Synthesis and *X*-Ray Structural Characterization† of Novel Binuclear Complexes of Copper(II), Nickel(II), and Cobalt(II) with an Octadentate Ligand, *N,N',N'',N'''*-Tetrakis(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane

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The ligand *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane(taec) and its binuclear metal complexes, $M_2(taec)X_nY_{4-n}$, were synthesized and characterized for M = Cu, Ni, or Co and where X and Y are anions (Cl^-, Br^-, ClO_4^-, or OH^-). The crystal structures of $Cu_2(taec)(ClO_4)_4$ (**1**), $Cu_2(taec)Br(ClO_4)_3$ (**2**), and $Ni_2(taec)(ClO_4)_4$ (**3**) were determined by single-crystal *X*-ray analysis. In all the complexes each taec molecule incorporates two metal ions, each of which is co-ordinated by two ring- and two pendant-nitrogen atoms. Complexes (**1**) and (**3**) adopt similar structures, different to (**2**). In (**1**) each copper is weakly co-ordinated by perchlorate oxygen forming an elongated square pyramid. In (**2**), the bromide ion is bound by both copper atoms. This structure accords with the proposed structure deduced from the unusually high stability of the Cu–Br linkage against hydrolysis in water. In (**3**) the co-ordination geometry is essentially square planar, and compatible with the observed diamagnetism and visible spectrum. From the magnetic data it was concluded that $Ni_2(taec)Cl_4{\cdot}H_2O$ consists of a diamagnetic nickel and a paramagnetic five- or six-co-ordinate nickel. All the cobalt(II) complexes are in the high-spin state. They are inert towards oxidation to cobalt(III), probably because of the difficulty of achieving six-co-ordination. In $Co_2(taec)(OH)(PF_6)_3$ and $Co_2(taec)(OH)(ClO_4)_3$ the hydroxide seems to be linked to both cobalt atoms, judging by the magnetic data.

A number of tetra-aza macrocycles with pendant arms on the nitrogen atoms have been prepared in the last several years, since they often showed specific complexation behaviour and gave metal complexes of interesting structure.[1–6] Cyclam (1,4,8,11-tetra-azacyclotetradecane) derivatives having pendant arms such as $-CH_2COOH$,[2] $-CH_2CH_2OH$,[3] $-CH_2CH_2CN$,[4] $-CH_2CH_2CONH_2$,[4] and $-CH_2CH_2CH_2NH_2$[5] were prepared. These ligands have always been reported to form 1:1 metal complexes incorporating a metal ion in the ring centre to form an essentially square-planar co-ordination, or distorted octahedral co-ordination by further donating two of the pendant groups,[6] except for one case where a poorly defined polymeric complex with metal:ligand ratio of 2:2 was observed.[5] In this study we have prepared the ligand *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane (taec) which is similar to the above ligands but interestingly always forms 2:1 (metal:ligand) complexes. It possesses eight amino-nitrogen atoms capable of forming co-ordination bonds with metal ions. Possible structures for the complexes are illustrated in Figure 1, for which there are a large number of possible conformations. In any of these the environment of a metal ion is so crowded that not only the co-ordination geometry, but also the ligation and substitution of an additional ligand would be significantly controlled by non-donating ligand atoms surrounding the co-ordination site. Thus, we may expect interesting properties specific for the complexes of this ligand.

