl group on the nitrogen atom: $R_2C{=}NR'$ ($R' \neq H$).

Secondary structure

Level of structural organization in proteins described by the folding of the polypeptide chain into structural ***motifs*** such as ***alpha helices*** and ***beta sheets***, which involve hydrogen bonding of backbone atoms. Secondary structure is also formed in ***nucleic acids***, especially in single-stranded ***RNA's*** by internal ***base pairing***.

Sequence

The order of neighbouring amino acids in a protein or the purine and pyrimidine bases in ***RNA*** or ***DNA***. See also ***primary structure***.

Sequence-directed mutagenesis

See ***mutagenesis***.

Serum

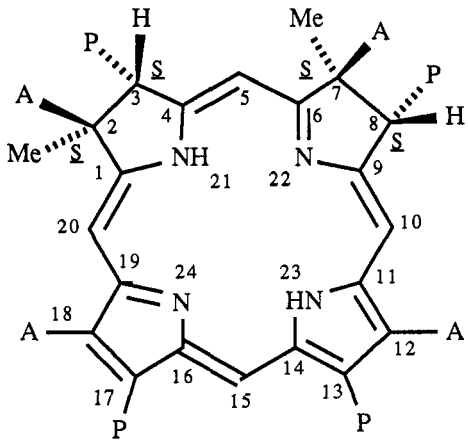
See ***plasma***.

Siderophore

Generic term for Fe(III)-complexing compounds released into the medium by bacteria for the purpose of ***scavenging*** iron.

Siroheme

A ***heme***-like ***prosthetic group*** found in a class of ***enzymes*** that catalyze the six-electron reduction of sulfite and nitrite to sulfide and ammonia, respectively. See also ***sulfite reductase*** and ***nitrite reductase***.



P = Propionic acid
A = Acetic acid
Me = Methyl

Site-directed mutagenesis

See ***mutagenesis***.

SOD

See ***superoxide dismutase***.

Soft acid

See ***hard acid***.

Soft base

See ***hard base***.

Solvation

Any stabilizing interaction of a solute (or solute moiety) and the solvent or a similar interaction with solvent of groups of an insoluble material (i.e., the ionic groups of an ion-exchange resin). They generally involve electrostatic forces and Van der Waals forces, as well as chemically more specific effects such as hydrogen bond formation.

Solvolysis

Reaction with a solvent involving the rupture of one or more bonds in the reacting solute.

Soret band

A very strong absorption band in the blue region of the optical absorption spectrum of a ***heme*** protein.

Speciation

Refers to the chemical form or compound in which an element occurs in both non-living and living systems. It may also refer to the quantitative distribution of an element. In biology, it refers to the origination of a new species. See also ***bioavailability.***

Spin label

A ***stable paramagnetic*** group that is attached to a part of another molecular entity whose microscopic environment is of interest and may be revealed by the ***electron paramagnetic resonance*** spectrum of the spin label. When a simple paramagnetic molecular entity is used in this way without covalent attachment to the molecular entity of interest it is frequently referred to as a "spin probe".

Spin-orbit coupling

The interaction of the electron spin magnetic moment with the magnetic moment due to the orbital motion of the electron.

Spin probe

See ***spin label.***

Spin-spin coupling

The interaction between the spin magnetic moments of different electrons and/or nuclei. In ***NMR spectroscopy*** it gives rise to multiplet patterns, and cross-peaks in two-dimensional NMR spectra. Between electron and nuclear spins this is termed the nuclear ***hyperfine*** interaction. Between electron spins it gives rise to relaxation effects and splitting of the ***EPR*** spectrum.

Spin trapping

In certain solution reactions a transient ***radical*** will interact with a ***diamagnetic*** reagent to form a more "persistent" radical. The product radical accumulates to a concentration where detection and, frequently, identification are possible by ***electron paramagnetic resonance spectroscopy***. The key reaction is usually one of attachment ; the diamagnetic reagent is said to be a "spin trap" , and the persistent product radical is then the "spin adduct".

Square plane

See ***coordination***.

Stability constant

An equilibrium constant that expresses the propensity of a species to form from its component parts. The larger the stability constant, the more ***stable*** is the species. The stability constant (formation constant) is the reciprocal of the instability constant (dissociation constant).

Stable

Stable is a term describing a system in a state of equilibrium corresponding to a local minimum of the appropriate thermodynamic potential for the specified constraints on the system. Stability cannot be defined in an absolute sense, but if several states are in principle accessible to the system under given

conditions, that with the lowest potential is called the stable state, while the other states are described as metastable. Unstable states are not at a local minimum. Transitions between metastable and stable states occur at rates which depend on the magnitude of the appropriate activation energy barriers which separate them.

