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CRITICAL SURVEY OF STABILITY CONSTANTS OF COMPLEXES OF THIOCYANATE ION**

(Technical Report)

Prepared for publication by
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Critical survey of stability constants of complexes of thiocyanate ion (Technical Report)

Abstract: Presdented is a review of the stability constants for metal complexes with thiocyanate ion. The literature data presented is critically discussed and recommended values, where warranted, listed from the many studies cited.

I. INTRODUCTION

The thiocyanate ion, SCN^-, is an interesting and widely studied ligand, which combines with a variety of metal ions, and whose chemistry is made the more challenging by its ambidentate nature, forming either thiocyanato (M-SCN) or isothiocyanato (M-NCS) complexes. Stable complexes are known in both aqueous and nonaqueous solution and the stability constants (and/or free energies of reactions) vary from very small to very large, depending on the metal ion in question. Investigations of these complexes are extensive, and the purpose here is to highlight these investigations, and to review their findings.

The measurement of metal-ligand stability constants can be carried out in many different ways, and a variety of possible methods have been applied in studying metal thiocyanate complexation. It is interesting to note that several of the classical experimental methods for measuring stability constants were in fact developed with measurements of metal thiocyanate complexes. Leden's graphical procedure, for instance, originated with potentiometric measurement of cadmium isothiocyanate (41L), and the spectrophotometric slope-ratio method of Harvey and Manning was first applied to iron(III) isothiocyanate (50H). Similarly the polarograpahic procedure of DeFord and Hume, to which numerous computer generated stability constant calculations have been compared, originated with studies of cadmium isothiocyanate complexes (51D).

The accurate measurement of stability constant values requires careful attention to experimental detail (77B). Results reported in the literature without complete citation of experimental details cannot be recommended (89T), for they cannot be reproduced in other laboratories, and unfortunately much of the reported data for metal thiocyanate complexes falls into this category. Among the experimental factors effecting β_j values are temperature control, accurate measurement of concentration of reacting species, effects of solvent upon the equilibrium of interest, choice of diverse ions for ionic strength adjustment, ability of the measurement type (optical, electrical, thermal, *etc.*) to perceive the desired reaction, method of data calculation, and effect of competing reactions. This latter point needs further explanation for there are several competing reactions that can influence the desired equilibrium between metal and ligand. The metal ion can, and frequently does, undergo other reactions with solvent and/or with ionic strength adjusting components. It must be known beforehand if these are sufficiently extensive to warrant adjustment of experimental conditions and/or corrective calculations. The ligand too, generally the salt of a weak acid, is often influenced by protonation and/or other side reactions significant with regard to the reaction of interest. Frequently proper pH control can minimize many of the possible side reactions. The alternative is to measure the respective stability constants for each side reaction and when appropriate calculate adjustment to the experimental data.

Thermochemical values of free energy, enthalpy and entropy are frequently studied along with stability constant values, and have been summarized elsewhere (63W, 67A, 73A). The same criteria of careful consideration to experimental detail apply here also. In addition these values sometimes result from calorimetric measurements. Here, too, careful control of temperature and heat losses is essential.

The thiocyanate ligand has been the subject of general reviews (75N, 79G). Its ambidentate nature, bonding through either sulfur or nitrogen, has been the focus of considerable interest (66Bu, 83R), with the mode of bonding used to describe the nature of central metal species as hard "class a" (M-N), or soft "class b" (M-S) (58A, 63P, 64Ba, 68A, 71N). With some metals the thiocyanate ion can also serve as a bridging ligand, forming either isopoly or heteropoly complexes (68B). Experimental evidence for the mode of bonding comes primarily from infrared data (60M, 62Tr, 65Fo, 65*K*, 66Cl, 67S, 71As, 71B) or other measurements (64T, 69Br, 74B, 82Z).

Stability constant values and other thermodynamic constants for metal thiocyanate complexes appear in the early compilations of such data (64S, 69Pe, 71S, 77Sm, 82H). This review presents, in tabular form, a comprehensive list of stability constant values for metal thiocyanate complexes in aqueous and nonaqueous solvents, along with reported enthalpy and entropy values, as found in the literature through the present time. Stability constant values in mixed water/nonaqueous media are cited in the text discussion but values do not appear in the tables. Innovative calculation procedures, utilizing previously reported data of other researchers in an attempt to improve calculated values, are also cited but do not appear in the table listings. Stability constant values for ternary complexes in which thiocyanate ion is one of the participating ligands are omitted from this review. Omitted also are the predicted stability constant values based upon a unified theory of metals (87B).

Data is given first for isothiocyanic acid, the proton complex. This is followed by data for the p group elements of the periodic table. Next data from the 3d transition metal ions is listed. After this comes data for the 4d transition metal ions. Last, stability constants and thermochemical data for the 4f and 5f metal ions are cited. Within each table, if available, the means of measurement, solvent if nonaqueous, ionic strength and ionic medium, and temperature are given. The overall stability constants are presented followed by the appropriate reference. Some indication of the suitability of each data set is made, being given as recommended (R), tentative (T), doubtful (D), or rejected (Rj). Criteria for choosing these categories has been established elsewhere (77B). All stability constant values are rounded to their first uncertain digit with the uncertainty, when available, following in parentheses. Studies carried out potentiometrically are identified by citing the composition of the indicating electrode. Other abbreviations indicating measuring techniques are as follows:

cal	calorimetry
con	conductivity
el	electrolysis
ext	extraction
elec	electrophoresis
gl	glass electrode
ix	ion exchange
ir	infrared spectrometry
ise	ion selective electrode
kin	kinetic measurement
nmr	nuclear magnetic resonance
pol	polarography
pj	pressure jump
Raman	Raman spectrometry
ri	refractive index
sf	stopped flow
sol	solubility
sp	spectrophotometry, uv/vis
tit	titration
tj	temperature jump

The following abbreviations are used to represent various nonaqueous solvents:

n-BuOH	butane-l-ol
DMAA	*N,N*-dimethylacetamide
DMF	*N,N*-dimethylformamide
DMSO	dimethyl sulfoxide
EtOH	ethanol
HMPT	hexamethylphosphoric triamide
MeOH	methanol
MBK	methyl isobutyl ketone
n-PrOH	propane-l-ol
py	pyridine
pyHCl	pyridinium chloride
TBP	tributyl phosphate
TMP	trimethyl phosphate

II. PROTON COMPLEXES OF THIOCYANATE ION

Hydrogen

It is difficult to measure the association constant of moderately strong acids, and hydroisothiocyanic acid is no exception. Not only is its acid dissociation affected by temperature and ionic strength (69B, 82B), but there is in addition a number of decomposition reactions which may yield H_2S, HCN, OCS, and in the presence of strong acid or high concentrations of NCS^- perhaps H_2NCS^+ or $H_2C_2N_2S_3$ (69Cr, 76C, 82N). With suitable precautions it is possible to prepare solutions of HNCS which are stable over extended periods up to several days at 4°C (75J). Bonding of hydrogen to the isothiocyanate group is through nitrogen (47Be, 77S).

Table II.1 lists literature protonation constants and Table II. enthalpy and entropy values. Other references to hydroisothiocyanic acid formation constant values are omitted because of the absence of one or more essential experimental details for example; temperature, ionic strength, or identity of the adjusting ionic strength medium (66T, 70Gu). From the tentative values listed in Table II.1 the protonation constant $\lg (K_{HNCS}/\mathrm{mol}^{-1}\ \mathrm{dm}^3) = -0.87(2)$ at $I = 2.0\ \mathrm{mol\ dm}^{-3}$ (82N) and $\lg (K_{HNCS}/\mathrm{mol}^{-1}\ \mathrm{dm}^3) = -0.52(1)$ at $I = 4.0\ \mathrm{mol\ dm}^{-3}$ (82T) are the best tentative values.

The value (2) in parenthesis, indicates the uncertainty in the last digit cited. Here –0.87(2) signifies -0.87±0.02. This notation is used throughout the review.

III. METAL STABILITY CONSTANTS

III.1. Complex formation with p group elements

Alkali metals

Stability constants for the association between sodium or potassium ions and isothiocyanate ion in nonaqueous solvents are given in Table III.2. The results in different solvents are not comparable.

Beryllium

Complexes formed between beryllium cation and isothiocyanate are weak, and only a few values for the stability constants of these complexes appear in the literature. The Be-7 isotope was employed in both studies cited in Table III.1 to follow the ion exchange (71Po) and extraction (71Se) behavior of these complexes.

Alkaline earth metals

No evidence for complex formation between any of these ions and thiocyanate ion was found in the literature search.

Boron

Boron triisothiocyanate has been prepared in liquid sulfur dioxide (62So) and readily forms adducts with electron-donor Lewis bases. No information on the stability of the $[B(NCS)_4]^-$ ion is available.

Aluminium

Das, *et al.*, in their study of thiocyanate complexes, concluded that the tendency to form complexes with group 3 metals increases in the order Al < Ga < In (68D) and they were unable to detect any complexes of aluminium by spectrophotometric or potentiometric measurements. In contract, Vasil'ev and Mukhina in a spectrophotometric study of auxiliary ion effects on absorbance values of $[Fe(NCS)]^{2+}$ observed a measurable decrease in absorbance when aluminium ion was present and attributed this to complex formation 63V).

The bonding of thiocyanate to aluminium, and indeed to all the elements of this group is through nitrogen (67P, 69P, 69Sc, 70Gl, 70P, 71G, 71P).

Gallium

The stability constant of monoisothiocyanatogallium(III) ion has been measured indirectly by observing the competing effect of Ga^{3+} upon the stability constants of other metal thiocyanate complexes (64*K*a, 68D, 74T). Experimental conditions of temperature and ionic strength vary considerably and the scarcity of values prevents direct comparisons. One reported value is cited by its authors as being only approximate (64*K*a). The remaining two studies were done using an excess of perchloric acid to prevent hydrolysis and with an excess of gallium to prevent formation of complexes with coordination values (j) greater than one. All values seem doubtful until further confirming studies are reported.

Indium

Indium isothiocyanate stability constant values have been studied in several laboratories, with divergent results. As many as five (70H) or six (63R) coordinated NCS^- groups have been observed in some experiments. A previous review summarizes all values (83T). The data of Suden (54S), and Radhakrishnan and Sundaram (63R), are frequently used as a basis for comparison by others seeking to measure stability constants for indium(III) isothiocyanate complexes, but the latter polarographic study is questionable. The polarographic values were measured over a restricted concentration range, were coupled with graphical procedures for determining stability constant values, and neglected the partially irreversible nature of the indium(III) reduction wave in the presence of thiocyanate ion. Momoki and Ogawa (71M) pointed out the difficulty of a graphical procedure with limited data; their and other recalculations of the results of Radhakrishnan and Sundaram (63R) incorporated correction terms for these effects and led to revised stability constant values (71M, 75M). Because of insufficient information some reported values for indium(III) isothiocyanate stability constant values are omitted from Table III.1 (62S, 67Pr).

Stability constant values in nonaqueous media are listed in Table III.2 and Table III.3 contains the only enthalpy and entropy values reported for these complexes.

The stability constant values of Suden $\lg(\beta_1/\text{mol}^{-1}\ \text{dm}^3) = 2.58(2)$ and $\lg(\beta_2/\text{mol}^{-2}\ \text{dm}^6) = 3.60(3)$ are recommended until further studies become available (54S).

Thallium

Although some have reported no complex formation (56S), thallium(I) appears to form a series of weak complexes with thiocyanate ion. One report lists complexation to a coordination number of six (58H). Polynuclear species have generally not been observed (57N, 58Pa, 71Fe) although the complex $Tl_2(NCS)_3^-$ is identified from solubility data (no stability constant reported (58B)). Golub and Kornilov, too, suggest a complex with a 2:3 Tl^+/NCS^- ratio, but conclude that their absorbance measurements may have involved a solution containing a mixture of Tl(NCS) and $Tl(NCS)_2^-$ (59Gl). Thiocyanate ion reacts with Tl^{III} producing cyanide ion and Tl^{I}. No stable complexes of Tl^{III} and thiocyanate ion were found (91B). The choice of counter ion influences the stability of thallium isothiocyanate complexes, due to ion association between alkali metal cations and anionic thallium isothiocyanate species (60*K*). Some reported stability constant values are not tabulated for thallium isothiocyanate because of insufficient available information (56L, 58B, 66Ol, 71Be, 73R). A series of studies reports the stability constants for thallium isothiocyanate complexes in mixed solvents containing water and methanol (62*K*l) or water and ethanol, propane-1-ol or propane-2-ol (62*K*u). In general, stability constant values increase with increasing alcohol content, and for the same water/alcohol ratio with increasing alcohol carbon number.

The enthalpy and entropy values for TlNCS have been measured (52S, 53B, 61Gl). Values listed in Table III.3 are doubtful as experimental details are lacking. The aqueous phase stability constant values of Kul'ba and Chernova (62*K*l) and Fedorov *et al.* (71Fe) are averaged and recommended at $I = 3.0$ mol dm^{-3} giving $\lg(\beta_1/\text{mol}^{-1}\ \text{dm}^3) = 0.10(3)$. At $I = 4.0$ mol dm^{-3} the recommended value of Kul'ba *et al.* (65*K*) is $\lg(\beta_1/\text{mol}^{-1}\ \text{dm}^3) = 0.20(1)$.

Germanium

Little has been done on germanium isothiocyanate complexation, and no stability constants are found in the available literature. In acetone, a 1 : 4 complex has been reported (75Ts). A solid $M_2[Ge(NCS)_6]$ species was isolated from acetonitrile media (M = alkali metal ion)(78S).

Tin

Stability constant values for tin(II) isothiocyanate complexes in aqueous, nonaqueous and mixed solvents are known. The values obtained by Golub *et al.* were the first for a variety of solvents. These authors postulated coordination numbers as high as four in methanol and acetonitrile media (61Go, 63Gu). The stability constants listed in Table III.2 for tin isothiocyanate species in nonaqueous solvents are tentative until independent confirmation is forthcoming. The aqueous stability constant values in Table III.1 are also tentative until confirmed by further studies.

Lead

The majority of those studying thiocyanate complexes of lead(II) used polarographic measurements in order to obtain stability constant values. The lead(II) thiocyanate wave is reversible (59T). Leonard *et al.* expressed concern over the reliability of the polarographic method, especially with graphical evaluation of various β_j values, since the error associated with each stepwise constant carries over from one value to the next (56Le). These data (56Le) were treated by others. (74Mi, 75B) using an alternative mathematical approach with slightly different results. The possible formation of lead nitrate complexes was overlooked by many who used nitrate salts to adjust ionic strength values (91S) and hydrolysis of lead salts was also frequently neglected. Polynuclear formation was not cited by any of those reporting stability constant values, except for Fedorov *et al.* (70F), who specifically and successfully set out to observe polynuclear halide and pseudohalide formation from solubility data. Five (69F) and six (58Pa) coordinate mononuclear complexes were also observed in some instances. Lead(II) thiocyanate complexes have been identified in various nonaqueous solvents including acetone (59G), dimethyl sulfoxide (67Po) and 1,4-dioxane (80R).