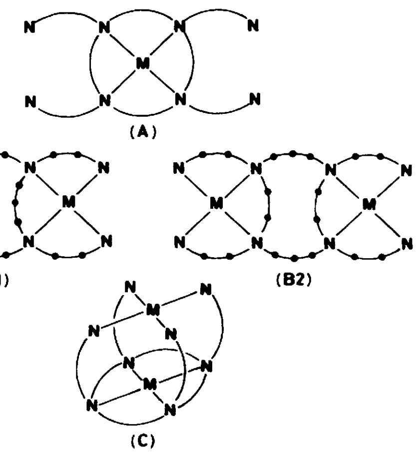

Figure 1. Co-ordination modes of taec

As reported in the previous communication,[7] we have isolated copper(II) complexes, $Cu_2(taec)(ClO_4)_4$, $Cu_2(taec)Br_4$, $Cu_2(taec)Br(ClO_4)_3$, and confirmed the type (**B1**) structure (Figure 1) for the tetraperchlorate complex by *X*-ray analysis. The tetrabromide and bromide triperchlorate complexes showed unusual stability towards the aquation of the Cu–Br bond. To account for this we proposed[7] a binuclear structure in which the bromide ion is incorporated into the complex such that it is bound by both copper ions. Thus, in this study, we have carried out the *X*-ray analysis of $Cu_2(taec)Br(ClO_4)_3$ in order to verify the assumption. We also report here the preparation and characterization of nickel(II) and cobalt(II) complexes of taec. In

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† *Supplementary data available* (No. SUP 56479, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. units employed: $\mu_B = 9.274 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

those complexes the steric effect of the ligand also strongly controls the co-ordination geometry and chemical properties.

Most metal enzymes conduct specific reactions which do not take place in ordinary metal complexes. This has been considered to be caused by the specific protein structure around the active site.[8] Thus, it is important to study the effect of non-donating ligand moieties on the co-ordination structure and stability of metal–ligand bonds. The present investigation can be one of such studies, and will contribute to the elucidation of sterically controlled complexation behaviour.

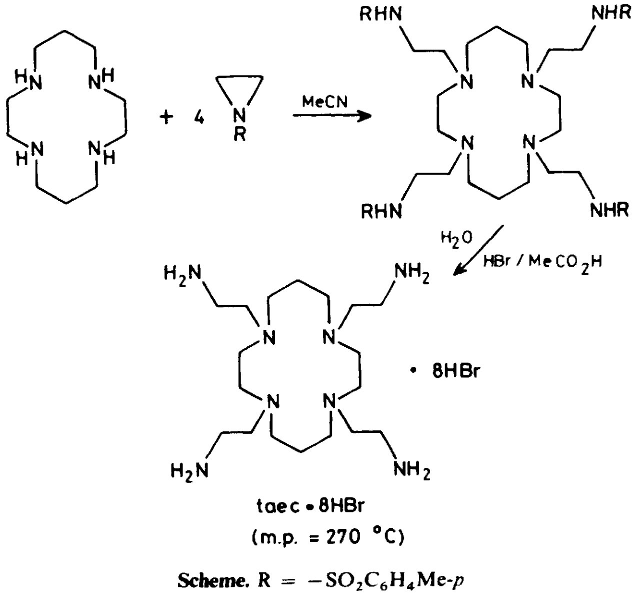
Experimental

Preparation of the Ligand.—The ligand taec was prepared according to the Scheme.

N,N′,N″,N‴-*Tetrakis*(2-N-*tosylaminoethyl*)-1,4,8,11-*tetra-aza-cyclotetradecane*.—A suspension of cyclam[9] (2.0 g, 0.1 mol) in acetonitrile (200 cm^3) was refluxed, and to this was added dropwise with stirring *N*-tosylaziridine (8 g, 0.44 mol) in acetonitrile (100 cm^3) during 3 h. The mixture became transparent near the end of the addition, and again became turbid after 15 h refluxing. The resulting precipitate was collected by filtration. Yield 8.5 g (85%). The product was recrystallized from dioxane, m.p. 209—210 °C (Found: C, 55.85; H, 7.00; N, 11.20. Calc. for $C_{46}H_{68}N_8O_8S_4$: C, 55.85; H, 6.95; N, 11.35%).

