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Thermodynamic, crystallographic and solvent extraction properties of cobalt(II), nickel(II) and copper(II) complexes of ethylenediamine-N,N,N′,N′-tetraacetanilide

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Abstract—Complexes of ethylenediamine-N,N,N′,N′-tetraacetanilide (edtan, $C_{34}H_{36}N_6O_{14}$) 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 changes) 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+}, 4.56 ± 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-21.4, 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 was isolated. The X-ray structure of $[Cu(edtan)(H_2O)][ClO_4]_2\cdot1.5H_2O$ (**1**) revealed a six-coordinate Cu centre with edtan acting as a pentadentate ligand (2N, 3O) with the coordination sphere completed by an oxygen atom from water. In striking contrast to the Cu complex, the Co centre in $[Co(edtan)(H_2O)][ClO_4]_2\cdot H_2O\cdot0.5C_2H_5OH$ (**2**) 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. © 1997 Elsevier Science Ltd

Keywords: ethylenediamine-N,N,N′,N′-tetraacetanilide; solvent extraction; metal complexes; formation constants; X-ray structures; thermodynamic parameters.

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 carries 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

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edtan and its solid complexes with nickel(II), cobalt(II) and copper(II) as their perchlorates, (ii) the thermodynamic data (stability constants, Gibbs energies, $\Delta_c G^0$, enthalpies, $\Delta_c H^0$ and entropies, $\Delta_c S^0$) for 1 : 1 complexation of the ligand with the same ions in water-saturated butan-1-ol as found from titration microcalorimetry, (iii) distribution data in the mutually saturated, two phase water: butanl-ol system, and (iv) the structures of the complexes formed between edtan and Cu^{II} and Co^{II} with perchlorate as the counter-anion in the solid state by single crystal X-ray crystallographic methods.

EXPERIMENTAL

Synthesis of edtan

The tetramethyl ester of H$_4$edta was synthesised by a modification of a previously reported [4] method in which a methanolic suspension of H$_4$edta is allowed to react with thionyl chloride. Found: C, 48.4; H, 7.1; N, 8.0. Calc. for $C_{14}H_{24}N_2O_8$: C 48.3; H, 6.9; N, 8.0%. ^{1}H NMR, CD$_3$COCD$_3$ δ_H (ppm): (300 MHz; standard SiMe$_4$) 2.86 (4H, s, NCH$_2$CH$_2$N), 3.61 (8H, s, NCH$_2$C), 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. Freshly distilled dmso (Fisons, 99%, 50 cm^3), sodium hydride (Aldrich, 60% dispersion in mineral oil, 3.1 g, 78 mmol) and freshly distilled aniline (BDH, Analar, 8.0 cm^3, 88 mmol) were placed in a three-necked flask under anhydrous conditions and the mixture cooled in an ice bath. A solution of the tetraester (5.3 g, 5 mmol) in dry dmso (30 cm^3) was added dropwise to allow a smooth reaction. After 19 h at room temperature, a brown solution was obtained at which stage the reaction had proceeded to completion (tlc). The brown solution was poured into cracked ice under vigorous stirring. The now yellow mixture was filtered under reduced pressure. The solid residue was washed several times with hexane, ethanol and then water. The white product was dried and finally recrystallised twice from hexane/ethanol (yield 35%). Found: C, 68.9; H, 6.1; H, 14.2. Calc. for $C_{34}H_{36}N_6O_4$: C, 68.9; H, 6.1; N, 14.2%. ^{1}H NMR, CDCl$_3$, δ_H (ppm): (300 MHz; standard SiMe$_4$) 2.86 (4H, s, NCH$_2$CH$_2$N), 3.46 (8H, NCH$_2$C), 7.07 (4H, t, *p*-H), 7.22 (8H, t, *m*-H), 7.54 (8H, d, *o*-H), 9.04 (4H, s, NH). IR (KBr pellet) ν_{max}/cm^{-1}, 3233 and 3183 (NH), 1682 (amide I), mp (uncorrected) 160–162°C, Chem. Abs. registry no. 107753-49-1.

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. For calorimetric titrations at 298.15 K the vessel was charged with a solution of edtan in water-saturated butan-1-ol (2.8 cm^3, 5.07×10^{-3} mol dm^{-3}) and the metal ion perchlorates in the same solvent [0.100 mol dm^{-3} for cobalt(II) and nickel(II), 0.0985 mol dm^{-3} for copper(II)] contained in a gas-tight, motor driven syringe (Hamilton, 500 μl) were used as titrants. In each titration about 12, 20 μl injections were made at 1 h intervals. 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.