The values for which reliable information was available are listed in Table III.2. All may be considered tentative until supported by other data. Insufficient experimental details result in the omission of some reported stability constant values for aqueous lead(II) thiocyanate solutions from Table III.1 (51Y, 59*K*, 61G). Of the values listed two are considered tentative because of the careful attention to experimental detail even though their values are divergent.

The lone set of enthalpy and entropy values for lead(II) thiocyanate is given in Table III.3.

Arsenic, Antimony

No evidence for complex formation between arsenic(III) and thiocyanate ion exists in the current literature. Antimony(III) thiocyanate was identified mass spectrometrically in a molten mixture of antimony(III) fluoride and ammonium thiocyanate (89Al).

Bismuth

The bismuth(III) ion forms a series of complexes with thiocyanate ion reaching a coordination number of six in aqueous solution if sufficient thiocyanate ion is present. Complex formation in acetone, acetonitrile, dimethylformamide and dimethyl sulfoxide has also been reported (71So). Stability constants in DMF and DMSO media are listed in Table III.2. The lone data set of enthalpy and entropy values (71Fd) is listed in Table III.3. Bonding of bismuth(III) to thiocyanate ion is through sulfur (68C). Details of some aqueous stability constant studies were not available for listing in Table III.1 (49G, 53Fu). Of the values that are listed, those of Fedorov, *et al.* (71Fd) at $I = 0$ $\lg(\beta_1/\text{mol}^{-1}\ \text{dm}^3) = 2.21$ and $I = 1.0\ \text{mol dm}^{-3}$ $\lg(\beta_1/\text{mol}^{-1}\ \text{dm}^3) = 1.28$ are considered tentative.

Selenium, Tellurium

Crystalline $Se(SCN)_2$ has been prepared (79H). No information regarding complexation and/or stability constant measurements is available. No reports of tellurium complexation with thiocyanate ion were found in the literature.

Iodine

Iodine, I_2, forms an adduct with thiocyanate ion in acid media, $[I_2(SCN)]^-$ or if an oxidizing agent is present $I(SCN)_2^-$. Table III.1 lists the available stability constant values for these complexes.

III.2 Complex formation with first-row transition metal ions

Scandium

Scandium(III) forms a stable 1 : 1 complex with thiocyanate ion. Stability constant values were generally measured by observing the competing effect of Sc^{III} on the absorbance value of the iron(III) isothiocyanate complex (64*K*a, 67*K*) or for thiocyanate ion and azo dyes (66*K*o). Values from a potentiometric procedure and an extraction procedure have also been reported (70S). No evidence of coordination between scandium(III) and thiocyanate ion with j values greater than one was observed in any of these studies. Two of the values in Table III.4 are tentative.

Titanium

Titanium is known to form isothiocyanate complexes in both Ti^{III} and Ti^{IV} states (58T, 59S, 60H). In aqueous solution, the titanium(IV) species with one bound isothiocyanate ion group, is variously reported as $[Ti(OH)(NCS)]^{2+}$ (58T), $[Ti(H_2O)(NCS)]^{3+}$ (60H), or $[TiO(NCS)]^{+}$ (77T). In acetonitrile (75Sy) and butane-1-ol (72Sy) $[Ti(NCS)_6]^{2-}$ is formed. Table III.4 lists tentative values for the Ti^{IV} complex. Other reported values, due to a lack of experimental details, are omitted from the table (53D, 77Vu). The single set of stability constant values for the complexes in acetonitrile is found in Table III.5.

Vanadium

Vanadium in various oxidation states combines with isothiocyanate ion to form complexes. With vanadium(IV) these take the form $[VO(NCS)]^{+}$, with vanadium(III) $[V(NCS)]^{2+}$, and with vanadium(II) $[V(NCS)]^{+}$. Stability constants for V^{V} complexes with j values above one were not observed in aqueous media from spectrophotometric measurements. Vanadium(IV) complexes have also been reported in mixed aqueous/acetone and aqueous/methanol solutions (63Go). Aqueous stability constants values are found in Table III.4. Two values for the V(III) complexes are recommended (51F, 67B). The remaining values are tentative until additional studies are performed.

Enthalpy and entropy values, primarily from spectrometric measurements, are listed in Table III.6.

Chromium

Stability constant values for thiocyanate ion complexes of Cr^{II}, Cr^{III} and Cr^{VI} are found in the literature. The chromium(III) isothiocyanate complexes were studied by N. Bjerrum in the 1920's (21B) but have received relatively little attention since then because of the very slow reactions of Cr(III) in solution. Reported stability constant values vary widely and in many instances experimental details are lacking. The chromium(VI) isothiocyanate complex is said to be $[(SCN)CrO_3]^{-}$ (69N). Bonding of thiocyanate to chromium(III) is either through nitrogen or nitrogen and sulfur (65H, 70Co) depending upon solution conditions. Polynuclear complexes with bridging thiocyanate groups are also known (72Bu).

Aqueous stability constant values are listed in Table III.4, the lone set of nonaqueous values, for acetone and methanol are in Table III.5, and the reported enthalpy and entropy data are in Table III.6. Some reported aqueous stability constant values are omitted from Table III.4 because of uncertain quality (60T, 71M). Values not rejected are considered doubtful because of the lack of supporting results.

Manganese

Manganese(II) isothiocyanate complexes have not received the extensive study to which those of some other first row transition elements have been subjected. The relatively recent data of Ishiguro and Ozutsumi (90I) for stability constants (Table III.5) and enthalpy and entropy values (Table III.6) in *N,N*-dimethylformamide can be considered tentative, since no other values are available for comparison in this medium. Some reported aqueous stability constant values are omitted from Table III.4 (67L, 68Pr) for lack of detail. Of the values listed those of Tribalat and Caldero from polarographic (63T) and spectrophotometric (64Tr) measurements are tentative until further values are reported.

Iron

One of the most extensively studied metal thiocyanate complexes is monoisothiocyanatoiron(III). Even after eliminating those stability constant values for which experimental details are incomplete (41B, 46B, 51S, 54J, 55I, 68Bu, 76V), subtle differences exist among the remaining values. Barring the presence of competing ligands, the hydrolysis of iron(III) is the most serious side reaction. Several reported values are corrected for this effect (47F, 51M, 55Li, 56L, 61Y). With colorimetric procedures, formation of higher complexes contributes to the observed absorbance (61Y). Some have taken advantage of this to measure stability constants of complexes with $j > 1$ (51M, 53Be, 55I, 55Li, 58Mi, 58Pe, 64Va, 85B). Others, generally, have maintained a small iron(III) concentration with equally small thiocyanate concentration (57Y, 61Y, 62V, 68Ms). Mψller (37M) established much of the present knowledge regarding interactions of iron(III), iron(II) and thiocyanate ions by electrochemical and spectrophotometric means. The contribution of others to our knowledge of iron isothiocyanate reactions is reviewed elsewhere (53L, 82Su). Stability constant values for iron(III) isothiocyanate are available in mixed aqueous/acetone (59B) and aqueous/methyl-ethyl-isopropyl alcohol solutions (76V). Values for nonaqueous media, excluding those for which complete data were missing (47B, 60O), are listed in Table III.5; they are doubtful, lacking agreement among themselves.

Aqueous stability constant values are given in Table III.4. At an ionic strength of 1.0–1.2 mol dm^{-3} the lg$(\beta_1/\mathrm{mol}^{-1}\ \mathrm{dm}^3)$ value of 2.11(4) is recommended (51M, 55Li, 68Po, 78M, 92O).

Enthalpy and entropy values, except where information was unavailable (69V), are found in Table III.6. The tentative entropy value for ΔH_1 = -6.7 kJ mol^{-1} was obtained in three independent studies (53Be, 56L, 81T) at ionic strengths of 0.4 mol dm^{-3} and zero.

Cobalt

Hydrolysis of cobalt(II) is considered to be negligible in measuring stability constant values of cobalt isothiocyanate complexes provided the solution is sufficiently acid. Various maximum pH values ranging from 3 to 6 are cited as being adequate to repress hydrolysis (58S, 62W, 64*K*), but rigid pH control has not generally been a factor in these experiments. HNCS, too, is considered completely dissociated although a possible correction for its incomplete ionization is suggested (62T). Formation of higher complexes is repressed by maintaining a cobalt concentration in excess of the thiocyanate present, but regrettably this fact was overlooked in one of the first reported determinations of β_1 (51L). Values for the formation constants of the higher isothiocyanate complexes of cobalt are acknowledged to be approximate (51L, 63T) and generally differ by more than the expected experimental error.

Stability constant values for cobalt(II) isothiocyanate formation in a variety of solvents are cited in Table III.5. The values are generally considered doubtful, lacking conformation from other studies. Aqueous stability constant values are found in Table III.4. A recommended value at I = 1.0 mol dm^{-3} is lg$(\beta_1/\mathrm{mol}^{-1}\ \mathrm{dm}^3)$ = 1.01(1) (58S, 71S*k*).

Table III.6 lists the available enthalpy and entropy values. Tentative agreement is found in some of these studies.

Nickel

Conditions for measurement of nickel(II) isothiocyanate complexes vary but, in general, experiments have been carried out in acidic solution and in the presence of excess nickel(II) to prevent formation of higher complexes. pH values of 3–4, or less, are satisfactory (53Fr, 61D, 62W) and perchlorate ions are frequently added to adjust ionic strength. Although polynuclear complexes are known (71L), their effect was not considered by those reporting stability constant values. In one instance a slightly different set of lg β_j values was obtained from the previous data (74*K*) by a revised mathematical treatment (76*K*). With nonaqueous solvents, agreement is lacking for those few systems where corresponding studies are available, and experimental details are often missing (Table III.5). Divergent results were also found for enthalpy and entropy values (Table III.6). The two thermodynamic studies for which agreement is approximate give values which are tentative, and other values must be considered doubtful pending further studies. Apart from those reports in which insufficient data were made available (68Pr, 68T), the aqueous phase stability constant values for nickel(II) isothiocyanate are given in Table III.4. A mean value for lg$(\beta_1/\mathrm{mol}^{-1}\ \mathrm{dm}^3)$ = 1.14(9) is obtained from the recommended values at I = 1.0 mol dm^{-3} (53Fr, 62T, 73Hu, 74*K*, 76M). This same value lg$(\beta_1/\mathrm{mol}^{-1}\ \mathrm{dm}_3)$ = 1.14(2) is also recommended at I = 1.5 mol dm^{-3} (64T).

From Table III.6 a mean enthalpy value of ΔH_1 = -13.2 kJ mol^{-1} is tentative (68Ma, 74*K*).

Copper

Both Cu$^{\mathrm{I}}$ and Cu$^{\mathrm{II}}$ combine with thiocyanate ion to form isothiocyanato complexes. With copper(I) only stability constant values for the four-coordinate species are found in the literature. Thiocyanate ion is known to reduce Cu$^{\mathrm{II}}$ to Cu$^{\mathrm{I}}$ (76*K*a) possibly with formation of mixed valence species (36*K*). Stability constant values for copper(I) and copper (II) complexation with thiocyanate ions in a variety of nonaqueous solvents are listed in Table III.5. The single study with each solvent lacks independent confirmation and is considered tentative.

Table III.4 lists the stability constants for aqueous phase Cu$^{\mathrm{I}}$ and Cu$^{\mathrm{II}}$ isothiocyanate complexes. Some of these have been modified by alternative mathematical treatments of the experimental data (62W, 76*K*);

these alternate values are omitted from the table. Of the listed values, these are in close agreement (73Hu, 74*K*, 88M) resulting in a $\lg(\beta_1/\text{mol}^{-1}\ \text{dm}^3) = 1.7(1)$ as a tentative value at $I = 1.0$ mol dm^{-3}.

In conjunction with the studies cited in Table III.5, various enthalpy and entropy values are reported in Table III.6, but they too are tentative until confirmed elsewhere.

Zinc

A review of the results in Table III.4 shows that many of the studies of zinc isothiocyanate complexes are unsatisfactory, either through lack of experimental detail or because of the failure to provide a non-complexing medium. Some have re-evaluated earlier data to correct mathematically for these shortcomings (56Tu, 71Mm, 84A). In addition to stability constant values in aqueous media, data have also been reported for zinc in molten $LiNO_3$-NH_4NO_3 (75Sp) and in water-ethanol mixtures (75A). Table III.5 lists reported values for various nonaqueous solvents. These values are considered tentative until confirmed by others. Some stability constant values for zinc isothiocyanate in aqueous systems are omitted from Table III.4 because of non-availability or inconsistencies (57Na, 66S, 68Pr). From the values given those of Ahrland and Kullberg $\lg(\beta_1/\text{mol}^{-1}\ \text{dm}^3) = 0.74$ at $I = 1.0$ mol dm^{-3} (71Ah) and Almeida Neves and Sant'Agostino $\lg(\beta_1/\text{mol}^{-1}\ \text{dm}^3) = 0.708(3)$ at $I = 2.0$ mol dm^{-3} (70A) are recommended. Data from other studies (66M, 71Mo, 73Hu, 85I) remain tentative until confirmed by independent work.

Table III.6 gives enthalpy and entropy data for zinc isothiocyanate complexes. Aqueous enthalpy values are in agreement from two independent studies and are recommended. At $I = 1.0$ mol dm^{-3} $\Delta H_1 = -5.8(2)$ kJ mol^{-1} (71Ah) and at $I = 5.0$ mol dm^{-3} $\Delta H_1 = -5.0(1)$ kJ mol^{-1} (85I). Alternate methods of thermodynamic value calculations for some of the reported studies are also available (66Ge, 74*K*).

III.3. Complex formation with 4d and 5d transition metal ions

Yttrium

The two sets of available stability constant values found for yttrium(III) isothiocyanate complexes are listed in Table III.7. Additional studies are needed.

Zirconium

Experimental details are generally lacking in publications of stability constant values for zirconium(IV) isothiocyanate complexes in aqueous solution. There is disagreement regarding the stoichiometry of the zirconium(IV) isothiocyanate complex. In various media, it is stated as $[Zr(NCS)_4]$ in (DMF) (70G), $[ZrO(NCS)_2]$ in (DMF) (83*K*), $[Zr(OH)(NCS)]^{2+}$(aq) (75T), and $[Zr(OH)_2(NCS)_2]$ in (cyclohexane) (70Go) and TBP (77Ts). As many as eight cumulative constants were reported by one laboratory for both aqueous (66Go) and DMF (70G) solutions. Available stability constant values for aqueous complexes are found in Table III.7 and for nonaqueous complexes in Table III.8. All are rejected because of the absence of missing experimental details.