Steady state

If during the course of a chemical reaction the concentration of an intermediate remains constant, the intermediate is said to be in a steady state. In a static system a reaction intermediate reaches a steady-state if the processes leading to its formation and those removing it are approximately in balance. The steady-state hypothesis leads to a great simplification in reaching an expression for the overall rate of a composite reaction in terms of the rate constants for the individual elementary steps. Care must be taken to apply the steady-state hypothesis only to appropriate reaction intermediates. An intermediate such as an atom or a free ***radical***, present at low concentrations, can usually be taken to obey the hypothesis during the main course of the reaction. In a flow system a steady-state may be established even for intermediates present at relatively high concentrations.

Stellacyanin

An ***electron transfer protein***, containing a ***type 1 copper*** site, isolated from exudates of the Japanese lacquer tree.

Stereochemical

Refers to the three-dimensional view of a molecule either as such or in a projection.

Stereoisomerism

Isomerism due to difference in the spatial arrangement of atoms without any difference in connectivity or bond multiplicity between the isomers.

Stock number

See ***oxidation number***.

Substrates

(1) A chemical species of particular interest, the reaction of which with some other chemical reagent is under observation (e.g. a compound that is transformed under the influence of a catalyst).

(2) The chemical entity whose conversion to a product or products is catalyzed by an ***enzymes***.

(3) A solution or dry mixture containing all ingredients which are necessary for the growth of a microbial culture or for product formation.

(4) A component in the nutrient medium, supplying the organisms with carbon (C-substrate), nitrogen (N-substrate) etc.

Subunit

An individual polypeptide chain in a protein, containing more than one polypeptide chain. Different types of subunits are frequently designated by α, β, γ, etc.

Sulfite reductase

Enzymes (***EC*** 1.8.99.1, 1.8.7.1, 1.8.1.2) which catalyze the reduction of sulfite to sulfide. All known enzymes of this type contain ***siroheme*** and ***iron-sulfur clusters***.

Superhyperfine

See ***electron paramagnetic resonance spectroscopy***.

Superoxide dismutases (*SOD*)

Enzymes (***EC*** 1.15.1.1) which catalyze the ***dismutation*** reaction of superoxide anion to dihydrogen peroxide and dioxygen. The enzymes have ***active sites*** containing either copper and zinc (Cu/Zn-superoxide dismutase), or iron (Fe-superoxide dismutase), or manganese (Mn-superoxide dismutase).

Supramolecular chemistry

This is defined as the chemistry of molecular assemblies and of the intermolecular bond, as "chemistry beyond the molecule", bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces. Thus, supramolecular chemistry may be considered to represent a generalized ***coordination*** chemistry extending beyond the coordination of ***transition elements*** by organic and inorganic ***ligands*** to the bonding of all kinds of ***substrates***; cationic, anionic and neutral species of either inorganic, organic or biological nature.

Syn

See ***anti***.

Synthase

An ***enzyme*** that catalyzes a reaction in which a particular molecule is synthesized, not necessarily by formation of a bond between two molecules (contrast ***synthetase***).

Synthetase

See ***ligase***.

Tertiary structure

The overall three-dimensional structure of a ***biopolymer***. For proteins this involves the side chain interactions and packing of ***secondary structure motifs***. For ***nucleic acids*** this may be the packing of stem-loops or supercoiling of ***double helices***.

Tetrahedron

See ***coordination***.

Tetrahydrofolates

Reduced ***folate*** derivatives that contain additional hydrogen atoms in positions 5, 6, 7 and 8. Tetrahydrofolates are the carriers of activated one carbon units and are important in the biosynthesis of amino acids and precursors needed for ***DNA*** synthesis. See also ***folate coenzymes***.

Thalassemia

A chronic inherited disease characterized by defective synthesis of ***hemoglobin***. Defective synthesis of the α chain of hemoglobin is called α-thalassemia and defective synthesis of the β chain of hemoglobin is called β-thalassemia. Thalassemias result in anemia that can be severe and are found more frequently in areas where malaria is endemic.

Therapeutic index

For a substance used to alleviate disease, pain or injury the therapeutic index is the ratio between toxic and therapeutic doses (the higher the ratio, the greater the safety of the therapeutic dose).

Thermolysin

A calcium- and zinc-containing neutral protease (***EC*** 3.4.24.27) isolated from certain bacteria.

Thermolysis

An uncatalyzed bond cleavage resulting from exposure of a compound to a raised temperature.

Thylakoids

Enclosed membrane structures inside ***chloroplasts*** and ***photosynthetic*** bacteria.

Toxicity

The action of poisons (including ***xenobiotics***) on biochemical reactions or processes in living organisms or ecological systems. A study of this action is the subject matter of toxicology.