taec·8HBr.—The crude *N*-tosylated compound obtained by the above procedure (8.0 g, 0.008 mol) was refluxed for 40 h with a mixture of hydrobromic acid (47%, 90 g) and glacial acetic acid (90 g). The reaction mixture was diluted with water (1 dm^3) and filtered. The filtrate was concentrated almost to dryness in a rotary evaporator, and was treated with hot ethanol. The undissolved product was collected and dried. Yield 8 g (95%). The sample was recrystallized from water–methanol solution and dried under vacuum at 100 °C, m.p. 270 °C (decomp.) (Found: C, 21.6; H, 5.10; N, 11.3. Calc. for $C_{18}H_{52}Br_8N_8$: C, 21.2; H, 5.15; N, 11.0%).

taec.—An aqueous solution of the octahydrobromide was passed through a column of anion-exchange resin (OH-form, Dowex 1 × 8), and the eluate was evaporated to dryness. The colourless sticky mass thus obtained was dried over P_2O_5 and used for the preparation of complexes without further purification. The yield was almost quantitative.



Scheme. R = $-SO_2C_6H_4Me$-*p*

Preparation of Metal Complexes.—$Cu_2(taec)Br_4$. The ligand hydrobromide, taec·8HBr (1.5 g, 1.5 mmol), was dissolved in water (50 cm^3). To this solution was added an excess of basic copper(II) carbonate. The mixture was filtered after heating on a water-bath for 1 h. The blue filtrate thus obtained was concentrated to one quarter of the volume on a water-bath. Ethanol was added to this solution to obtain blue fine crystals, which were recrystallized from ethanol–water and dried over P_2O_5 under vacuum; yield 445 mg (37%) (Found: C, 26.3; H, 5.40; N, 13.6. Calc. for $C_{18}H_{44}Br_4Cu_2N_8$: C, 26.4; H, 5.40; N, 13.7%).

$Cu_2(taec)Br(ClO_4)_3$. To an aqueous solution of $Cu_2(taec)Br_4$ was added an excess of sodium perchlorate. The mixture was concentrated to obtain fine blue crystals, which were recrystallized from water and dried over P_2O_5 under vacuum; yield 44% (Found: C, 24.75; H, 5.10; Cu, 14.15; N, 12.8. Calc. for $C_{18}H_{44}BrCl_3Cu_2N_8O_{12}$: C, 24.65; H, 5.05; Cu, 14.5; N, 12.75%).

$Cu_2(taec)(ClO_4)_4$. To an aqueous solution of $Cu_2(taec)Br_4$ was added an aqueous silver perchlorate solution to precipitate silver bromide, and the mixture was filtered. An excess of sodium perchlorate was added to the filtrate, and the solution was concentrated until fine violet crystals began to deposit. The crude product was recrystallized from water to give violet needles; yield 36% (Found: C, 24.05; H, 5.00; Cu, 14.35; N, 12.3. Calc. for $C_{18}H_{44}Cl_4Cu_2N_8O_{16}$: C, 24.1; H, 4.95; Cu, 14.15; N, 12.5%).

$Ni_2(taec)(ClO_4)_4$. The ligand hydrobromide, taec·8HBr (0.2 g, 0.2 mmol), and nickel(II) perchlorate hexahydrate (0.2 g, 0.6 mmol) were dissolved in warm water (20 cm^3). The pH of the solution was adjusted to 6 by adding 10% aqueous sodium hydroxide, and the solution was filtered. The yellow-brown filtrate was concentrated to one third of its volume. Fine yellow crystals were separated from the solution, when excess sodium perchlorate and methanol (half the solution volume) were added. The crystals were recrystallized from methanol–water; yield 98 mg (36%) (Found: C, 24.05; H, 5.15; N, 12.35; Ni, 13.2. Calc. for $C_{18}H_{44}Cl_4N_8Ni_2O_{16}$: C, 24.35; H, 5.00; N, 12.6; Ni, 13.2%).