Niobium

Results of niobium isothiocyanate complex studies dissolved in various nonaqueous and mixed solvents are available. Differing numbers of bound thiocyanate groups are observed with j values as high as seven in dimethylformamide at sufficiently high thiocyanate concentrations (66Gl). Complexes containing a niobium oxygen bond (74Sc), a niobium hydroxo bond (76Sy), and various counter ions and/or solvent species (66Gl, 74Sc) are possible. During extraction with tributyl phosphate and acid, for example, the protonated forms of $[NbO(NCS)_4]^-$ (74Sc) and $[Nb(NCS)_6]^-$ (66Gl) are presumed to be in the tributyl phosphate phase. Only monomeric niobium species are present, provided that sufficient thiocyanate ion is in solution (74Sc, 76Sy). The stability constant values in various nonaqueous solvents given in Table III.8 are rejected because of necessary experimental details.

Molybdenum

Molybdenum in its various oxidation states forms complexes with isothiocyanate ion, although with varying degrees of stability. Mo^V complexes are the most extensively studied although with divergent results. The stoichiometry of the complexes formed is questionable being reported as monomeric (59N), or dimeric $[Mo_2O_4(NCS)]^+$ (75S) or other compositions including a tetramolybdenum complex $[Mo_4O_4(OH)_8(NCS)]^{3+}$ (68L). Thiocyanate ions slowly reduce Mo^{VI} to Mo^V in acid solutions. Stability constants for molybdenum(V) isothiocyanate complexes have been measured in a mixed acetone-water solvent (58P). Values for Mo^{V} in pure acetone and in methanol are given in Table III.8 although experimental details are lacking.

Available stability constant values for aqueous molybdenum complexes in various oxidation states are found in Table III.7. The value of Sasaki, Taylor and Sykes, $\lg(\beta_1/\mathrm{mol^{-1}\ dm^3}) = 2.41(4)$ (75S) is tentative and further studies are needed.

Enthalpy and entropy values for the Mo^{IV} complex are stated in Table III.9. They are doubtful, lacking independent confirmation.

Technetium

Isothiocyanate complexes of technetium find application in the spectrophotometric determination of the element, but no values for the stability constants of these complexes were found in the literature. $[Tc(NCS)_6]^-$ forms salts with R_4N^+ cations stable in both the solid state (73H) and in solution (64O). Complexes of the form $[TcO(NCS)_5]^{2-}$ (81D) and $[Tc(NCS)_6]^{3-}$ (80T) are also reported.

Ruthenium

The composition of ruthenium complexes with thiocyanate ion is uncertain. Thiocyanate ions reduce ruthenium from higher oxidation states to Ru^{III} (66O) or Ru^{II} (84Al) depending upon solution conditions. Mixed valence dinuclear ruthenium complexes are also known (85P). Reported values for $[Ru(SCN)]^{2+}$ are cited in Table III.7. The value of Yaffe and Voigt $\lg(\beta_1/\mathrm{mol^{-1}\ dm^3}) = 1.78(1)$ (52Ya) is tentative until confirmed elsewhere.

Rhodium

Rhodium thiocyanate complexes are known to form in nonaqueous (67Sc, 72P) and mixed aqueous-alcohol (83B) solvents. No stability constant values were found in the literature.

Palladium

Studies of palladium(II) complexes with thiocyanate have centered upon the overall stability constant for the 1 : 4 complex. Shlenskaya *et al.*, who were first to report a value for β_2, state that their result is only approximate (62Sh). The potentiometric study of Grinberg *et al.* (63Gr) has been criticized for using palladium sponge as part of the measuring electrode, since adsorption of Pd^{II} upon the surface of the sponge may have caused an unpredictable change in the concentration of Pd^{II} ions in solution (65F). Available literature values for Pd^{II} thiocyanate stability constants are listed in Table III.7. All are considered doubtful.

Silver

Complex formation between Ag^{I} and thiocyanate ion is complicated by the insolubility of AgSCN. Although some workers report a β_1 value, in addition to K_{sp} for AgSCN, others elect to begin their evaluation of silver thiocyanate complexes with β_2. Data are generally reported from potentiometric measurements using a Ag electrode or more recently a Ag ion-selective electrode. Many of the studies lack complete disclosure of experimental details, making an evaluation of the results difficult. Further complications arise from the existence of polynuclear complexes in both aqueous (55L, 68Gy) and nonaqueous solutions (68Lr, 68Mi, 70L). Stability constants for silver thiocyanate complexes in mixed water/acetone (82Tu), water /alcohol (54*K*) and water/DMSO (90T) solutions have been measured. Values in a variety of pure organic solvents are listed in Table III.8. Those values resulting from good laboratory practice but lacking independent confirmation are considered tentative. All others are doubtful or rejected.

Some aqueous stability constants for the silver(I) thiocyanate complexes are unavailable or unsatisfactory (52Y, 54*Kr*, 68Gy). Available values are found in Table III.7. Considering their divergence all are assumed doubtful until additional supporting data are forthcoming.

Table III.9 lists the thermodynamic constants found for silver thiocyanate. The aqueous values differ considerably and are doubtful.

Cadmium

Cadmium complexes with thiocyanate ion have been extensively studied (41L, 51H), but re-evaluation of earlier stability constant values by computer refinement often lead to different, and in some cases divergent, results (56Tu, 60I, 74Mi, 75M, 80L, 84C, 85S). Bonding within the complexes is via N, S or both depending upon the counter ion, coordination number or solvent (74A, 78Fr, 81Ah, 86I). Casassas and Arino (86C) have shown that failure to account for adsorption of thiocyanate ion upon the surface of a dropping mercury electrode in their polarographic work causes an error in the results compared to values obtained from potentiometric data. They also found divergent values depending upon the type of voltammetric technique employed. Stability constants for cadmium with thiocyanate ion have been measured in various mixed water-acetonitrile (64G), alcohols (59Tu, 77Ar, 80Ro, 82Ts) and dioxane (77A) solvents. Values for these constants in pure nonaqueous media are found in Table III.8. Some are considered tentative pending further studies. Table III.7 contains the available aqueous stability constant values for cadmium isothiocyanate. There is agreement among several reported β_1 values at various ionic strengths.

Recommended at an ionic strength of one mol dm^{-3} is the mean value $\lg(\beta_1/\mathrm{mol^{-1}dm^3}) = 1.31(6)$ (63T,68G,73Hu,78A) and at an ionic strength of 3.0 mol dm^{-3} $\lg(\beta_1/\mathrm{mol^{-1}dm^3}) = 1.38(3)$ (41L,57Ts,66Ge,86I).

Table III.9 lists reported enthalpy and entropy values for cadmium complexes. The values are wide ranging. Those with some agreement are considered tentative and are at $I = 1.0$ mol dm^{-3} $\Delta H_1 = -9.58(4)$ kJ mol^{-1} (68Ge) and at $I = 3.0$ mol dm^{-3} $\Delta H_1 = -10.19(6)$ kJ mol^{-1} (86I).

Hafnium

Experimental details are generally lacking in reports of determinations of stability constant values for hafnium(IV) isothiocyanate complexes in aqueous solution. The stoichiometry of the hafnium isothiocyanate complex is variously reported as [$Hf(NCS)_4$] (70G), or [$HfO(NCS)_2$] (83*K*) in dimethylformamide and as [$Hf(OH)_2(NCS)_2$] (77V) in cyclohexanone. As many as eight cumulative constants were reported by one laboratory for both aqueous (66Go) and DMF (70G) solutions. Available stability constant values for aqueous complexes are found in Table III.7 and for nonaqueous complexes in Table III.8. All are rejected because of missing experimental details.

Tantalum

Studies of tantalum isothiocyanate complexes in various nonaqueous and mixed solvents are available with reported stability constant values listed in Table III.8 for alcohol and DMF solutions. Only monomeric tantalum species are assumed present provided sufficient excess thiocyanate ion is in solution (77Sy).

Tungsten

Although most investigations were commonly associated with the colorimetric determination of tungsten, no thorough studies of the stability constant values for tungsten isothiocyanate complexes were found. Formulae for the complexes are uncertain. Stability constants for mixed W-Cl-NCS complexes in various ketone solvents have been measured (67U).

Rhenium

Rhenium, in its various oxidation states, is known to form complexes with thiocyanate ion (81D). Stability constants for the red complex formed from Re^{IV} and thiocyanate ion in the presence of tin(II) chloride are given in Table III.7. Additional studies of rhenium thiocyanate complexation are needed before any recommendation can be made.

Osmium

Osmium complexes with thiocyanate ion are stabilized in various organic solvents (79M) and widely used for quantitative spectrophotometric measurements (68Q). No reported values for stability constants, however, were found in the literature.

Iridium

Iridium complexes with thiocyanate ion are known but no stability constant values have been measured. Iridium(IV) is reduced to iridium(III) by thiocyanate ion in acid solution (80St).

Platinum

Platinum(II) forms complexes with thiocyanate ion (60Gr). The single reported stability constant value (77H) is found in Table III.7 and is tentative until additional values become available.

Gold

Both Au^I and Au^{III} ions complex with thiocyanate ion, the latter being studied initially in 1918 by N. Bjerrum and Kirshner (18B). Thiocyanate ions reduce gold(III) to gold(I) upon prolonged exposure (18B). Stability constant values for aqueous Au^I complexes are in Table III.7 with a tentative value of lg(β_1/mol^{-1}dm^3) = 15.3(2) (66*K*).

Available stability constant values for Au^I complexes in acetonitrile and pyridine are given in Table III.8, and enthalpy and entropy values for the pyridine solution are in Table III.9.

Mercury

Of the various mercury(II) thiocyanate complexes those with coordination numbers 2 and 4 predominate. Among the several nonaqueous media utilized for the study of mercury(II) thiocyanate complexes close agreement was obtained for stability constant values in acetone and in *N,N*-dimethylformamide as shown in Table III.8. Single studies in other solvents are tentative until further reports are available. Stability constant values in mixed water/acetone (60G), alcohols (60G), pyridine (68P) or other solvent mixtures (81H) are also known. Some reported aqueous stability constant studies lack sufficient information and were omitted from this review (46G, 57Go, 70Se). Many of the reported aqueous stability constant values listed in Table III.7 were measured in media containing nitrate ion, and the competing effect of nitrate ligand uncertain. There was agreement for β_2 and β_4 stability constant values in perchlorate ion media at I = 1.0 mol dm^{-3} with a mean value of lg(β_2/mol^{-2}dm^6) = 16.5(4) accepted as tentative (60N, 70C).

Enthalpy and entropy data for mercury(II) thiocyanate complexes are found in Table III.9. A mean ΔH_1 = -50.11(4) kJ mol^{-1} is recommended (71A, 84V) at I = 1.0 mol dm^{-3}.

III.4. Complex formation with 4f and 5f transition metal ions

Lanthanum

Divergent stability constant values for lanthanum isothiocyanate complexes appear in the literature. They are listed in Table III.10. The values lg(β_1/mol^{-1}dm^3) = 0.20 at I = 2 .0 mol dm^{-3} (82Ch, 86G) and lg(β_1/mol^{-1}dm^3) = 0.24(8) at I = 5.0 mol dm^{-3} (64Se, 65Se) are tentative pending further study.

Lanthanides

The chemistry of lanthanide isothiocyanate complexes has been reviewed (69J, 86G). With the exception of praseodymium, for which no stability constant values could be found, values for the stability constants of the lanthanide ion with isothiocyanate ion are listed in Table III.10. In all cases, the tendency to form complexes is small and the trend is to slightly increasing β_j values with increasing lanthanide atomic number (64*K*u, 74*K*h). It may be that thiocyanate ions reduce rare earth ions upon prolonged contact (64B). No studies of rare earth isothiocyanate complexes in nonaqueous solvents were found in the literature. Because of the limited number of studies for each individual set of lanthanide ion complexes, often with divergent results, the majority of values reported in Table III.10 are taken as tentative pending further studies.

Enthalpy and entropy values for Nd^{3+} and Eu^{3+} are given in Table III.12. They are considered tentative until confirmed elsewhere.

Actinium

The lone available set of stability constant values for actinium isothiocyanate complexes is listed in Table III.10.

Thorium

Thorium isothiocyanate complexes have not been studied extensively and the few reported stability constant values lack information on experimental details. Table III.10 lists available values in aqueous solvents and Table III.11 those in nonaqueous medium. The paper by Waggener and Stonghton (50W) gives the most extensive experimental information.

Uranium

Both uranium(IV) and uranium(VI), as uranyl ion UO_2^{2+}, form complexes with isothiocyanate ion. The original data of Ahrland (49A) has been recalculated (69S, 78A) resulting in different values, especially for β_2 and β_3. Stability constant values have also been measured in mixed water/methanol solutions (57B). Table III.10 lists stability constants for aqueous complexes. Those for the U^{IV} species are tentative with a $\lg(\beta_1/\text{mol}^{-1}\text{dm}^3) = 1.49$ reported at both 1.0 mol dm^{-3} = 1.0 (54A) and $I = 2.0$ mol dm^{-3} (55D). Those for the U^{VI} complexes are tentative pending further studies.

Enthalpy and entropy values for the uranyl ion complexes are found in Table III.12, with a tentative $\Delta H_1 = -3.22(6)$ kJ mol^{-1} (71A).

Other actinides

Stability constant values for isothiocyanate complexes of the remaining actinide ions, Np, Pu, Am, Cm, B*k*, Cf and Es are listed in Table III.10. As with the corresponding lanthanide species complex formation is weak. Exact formulae for these complexes are uncertain. Neptunium, for example, is reported by one group (77M) to be $[NpO_2(NCS)_4]^{2-}$ when joined to isothiocyanate ion. The majority of the aqueous stability constant values are tentative lacking supporting confirmation.

The enthalpy and entropy values reported for Pu, Am, Cm and Bk isothiocyanates are given in Table III.12. Most values are listed as tentative and further work is needed.

IV. SUMMARY

Table III.13 summarizes recommended and tentative lg β_1 values for the various metal thiocyanate complexes reported.

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APPENDIX

Table II.1. Protonation constants of thiocyanate ion.