Trace elements

Elements required for physiological functions in very small amounts that vary for different organisms. Included among the trace elements are Co, Cu, F, Fe, I, Mn, Mo, Ni, Se, V, W, and Zn. Excess mineral intake may produce toxic symptoms.

trans

In inorganic nomenclature a structural prefix designating two groups directly across a ***central atom*** from each other (not generally recommended for precise nomenclature purposes of complicated systems). See also ***cis***.

Transcription

The process by which the ***genetic*** information encoded in a linear ***sequence*** of ***nucleotides*** in one strand of ***DNA*** is copied into an exactly complementary sequence of ***RNA***.

Transduction

(1) The transfer of ***genetic*** information from one bacterium to another by means of a transducing bacteriophage. When the phage is grown on the first host, a fragment of the host ***DNA*** can be incorporated into the phage particles. This foreign DNA can be transferred to the second host upon infection with progeny phage from the first experiment.

(2) In cell biology the transduction of a signal (mechanical signal, hormone, etc.) to cells or tissues summarizes the chain of events between the primary reception of the signal and the final response (change in growth and/or ***metabolism***) of the target cells or tissues. Inorganic substances (e.g., calcium ions) are frequently involved in the transduction of signals.

Transferase

An ***enzyme*** of ***EC*** class 2, which catalyzes the transfer of a group from one ***substrate*** to another.

Transferrin

An iron-transport protein of blood ***plasma***, which comprises two similar iron-binding ***domains*** with high affinity for Fe(III). Similar proteins are found in milk (lactoferrin) and eggs (ovotransferrin).

Transition element

A transition element is an element whose atom has an incomplete **d**-sub-shell, or which gives rise to a cation or cations with an incomplete **d**-sub-shell. The First Transition Series of elements is Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu. The Second and Third Transition Series are similarly derived : these include the lanthanoids (lanthanides) and actinoids (actinides) respectively which are designated inner (or **f**) transition elements of their respective Periods in the Periodic Table.

Translation

The unidirectional process that takes place on the ***ribosomes*** whereby the ***genetic*** information present in an ***mRNA*** is converted into a corresponding ***sequence*** of amino acids in a protein.

Trapping

The interception of a reactive molecule or reaction intermediate so that it is removed from the system or converted into a more ***stable*** form for study or identification.

Type 1, 2, 3 copper

Different classes of copper-***binding sites*** in proteins, classified by their spectroscopic properties as Cu(II). In type 1, or ***blue copper*** centers the copper is ***coordinated*** to at least two imidazole nitrogens from histidine and one sulfur from cysteine. They are characterized by small copper ***hyperfine*** couplings and a strong visible absorption in the Cu(II) state. In type 2, or non-blue copper sites, the copper is mainly bound to imidazole nitrogens from histidine. Type 3 copper centers comprise two spin-coupled copper ions, bound to imidazole nitrogens.

Tyrosinase

A copper protein containing an ***antiferromagnetically*** coupled ***dinuclear*** copper unit (***type 3*** like site) which oxygenates the tyrosine group to catechol and further oxidizes this to the quinone.

Urease

A nickel ***enzyme***, urea amidohydrolase (***EC*** 3.5.1.5), that catalyzes the ***hydrolysis*** of urea to ammonia and carbon dioxide. The ***active site*** comprises two Ni(II) ions, bridged by a carbamate.

Vitamin B-12

See ***cobalamin***.

Wild type

The most frequently encountered genotype in natural breeding populations.

Wilson's disease

An inherited condition in which copper fails to be excreted in the bile. Copper accumulates progressively in the liver, brain, kidney and red blood cells. As the amount of copper accumulates hemolytic anaemia, chronic liver disease and a neurologic syndrome develop. See also ***chelation therapy***.

XANES

Acronym for X-ray absorption near edge structure. See ***extended X-ray absorption fine structure***.

Xenobiotic

A xenobiotic (Greek, xenos "foreign"; bios "life") is a compound that is foreign to a living organism. Principal xenobiotics include: drugs, carcinogens and various compounds that have been introduced into the environment by artificial means.

X-ray absorption near edge structure (XANES)

See ***extended X-ray absorption fine structure***.

Zinc finger

A ***domain***, found originally in certain ***DNA***-binding proteins and subsequently in other classes of proteins, comprising a ***helix***-loop structure in which a zinc ion is ***coordinated*** to 2–4 cysteine sulfurs, the remaining ***ligands*** being histidines. In many proteins of this type the domain is repeated several times.

Zwitterionic compound

A neutral compound having electrical charges of opposite sign, delocalized or not, on adjacent or non-adjacent atoms.