$Ni_2(taec)Br_4$. Nickel(II) bromide (328 mg, 1.5 mmol) was dissolved in dmf (25 cm^3) and mixed with taec (186 mg, 0.5 mmol) dissolved in methanol (5 cm^3). Yellow powder immediately separated from the mixture. It was collected, washed with methanol, and dried over P_2O_5 under vacuum; yield 425 mg (35%) (Found: C, 26.35; H, 5.45; N, 13.55; Ni, 14.3. Calc. for $C_{18}H_{44}Br_4N_8Ni_2$: C, 26.7; H, 5.50; N, 13.85; Ni, 14.5%).

$Ni_2(taec)Cl_4 \cdot H_2O$. Nickel(II) chloride hexahydrate (357 mg, 1.5 mmol) and taec (186 mg, 0.5 mmol) were stirred in methanol (15 cm^3). The resulting deep green solution was filtered. Green needles were separated from the filtrate after 24 h. The product was washed with methanol and dried in a P_2O_5 desiccator under vacuum; yield 38 mg (12%) (Found: C, 33.2; H, 7.05; N, 17.05; Ni, 17.5. Calc. for $C_{18}H_{46}Cl_4N_8Ni_2O$: C, 33.25; H, 7.15; N, 17.25; Ni, 18.1%).

$Co_2(taec)Cl_2(BPh_4)_2$. Cobalt(II) chloride hexahydrate (238 mg, 1 mmol) and taec (186 mg, 0.5 mmol) were stirred in methanol (30 cm^3). To this was added sodium tetraphenylborate (684 mg, 2 mmol) dissolved in methanol (10 cm^3). The mixture immediately became violet and turbid. The violet precipitate was collected, washed with methanol, and dried over P_2O_5 under vacuum; yield 38 mg (12%) (Found: C, 66.0; H, 7.10; Co, 9.7; N, 9.60. Calc. for $C_{66}H_{84}B_2Cl_2Co_2$: C, 66.05; H, 7.05; Co, 9.8; N, 9.35%).

$Co_2(taec)(OH)(ClO_4)_3$. Cobalt(II) perchlorate hexahydrate (300 mg, 1 mmol) and taec (186 mg, 0.5 mmol) were mixed in water (30 cm^3), and heated on a water-bath with stirring for 15 min. The resulting purple solution was filtered and allowed to stand overnight. The purple needles which separated from the solution were collected, washed with water and methanol, and dried in a P_2O_5 desiccator; yield 64 mg (16%) (Found: C, 26.8; H, 5.65; Co, 14.6; N, 13.9. Calc. for $C_{18}H_{45}Cl_3Co_2N_8O_{13}$: C, 26.8; H, 5.65; Co, 14.6; N, 13.9%).

Co_2(taec)(OH)$(PF_6)_3$. Cobalt(II) chloride hexahydrate (238 mg, 1 mmol) and taec (186 mg, 0.5 mmol) were mixed in water (30 cm^3). Ammonium hexafluorophosphate (326 mg, 2 mmol) was added to this solution, and the mixture was heated on a water-bath with stirring. The resulting purple solution was filtered and allowed to stand overnight. Purple needles separated from the solution, which were collected, washed with water and methanol, and dried over P_2O_5; yield 48 mg (10%) (Found: C, 22.75; H, 4.85; Co, 12.4; N, 11.8. Calc. for $C_{18}H_{45}Co_2F_{18}N_8OP_3$: C, 22.95; H, 4.80; Co, 12.5; N, 11.9%).

Physical Measurements.—Infrared spectra were measured with a Hitachi 215 spectrometer. Electronic spectra were recorded with a Shimadzu MPS-5000 multipurpose spectrophotometer and a Shimadzu UV-240 u.v.–visible recording spectrometer. Magnetic susceptibilities were measured by the Faraday method, and calibrated using $[Ni(H_2NCH_2CH_2NH_2)_2]S_2O_3$. Diamagnetic corrections were made with Pascal's constants.