Method	Solvent Medium	I mol dm^{-3}	Temp C	lg K_{HL} mol^{-1} dm^3	Ref	Category
gl	--	--	25	0.84(3)	42S	Rj
sp	--	~0	25	-1.32	75Y	Rj
gl	--	0.06	26	0.97	66Bo	Rj
gl	$NaClO_4$	0.1	25.0(2)	0.01(6)	84S	D
Raman	NH_4NCS	1.0	20	-1.1	76C	D
ext	$HClO_4$	1.8	25.0(1)	-1.85(2)	65M	D
Hg	$NaClO_4$	2.0	25.0(1)	-0.87(2)	82N	T
pol	$HClO_4$	3.5	--	-0.88(1)	72T	Rj
pol	H^+-$NaClO_4$	4.0	25.0(2)	-0.52(1)	82T	T

Table II.2. Thermodynamic constants for the protonation of thiocyanate ion.

Method	I mol dm^{-3}	T C	H kJ mol^{-1}	S J mol^{-1}K^{-1}	Ref	Category
gl	~0	26	54	170	66Bo	Rj
gl	0.1($NaClO_4$)	25.0(2)	2	6.7	84S	D

Table III.1. Stability constants for complexes of thiocyanate with main group elements

Metal Ion	Method	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Be^{2+}	ix	1(H^+-$NaClO_4$)	18	0.13(4)	0.0(1)					71Po	T
	ext	4.0(HOAc-$NaClO_4$)	25	0.69	0.25					71Se	T
Al^{3+}	sp	0	22	0.42						63V	T
Ga^{3+}	pol	0	25.0(2)	2.32(6)						74T	D
	sp	0($HClO_4$)	35.0(1)	2.26(3)						68D	D
	sp	0.6($HClO_4$)	20	1.18(6)						64Ka	D
	pol	1.06($HClO_4$)	25.0(2)	1.31(4)						74T	D
In^{3+}	sp	0	30(1)	3.15(1)						68D	T
	sp	0.6($HClO_4$)	20	2.34(2)						64K	T
	In(Hg)	2	20	2.58	4.00	4.74	4.80			63Gl	T
	In	2.0(H^+-$NaClO_4$)	20	2.58(2)	3.60(3)	4.63(5)				54S	R
	pol	2(H^+-$NaClO_4$)	25.0(1)	2.54(3)	3.77(5)	4.79(3)	4.45(3)			71M	T
	pol	2.0(H^+-$NaClO_4$)	25.0(1)	1.7	2.3	2.1	3.2			65N	D
	pol	2($NaNO_3$)	27.0(1)	0.78	2.49	3.91				73R	D
	pol	2(H^+-$NaClO_4$)	30.0(1)	2.08(7)	3.20(7)	4.24(7)	4.23(7)			63R	T
	ext	4(H^+-$NaClO_4$)	25.0(5)	2.44	4.11	5.10	4.57			70H	D
Tl^+	Tl(Hg)	3.0($LiClO_4$)	25.0(1)	0.10(2)	-0.10(3)	-0.55(3)	-1.4(2)			71Fe	R
	pol	3.0($NaClO_4$)	25	0.64(0)	0.88(1)	0.70(2)	0.73(4)			58H	T
	Tl(Hg)	3($LiClO_4$)	25.0(2)	0.11	-0.06	-0.43	-1.35			62Kl	R
	sol	3($LiClO_4$)	25.0(2)	0.19	-0.03	-0.43	-1.44			62Kl	T

III.1 continued

Metal Ion	Method	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
	pol	3(KNCS)	25	0.19	-0.20	-0.62	-0.96			58Pa	T
	sol	4(LiClO$_4$)	25	0.20(1)	-0.04(4)	-0.6(1)	-0.8(1)			65K	R
	Tl(Hg)	4(NaClO$_4$)	25	0.15(6)	0.00(9)	-0.46(6)	-0.9(2)			57N	T
	sol	4.6(NaClO$_4$)	20.0(2)	0.66	0.55	0.17				61Gl	D
	sol	8(NaClO$_4$)	25.0(1)	0.65	0.60	0.17	-0.39			60K	D
Sn^{2+}	Sn(Hg)	0	25	1.7(2)	2.0(1)					80F	T
	Sn(Hg)	1((H$^+$-NaClO$_4$)	25	0.83(6)	1.1(1)					80F	T
	Sn(Hg)	1(NaClO$_4$)	25	1.03(6)	1.57(3)					76Sa	T
	Sn(Hg)	2.2(NaClO$_4$)	20	1.2	1.8	1.7				61Go	T
Pb^{2+}	pol	1.0(NaClO$_4$)	25.0(5)	0.20	0.94					80R	D
	pol	1.0(NaClO$_4$)	25.0(1)	0.15	0.96					85R	D
	ext	1Na$^+$(ClO$_4^-$,SCN$^-$)	25	0. 49						81Ku	
	pol	2.00(H$^+$-NaClO$_4$)	25.0(1)	0.54(8)	0.88(3)	0.84(4)				56Le	D
	pol	2.0(KNO$_3$)	25	1.3(2)	0.9(1)	1.1(2)				57I	Rj
	pol	2(NH$_4$NO$_3$)	25	1.70	0.92	0.30	1.1			59T	Rj
	pol	3(NaClO$_4$)	25	1.08	1.15	0.83	1.16			58Pa	D
	Pb(Hg)	3(H$^+$-LiClO$_4$)	25	0.46						69F	T
	sol	3(H$^+$-LiClO$_4$)	25	0.4(1)	0.7(1)	0.9(1)	0.6(3)			69F	D
	Pb(Hg)	4(LiClO$_4$)	25.0(2)	1.08(7)	1.48(7)	2.58(2)				63M	T
	Pb(Hg)	5.8(NaNO$_2$)	20					0 .57	1 .01	59C	Rj

III.1 continued

Metal Ion	Method	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Bi^{3+}	Bi(Hg)	0	25.0(1)	2.21(6)	3.7(1)	4.4(1)	5.2(3)	5.8(1)	5.4(3)	71Fd	T
	sp	0.4(HClO$_4$)	--	1.15(2)	2.26		3.40		4.23	49K	Rj
	Bi(Hg)	0.4(KNO$_3$)	20	0.82	1.91	2.74	3.40	3.25	3.19	59Go	Rj
	Bi(Hg)	1(H$^+$-LiClO$_4$)	25.0(1)	1.28(5)	2.67(4)	3.4(1)	4.0(1)	5.4(1)	6.4(1)	71Fd	T
	ext	2.2(?)	25	0.79	1.53	2.24	2.91	3.54	4.12	64C	Rj
I_2	sp	0.1(NaClO$_4$)	25	1.73(6)						72O	T
	sp	1(NaClO$_4$)	25	1.93						62Le	T
	sp	1.2(H$^+$-NaClO$_4$)	25		4.1					66L	T

Table III.2. Stability constants for complexes of thiocyanate ion with main group elements in non-aqueous media.

Metal Ion	Method	Solvent	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	Ref	Category
Na^+	con	DMF	--	25	0.89				55A	Rj
	con	sulfolane	--	30	0.66				62A	Rj
K^+	con	adipo-nitrile	--	25	1.3				67Se	Rj
In^{3+}	In(Hg)	DMF	1(LiClO$_4$)	25	4.18	6.40	8.30	10.34	71Sm	T
	In(Hg)	DMSO	1(LiClO$_4$)	25	2.04(8)	4.4(2)	5.1(1)		73R	T
	In(Hg)	form-amide	1.1(NaNO$_3$)	25	2.10	2.70	3.18	3.76	72S	D
	In (Hg)	MeOH	1(Na$^+$-LiClO$_4$)	25	4.78(7)	8.00(9)	11.2(2)	14.23(5)	80S	T
Sn^{2+}	Sn(Hg)	DMAA	1(NaClO$_4$)	25	2.55(2)	4.35(1)	5.98(1)		87G	T
	Sn(Hg)	DMF	1(NaClO$_4$)	25	1.9(1)	2.49(4)	4.43(3)		76Sa	T
	Sn(Hg)	DMSO	1(NaClO$_4$)	25	0.93(1)				73S	T
	Sn(Hg)	EtOH	1(NaClO$_4$)	25	4.70(1)	6.40(6)	7.93(3)		76Sa	T
	Sn(Hg)	MeOH	1(NaClO$_4$)	25	4.48(5)	5.93(1)	6.79(2)		76Sa	T
Pb^{+2}	Pb(Hg)	DMAA	1(NaClO$_4$)	25	1.70(2)	2.62(2)	3.18(6)		82S	T
	Pb(Hg)	DMF	0	25	1.30	1.80	1.90	2.04	68S	T
	Pb(Hg)	DMSO	1(NaClO$_4$)	25	0.00(4)	0.86(2)			73S	T
	pol	MeOH	2(NH$_4$NO$_3$)	25	3.31	2.92	3.28		59T	T
Bi^{3+}	Bi(Hg)	DMF	1(Li$^+$-NaClO$_4$)	25	1.93(5)	2.8(1)	6.2(1)	7.8(1)	83S	T
	Bi(Hg)	DMSO	1(H$^+$-NaClO$_4$)	25	1.40(6)				76S	T

Table III.3. Thermodynamic constants for formation of metal complexes of thiocyanate with main group elements.

Metal Ion	Method	*I* mol dm $^{-3}$	T °C	j	ΔH_i kJmol^{-1}	ΔSj J mol^{-1}K^{-1}	Ref	Category
In^{3+}	cal	2.0(H^+-$NaClO_4$)	25	j1	-6.9(1)	+25.5(8)	0.00	T
				j2	-15.9(8)	-35(2)		
				j3	+10.0(1)	+53(4)		
Tl^+	Tl(Hg)	--		j1	+12(2)	+27(5)	53B	D
Pb^{2+}	sol	3($LiClO_4$)	25	j1	-17(6)	-50(20)	69F	T
				j2	-0.7(6)	-0.6(6)		
				j3	-1.3(5)	-1.3(7)		
				j4	-0.9(5)	-1.0(8)		
				j5	-2.8(5)	-3.1(8)		
Bi^{3+}	Bi(Hg)	3(H^+-$LiClO_4$)	25.0(1)	j1	+34(2)	+140(20)	71Fd	T
				j2	+42(4)	+200(20)		
				j3	+46(8)	+130(30)		
				j4	+30(20)	+190(40)		

Table III.4. Stability constants for complexes of thiocyanate with 3d transition elements.

Metal Ion	Method	I mol dm^{-3}	T °C	lg β_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Sc^{3+}	sp	0.6($HClO_4$)	20	0.20(5)						64Ka	T
	ext	1.0($NaClO_4$)	20.0(5)	0.36(4)	0.65(6)	0.88(7)	1.1(5)			70S	T
	sp	4.75(H^+-$NaClO_4$)	20	0.89						67K	D
Ti^{4+}	sp	0.1(H^+-$LiClO_4$)	25	0.5(1)						77T	T
	sp	1.0(H^+NaClO_4)	25	0.36(8)						80M	T
V^{2+}	sp	0.5($LiClO_4$)	25.0	1.4(1)						83N	T
	sp	0.84(H^+-$LiClO_4$)	25	1.43(8)						68M	T
V^{3+}	sp	1.0($HClO_4$)	25.0	2.07(3)						67B	R
	sp	2.5(H^+-$NaClO_4$)	25(1)	1.9(1)						51F	R
VO_2^+	Ag	0	25	2.32(2)	3.68(6)					68Sc	T
	sp	2.6(H^+-$NaClO_4$)	25(1)	0.92(3)						51F	T
Cr2+	sp	0	25	1.05(5)	1.86(1)					58Y	D
Cr^{3+}	con	--	--	2.52	3.76	4.42	4.70	4.61	4.22	21B	Rj
	tit	1(H^+-$NaClO_4$)	25	1.87(1)						54P	D
	elec	1($NaNO_3$)	100	2.30	3.72	4.06	4.20	3.68		75L	Rj
Cr^{VI}	sp	0.15(H^+-$NaClO_4$)	25.0(1)	0.96(4)						69N	D
Mn^{2+}	sp	0	23-24	1.24(2)						58Y	Rj
	sp	1.25(?)	23-24	1.06						58Y	Rj
	sp	1.00(H^+-$NaClO_4$)	25	0.65(5)						73Hu	D
	pol	1.5(H^+-$NaClO_4$)	25.0(1)	0.73(1)						63T	T
	sp	1.5(H^+-$NaClO_4$)	25.0(1)	0.73(2)	1.3(1)					64Tr	T
	ir	3($NaClO_4$)	--	0.64						62F	Rj
Fe^{2+}	sp	3.0(H^+-M-g(ClO_4)$_2$)	25.0	0.84(4)						67C	T
Fe^{3+}	sp	0	--	2.95						47F	Rj
	sp	0	--	3.12						62V	Rj
	sp	0	18	3.04	4.64					58Pe	D
	sp	0	22-23	3.10	5.30	6.22				64Va	Rj
	sp	0	25	2.94						53Be	D

III.4 continued

Metal Ion	Method	I mol dm^{-3}	T C	lg$_1$ mol^{-1}dm^3	lg$_2$ mol^{-2}dm^6	lg$_3$ mol^{-3}dm^9	lg$_4$ mol^{-4}dm^{12}	lg$_5$ mol^{-5}dm^{15}	lg$_6$ mol^{-6}dm^{18}	Ref	Category
	Au	0	25	3.03						56L	R
	sf	0	25.0(1)	3.08						78B	D
	sp	0.1(HCl)	25	2.29	3.87	3.65				37M	Rj
	sp	0.2(H$^+$-NO$_3$–)	20.0(1)	2.32(4)						82D	Rj
	sp	0.2(H$^+$-NaClO$_4$)	25.0(1)	2.18(2)						76J	D
	sf	0.4(H$^+$-NaClO$_4$)	25.0(1)	2.22						78B	D
	tj	0.40(H$^+$-NaClO$_4$)	25.0	2.12						81T	T
	sf	0.4(H$^+$-NaClO$_4$)	25	2.15						83M	T
	sp	0.5(HClO$_4$)	--	2.14(1)						47F	Rj
	pol	0.5(HClO$_4$)	--	1.83(3)						60T	Rj
	sp	0.5(KNO$_3$)	25	2.26(4)						76V	Rj
	sp	0.5(H$^+$-NaClO$_4$)	25	2.14	3.46					56L	T
	sp	0.6(H$_2$SO$_4$)	--	1.78(2)						50H	Rj
	sp	0.6(HClO$_4$)	20	2.15(1)						64K	D
	Pt	0.65(H$^+$-NaClO$_4$)	18	2.12	3.12					58Pe	T
	sp	1(HClO$_4$)	--	2.10(4)						41E	Rj
	sp	1.0(NaClO$_4$)	--	2.05						62V	Rj
	ext	1.0(H$^+$-NaClO$_4$)	18.0(1)	2.11(3)						51M	R
	sp	1(KNO$_3$)	20(1)	2.11						57Y	Rj
	ext	1(NaCF3SO$_4$)	24	2.30(5)	3.99(7)	4.4(1)				85B	D
	ext	1-10(KNCS)	24				4.2	3.2	1.5	85B	T
	Pt	1(H$^+$-NaClO$_4$)	25.0(1)	2.10(1)	3.14					68Po	R
	sf	1.0(H$^+$-NaClO$_4$)	25	2.11(2)	2.75(1)					78M	R
	sf	1.0(H$^+$-NaClO$_4$)	25	2.07(2)						80G	T
	sp	1.0(H$^+$-NaClO$_4$)	25	2.06						81Kr	T
	sp	1(H$^+$-NaClO$_4$)	25	2.11(1)	3.34(2)	3.82(9)	3.6(3)	4.3(2)	5.0(2)	92O	R
	sp	1(HClO$_4$)	26.7	2.15						61Y	T
	sp	1.2(?)	20	2.12(1)						68Ms	Rj
	sp	1.2(H$^+$-NaClO$_4$)	25.0(1)	2.11(1)	3.20					55Li	R
	sp	1.28(HClO$_4$)	25	2.06	3.36					53Be	T
	sp	1.4(H$^+$-NaClO$_4$)	--	2.34	3.90	5.21	5.86	6.07		64J	Rj
	ext	2(H$^+$-NaClO$_4$)	20.0(1)	2.09	3.57	4.57	5.24	5.42	5.36	73M	D
	sf	2(H$^+$-Mg(ClO$_4$)$_2$)	25.0	2.23						76H	Rj

