Synthesis and thermodynamic characterisation of cobalt(II), nickel(II) and copper(II) complexes of ethylenediamine-N,N,N',N'-tetraacetanilide

Angela F. Danil de Namor, Jaime D. Cardenas Garcia and Joseph I. Bullock

Laboratory of Thermochemistry, Chemistry Department, University of Surrey, Guildford, Surrey GU2 5XH, UK.

Abstract: Complexes of ethylenediamine-N,N,N',N'-tetraacetanilide (edtan) with cobalt (II), nickel (II) and copper (II) in the solid state and in solution are reported for the first time. Thermodynamic data (stability constant, and derived Gibbs energy, enthalpy and entropy) for the 1:1 complexation of edtan with the metal ions at 298.15 K in water-saturated butan-1-ol gave the selectivity sequence $\log_{10}K_s$: Ni^{2+}, 4.65 ±0.02; Cu^{2+}, 4.41 ±0.01; Co^{2+}, 4.18 ±0.04 as found from microcalorimetric titration studies. The entropies suggested that the structure of the 1:1 complex with copper (II) contains fewer chelate rings than those for nickel (II) and cobalt (II) ($\Delta_c S^0$: Cu, -19.3; Co, 5.7; Ni, 3.9 J mol^{-1} K^{-1}). Solid complexes of the metal ions with edtan and perchlorate as the counter anion were prepared. For each a complex with a 1:1 metal : edtan stoichiometry with non-coordinated perchlorate (ir) was isolated. Subsequent X-ray crystallographic research has shown that $[Cu(edtan)(H_2O)][ClO_4]_2.1.5H_2O$ has a six-coordinate Cu center with edtan acting as a pentadentate ligand (2N, 3O) with the coordination sphere completed by an oxygen atom from water. Conversely and in striking contrast to the Cu complex, in $[Co(edtan)(H_2O)][ClO_4]_2.H_2O.\frac{1}{2}C_2H_5OH$ the Co center is seven-coordinate with hexadentate edtan (2N, 4O) and one coordinated water molecule. There is thus an excellent confirmation of the results obtained from the microcalorimetric study in that edtan forms four chelate rings to Cu but five to Co in the solid state. The ability of the ligand to extract metal ions from water to the water-saturated butan-1-ol phase was assessed from distribution data as a function of the aqueous phase hydrogen ion concentration and of the ligand concentration in the organic phase. The data showed that Cu^{2+} is selectively extracted over a wide range of aqueous phase hydrogen ion concentrations.

INTRODUCTION

Although edta (edta = ethylenediaminetetraacetate) has remarkable complexing powers, its use as an extracting agent is limited by the polarity of the tetraanion, its various protonated forms and the metal complexes which have limited solubility in the organic solvents commonly used for extraction purposes. Most of the work[1,2] using edta as extraction agent for metal cations thus involves the presence of (i) a negatively charged edta-metal ion complex in the aqueous phase and (ii) a lipophilic counter cation to favour the extraction of an ion-pair, which , in turn, requires the use of an organic phase capable of solvating the ion-pair. For applications requiring a neutral extractant which is insoluble in water, it would be of use to retain as far as possible the complexing powers of edta by synthesising derivatives of it which carry lipophilic substituents such as the edta amides. We selected ethylenediamine tetracetanilide (edtan) for this purpose which was reported[3] briefly in 1986. In order to fully assess edtan as an extracting agent we report (i) the

synthesis and characterisation of edtan and its solid complexes with nickel (II), cobalt (II) and copper (II) as their perchlorates, (ii) the thermodynamic data (stability constants, Gibbs energies, $\Delta_c G°$, enthalpies, $\Delta_c H°$ and entropies, $\Delta_c S°$) for 1:1 complexation of the ligand with the same metal ions in water-saturated butan-1-ol as found from titration microcalorimetry, (iii) distribution data in the mutually saturated, two phase water : butan-1-ol system and (iv) a preliminary statement concerning the X-ray crystallographic structures of the complexes formed between edtan and Cu(II) and Co(II) with perchlorate as the counter-anion in the solid state.