Elemental Analyses.—The carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. The copper, nickel, and cobalt analyses were made with a Shimadzu AA-610 atomic absorption flame spectrometer.

Crystal Structure Determination.—The crystals used for the *X*-ray analysis were grown by the slow evaporation of aqueous solutions. A Rigaku AFC-5 automated four-circle diffractometer was used for all measurements. Crystal data and details of the data collection are given in Table 1. Lattice constants were determined by least-squares refinement based on 40 reflections with $20 < 2\theta < 30°$. The intensity data were corrected for Lorentz-polarization effects, but not for absorption.

The structures were solved by direct methods. Refinements were carried out by the block-diagonal least-squares methods. Hydrogen atoms were inserted in their calculated positions and included in the refinement. The final R values were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.069$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.111$ for Cu_2(taec)$(ClO_4)_4$, $R = 0.071$, $R' = 0.109$ for Cu_2(taec)Br$(ClO_4)_3$, and $R = 0.086$, $R' = 0.130$ for Ni_2(taec)$(ClO_4)_4$. The weighting schemes were $w = (5.70 + |F_o| + 0.008|F_o|^2)^{-1}$ for Cu_2(taec)$(ClO_4)_4$, $(17.3 + |F_o| + 0.005|F_o|^2)^{-1}$ for Cu_2(taec)Br$(ClO_4)_3$, and $(11.5 + |F_o| + 0.006|F_o|^2)^{-1}$ for Ni_2(taec)$(ClO_4)_4$. The final difference Fourier syntheses were featureless.

The atomic scattering factors for Br, Cu, Ni, Cl, O, N, C, and H and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, for Br, Cu, Ni, Cl, O, N, and C were taken from ref. 10. All calculations were carried out on the FACOM M-200 computer at the Computer Center of Kyushu University using a local version of the UNICS III[11] and the ORTEP programs.[12] Atomic co-ordinates are in Table 2.

Results

Description of the Structures.—Cu_2(taec)$(ClO_4)_4$. The ORTEP diagram was included in the previous report.[7] It is similar to that of the nickel analogue except for the perchlorate co-ordination. The Cu_2(taec) unit assumes the (**B1**) structure (Figure 1), and the cyclam ring adopts the *trans* III form of Bosnich *et al.*[13] The complex cation $[Cu_2(taec)(ClO_4)_2]^{2+}$ has a centre of symmetry and a symmetry plane formed by C(3), Cu, O(1), C(3′), Cu′, and O(1′), where the atom numbering system is the same as that of the nickel analogue.

The co-ordination geometry of each copper ion is an

Table 1. Crystal data and data collection details[*]

Complex	Cu_2(taec)$(ClO_4)_4$	Cu_2(taec)Br$(ClO_4)_3$	Ni_2(taec)$(ClO_4)_4$
Formula	$C_{18}H_{44}Cl_4Cu_2N_8O_{16}$	$C_{18}H_{44}BrCl_3CuN_8O_{12}$	$C_{18}H_{44}Cl_4N_8Ni_2O_{16}$
M	897.59	877.95	887.82
T/K	296 ± 1	295 ± 1	291 ± 1
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnnm*	$Pca2_1$	*Pnnm*
a/Å	11.709(1)	15.590(1)	11.655(1)
b/Å	14.948(3)	14.460(1)	15.076(1)
c/Å	9.938(2)	14.602(1)	9.872(1)
U/Å^3	1 739.4(4)	3 291.7(3)	1 734.7(2)
Z	2	4	2
D_c/g cm^{-3}	1.71	1.77	1.70
D_m/g cm^{-3}	1.75	1.76	1.76
F(000)	924	1 792	920
μ(Mo-K_α)/cm^{-1}	16.1	28.1	14.8
Crystal dimensions (mm)	0.23 × 0.25 × 0.50	0.35 × 0.45 × 0.50	0.10 × 0.25 × 0.29
Standard reflections	(2, 0, 0)	(4, 0, 0)	$(\bar{2}, 0, 0)$
	$(0, \bar{4}, 0)$	(0, 5, 0)	$(0, \bar{4}, 0)$
	(0, 0, 2)	(0, 0, 4)	$(0, 0, \bar{2})$
Decay of standard	±2%	±3%	±2%
2θ range (°)	2.5—64.0	2.5—64.0	2.5—65.0
Total no. of observed reflections	6 530	6 313	3 540
No. of unique reflections with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	2 397	2 493	1 521
Final no. of variables	194	574	194
Final residuals			
R	0.069	0.071	0.086
R'	0.111	0.109	0.130