III.4 continued

Metal Ion	Method	I mol dm^{-3}	T C	lg$_1$ mol^{-1}dm^3	lg$_2$ mol^{-2}dm^6	lg$_3$ mol^{-3}dm^9	lg$_4$ mol^{-4}dm^{12}	lg$_5$ mol^{-5}dm^{15}	lg$_6$ mol^{-6}dm^{18}	Ref	Category
	nmr	3Na(ClO_4,SCN)	25	2.53	3.88	5.19	6.52	6.20		83Ko	Rj
	sp	4(H^+-$NaNO_3$)	22-23	2.1	3.4	3.9	0	3.8	3.7	64Va	Rj
Co^{2+}	sp	--	--	0.95(7)	1.6(2)	1.8(2)	-0.3(3)			62Ti	Rj
	AgSCN	--	25.0	1.87(2)						71D	Rj
	AgSCN	--	35	1.77						68Pr	Rj
	ix	NO_3—(Li^+,NH_4^+)	150	0.36						75Si	Rj
	sp	0	23-24	1.51(3)						58Ya	Rj
	sp	0	22-24	1.75(7)						64K	Rj
	sp	0.16(H^+-$NaClO_4$)	25	1.72						62W	D
	sp	0.5	1.5	1.20						61D	Rj
	sp	0.5($NaClO_4$)	25	1.08(3)	1.73(5)	2.0(1)	-0.078(2)			85S	T
	sp	0.5($NaClO_4$)	25	1.2(2)	1.6(3)					88I	T
	sp	0.6($HClO_4$)	20	1.10(2)						64Ka	T
	sp	0.6($HClO_4$)	25	1.15						51S	T
	pol	0.85	20	1.06(2)						60T	Rj
	sp	1.0($NaClO_4$)	20(1)	0.40						58Sm	Rj
	sp	1(H^+-$NaClO_4$)	25(1)	1.01(1)						58S	R
	pol	1.0(H^+-KNO_3)	25	1.04(2)						68Tu	Rj
	sp	1($NaClO_4$)	25	1.00	1.32					71Sk	R
	sf	1.0(H^+-$NaClO_4$)	25	0.95(4)						73Hu	T
	ir	1.1($KClO_4$)	--	0.95						62F	Rj
	sp	1.5(H^+-$NaClO_4$)	25	0.98(2)						62T	T
	pol	1.5($NaClO_4$)	25.0(1)	0.98(2)	2.00(9)	3.4(2)				63T	T
	nmr	1.5($NaClO_4$)	27	1.18(4)	1.6(2)	1.0(1)	-0.30(7)			70Z	T
	sp	3.0(KNO_3)	22-24	0.63	0	-0.38				64K	Rj
	ext	3($NaClO_4$)	25	-0.46	-1.08					63D	Rj
	sp	3($LiClO_4$)	25	1.27						70M	T
Ni^{2+}	ix	--	--	2.22	2.43	2.62	2.15			71L	Rj
	AgSCN	--	25.0(1)	1.98(2)						71D	Rj
	kin	O	20	1.83						74D	T
	sp	0.06(Ni(ClO_4)$_2$)	25	1.50						61M	D

III.4 continued

Metal Ion	Method	I mol dm^{-3}	T °C	lg$_1$ mol^{-1}dm^3	lg$_2$ mol^{-2}dm^6	lg$_3$ mol^{-3}dm^9	lg$_4$ mol^{-4}dm^{12}	lg$_5$ mol^{-5}dm^{15}	lg$_6$ mol^{-6}dm^{18}	Ref	Category
	sp	0.2	25-27	1.20						62K	Rj
	sp	0.4(NaClO$_4$)	25	1.76(6)						62W	T
	sp	0.5	1.4	1.38						61D	Rj
	pol	0.65(HClO$_4$)	25	1.24(2)						68Ma	T
	ix	1(H$^+$-NaClO$_4$)	20.0	1.18(2)	1.64(4)	1.81(7)				53Fr	R
	sp	NO$_3$—(H$^+$-Mg^{2+})	23-24	0.96						58Y	Rj
	pol	1(NaClO$_4$)	25	1.17(2)						63T	R
	sp	1.0(H$^+$-NaClO$_4$)	25	1.13(5)						73Hu	R
	cal	1.0(NaClO$_4$)	25.0	1.14(2)	1.58(5)	1.6(2)				74K	R
	ext	1.0(NaClO$_4$)	25.0(3)	1.1	1.6					76M	R
	ext	1.5(H$^+$-NaClO$_4$)	20	1.14(2)	1.75(5)	1.70(4)	2.0(1)			64T	R
	sp	2(NaClO$_4$)	25(2)	1.27(2)						59U	D
	ir	3(NaClO$_4$)	--	1.18						62F	Rj
	sp	3(LiClO$_4$)	25	1.34(1)						70M	D
Cu$^+$	pol	(NH$_4$SCN)	--				9.15			50K	Rj
	Cu	(NaNO$_3$)	20				10.1			56Go	Rj
	sol	5(NaNO$_3$)	25				10.5			59F	Rj
Cu^{2+}	sp	0	23-24	2.57						58Ya	Rj
	sp	0	30	2.39						68D	D
	sp	0.2(?)	25-27	1.72						62K	Rj
	sp	0.5(KNO$_3$)	25	1.74	2.54	2.69	2.99			59Ta	Rj
	ext	1(NaClO$_4$)	25	1.6	2.7					95S	T
	sp	1.0(NaClO$_4$)	25	1.76(7)						73Hu	T
	cal	1(NaClO$_4$)	25.0	1.74(2)	2.74(4)					74K	T
	ext	1(NaClO$_4$)	25	1.7	2.8	3.1				88M	T
	sp	3(LiClO$_4$)	25	1.91(3)						70Mi	D
Zn^{2+}	ix	--	--	1.57	1.56	1.51	3.02			68N	Rj
	Zn(Hg)	--	20	1.46	2.16	2.33	2.01			58G	Rj
	sp	0	23-24	1.2						58Y	Rj

III.4 continued

Metal Ion	Method	I mol dm^{-3}	T C	lg$_1$ mol^{-1}dm^3	lg$_2$ mol^{-2}dm^6	lg$_3$ mol^{-3}dm^9	lg$_4$ mol^{-4}dm^{12}	lg$_5$ mol^{-5}dm^{15}	lg$_6$ mol^{-6}dm^{18}	Ref	Category
	AgSCN	(HClO$_4$)	25	1.49(3)						71D	Rj
	Zn(Hg)	0.02(ZnSO$_4$)	--	1.7						36F	Rj
	sp	0.2	25-27	0.65						62K	Rj
	pol	1	?	0.8	0.8		1.6			75A	Rj
	ix	1	20	1.54						73Cz	Rj
	sp	1.0(HNO$_3$)	20	0.5						57Y	Rj
	ext	1(H$^+$-NaClO$_4$)	20	-0.3(3)	0.8(3)	0.3(3)	0.9(3)			60Tr	D
	Zn(Hg)	1.0(NaClO$_4$)	25.0	0.708(3)	1.04(2)	1.2(1)	1.50(7)			71Ah	R
	ext	1(H$^+$-NaClO$_4$)	25.0(5)	0.56a	1.32	1.18				71Mo	T
	sp	1(H+-NaClO$_4$)	25.0	0.41(6)						73Hu	T
	Zn(Hg)	1.7(KNO$_3$)	--	1.53	2.18					56N	Rj
	Zn(Hg)	2.0(H$^+$-NaClO$_4$)	25.0	0.74	1.15	1.30	1.68			70A	R
	pol	2.0(KNO$_3$)	30	0.48(7)	0.8(2)	0.0(2)	1.30(4)			53F	Rj
	ir	3.0(NaClO$_4$)	--	0.91						62F	Rj
	pol	3.0(NaClO$_4$)	25	-0.14	0.90	1.20	1.29			59Ch	D
	Zn(Hg)	4(LiClO$_4$)	25	1.11	1.81	2.81	2.80			66M	T
	cal	5(NaClO$_4$)	25.0	0.92(2)	1.59(3)	2.17(4)	2.51(3)			85I	T

Table III.5. Stability constants for complexes of thiocyanate with 3d transition elements in non-aqueous media.

Metal Ion	Method	Solvent	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Ti^{4+}	sp	aceto-nitrile	--	--	3.00	6.36	9.74	12.72			74Sy	Rj
Cr^{3+}	sp	acetone	--	--			5.72				63Go	Rj
		MeOH	--	--			4.15			8.26	63Go	Rj
Mn^{2+}	cal	DMF	0.4(Et_4NClO_4)	25.0(2)	0.36(3)	0.58(2)	0.66(2)	0.75(2)			90I	T
Fe^{3+}	sp	aceto-nitrile	1((H^+-$NaClO_4$)	25	2.92	5.50	7.69				81K	D
	cal	DMAA	0.4(Et_4NClO_4)	25.0	5.2(3)	9.3(5)	12.5(5)	14.9(5)	16.4(6)	17.1(6)	93Oz	R
	cal	DMF	1(NH_4ClO_4)	25.0	2.6(2)	4.9(3)	6.8(3)	8.1(3)	8.5(3)		93O	R
	sp	DMSO	0.024($NaNO_3$)	25	3.07						68L	Rj
	sp	DMSO	0.1(H^+-$NaClO_4$)	25	2.92(6)	2.91	4.91				71W	D
	sp	DMSO	1.0(H^+-$NaClO_4$)	25	2.08(1)	4.15(2)	6.16(4)	8.05(6)			81K	D
Co^{2+}	sp	acetone	--	--				13.72			51K	Rj
	ir	aceto-nitrile	--	--	2.89(9)						73M	Rj
	ir	DMAA	--	--	2.69(9)						73M	Rj
	cal	DMF	0.4(Et_4NClO_4)	25	2.4(1)	4.2(6)	6.6(5)	9.9(2)			90I	T
	ir	DMSO	--	--	2.18(9)						73M	Rj
	sp	DMSO	~0($LiClO_4$)	25.0(2)	2.67(7)	4.71(2)		6.76(6)			72Ma	D
	sp	DMSO	0.5($NaClO_4$)	25	1.64	2.50		3.45			73S	D
	sp	MIBK	1.5($NaClO_4$)	20	0.95(7)						62T	D
	ir	TMP	--	--	2.70(9)						73M	Rj

III.5 continued

Metal Ion	Method	Solvent	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
$Ni^{2\bullet}$	ir	aceto-nitrile	--	--	3.70	4.34	2.40				74M	Rj
	kin	aceto-nitrile	0	20	5.52	9.82					74D	T
	ir	DMAA	--	--	3.45(6)	6.30	8.4	9.11			74M	Rj
	kin	DMF	0	20	3.92	6.29					74D	T
	cal	DMF	0.4(Et_4NClO_4)	25	2.7(1)	4.6(1)	5.6(2)	6.3(4)			90I	T
	ir	DMSO	--	--	2.65(2)	2.66					74M	Rj
	kin	DMSO	0	20	3.0	4.54					74D	T
	AgSCN	MeOH	0.03($NaClO_4$)	--	4.78(5)	7.62(8)					70D	Rj
	ir	TMP	--	--	3.28(8)	5.26					74M	Rj
Cu^+	Cu(Hg)	aceto-nitrile	0.1(Et_4NClO_4)	25	3.53(5)	7.08(3)	9.13(6)				83Ah	T
	Cu	DMSO	0.1(Et_4NClO_4)	25	4.3(3)	9.3(1)					72Fo	T
	Ag(Hg)	pyridine	0.1(Et_4NClO_4)	25	2.62(1)	3.83(2)					86Ah	T
Cu^{2+}	sp	acetone	--	0.0(1)				11.52			80C	Rj
	sp	n-BuOH	0.05(Bu_4NClO_4)	0.0(1)				15.15			82C	T
	Cu	DMSO	0.1(Et_4NClO_4)	25	3.2	5.3					72F	T
	sp	EtOH	0.05(Bu_4NClO_4)	0.0(1)		9					82C	T
	cal	MeOH	--	20(1)	3.50(4)	6.13(6)	7.1(2)				76R	Rj
	sp	MeOH	0.05(Bu_4NClO_4)	0.0(1)		8					82C	T
	sp	n-$C_5H_{11}OH$	0.05(Bu_4NClO_4)	0.0(1)				16.23			82C	T

III.5 continued

Metal Ion	Method	Solvent	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
	sp	n-PrOH	0.05(Bu_4NClO_4)	0.0(1)				13.76			82C	T
Zn^{2+}	Zn(Hg)	DMAA	1($NaClO_4$)	25	3.3(1)						82S	T
	cal	DMF	0.40(Et_4NClO_4)	25.0(2)	3.33(5)		10.23(6)	13.31(7)			90I	T
	Zn(Hg)	DMF	1.5($LiClO_4$)	25.0(1)	2.0(6)	4	6.5(4)	8.6(1)	7.6		79L	T
	Zn(Hg)	DMSO	1.00(NH_4Cl)	25	1.38(4)	2.8(4)	5.20(9)	6.86(4)			76Ac	T
	Zn(Hg)	DMSO	1($LiClO_4$)	25	3.53(9)	4.1(1)	5.6(7)				73S	T
	ise	MeOH	0	25.0(1)	5.24(1)	7.83	10.85	12.96			83D	T
	ise	MeOH	0	25.0(1)	5.32(1)	8.3(3)					87D	T
	ise	MeOH	0.05($NaClO_4$)	25.0(1)	4.31(1)	7(3)					87D	T