EXPERIMENTAL SECTION

Synthesis of Edtan

The tetramethyl ester of H_4edta was synthesised by a modification of a previously reported[4] method in which a methanolic suspension of H_4edta is allowed to react with thionyl chloride.
[Found : C, 48.4; H, 7.15; N, 8.05. $C_{14}H_{24}N_2O_8$ requires C, 48.3; H, 6.95; N, 8.05%. δ_H(300 MHz; solvent CD_3COCD_3; standard $SiMe_4$) 2.86 (4H, s, NCH_2CH_2N), 3.61 (8H, s, NCH_2C), 3.64 (12H, s, CH_3). b.p. 174 - 176°C at 0.02 mm Hg, lit.[4] 189 -191°C at 3 mm Hg]

Edtan was synthesised by aminolysis of the tetraester using freshly distilled dmso, sodium hydride, and freshly distilled aniline.
[Found: C, 68.95; H, 6.1; N, 14.25. $C_{34}H_{36}N_6O_4$ requires C, 68.9; H, 6.1; N, 14.2%. δ_H (300 MHz; solvent $CDCl_3$; standard $SiMe_4$) 2.86 (4H, s, NCH_2CH_2N), 3.46 (8H, NCH_2), 7.07 (4H, t, p-H), 7.22 (8H, t, m-H), 7.54 (8H, d, o-H), 9.04 (4H, s, NH). ν_{max}/cm^{-1}, KBr disc, 3233 and 3183 (NH), 1682 (amide I), mp (uncorrected) 160 - 162°C, Chem. Abs. registry no. 107753-49-1]

Synthesis of the Metal Complexes

1. Aqua(ethylenediamine-N,N,N',N'-tetraacetanilide)copper(II) perchlorate 1½hydrate, [Cu(edtan)(H_2O)][ClO_4]$_2$.1.5H_2O

An excess of Cu(ClO_4)$_2$·6H_2O (3.159 g., 8.5 mmol), was added to a suspension of ligand edtan (1.072 g., 1.8 mmol) in 50 ml of butan-1-ol which had been previously saturated with water. After various stages of purification, pale blue-green needles formed.
[Found : C, 45.55; H, 4.6: N, 9.5. $CuC_{34}H_{41}N_6O_{14.5}Cl_2$·requires C, 45.8; H, 4.6; N, 9.45%. υ_{max}/cm^{-1} KBr disc, 3344 (NH), 1663 (amide I), 1100 (υ_3, [ClO_4]$^-$)]

2. Aqua(ethylenediamine-N,N,N',N'-tetraacetanilide)cobalt(II) perchlorate monohydrate ½ethanol [Co(edtan)(H_2O)](ClO_4)$_2$·H_2O.½C_2H_5OH

An excess of Co(ClO_4)$_2$.6H_2O (2.5 g, 6.8 mmol, Johnson Matthey) was added to a suspension of the ligand (0.5 g, 0.8 mmol) in ethanol (40 ml) under stirring. After work-up of the pink compound which formed, pink crystals were separated.
[Found : C, 46.1; H, 4.8; N, 9.05. $CoC_{35}H_{43}N_6O_{14.5}Cl_2$·requires C, 46.2; H, 4.8; N, 9.2%. υ_{max}/cm^{-1}, KBr disc, 3381(NH), 1665 (amide I), 1100 (υ_3, [ClO_4]$^-$)]

3. (Ethylenediamine-N,N,N',N',-tetraacetanilide)nickel(II) perchlorate hexahydrate [Ni(edtan)](ClO_4)$_2$·6H_2O

Pale-blue needles of the Ni(II) complex were prepared from the perchlorate salt by the same method as for the Cu(II) and Co(II) compounds.
.[Found : C, 42.7; H, 4.8; N, 8.55. $NiC_{34}H_{48}N_6O_{10}Cl_2$·requires C, 42.6; H, 5.05; N, 8.75%. υ_{max}/cm^{-1}, KBr disc, 3336 (NH), 1654 (amide I), 1100 (υ_3, [ClO_4]$^-$)]

Microcalorimetric Studies

The LKB 2277 Thermal Activity Monitor (TAM) was the microcalorimetric system used to perform these studies. The instrument was chemically calibrated using a standard reaction[5] between 18-crown-6 and barium (II) in water at 298.15 K. Corrections for the heat of dilution of the titrant in the solvent were carried out in all cases. Stability constants and enthalpy data for the complexation process were calculated using a locally written, minimisation program.