Synthesis of the metal complexes

CAUTION! Perchlorates may detonate on warming or scraping.

Aqua(ethylenediamine-N,N,N′,N′-tetraacetanilide) copper(II) perchlorate 1.5 *hydrate*, [Cu(edtan)(H$_2$O)][ClO$_4$]$_2$·1.5H$_2$O (**1**). An excess of Cu(ClO$_4$)$_2$·6H$_2$O (3.159 g, 8.5 mmol), was added to a suspension of ligand edtan (1.072 g, 1.8 mmol) in 50 cm^3 of butan-1-ol which had been previously saturated with water. A green precipitate was formed after stirring at room temperature. The reaction mixture was left overnight and then filtered *in vacuo* and the product washed with cold butan-1-ol. Small amounts of solid remaining were discarded. The filtrate was recovered and most of the solvent removed using a rotary evaporator. Then, distilled water (25 cm^3) and sodium perchlorate (3 g) were added. The insoluble product was refluxed and ethanol was added dropwise to the suspension until the product was completely dissolved. The solution was left under reflux for several minutes and immediately filtered hot under reduced pressure. The reaction mixture was left for several days. The pale blue–green needles formed were dried at room temperature in a desiccator over calcium chloride. Found: C, 45.5; H, 4.6; N, 9.5. Calc. for $CuC_{34}H_{41}Cl_2N_6O_{14.5}$. C, 45.8; H, 4.6; N, 9.4%. IR (KBr pellet) ν_{max}/cm^{-1} 3344 (NH), 1663 (amide I), 1100 (ν_3, [ClO$_4$]$^-$).

Aqua(ethylenediamine-N,N,N′,N′,-tetraacetanilide) cobalt(II) perchlorate monohydrate 0.5 *ethanol* [Co(edtan)(H$_2$O)](ClO$_4$)$_2$·H$_2$O·0.5C$_2$H$_5$OH (**2**). An excess of Co(ClO$_4$)$_2$·6H$_2$O (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 cm^3) under stirring. The pink compound formed was filtered *in vacuo* and transferred to a round bottomed flask containing sodium perchlorate (2 g) and a small amount of ethanol. The mixture was refluxed and additional ethanol was added dropwise until the product dissolved completely. The solution was refluxed for a few minutes and immediately filtered *in vacuo*. The solution was left for several weeks after which pink crystals separated out. These were filtered and dried at the water pump. Found: C, 46.1; H, 4.8; N, 9.0. Calc. for $CoC_{35}H_{43}Cl_2N_6O_{14.5}$. C, 46.2; H, 4.8; N, 9.2. IR (KBr pellet) ν_{max}/cm^{-1}, 3381 (NH), 1665 (amide I), 1100 (ν_3, $[ClO_4]^-$).

(Ethylenediamine-N,N,N′,N′,tetraacetanilide)nickel (II) perchlorate hexahydrate $[Ni(edtan)](ClO_4)_2 \cdot 6H_2O$. An excess of $Ni(ClO_4)_2 \cdot 6H_2O$ (2.131 g, 5.8 mmol) was added in small amounts to a suspension of the ligand, edtan (0.5 g, 0.8 mmol) in ethanol under continuous stirring. The reaction was carried out at room temperature. After a while, the blue pale product which precipitated was filtered off. The solid was transferred to a round bottom flask (100 cm^3) containing sodium perchlorate (2 g) and a small amount of ethanol. The mixture was refluxed and ethanol was added dropwise until full dissolution of the product. It was then filtered in hot *in vacuo* and the solution was left for several days. The pale-blue needles formed were isolated. Found: C, 42.7; H, 4.8; N, 8.55. Calc. for $NiC_{34}H_{48}Cl_2N_6O_{10}$. C, 42.6; H, 5.0; N, 8.7%. IR (KBr pellet) ν_{max}/cm^{-1}, 3336 (NH), 1654 (amide I), 1100 (ν_3, $[ClO_4]^-$).