Table III.6. Thermodynamic constants for formation of metal complexes of thiocyanate with 3d transition elements

Metal Ion	Method	I mol dm^{-3}	T °C	j	ΔH_j kJ mol^{-1}	ΔS_j J mol^{-1} K^{-1}	Ref	Category
V^{2+}	sp	0.84((H^+-$NaClO_4$)	25	j1	-22(3)		-50(10)	
V^{3+}	sp	1.0($HClO_4$)	25.0	j1	-15(1)	-9(5)	67B	
	sp	2.5(H^+-$NaClO_4$)	25(1)	j1	-15		51F	T
VO^{2+}	Ag	0	25	j1	-17(2)	-11(8)	68Sc	T
	sp	2.6(H^+-$NaClO_4$)	25(1)	j1	+2(2)		51F	T
Cr^{3+}	sp	--	25	j1	-8.9	+29	55P	Rj
Mn^{2+}	cal	0	25	j1	-3.8(8)	+10(3)	67N	Rj
	AgSCN	0	25	j1	-13.8(2)	-24.1(2)	71D	Rj
	cal	0.4(Et_4NClO_4) DMF solvent	25	j1	-1.0(1)		90I	T
				j2	-2.6(4)			
				j3	+7(4)			
				j4	+15(1)	+159		
Fe^{3+}	sp	0	25	j1	-6.7	+35	53Be	R
	sp	0	25	j1	-6.7	+36	56L	R
				j2	-8			
	Pt	0	25	j1	-2.2	+50	61Y	D
	sp	0.2(H^+-$NaClO_4$)	25.0(1)	j1	-15.1		76J	Rj
	tj	0.40(H^+-$NaClO_4$)	25.0	j1	-6.7		81T	R
	cal	0.50(HNO_3)	25	j1	-6.2(4)	+23(2)	76V	Rj
	sf	1.0(H^+-$NaClO_4$)	25	j1	-8.8(4)	+20(10)	78M	D

III.6 continued

Metal Ion	Method	I mol dm^{-3}	T °C	j	ΔH_j kJ mol^{-1}	ΔS_j J mol^{-1} K^{-1}	Ref	Category
	cal	1.0(H$^+$-NaClO$_4$)	25.0	j1	-5.6(2)	+22(6)	92O	T
				j2	-11.0(4)	+30(10)		
				j3	--18.9(6)	+10(20)		
	sp	1.1(H$^+$-LiClO$_4$)	22	j1	-6.2	+20	65Mi	T
	cal	0.4(Et$_4$NClO$_4$) DMAA solvent	25.0	j1	+1.8(1)	+106(5)	93Oz	R
				j2	-0.1(2)	+178(6)		
				j3	-5.6(1)	+221(6)		
				j4	-14.1(3)	+237(6)		
				j5	-24(1)	+234(8)		
				j6	-36(1)	+200(10)		
	cal	1(NH$_4$ClO$_4$) DMF solvent	25	j1	+2.7(2)	+59	93O	
				j2	+1.9(4)	+101		
				j3	-1.1(4)	+126		
				j4	-6.8(9)	+133		
				j5	-22.1(6)	+89		
Co^{2+}	AgSCN	0	25.0(1)	j1	-19(2)	-27(2)	71D	D
	cal	0	25	j1	-6.8(7)	+9(3)	67N	T
	sp	0.5(NaClO$_4$)	25	j1	-20(2)	-47(9)	85S	T
				j2	-45(4)	-120(10)		
				j3	-72(4)	-200(10)		
				j4	-45(9)	-30(30)		
	sp	0.5(Et$_4$NClO$_4$)	25	j1	-8(2)	-4	88I	T

III.6 continued

Metal Ion	Method	I mol dm^{-3}	T °C	j	ΔH_j kJ mol^{-1}	ΔS_j J mol^{-1} K^{-1}	Ref	Category
				j2	-22(2)	-45		
	nmr	1.5($NaClO_4$)	27	j1	+17(6)		70Z	Rj
				j2	-7(9)			
				j3	1(10)			
				j4	8(30)			
	cal	0.4(Et_4NClO_4) DMF solvent	25	j1	-0.9(4)		90I	T
				j2	-20(20)			
				j3	+30(40)			
				j4	+5.7(1)	+209		
Ni^{2+}	cal	0	25	j1	-9.4(3)	+2(2)	62W,67N	D
	AgSCN	0	25.0(1)	j1	-23(2)	-34(2)	71D	D
	sp	0.06($Ni(ClO_4)_2$)	25	j1	-55	+214	61M	D
	pol	0.65($HClO_4$)	25	j1	-14.4	-24	68Ma	T
	cal	1.0($NaClO_4$)	25.0	j1	-12.0(2)	-18.5(6)	74K	T
				j2	-21(2)	-40(3)		
				j3	-29(4)	-70(10)		
	cal	0.4(Et_4NClO_4) DMF solvent	25	j1	-0.72(2)		90I	T
				j2	-2.5(1)			
				j3	-6(1)			
				j4	-4.0(5)	+107		

III.6 continued

Metal Ion	Method	I mol dm^{-3}	T °C	j	ΔH_j kJ mol^{-1}	ΔS_j J mol^{-1} K^{-1}	Ref	Category
Cu$^+$	cal	0.1(Et$_4$NClO$_4$) acetonitrile solvent	25	j1	-5.4(8)		83A	T
				j2	+0.6(7)			
	cal	0.1(Et$_4$NClO$_4$) pyridine solvent	25	j1	+4.7	+66	86Ah	T
				j2	+11.6	+112		
Cu^{+2}	cal	0	25	j1	-12.6(7)	+2(2)	67N	T
	sp	0.5(Bu$_4$NClO$_4$) n-BuOH solvent	0.0(1)	j1	-14		82C	T
				j2	-24			
	sp	0.5(Bu$_4$NClO$_4$) EtOH solvent	0.0(1)	j2	-36		82C	T
	sp	-- MeOH solvent	--	j1	+2.5(4)	+100(8)	76R	Rj
				j2	+4.2(6)	+160(10)		
				j3	-23(4)	+80(20)		
	sp	0.5(Bu$_4$NClO$_4$) n-C$_5$H$_{11}$OH solvent	0.0(1)	j1	-8.8		82C	T
				j2	-18			
	sp	0.5(Bu$_4$NClO$_4$) n-PrOH solvent	0.0(1)	j1	-23		82C	T
				j2	-36			
Zn^{2+}	cal	0	25	j1	+0.9(8)	+38(3)	67N	Rj
	con	--	20	j4	-24		58G	Rj
	AgSCN	(HClO$_4$)	25	j1	-11(2)	-8(2)	71D	Rj
	cal	1.00(NaClO$_4$)	25.0	j1	-5.8(2)	-5.9(5)	71Ah	R

III.6 continued

Metal Ion	Method	I mol dm^{-3}	T °C	j	ΔH_j kJ mol^{-1}	ΔS_j J mol^{-1} K^{-1}	Ref	Category
				j2	-2(1)	0(4)		
				j3	-1(3)	0(10)		
				j4	-8(4)	-20(10)		
	cal	5(NaClO$_4$)	25.0	j1	-5.0(1)	+1	85I	R
				j2	-2.1(1)	+23		
				j3	-8.4(4)	-10		
				j4	-12.8(2)	-8		
	cal	-- DMF solvent	25	j4	-8.4		74Go	Rj
	cal	0.40(Et$_4$NClO$_4$) DMF solvent	25.0(2)	j1	+4.9(3)	+0.08	90Is	T
				j3	+9.5(4)	+0.23		
				j4	-7.9(1)	+0.23		
	cal	1(NH$_4$ClO$_4$) DMSO solvent	25	j1	+5.5(7)	+45(3)	76Al	T
				j2	+24(4)	+10(20)		
				j3	-18(4)	-10(10)		
				j4	-10.7(6)	-4(3)		

Table III.7. Stability constants for complexes of thiocyanate with 4d and 5d transition elements

Metal Ion	Method	I mol dm^{-3}	T °C	lg β_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Y^{3+}	sp	0.6(HClO$_4$)	20	-0.06(2)						64Ka	T
	ix	2.0(NaClO$_4$)	25	-0.27	-0.43	-0.66				86G	T
Zr^{IV}	sp	0.1(HClO$_4$)	--	2.0	3.4	4.7	5.8			66Go	Rj
	ext	3(HClO$_4$)	--	1.08(8)	2.33(0)		2.31(4)			71La	Rj
	ext	3.5(HClO$_4$)	--	0.95(3)						76T	Rj
Mo^{III}	sp	--	25	5						73Ss	Rj
Mo^{IV}	sp	2.0(LiClO$_4$)	25	2.6(3)						76F	D
Mo^{V}	sp	1.6(HCl,KNCS)	20(1)	1.6(1)						58P	D
	sp	2(NaClO$_4$)	25	2.41(4)						75S	T
	sp	3.1(H$_2$SO$_4$)	--			2.2(1)	4(2)	5(2)		59N	Rj
Mo^{VI}	sp	1(H$_2$SO$_4$)	--	2.55	3.44	4.39	4.47			63Mu	Rj
Ru^{3+}	sp	1	--	1.63(1)						64Sh	Rj
	sp	1.0(H$^+$-LiClO$_4$)	25(1)	1.78(1)						52Ya	T
Pd^{2+}	sp	--	--		7.5					62Sh	Rj
	sp	(NaClO$_4$)	25		8.38		19.46			64G	Rj
	sp	0	27		16.8		25.6			73J	D
	sp	0.1(HClO$_4$)	27		16.2		25.6			73J	D
	Pd	1(KNO$_3$)	18-20				27.6(3)			63Gr	D
	gl	1(NaClO$_4$)	20				27.6			76An	D
	pol	1	25	1.04	1.87	1.0	2.4			60D	Rj
	Pd	1(KNCS)	25				26.2			65F	D
	sp	1.1(H$^+$-NaClO$_4$)	25.0(2)				28.22			66B	D
	sp	1.1((H$^+$-NaCl)	25.0(2)				28.7(3)			67Bi	Rj

III.7 continued

Metal Ion	Method	I mol dm^{-3}	T °C	lg β_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Ag^+	Ag	--	--	10.43	10.60	10.74				36F	Rj
	Ag	--	20				10.54			56G	Rj
	Ag	--	25		8.20					67Al	Rj
	sol	0	25		8.39	9.62	9.90			53C	D
	ise	0.10	25.0	5.2(1)						75La	Rj
	Ag	0.11(NaClO$_4$)	25	4.26(3)	8.0(1)	11(5)				55L	D
	Ag	0.4(LiClO$_4$)	--	4.4	7.9	9.0	9.7			81Tu	Rj
	Ag	1(NaNO$_3$)	20				10.19			53J	D
	Ag	1(KNO$_3$)	25	7.03	8.64	9.97	10.59			80D	D
	sol	1.1	25		1.11					30R	Rj
	sol	2.2(KNO$_3$)	25		7.57	9.08	10.08			53C	D
Cd^{2+}	Cd(Hg)	--	--	2.10						36F	Rj
	ix	--	--	1.74	2.40	1.40	2.91			66A	Rj
	sp	--	--	1.19						67L	Rj
	pol	(NH$_4$SCN)	25			1.28	1.34		1.33	51Ko	Rj
	sp	(HClO$_4$)	25	2.11(1)						71D	Rj
	ext	(HClO$_4$)	30.0(5)	0.7	1.5					65He	Rj
	Cd(Hg)	0	25.0(1)	1.89(3)	2.78(5)	2.85(8)	2.3(1)			73Ru	T
	Ag(Hg)	0	35	2.08						68Pr	D
	Cd(Hg)	0.3(HClO$_4$)	25	0.67	1.98					76L	Rj
	Cd(Hg)	0.1(KNO$_3$)	20	1.4	2.5					71Pl	Rj
	pol	0.1(KNO$_3$)	25.0(3)	1.74(7)						57T	Rj
	sp	0.2(?)	25-27	1.23						62K	Rj
	pol	0.5(LiClO$_4$)	25.0(2)	1.42	2.15					82Ts	Rj
	sp	0.6(H$^+$-Fe(ClO$_4$)$_3$)	20	1.32(1)						64Ka	R
	pol	1(H$^+$-NaClO$_4$)	25.0(5)	1.31(4)	2.0(2)	4.8(1)				63T	R

III.7 continued

Metal Ion	Method	I mol dm^{-3}	T °C	lg β_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
	Cd(Hg)	1.00(H$^+$-NaClO$_4$)	25.0	1.32(1)	1.99(3)	2.03(8)	1.9(2)			68G	R
	sp	1.00(NaClO$_4$)	25.0	1.34(4)						73Hu	R
	pol	1.0(NaClO$_4$)	25.00(5)	1.28(2)	1.95(3)	2.26(2)				78A	R
	pol	1.0(NaClO$_4$)	25.0(1)	1.44	1.81	2.13	2.36			86C	T
	ext	1.5(H$^+$-NaClO$_4$)	--	1.32(2)	2.00(3)	2.55(7)				64T	Rj
	Cd(Hg)	2(KNO$_3$)	20	1.90	2.24	2.36				57G	Rj
	sp	2(KNO$_3$)	22-23	1.11						63V	Rj
	pol	2(NH$_4$NO$_3$)	25	1.08	1.62	0.96	1.64			59Tu	Rj
	pol	2.0(H$^+$-NaClO$_4$)	25.0(1)	1.40	1.88	1.93	2.38			61S	D
	pol	2.00(H$^+$-KNO$_3$)	25	1.12(7)	1.67(6)		1.93(2)			67M	Rj
	pol	2.0(NaClO$_4$)	25.0(1)	1.26(3)	2.14(5)	1.9(1)	2.25(4)			69M	T
	pol	2.0(NaNO$_3$)	25.0(1)	1.04	1.75	0.78	1.78			81K	Rj
	pol	2.0(KNO$_3$)	30.0(1)	1.04(2)	2.79(3)	3.6(2)	5.4(2)			51H	Rj
	pol	2(KNO$_3$)	30.0(1)	1.00	1.74	1.87	1.64			67H	Rj
	Cd(Hg)	3(NaClO$_4$)	25	1.39	1.98	2.58				41L	R
	pol	3.0(NaClO$_4$)	25	1.36(0)	2.09(1)	2.38(2)	2.48(4)	2.22(7)	1.7(1)	57Ts	R
	Cd(Hg)	3.0(H$^+$-NaClO$_4$)	25.0	1.41(2)	2.24(4)	2.48(7)	2.5(2)			66Ge	R
	cal	3(NaClO$_4$)	25.00(1)	1.37	1.77	1.82	2.00			86I	R
	Cd(Hg)	4(NaClO$_4$)	25	1.26(5)	2.38(4)	2.73(5)	2.91(5)			78Fr	T
Hf^{IV}	sp	0.1(HClO$_4$)	--	2.0	4.0	5.6	7.2			66Go	Rj
	ext	3(HClO$_4$)	--	1.1(1)	2.33(4)	2.22(8)				71La	Rj