Distribution experiments

For these experiments, the water-butan-1-ol solvent system was used. Both solvents were mutually previously saturated in order to avoid phase volume changes during the extraction process. All experiments were carried out at 298 K and the ionic strength of the aqueous phase was kept constant ($I = 0.1$ mol dm^{-3} LiClO$_4$). Two variables were considered; these were the concentrations of (i) hydrogen ion in the aqueous phase and (ii) ligand in the organic phase.
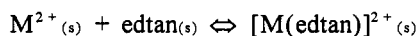
RESULTS AND DISCUSSION

Characterisation of ethylenediamine-N,N,'N'-tetraacetanilide and its metal complexes

The ^{1}H NMR and microanalytical data for edtan (see experimental) are entirely consistent with the tetrakisacetanilide of edta. The compound is soluble in chloroform, butan-1-ol and N,N-dimethylformamide as expected for a neutral molecule containing lipophilic substituents. The IR spectrum of edtan has absorption bands at 3233 and 3183 cm^{-1} assigned to the N-H stretching vibrations of a secondary amide with the two components attributed[6] to <u>cis</u> and <u>trans</u> rotational isomers formed as a result of hydrogen bonding. There was no absorption characteristic of a carboxylic acid group in the region above 2000 cm^{-1}.

The absorption at 1682 cm^{-1} in edtan is assigned to the amide I band since in anilides this is usually found[6] towards the upper end of the range. This band falls in wavenumber on complexation to the metal ions consistent with coordination through carbonyl oxygen rather than amide nitrogen. There are a number of other vibrations expected[6] in this region (CH$_2$ and NH deformations, aromatic ring, coordinated or lattice water in the complexes) so that the amide I band assignments are tentative. All of the IR spectra of the neutral complexes had a strong, symmetrical absorption near 1100 cm^{-1} suggesting[7] the presence of ionic (T$_d$) perchlorate.

Thermodynamic studies[8]

Stability constants and derived Gibbs energies, enthalpies and entropies for the complexation process are shown in Table 1. The data gave an excellent fit for the formation of 1:1 stoichiometric complexes in all three cases. and are referred to the process:

$$M^{2+}_{(s)} + edtan_{(s)} \Leftrightarrow [M(edtan)]^{2+}_{(s)}$$

where s denotes the water-saturated butan-1-ol solvent and M^{2+} = copper, cobalt and nickel.

It is assumed that neither the hydrated metal cations nor the complexes with edtan form ion-pairs with the perchlorate counter anion. The solutions were dilute (Table 1) and the solvent contained large quantities of water which would increase the dielectric constant above that of pure butan-1-ol.

For the three complexation equilibria, the process is enthalpically favoured. The stability constant data show that the ligand selectively recognised the cations in the order $Ni^{2+} > Cu^{2+} > Co^{2+}$ which is different from that expected from the Irving-Williams series[9] suggesting a ligand specific effect for copper (II). It is therefore interesting to note that while favourable (positive) entropies are found for the complexation of nickel (II) and cobalt (II) that for copper (II) is negative which also suggests a structural anomaly for copper (II). For the

TABLE 1. Thermodynamic parameters of complexation of ethylenediamine - N,N,N',N'-tetraacetanilide and transition metal cations in butan-1-ol saturated with water at 298.15 K.

Cation[a]	log K_S	$\Delta_c G^\circ$ kJ mol^{-1}	$\Delta_c H^\circ$ kJ mol^{-1}	$\Delta_c S^\circ$ J mol^{-1} K^{-1}
Cu^{2+}	4.41 ±0.01	-25.80 ±0.2	-31.54 ±1.4	-19.3
Co^{2+}	4.18 ±0.04	-23.85 ±0.2	-22.16 ±1.2	5.7
Ni^{2+}	4.65 ±0.02	-26.54 ±0.1	-25.38 ±0.7	3.9

[a]Concentration ranges mol dm^{-3}; Cu^{2+} 6.97x10^{-4}- 9.52x10^{-3}, edtan 7.92x10^{-3}- 7.21x10^{-3}, 15 injections; Co^{2+} 7.093x10^{-4} - 7.897x10^{-3}, edtan 4.965x10^{-3} - 4.605x10^{-3}, 12 injections; Co^{2+} 7.08x10^{-4} - 7.88x10^{-3}, edtan 4.97x10^{-3} - 4.61x10^{-3}, 12 injections.

entropy associated with chelation reactions, Chung[10] has suggested that overall positive entropy changes (implying favourable contributions from both the translational and intrinsic entropies) are due to the presence of additional chelate rings in the complexes. This would appear to indicate that the nickel (II) and cobalt (II) complexes formed in solution may have an additional chelate ring relative to the copper (II) complex. This study confirms the importance of acquiring both stability constant and directly determined enthalpy data in understanding complexation reactions.