Distribution experiments

For these experiments, the water–butan-1-ol solvent system was used. Both solvents were previously mutually 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} $LiClO_4$). For the distribution studies, equal volumes (10 cm^3) of the aqueous phase containing the metal cation salt (2.5×10^{-4} mol dm^{-3}) and the organic phase containing the ligand were used. Two variables were considered; these were the concentrations of (i) hydrogen ion in the aqueous phase and (ii) ligand in the organic phase. For the former, different concentrations of aqueous perchloric acid (0.0508 mol dm^{-3} standardised with tris-hydroxyaminomethane) were added to the aqueous phase (saturated with butan-1-ol) containing the appropriate cation perchlorate. For the latter, different concentrations of ligand (from 0 to 2.9×10^{-4} mol dm^{-3}) were used in the organic phase. The mixtures were left under continuous shaking for ten minutes and then overnight in a thermostatic bath at 298 ± 0.05 K. After separation of the two layers, the equilibrium concentrations of the metal cation on the aqueous phase was determined by edta complexometric titrations and that of the organic phase by UV spectrophotometry.

X-ray crystallography (Table 1)

$[Cu(edtan)(H_2O)][ClO_4]_2 \cdot 1.5H_2O$ (**1**). 4018 reflections were measured with 2444 unique reflections ($I > 2.5\sigma(I)$) used in refinement. The total intensity change during the measurements was −1.5%. The structure was solved by direct methods and difference Fourier syntheses with neutral atomic form factors [6]. The highest residual electron density in the final difference map was 0.55 e/Å^3, 0.66 Å from O(16). The ligand phenyl rings were refined as rigid groups with isotropic thermal parameters. All other non-hydrogen atoms were refined with anisotropic thermal parameters except for O(12) (water of crystallisation) which was refined with an isotropic thermal parameter and population parameter of 0.5. Thermal parameters of one of the perchlorate anions were found to be very high. Resolution of a disordered model was not successful. Cl—O distances for this group were restrained during refinement. The relatively high R_w value is derived in the main from the apparent disorder in this perchlorate group. Hydrogen atoms for the ligand were placed in calculated positions, riding on the parent carbon atoms during refinement with fixed

Table 1. Crystal data for $[Cu(edtan)(H_2O)][ClO_4]_2 \cdot 1.5H_2O$ (**1**) and $[Co(edtan)(H_2O)][ClO_4]_2 \cdot H_2O \cdot 0.5C_2H_5OH$ (**2**)

Formula	$CuC_{34}H_{41}Cl_2N_6O_{14.5}$	$CoC_{35}H_{43}Cl_2N_6O_{14.5}$
Fw	900.18	909.59
Space group	$Pna2_1$	$P2_1/c$
Cryst system	orthorhombic	nomoclinic
a (Å)	27.531(4)	14.612(3)
b (Å)	12.253(1)	19.562(4)
c (Å)	11.984(3)	14.648(5)
β (°)		94.08(2)
V (Å^3)	4043(2)	4176(2)
Z	4	4
d_{calc} (g/cm^3)	1.48	1.45
Crystal dimensions (mm)	$1.30 \times 0.13 \times 0.07$	$0.8 \times 0.4 \times 0.1$
Data colln (room temp)	Enraf-Nonius CAD4	Enraf-Nonius CAD4
μ (Mo-K_α) (cm^{-1})	7.04	6.07
Radiation (Å)	Mo K_α (0.71069)	Mo K_α (0.71069)
F (000)	1864	1888
Scan techn ($0 < 2\theta < 50°$)	$6\omega/10\theta$	$\omega/2\theta$
R	0.063	0.105
R_w	0.067	0.300

isotropic thermal parameters. The positions of four water molecule hydrogen atoms were found in the difference Fourier map and refined with an O—H distance restriction. No hydrogen atom positions could be found for water molecule O(12) and were therefore not included in the structure factor calculation. The weighting scheme was:

$$w = [\sigma^2(F_0) + 0.001439F_0^2]/1.6224$$

$[Co(edtan)(H_2O)][ClO_4]_2 \cdot H_2O \cdot 0.5C_2H_5OH$ (**2**). 7258 reflections were measured with 4921 unique reflections ($I > 2\sigma(I)$) used in refinement. Standard reflections remained constant during data collection. Direct methods were used to solve the structure which was refined by least-squares methods. The two perchlorate anions show disorder and were isotropically refined with restrained geometries. Hydrogen atoms were introduced in calculated positions with isotropic temperature factors. The rest of the atoms were refined anisotropically. Some residual electron density peaks near to a perchlorate group (maximum value 1.59 e/Å^3) indicated the presence of disordered solvent ethanol. Disorder in the perchlorate groups and in the solvent ethanol is the main cause of the relatively high R(w) value. The weighting scheme was:

$$w = [\sigma^2(F_o^2) + (0.1524P)^2 + 29.71P]$$

where

$$P = [\max(F_o^2, 0) + 2F_o^2]/3$$

RESULTS AND DISCUSSION

Characterisation of ethylenediamine-N,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 [7] to the N—H stretching vibrations of a secondary amide with the two components attributed to *cis* and *trans* rotational isomers formed as a result of hydrogen bonding. There was no absorption characteristic [7] 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 [7] 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 [7] 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 [8] the presence of ionic (T_d) perchlorate.