III.7 continued

Metal Ion	Method	I mol dm^{-3}	T °C	lg β_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
	ext	3.5($HClO_4$)	--	1.04(2)						76T	Rj
Re^{IV}	sp	--	--	4.2						69Mu	Rj
	sp	--	--		3.95					71Mu	Rj
Pt^{2+}	Pt	0.5(KNCS)	25				33.6			77H	T
Au^{+}	Au	0.1(NaNCS)	25		25					70Ha	Rj
	Au	3($NaClO_4$)	25(1)	15.3(2)	17.0(1)					66K	T
Hg^{2+}	Hg	--	--					22.05	2 1.67	60G	Rj
	Hg	--	25				21.99			O5S	Rj
	pol	0	25		17.25	19.97	21.69			62Ta	T
	sp	0.10($HClO_4$)	25		16.43					71F	T
	pol	0.1(KNO_3)	25.0(1)		16.5(6)					86E	D
	pol	0.1(KNO_3)	30.0(1)		17.60	20.40	21.23			64St	D
	pol	0.2(KNO_3)	18				19.30			49Ko	Rj
	pol	0.2(KNO_3)	25		16.43(3)	19.14(1)	21.12(1)			62Ta	T
	Hg	0.3($NaNO_3$)	25				21.89			56T	T
	sp	0.35(H^+-$Fe(NO_3)_3$)	25(1)		17.47					56Y	Rj
	Hg	1(KNO_3)	18				22.4			05G	D
	pol	1.0($NaClO_4$)	25		16.07(3)	18.95(1)	20.94(4)			60N	R
	Hg	1($NaClO_4$)	25	9.08(3)	16.86(5)	19.7(1)	21.67(3)			70C	R

Table III.8. Stability constants for complexes of thiocyanate with 4d and 5d transition elements in non-aqueous media.

Metal Ion	Method	Solvent	I mol dm^{-3}	T °C	$lg\beta_1$ mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Zr^{IV}	sp	DMF	–	20	2.17	3.17	6.04	7.80	9.43	10.96	70G	Rj
Nb^V	sp	n-BuOH	–	20	4.37	8.58		16.92			64Gu	Rj
	sp	DMF	–	20	3.08	6.11	8.92	11.55	14.15	16.72	64Gu	Rj
	sp	MeOH	–	20	3.58	6.74	9.23				64Gu	Rj
Mo^V	sp	acetone	–	–	4.95	8.72	12.68	16.1			65U	Rj
		MeOH	–	–	3.85	6					65U	Rj
Ag$^+$	Ag	DMAA	0.01-0.05 (Et_4Npicrate)	25		11.4					67Al	D
	Ag	DMF	0.01-0.05 (Et_4Npicrate)	25		11.9					67Al	D
	Ag	DMF	0.1($LiClO_4$)	–	11.0(3)	11.9(3)					70Br	Rj
	Ag	DMSO	0.01-0.05 (Et_4Npicrate)	25		7.4					67Al	D
	Ag	DMSO	0.1(Et_4NClO_4)	–		8.4					70L	Rj
	Ag	ethylene glycol	0.1($HClO_4$)	–		16.8(3)					72Br	Rj
	Ag	HMPT	0.01-0.05 (Et_4Npicrate)	25	9.7						67Al	D
	Ag	N-methyl-pyrrolidone	0.1($LiClO_4$)	–	10.2(3)	11.3(3)					70B	Rj
	Ag	propylene carbonate	0.1(Et_4NClO_4)	22		16.0(1)	18.7(1)				69Co	T
	Ag(Hg)	pyridine	0.1(Et_4NClO_4)	25	3.64(1)	5.56(2)					86A	T
	ir	pyridine	1(KNCS)	–	2.55(3)	4.44(4)	4.5(1)				68Lr	Rj
	Ag	pyridine	1.5(py HCl)	25	2.26(3)	3.83(2)	3.69(3)				68Mi	T
	Ag	2-pyrrolidone	0.1(Et_4NClO_4)	30		8.7(3)					71Ba	T
	Ag	sulfolane	0.1(Et_4NClO_4)	30.0(2)		16.04					68De	T

III.8 continued

Metal Ion	Method	Solvent	I mol dm^{-3}	T °C	lgβ^1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
	Ag	sulfolane	0.1(Et_4NClO_4)	30.0(1)		14.9(4)					82A	T
Cd^{2+}	Cd(Hg)	acetone	?(KNO_3)	20			0.18				57G	Rj
	Cd(Hg)	acetonitrile	1.6($NaClO_4$)	20				13.33	14.00		64G	T
	Cd(Hg)	DMAA	1($NaClO_4$)	25	2.78(2)	4.65(5)	6.81(3)				81S	T
	cal	DMF	1(NH_4ClO_4)	25.0(2)	2.77(8)	4.6(1)	5.7(1)	6.6(1)			88Is	T
	Cd(Hg)	DMF	1.2($NaClO_4$)	20	3.00	4.51	6.30	6.68			64G	T
	Cd(Hg)	DMF	1.60($LiClO_4$)	25.0(1)	3.62(9)	4.41(1)	5.6(1)	6.5(2)	7.3(1)		79L	T
	Cd(Hg)	DMSO	1($LiClO_4$)	25	1.79(4)	2.54(3)	2.72(2)				74S	R
	Cd(Hg)	DMSO	1.00(NH_4ClO_4)	25.0	1.81(1)	2.72(3)	2.93(5)				76A	R
	Cd(Hg)	dioxane	(KNO_3)	20	2.18	2.36					57G	Rj
	pol	formamide	1($NaClO_4$)	--	1.78	2.50	1.78	3.80			60Hs	Rj
	Cd(Hg)	formamide	1.1($NaNO_3$)	25	1.48(3)	2.18(2)	3.04(8)				71Sa	Rj
	ise	MeOH	0	25.0	5.86(1)	9.1(3)					87D	T
	ise	MeOH	0.05($NaClO_4$)	25.0	4.77(1)	7.43(3)					87D	T
	Cd(Hg)	MeOH	1.6($NaClO_4$)	20	3.00	5.51	5.89	6.77			64G	T
	pol	MeOH	2(NH_4NO_3)	25	2.77	3.92	4.28	4.85			59Tu	Rj
Hf^{IV}	sp	DMF	--	20	2.77	3.49	4.12	6.68	8.13	9.49	70G	Rj
Ta^{V}	sp	i-BuOH	--	--	3.68	7.04	11.42				64Gl	Rj
	sp	DMF	--	--	3.15	5.92	8.55	11.06	13.52	15.96	64Gl	Rj
	sp	MeOH	--	--	3.13	5.48	7.77				64Gl	Rj
Au^{+}	Au	acetonitrile	0.10(Et_4NClO_4)	24.0(5)		20.18					68Go	R
	Au	acetonitrile	0.1(Et_4NClO_4)	25		20.0(2)					89A	R
	Au	pyridine	0.1(Et_4NClO_4)	25	4.63(0)	8.36(4)					89A	T

III.8 continued

Metal Ion	Method	Solvent	I mol dm^{-3}	T °C	lgβ^1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Hg^{2+}	Hg	acetone	–	20			27				60G	Rj
	sol	acetone	0.5($NaNO_3$)	20			7.24				60C	R
	sol	acetone	1.4($LiNO_3$)	20			6.97				59Cz	R
	pol	DMAA	0.1($LiClO_4$)	–				26.8(3)			71Br	Rj
	–	DMF	–	–	10.10						75B	Rj
	pol	DMF	0.1($HClO_4$)	–				22.50			66Br	Rj
	Hg	DMF	0.1(Et_4NClO_4)	40.0(2)		17.7(2)		25.2(2)			69Pu	T
	–	DMSO	–	–	10.70						75Ba	Rj
	Hg	DMSO	0.1(Et_4NClO_4)	25		16.1	19.1	21.2			72F	D
	Hg	DMSO	1($LiClO_4$)	25		16.11(7)	19.0(1)	20.41(4)			74S	D
	Hg	DMSO	1.0(NH_4ClO_4)	25	7.48(4)	13.08(3)	16.03(3)	18.27(7)			85A	T
	–	N-methyl-acetamide	–	–	9.50						75Ba	Rj
	Hg	N-methyl-acetamide	0.1(Et_4NClO_4)	40.0(2)		14.6(3)	18.4(3)	20.5(3)			69Pu	T
	pol	N-methyl-pyrrolidone	0.1($HClO_4$)	23(3)				25.6(3)			70B	T
	Hg	pyridine	0.1(Et_4NClO_4)	25	6.77(4)	11.7(2)	14.8(4)				85A	T

Table III.9. Thermodynamic constants for formation of metal complexes of thiocyanate with 4d and 5d transition elements.

Metal Ion	Method	I mol dm^{-3}	T °C	j	ΔH_j kJ mol^{-1}	ΔS_j J mol^{-1} K^{-1}	Ref	Category
Mo^{IV}	sp	2.0($LiClO_4$)	25	j1	-28(4)	-40(10)	76F	D
Ag^+	Ag	--	20	j4	+107		56G	Rj
	Ag	1($NaNO_3$)	20	j4	+84		53J	D
	Ag	1(KNO_3)	25	j1	-62(3)	-70(150)	80D	D
				j2	-76(5)	-90(230)		
				j3	-57(1)	+0(100)		
				j4	-103(7)	-100(180)		
	cal	0.1(Et_4NClO_4) pyridine solvent	25	j1	-1.5	+65	86A	T
				j2	+0.1	+37		
Cd^{2+}	sp	?($HClO_4$)	25	j1	-14(2)	-7(2)	71D	Rj
	cal	0	25	j1	-2.9(4)	+38(2)	67N	Rj
	Cd(Hg)	0.03($HClO_4$)	25	j1	-14.6	-62	76L	D
				j2	-4.9	+21		
	cal	1.00($NaClO_4$)	25.00	j1	-9.58(4)	-6.7(4)	68Ge	T
				j2	-8.1(4)	-14(1)		
				j3	-9(4)	-30(10)		
	Cd(Hg)	2(KNO_3)	20	j2	-18	-16.7	57G	Rj
				j3	-25	-38		
	cal	3.00(H^+-$NaClO_4$)	25.0	j1	-18	-17	66Ge	D
	cal	3($NaClO_4$)	25.00	j1	-10.19(6)	-8	86I	T
				j2	-30.3(3)	-68		
				j3	-7.7(6)	+9		

III.9 continued

Metal Ion	Method	I mol dm^{-3}	T °C	j	ΔH_j kJ mol^{-1}	ΔS_j J mol^{-1} K^{-1}	Ref	Category
				j4	-30.5(2)	-64		
	cal	-- DMF solvent	25	j4	+15		74G	Rj
	cal	1(NH_4ClO_4) DMF solvent	25.0(2)	j1	-5.8(1)		88Is	T
				j2	-11.7(3)			
				j3	-11.2(4)			
				j4	-2.3(1)	+118		
	cal	-- DMSO solvent	25	j4	+7.8		74G	Rj
	cal	1.00(NH_4ClO_4)^b DMSO solvent	25.0	j1	-2.97(2)	+24.6(2)	76Ah	T
				j2	-2.8(2)	+8(1)		
				j3	+4.2(6)	+18(3)		
Au^+	Au	0.1(Et_4NClO_4) pyridine solvent	25	j1	-4.5(7)	+73	89A	T
				j2	-3.7(8)	+147		
Hg^{2+}	pol	0.2(KNO_3)	25	j2	-125	-84	62Ta	T
				j3	-121	-25		
				j4	-150	-84		
	Hg	0.3($NaNO_3$)	25	j4	-150	-84	56T	T
	cal	1.00($NaClO_4$)	25.0	j1	-49.7(3)	+7(1)	71A	R
				j2	-100.2(5)	-13(2)		
				j3	-120.2(9)	-17(4)		

III.9 continued

Metal Ion	Method	I mol dm^{-3}	T °C	j	ΔH_j kJ mol^{-1}	ΔS_j J mol^{-1} K^{-1}	Ref	Category
				j4	-141(2)	-50(6)		
	cal	1.00($NaClO_4$)	25.0	j4	-145.3(8)	-72(4)	74Ku	R
	cal	1.0(H^+-$NaClO_4$)	25.0	j2	-51.2(8)	-23(4)	75C	D
				j3	-69(1)	-30(6)		
				j4	-87(2)	-52(8)		
	cal	1.0(H^+-$NaClO_4$)	25	j1	-50.5(3)	+4(1)	84V	R
				j2	-101.7(2)	-18(1)		
	cal	-- DMF solvent	25	j4	-40		74Go	Rj
	cal	-- DMSO solvent	25	j4	-15		74Go	Rj
	Hg	1(NH_4ClO_4) DMSO solvent	25	j1	-28(1)	+50	85A	T
				j2	-59(1)	+52		
				j3	-69(2)	+76		
				j4	-86(3)	+60		
	Hg	0.1(Et_4NClO_4) pyridine solvent		j1	-2.5(3)	+121	85A	T
				j2	+0.6(4)	+223		
				j3	+0.7(5)	+283		

Table III.10. Stability constants for complexes of thiocyanate with 4f and 5f transition elements.