Structural Studies

The main purpose of the crystallographic study[11] was to investigate the conclusion drawn from the thermodynamic evaluation of the entropy changes that the Cu(II) complex cation is structurally different from the other two.

(a) [Cu(edtan)(H$_2$O)][ClO$_4$]$_2$.1.5H$_2$O (1). The potentially hexadentate amide was clearly shown to coordinate through 2 nitrogen atoms of the ethylenediamine linkage and only three of the four amide oxygen atoms. The sixth coordination site is occupied by a water molecule (O1). A nitrogen atom (N2), two amide oxygen atoms (O4 and O2) and the water molecule (O1) form a distorted square planar arrangement with bond lengths which might be described as normal for coordination to Cu(II); Cu1 - O1 = 1.978(8) Å, Cu -O 2 = 2.018(7) Å, Cu - O4 = 2.007(8) Å and Cu - N2 = 2.061(8) Å . The remaining bond lengths to the ligand are long (Cu - O3 = 2.214(8) Å and Cu - N1 = 2.295(9) Å. The N1- Cu1- O3 angle = 156.9(3) ° and inclined towards N2 and O21. Edta is known [12] to be five coordinate [13]in [Cu(Hedta)(H$_2$O)]$^-$ in which the water molecule is trans to nitrogen. The 'four short, two long' bond length pattern with complexity in the detailed structural arrangements are well established for Cu(II). Overall, edtan forms four chelate rings to Cu(II).

(b) [Co(edtan)(H$_2$O)][ClO$_4$]$_2$.H$_2$O.½C$_2$H$_5$OH (2). The ligand edtan is hexadentate forming five chelate rings to Co and coordinated through the two nitrogen atoms of the ethylenediamine linkage and the four amide oxygen atoms with seven coordination completed by the presence of a water molecule. The coordination geometry approximates to a monocapped trigonal prism with the water molecule capping the rectangular plane defined by the four amide oxygen atoms (O1, O2, O3, O4). One of the Co to amide oxygen bonds (Co - O3 = 2.263(7) Å) is considerably longer than the other four Co to O contacts (average 2.134 Å). This may reflect the generally crowded situation with respect to coordination of edtan to a 3d divalent metal ion. The Co to N bond lengths are approximately equal in terms of the likely overall experimental errors.

The coordination of edtan to Cu and Co is thus strikingly different in the solid state with five chelate rings to Co but only four to Cu even though the coordination shell contains one molecule of edtan and one water

molecule in each case. There is thus an excellent corroboration of the conclusion drawn from the calorimetric study which indicated a structural difference between Cu and Co based on the estimation of the entropy changes on complexation.

Distribution experiments

The results are illustrated in Figure 1 and Table 2 . These show that under the conditions employed the distributions are in the order $Cu^{2+} > Co^{2+} > Ni^{2+}$. At low hydrogen ion concentrations (Figure 1) there is an important and marked preference for Cu^{2+} such that complete separation of copper from cobalt and nickel is feasible.
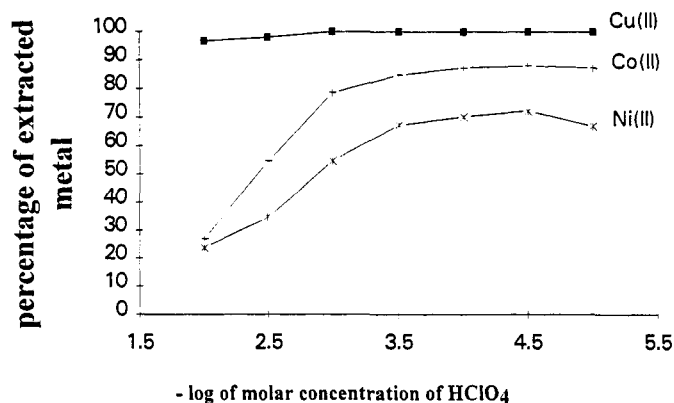

Fig. 1. Extraction Process at 298 K, I=0.1 mol·dm^{-3} and a Ligand concentration of 1.0 x 10^{-3} mol·dm^{-3}.