Thermodynamic studies [9]

Stability constants and derived Gibbs energies, enthalpies and entropies for the complexation process are shown in Table 2. The data gave an excellent fit for the formation of 1 : 1 stoichiometric complexes in all three cases and are referred to the process:

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

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 2) 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 [10] suggesting a ligand specific effect for copper(II). It is therefore interesting to note that while favourable (positive) entropy changes 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 entropy associated with chelation reactions, Chung [11] has suggested that overall positive entropy changes (implying favourable contributions from both the transitional 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. In solution it is very difficult to obtain unequivocal evidence as to the number of amide groups coordinated to the metal ion. Whatever the number it would appear that there are fewer in the copper(II) complex. Equally it is difficult or impossible to say that the structures are the same in both solution and the solid state particularly as the metal ions are paramagnetic and thus the solutions are not amenable to study by NMR. However, results from the solid state can be used as corroborative evidence and this was the purpose of the X-ray crystallographic study reported below. Our calorimetric work confirms the importance of acquiring both stability constant and directly determined enthalpy data in understanding complexation reactions. It is difficult however to compare the values of the thermodynamic parameters with other amides as there appears to be no other published data in water saturated butanol as solvent.

Table 2. 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$_S$	$\Delta_c G^0$ (kJ mol^{-1})	$\Delta_c H^0$ (kJ mol^{-1})	$\Delta_c S^0$ (J mol^{-1} K^{-1})
Cu^{2+}	4.41 ± 0.01	-25.17 ± 0.24	-31.54 ± 1.45	-21.4
Co^{2+}	4.18 ± 0.04	-23.85 ± 0.22	-22.16 ± 1.24	5.7
Ni^{2+}	4.65 ± 0.02	-26.54 ± 0.12	-25.38 ± 0.74	3.9

^{a}Concentration ranges mol dm^{-3}; Cu^{2+} 6.97×10^{-4}–9.52×10^{-3}, edtan 7.92×10^{-3}–7.21×10^{-3}, 15 injections; Co^{2+} 7.093×10^{-4}–7.897×10^{-3}, edtan 4.965×10^{-3}–4.605×10^{-3}, 12 injections; Co^{2+} 7.08×10^{-4}–7.88×10^{-3}, edtan 4.97×10^{-3}–4.61×10^{-3}, 12 injections.

Structural studies

The main purpose of the crystallographic study 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.

[Cu(edtan)(H_2O)][ClO_4]$_2$ · 1.5H_2O (**1**). A Pluto plot of the molecule with a partial numbering scheme and selected bond lengths and angles are given in Fig. 1 and Table 3 respectively. The potentially hexadentate amide is clearly shown to coordinate through two nitrogen atoms of the ethylenediamine linkage and only three of the four amide oxygen atoms. The free amide oxygen atom is shown as O(11) in Fig. 1. The sixth coordination site is occupied by a water molecule O(1). A nitrogen atom N(2), two amide oxygen atoms O(41) and O(21) and the water molecule O(1) form a distorted square planar arrangement with bond lengths which might be described as normal for coordination to Cu^{II}; Cu(1)—O(1) = 1.978(8), Cu—O(21) = 2.018(7), Cu—O(41) = 2.007(8) and Cu—N(2) = 2.061(8) Å. The remaining bond lengths to the ligand are long (Cu—O(31) = 2.214(8) and Cu—N(1) = 2.295(9) Å). The N(1)—Cu(1)—O(31) angle = 156.9(3)° and inclined towards N(2) and O(21). Edta is known [12] to be five coordinate in [Cu(H_2edta)(H_2O)] in which the water molecule is *trans* to nitrogen and, as in **1**, the water molecule, two acetate oxygen atoms and a nitrogen atom are the four short contacts (1.978, 1.929, 1.970 and 2.066 Å, respectively) with an acetate oxygen atom and the remaining nitrogen atom at longer distances (2.467 and 2.291 Å respectively). 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}.