Metal	Method	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
lanthanum and lanthanides											
La^{3+}	sp	0.6($HClO_4$)	20	-0.4(3)						64Ka	D
	ext	1(H^+-$NaClO_4$)	27	0.06(4)	0.04(5)					68R	D
	ext	1(NH_4ClO_4)	30.0(1)	0.12(3)	0.22(3)					74Kh	D
	ix	2.0($NaClO_4$)	25	0.20	-0.28	-0.89				82Ch,86G	T
	ext	5($NaClO_4$)	25	0.24(6)	-0.62	-0.7(1)				64Se	T
	ext	5($NaClO_4$)	25	0.24(6)	-0.62	-0.7(1)				65Se	T
Ce^{3+}	ix	0	--	-0.28						62L	Rj
	ix	0.5(NH_4ClO_4)	--	0.59(1)						62L	Rj
	ext	2.01(NH_4NO_3)	25	-0.3(3)	0.20(6)					73C	Rj
	ext	5.0(H^+-$NaClO_4$)	25	0.58(6)						74Ki	T
Ce^{4+}	pol	0	25	1.06	-0.21					68Tr	T
Pr^{3+}	ix	2.0($NaClO_4$)	--	0.11	-0.33	-0.92				82Ch,86G	T
	ir	3($LiClO_4$)	--	0.4(1)						74N	Rj
Nd^{3+}	sp	0.1-4(?)	--	-0.27(2)						69Z	Rj
	sp	0.6($HClO_4$)	20	-0.3(2)						64Ka	T
	ext	1.0(H^+-$NaClO_4$)	25.0(1)	0.8(1)	0.92(7)					65C	T
	ix	2.0($NaClO_4$)	25	-0.05	-0.31	-0.60				82Ch,86G	T
Sm^{3+}	sp	0.6($HClO_4$)	20	0.09(6)						64Ka	T
	ix	2.0($NaClO_4$)	25	0.09	-0.26	-0.60				82Ch,86G	T

III.10. continued

Metal	Method	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Eu^{3+}	sp	0	25	0.7						64B	Rj
	ext	1.0(H^+-$NaClO_4$)	25.0(1)	0.70(6)	0.83(9)					65C	T
	ext	1($LiClO_4$)	30.0(1)	0.13(3)	0.18(2)					71K	R
	ext	1(NH_4ClO_4)	30.0(1)	0.13(5)	0.28(5)					74Kh	R
	ext	2.01(NH_4NO_3)	25	0.23(8)	0.49(9)					73C	Rj
	ext	5($NaClO_4$)	25	0.32(9)	-0.1	-0.4(2)				64Se	T
	ext	5($NaClO_4$)	25	0.32(9)	-0.1(2)	-0.4(2)				65Se	T
	ext	5.0(H^+-$NaClO_4$)	25	0.43(2)						74Ki	T
Dy^{3+}	sp	0.6($HClO_4$)	20	0.12(4)						64Ka	T
	ix	2.0($NaClO_4$)	25	0.25	-0.08	-0.57				82Ch,86G	T
Ho^{3+}	ix	2.0($NaClO_4$)	25	0.24	-0.15	-0.62				82Ch,86G	T
	ir	3($LiClO_4$)	--	0.2(2)						74N	Rj
Gd^{3+}	sp	0.6($HClO_4$)	20	0.21(5)						64Ka	T
	ix	2.0($NaClO_4$)	25	0.09	-0.17	-0.66				82Ch,86G	T
Tb^{3+}	ext	1(NH_4ClO_4)	30.0(1)	0.22(3)	0.34(2)					74Kh	T
	ix	2.0($NaClO_4$)	25	0.18	-0.12	-0.64				82Ch,86G	T
Er^{3+}	sp	0.6($HClO_4$)	20	0.16(8)						64Ka	T
	ix	2.0($NaClO_4$)	25	0.30	-0.55	-0.60				82Ch,86G	T
Tm^{3+}	ext	1.0(NH_4ClO_4)	30	0.07	0.42					80K	T
	ix	2.0($NaClO_4$)	25	0.26	-0.23	-0.68				82Ch,86G	T
Yb^{3+}	ix	2.0($NaClO_4$)	25	0.18	-0.24	-0.62				82Ch,86G	T

III.10. continued

Metal	Method	*I* mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^{3}	lgβ_2 mol^{-2}dm^{6}	lgβ_3 mol^{-3}dm^{9}	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Lu^{3+}	ext	1(NH$_4$ClO$_4$)	30.0(1)	0.21(6)	0.35(4)					74Kh	T
	ix	2.0(NaClO$_4$)	25	0.20	-0.24	-0.82				82Ch,86G	T
	ext	5(NaClO$_4$)	25	0.45(9)	-1.3	-0.1(2)				64Se	D
	ext	5(NaClO$_4$)	25	0.45(9)	-1.3(1)	-0.1(2)				65Se	D
actinium and actinides											
Ac^{3+}	ext	1(H$^+$-NaClO$_4$)	27	0.04(3)	-0.09(5)					68R	T
	ext	5(NaClO$_4$)	25	-0.75	-0.46					69Se	T
Th^{IV}	pol	--	--	1.09	1.45					66S	Rj
	ext	3(HClO$_4$)	--	0.85(7)	1.53(7)	1.2(2)	1.51(4)			71La	Rj
	ext	1(NaClO$_4$)	25	1.08	1.78					50W	T
U^{IV}	Au	1(H$^+$-NaClO$_4$)	20	1.49(3)	2.0(2)					54A	T
	sp	2.0(H$^+$-NaClO$_4$)	25	1.49	2.11					55D	T
UO$_2$$^{2+}$	sp	0.08(H$^+$-NaClO$_4$)	25	0.93(3)						57D	T
	sp	0.1(HClO$_4$)	20	0.76(3)	0.75(1)	1.18(8)				49A	T
	ix	1(H$^+$-NaClO$_4$)	32.00	-1.30	1.05	1.08				61B	Rj
	sp	2.5(H$^+$-NaNO$_3$)	22-23	0.7(2)	0.70(2)					64V	Rj
	sp	4.0(H$^+$-NaNO$_3$)	22-23	0.7(2)	0.71(2)					64V	Rj
Np^{3+}	ext	2.0((H$^+$-NaClO$_4$)	--	1.50(7)	2.06(8)	2.53(3)				78V	Rj
	ir	9	--	1.14	1.77	1.87	1.65	0.28		77M	Rj
	ext	2.0(H$^+$-NaClO$_4$)	25	0.32(2)						79V	T
Pu^{3+}	ext	1.0(H$^+$-NaClO$_4$)	25.0(5)	0.046(5)	0.075(7)					65C	T

III.10. continued

Metal	Method	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
	ix	1((H$^+$-NaClO$_4$)	25.0(5)	0.041	-0.095	-0.73				66C	T
	ext	1(NH$_4$ClO$_4$)	30.0(1)	0.34(4)	0.61(3)					74Kh	T
	ext	2.0(H$^+$-NaClO$_4$)	--	0.33(3)						78V	Rj
Am^{3+}	ix	0	--	0.24		-0.04				62L	Rj
	ix	0.5(NH$_4$ClO$_4$)	--	0.66						62L	Rj
	sp	1.0(NaClO$_4$)	--	0.76(3)	0.83(7)					72B	Rj
	ext	1.0(H$^+$-NaClO$_4$)	25.0(1)	0.50(2)	0.85(6)					65C	T
	ext	1.0(H$^+$-NaClO$_4$)	25	0.36(3)	0.0(2)	-0.1(2)				72H	T
	ext	1(LiClO$_4$)	30.0(1)	0.17(4)	0.51(3)					71K	R
	ext	1(NH$_4$ClO$_4$)	30.0(1)	0.17(7)	0.62(3)					74Kh	R
	ext	2.01(NH$_4$NO$_3$)	25	-0.5(2)	0.74(4)	0.87(5)				73C	Rj
	ext	5(NaClO$_4$)	25	0.85(5)		0.6(1)	0.0(2)			64Se	T
	ext	5(NaClO$_4$)	25	0.85(5)		0.6(2)	0.0(2)			65Se	T
	ext	5.0(H$^+$-NaClO$_4$)	25	0.60(6)						74Ki	T
Cm^{3+}	ix	0	--	0.27	-0.0044					62L	Rj
	ix	0.5(NH$_4$ClO$_4$)	--	0.67(4)						62L	Rj
	ext	1.0(H$^+$-NaClO$_4$)	25.0(1)	0.43(3)	0.85(4)					65C	R
	ext	1.0(H$^+$-NaClO$_4$)	25	0.45(3)	-0.1(4)	0.1(3)				72H	R
	ext	1(NH$_4$ClO$_4$)	30.0(1)	0.18(6)	0.61(3)					74Kh	T
	ext	2.01(NH$_4$NO$_3$)	25	-0.6	0.48(6)	1.15(2)				73C	Rj
	ext	5.0(H$^+$-NaClO$_4$)	25	0.62(3)						74Ki	T
Bk^{3+}	ext	1.0(H$^+$-NaClO$_4$)	25	0.49(3)	-0.51(1)	0.4(1)				72H	T
	ext	5.0(H$^+$-NaClO$_4$)	25	0.86(4)						74Ki	T

III.10. continued

Metal	Method	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
Cf^{3+}	ext	1.0(H^+-$NaClO_4$)	25.0(1)	0.48(3)						65C	T
	ext	1.0(H^+-$NaClO_4$)	25	0.57(3)	-0.55(2)	0.42(8)				72H	T
	ext	2.01(NH_4NO_3)	25	-0.2	0.91(5)	1.38(4)				73C	D
Es^{3+}	ext	1.0(H^+-$NaClO_4$)	25	0.56(3)	-1.04(6)	0.47(8)				72H	T

Table III.11. Stability constants for complexes of thiocyanate with 4f and 5f transition elements in non-aqueous media

Metal Ion	Method	Solvent	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	lgβ_2 mol^{-2}dm^6	lgβ_3 mol^{-3}dm^9	lgβ_4 mol^{-4}dm^{12}	lgβ_5 mol^{-5}dm^{15}	lgβ_6 mol^{-6}dm^{18}	Ref	Category
actinides												
Th^{IV}	sp	acetone	--	20	3.51	9.57	12.55				66G	Rj
	sp	DMF	--	20	3.20	6.28	9.26	12.12	14.92	17.17	66G	Rj
	sp	MeOH	--	20	3.37	6.66	9.82	12.89			66G	Rj

Table III.12. Thermodynamic constants for formation of metal complexes of thiocyanate with 4f and 5f transition elements.

Metal Ion	Method	I mol dm^{-3}	T °C	j	ΔH_j kJ mol^{-1}	ΔS_j J mol^{-1} K^{-1}	Ref	Category
lanthanides								
Nd^{3+}	ext	1.0(H^+-$NaClO_4$)	25.0(1)	j1	-22.9(8)	-62(3)	65C	T
Eu^{3+}	ext	1(NH_4ClO_4)	30.0(1)	j1	-3.5(8)	-9(3)	74Kh	T
				j2	-6.8(5)	-17(2)		
	ext	5.0(H^+-$NaClO_4$)	25	j1	+3.35(4)	+19.2(4)	74Ki	T
actinides								
UO_2^{2+}	cal	1.0($HClO_4$)	25.00	j1	-3.22(6)	+3.5(5)	71A	T
				j2	-5.7(6)	-20(3)		
				j3	+3(1)	+18(5)		
Pu^{3+}	ext	1(NH_4ClO_4)	30.0(1)	j1	+0.2(8)	+7(2)	74Kh	T
Am^{3+}	ext	1.0(H^+-$NaClO_4$)	25.0(1)	j1	-18(1)	-52(4)	65C	D
	ext	1.0(H^+-$NaClO_4$)	25	j1	+7(3)	+29(8)	72H	T
				j3	-20(20)	-80(60)		
	ext	1(NH_4ClO_4)	30.0(1)	j1	+2(4)	+10(8)	74Kh	D
				j2	-5(1)	-4(4)		
	ext	5.0(H^+-$NaClO_4$)	25	j1	+12(2)	+50(7)	74Ki	T
Cm^{3+}	ext	5.0(H^+-$NaClO_4$)	25	j1	+12(2)	+51(7)	74Ki	T
Bk^{3+}	ext	5.0(H^+-$NaClO_4$)	25	j1	+3(2)	+26(6)	74Ki	T

Table III.13. Summary of recommended and tentative log β_1 values for complexes of thiocyanate ion[a].

Metal Ion	Method	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	Ref	Category
H^+	Hg	2	25	-0.87(2)	82N	T
	pol	4	25	-0.52(1)	82T	T
In^{+3}	In	2	20	2.58(2)	54S	R
Tl^+	Tl(Hg)	3	25	0.10(3)	62Kl,71Fe	R
	sol	4	25	0.20(1)	65K	R
Sn^{2+}	Sn(Hg)	1	25	0.93(8)	76Sa,80F	T
Pb^{2+}	Pb(Hg)	4	25	1.08(7)	63M	T
Bi^{3+}	Bi(Hg)	1	25	1.28(5)	71Fd	T
I_2	sp	1	25	1.93	62Le	T
Ti^{4+}	sp	1	25	0.36(8)	80M	T
V^{2+}	sp	0.5-0.8	25	1.4(1)	68M,83N	T
V^{3+}	sp	1	25	2.07(3)	67B	R
	sp	2.5	25	1.9(1)	51F	R
V^V	sp	2.6	25	0.92(3)	51F	T
Fe^{3+}	ext,Pt sf,sp	1-1.2	18-25	2.11(4)	51M,55Li, 68Po 78M,92O	R
Co^{2+}	sp	1	25	1.01(1)	58S,71Sk	R
Ni^{2+}	cal,ext,ix,pol,sp	1	20-25	1.14(9)	53Fr,62T,73Hu,74K,76M	R
	ext	1.5	25	1.14(2)	64T	R
Cu^{2+}	cal,ext,sp	1	25	1.7(1)	73Hu,74K, 88M	T

III.13 continued

Metal Ion	Method	I mol dm^{-3}	T °C	lgβ_1 mol^{-1}dm^3	Ref	Category
Zn^{2+}	Zn(Hg)	1	25	0.708(3)	71Ah	R
	Zn(Hg)	2	25	0.74	70A	R
Cd^{2+}	sp	0.6	20	1.32(1)	64Ka	R
	Cd(Hg) pol,sp	1	25	1.31(6)	63T,68G 73Hu,78A	R
	cal,Cd(Hg) pol	3	25	1.38(3)	41L,57Ts 66Ge,86I	R
Hg^{2+}	Hg,pol	1	25	lgβ_2=16.5(4) mol^{-3}dm^6	60N,70C	T
La^{3+}	ix	2	25	0.20	82Ch,86G	T
	ext	5	25	0.24(8)	64Se,65Se	T
Eu^{3+}	ext	1	30	0.13(6)	71K,74Kh	T
U^{IV}	Au	1	20	1.49(3)	54A	T
	sp	2	25	1.49	55D	T
Am^{3+}	ext	1	30	0.17(8)	71K,74Kh	R
Cm^{3+}	ext	1	25	0.44(4)	65C,72H	R

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[a] When two or more recommended or tentative values occur under corresponding experimental conditions a mean value is reported.

Some elements and especially the majority of 4f and 5f transition metals complexed with thiocyanate ion have too few reported values for comparison of lgβ and are omitted from this table.