TABLE 2. Percentage metal extraction at 298 K at different ligand concentrations (I = 0.1 mol dm^{-3})

Initial Ligand Concentration i Organic Phase (mol dm^{-3})	Cu^{2+}	Ni^{2+}	Co^{2+}
2.5 x 10^{-4}	97.3	48.3	72.5
2.4 x 10^{-4}	93.8	47.3	74.3
2.2 x 10^{-4}	87.7	45.7	68.8
2.0 x 10^{-4}	81.6	43.8	64.0
1.8 x 10^{-4}	73.4	40.4	62.8
1.6 x 10^{-4}	65.6		55.4
1.4 x 10^{-4}	58.4	38.6	50.7
1.2 x 10^{-4}	50.9	35.5	45.8
1.0 x 10^{-4}	44.5	37.8	39.5
8.0 x 10^{-5}	40.0	32.1	36.6
7.0 x 10^{-5}	33.8	30.3	32.9
6.0 x 10^{-5}		26.5	30.5
5.0 x 10^{-5}	25.8	23.3	26.5
4.0 x 10^{-5}	22.0	19.4	22.5
3.0 x 10^{-5}	17.3	15.9	21.2
2.0 x 10^{-5}	13.6	12.3	19.6
1.0 x 10^{-5}	9.1	8.5	16.0
0	5.1	5.0	12.0

The data in Table 2, in which the ligand effect on the distribution data is clearly demonstrated, were obtained without the addition of perchloric acid to the aqueous phase. In the absence of ligand cobalt is better transferred to the organic phase than the other two metal ions. The separation ratio for copper relative to nickel is approximately unity while there is a considerable reduction of this value with respect to cobalt. The presence of edtan in the organic phase leads to a different selectivity pattern to the extent that at the highest ligand concentration (2.5×10^{-4} mol dm^{-3}) the selectivity ratios for copper with respect to cobalt and nickel are increased to 1.3 and 2.0 respectively. Several processes contribute to the overall extraction of metal cations by neutral ligands. These include (i) the transfer of the electrolyte (in the present case metal ion perchlorates) from water to the non-aqueous solvent, (ii) the degree of ion-pair formation of the electrolyte in the organic phase, (iii) the nature and the number of ligand : metal species formed in the non-aqueous phase, (iv) the degree of ion-pair formation between the complexed cation and the counter anion and (v) the formation constants of the ligand : metal species in the organic phase.

As discussed earlier, there is little evidence in this work to suggest that significant ion-pair formation (factors ii and iv) in the water-saturated butan-1-ol phase occurs. However, it seems clear that for Co^{2+} and Ni^{2+} the overall extraction of the cations is mainly influenced by the transfer (i) and the complexation process (iv). Thus, it would appear that the higher stability of the nickel complex relative to cobalt (see $\Delta_c G^0$ values, Table 1) is insufficient to overcome the favourable transfer of the latter as the perchlorate (factor i). As a result cobalt is better extracted than nickel. On the other hand, the marked preference for copper in the extraction process may be attributed to an additional contribution resulting from the formation of a complex ion with five rather than six coordinate edtan molecule demonstrated by the X-ray crystallogrphic structures discussed above. The thermodynamic data derived from microcalorimetry also indicated that the 1:1 complex with Cu^{2+} is structurally different from those for Ni^{2+} and Co^{2+}.

Acknowledgement

References

1. Y.A.Zolotov, O.M.Petrukhin and I.P.Alimarin, Z. Anal. Khim., 1965, **20**, 347.
2. F.L.Moore, Anal. Chem., 1965, **37**, 1235.
3. K.Iiyama and N.Inaba, Ger. Offen. DE 3610588, 2 Oct 1986; Chem. Abs., 1987, **106**, P 166312 k.
4. R.W.Hay and K.B.Nolan, J.Chem. Soc. Dalton Trans., 1975, 1348.
5. L.E.Brignner and I.Wadso, J.Biochem. Biophys., 1991, **22**, 101.
6. L.J.Bellamy, *The Infrared Spectra of Complex Molecules*, 3rd ed., Chapman and Hall, London, 1975.
7. K.Nakamoto, *Infrared Spectra of Inorganic and Coordination Complexes*, 4th ed., Wiley, New York, 1986.
8. N.M.Gorman, J.Laynez, A.Schon, J.Swirkuwsk and I.Wadso, J.Biochem. Biophys. Methods, 1984, **10**, 187.
9. H.Sigel and D.B.McCormick, Acc. Chem. Res., 1970, **3**, 201.
10. C.S.Chung, J.Chem.Ed., 1984, **61**, 1062.
11 Private Communication, Autonoma University, Barcelona, Spain.
12 Stevens, J. Chem. Soc. (A), 1969, 1723