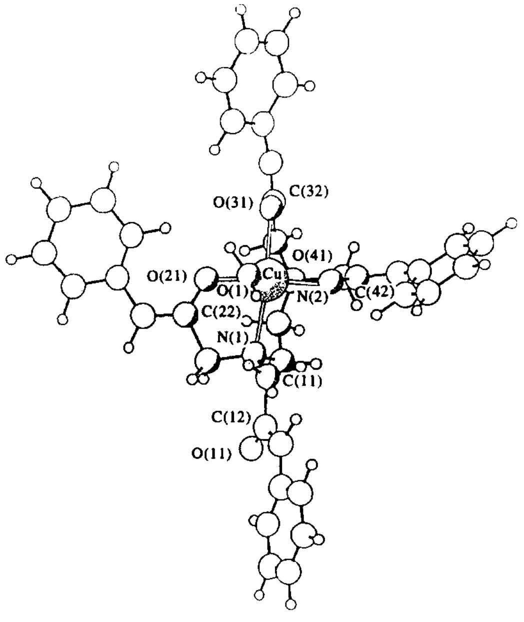

Fig. 1. Pluto drawing of the coordination sphere in [Cu(edtan)H_2O]$^{2+}$ (**1**).

[Co(edtan)(H_2O)][ClO_4]$_2$ · H_2O · 0.5C_2H_5OH (**2**). A Pluto plot of the molecule and a partial numbering scheme are given in Fig. 2 and selected bond lengths and angles in Table 3. The ligand edtan is hexadentate forming five chelate rings to Co and coordinated through the two nitrogen atoms of the entylenediamine 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 occupying the rectangular plane defined by the four amide oxygen atoms [O(1), O(2), O(3), O(4)]. One of the Co to amide oxygen bonds [Co—O(3) = 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 3 d divalent metal ion. The Co—N bond lengths are approximately equal in terms of the likely overall experimental errors. With edta both six and seven coordinate aqua complexes of Co^{II} are known. Thus, for example, [Co(H_2edta)(H_2O)] · 2H_2O has [13] six coordinate H_2edta (2N at 2.232 and 2.252 Å, 4O at 2.072, 2.116, 2.273 and 2.472 Å) with the water molecule (at 2.070 Å) completing the seven coordinate arrangements described [13] as '(6+1)', whereas in [Co(H_2O)$_6$] [Co(Hedta)H_2O]$_2$ Hedta is [14] five coordinate (2N at 2.146 and 2.215 Å, 3O at 2.114, 2.088 and 2.062 Å) with the water molecule (at 2.055 Å) completing six coordination.

Table 3. Selected bond distances (Å) and angles (°) and their estimated standard deviations for $CuC_{34}H_{41}Cl_2N_6O_{14.5}$ (**1**) and $CoC_{35}H_{43}Cl_2N_6O_{14.5}$ (**2**)

Compound **1**			
Cu—N(1)	2.295(9)	Cu—N(2)	2.061(8)
Cu—O(21)	2.018(7)	Cu—O(31)	2.214(8)
Cu—O(41)	2.007(8)	Cu—O(1)	1.978(8)
N(2)—Cu—N(1)	84.1(3)	O(21)—Cu—N(1)	78.4(3)
O(31)—Cu—N(1)	156.9(3)	O(21)—Cu—N(2)	93.4(3)
O(31)—Cu—O(21)	86.8(3)	O(31)—Cu—N(2)	79.1(3)
O(41)—Cu—N(2)	84.0(3)	O(41)—Cu—N(1)	100.7(3)
O(41)—Cu—O(31)	93.3(3)	O(41)—Cu—O(21)	177.3(3)
O(1)—Cu—N(2)	174.2(3)	O(1)—Cu—N(1)	100.2(3)
O(1)—Cu—O(31)	97.8(3)	O(1)—Cu—O(21)	91.4(3)
		O(1)—Cu—O(41)	91.3(3)
Compound **2**			
Co—O(1)	2.099(7)	Co—O(2)	2.186(7)
Co—O(3)	2.263(7)	Co—O(4)	2.157(7)
Co—N(12)	2.273(8)	Co—N(34)	2.263(7)
Co—O	2.093(7)		
N(12)—Co—N(34)	77.8(3)	O(34)—Co—N(34)	74.3(3)
O(4)—Co—N(12)	102.8(3)	O(3)—Co—N(34)	71.1(3)
O(3)—Co—N(12)	124.6(3)	O(3)—Co—O(4)	111.0(3)
O(2)—Co—N(34)	133.1(3)	O(2)—Co—N(12)	73.2(3)
O(2)—Co—O(4)	77.2(3)	O(2)—Co—O(3)	155.2(3)
O(1)—Co—N(34)	113.5(3)	O(1)—Co—N(12)	76.7(3)
O(1)—Co—O(4)	171.5(3)	O(1)—Co—O(3)	75.5(3)
O(1)—Co—O(2)	94.6(3)	O—Co—N(34)	133.0(3)
O—Co—N(12)	148.9(3)	O—Co—O(4)	85.7(3)
O—Co—O(3)	77.6(3)	O—Co—O(2)	79.9(3)
O—Co—O(1)	90.6(3)		

Oxygen atom from coordinated water molecule, O(1) in **1**, O in **2**.

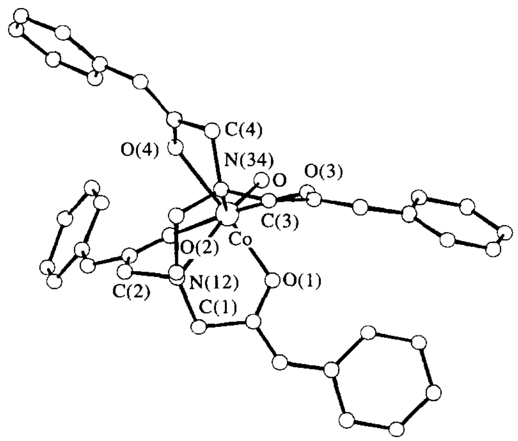

Fig. 2. Pluto drawing of the coordination sphere in $[Co(edtan)H_2O]^{2+}$ (**2**).

In both structures the metal ion to N and the shorter metal ion to O bond lengths are similar [15] to those found for amides of ethylenediamine derivatives. For example, a Cu^{II} complex [5] of NN′-bis(2-carbamoylethyl)ethylenediamine which is four coordinate, has Cu to N contacts at 1.997 and 1.983 Å, with Cu to O at 1.953 and 1.962 Å.

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 Tables 4 and 5. These show that under the conditions employed the distributions are in order $Cu^{2+} > Co^{2+} > Ni^{2+}$. At high hydrogen ion concentrations (Table 5) there is an important and marked preference for Cu^{2+} such that complete separation of copper from cobalt and nickel is feasible.

The data in Table 4, 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 rela-

Table 4. Percentage metal extraction at 298 K at different ligand concentrations ($I = 0.1$ mol dm^{-3})

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

Table 5. Distribution of metal cations in the water/butan-1-ol/edtan system at different concentrations of aqueous perchloric acid (298 K; $I = 0.1$ mol dm^{-3}, $LiClO_4$; edtan 1.0×10^{-3} mol dm^{-3}; initial metal ion concentrations 2.4×10^{-4} mol dm^{-3})

$HClO_4$ (mol dm^{-3})	Cu^{II}	Co^{II}	Ni^{II}
1.0×10^{-5}	100	87.5	66.9
3.2×10^{-5}	100	88.1	72.4
1.0×10^{-4}	100	87.5	70.3
3.2×10^{-4}	100	84.8	67.2
1.0×10^{-3}	100	78.6	54.8
3.2×10^{-3}	98.1	54.6	34.5
1.0×10^{-2}	96.7	26.8	23.8

tive to nickel is of approximate 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 [16] 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.

Because the thermodynamic data gave an excellent fit for the formation of 1 : 1 complexes assuming no ion association, it would seem that factors (ii) and (iv) are insignificant in the water-saturated butan-1-ol phase. 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 (v) since there is a significant difference in their log K_s values. Thus, it would appear that the higher stability of the nickel complex relative to cobalt (see $\Delta_c G^0$ values, Table 2) is insufficient to overcome the favourable transfer of the latter as the perchlorate [factor (i)]. As a result, cobalt is better extracted than nickel. The marked preference for copper in the extraction process may then be attributed to an additional contribution resulting from the formation of a complex ion with a five rather than a six coordinate edtan molecule (as demonstrated by the X-ray crystallographic structures discussed above) which then alters the solvation of the complex ion in the butan-1-ol phase in a beneficial manner. 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+}.

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Supplementary material available—Tables of complete data including methods of data collection, refinement, atomic coordinates and *U* values, bond distances and angles, and thermal parameters for both structures (6 pages).

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