[*] Common data: graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,73$Å), scan type θ—2θ, scan speed 3° min^{-1}, scan width (1.4 + 0.5 tan θ)°.

Table 2. Fractional atomic co-ordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $Cu_2(taec)(ClO_4)_4$							
Cu	0.207 4(1)	−0.084 8(1)	0.5000	O(6)	0.245 0(10)	0.124 1(9)	0.114 0(11)
Cl(1)	0.352 5(1)	0.140 1(1)	0.5000	N(1)	0.090 8(3)	−0.105 9(2)	0.347 1(4)
Cl(2)	0.179 4(2)	0.141 7(2)	0.0000	N(2)	0.325 3(4)	−0.089 6(4)	0.354 5(7)
O(1)	0.255 1(6)	0.082 5(4)	0.5000	C(1)	−0.012 9(4)	−0.049 2(3)	0.329 8(5)
O(2)	0.316 6(9)	0.228 0(6)	0.5000	C(2)	0.055 1(4)	−0.200 4(3)	0.369 7(6)
O(3)	0.417 3(6)	0.119 1(7)	0.613 7(9)	C(3)	−0.008 2(6)	−0.217 3(5)	0.5000
O(4)	0.082 0(7)	0.086 9(6)	0.0000	C(4)	0.157 0(6)	−0.101 0(4)	0.218 2(5)
O(5)	0.163 2(15)	0.231 3(7)	0.0000	C(5)	0.277 8(5)	−0.134 6(5)	0.236 4(6)
(*b*) $Cu_2(taec)Br(ClO_4)_3$							
Br	0.493 3(2)	0.354 4(1)	0.179 8(2)	N(5)	0.568 2(15)	0.186 0(13)	0.328 8(13)
Cu(1)	0.566 4(1)	0.182 9(1)	0.186 1(2)	N(6)	0.686 1(12)	0.234 0(14)	0.175 8(19)
Cu(2)	0.405 4(2)	0.403 6(1)	0.030 1(2)	N(7)	0.500 1(18)	0.486 8(16)	−0.007 6(23)
Cl(1)	0.713 7(3)	−0.025 6(3)	0.362 6(3)	N(8)	0.342 5(14)	0.504 2(14)	0.104 6(13)
Cl(2)	0.495 0(4)	0.731 3(4)	0.095 7(5)	C(1)	0.481 5(11)	0.014 2(12)	0.133 2(16)
Cl(3)	0.248 4(5)	0.625 2(4)	0.387 9(6)	C(2)	0.569 2(18)	0.017 7(18)	0.101 0(19)
O(11)	0.648 0(11)	−0.003 0(16)	0.426 6(13)	C(3)	0.555 9(18)	0.134 5(16)	−0.020 5(16)
O(12)	0.780 9(10)	−0.069 1(12)	0.409 7(13)	C(4)	0.541 4(15)	0.230 6(21)	−0.039 2(17)
O(13)	0.680 0(15)	−0.084 9(15)	0.296 6(15)	C(5)	0.465 8(19)	0.250 4(20)	−0.099 9(15)
O(14)	0.741 1(14)	0.054 1(12)	0.320 9(16)	C(6)	0.334 2(21)	0.338 5(19)	−0.122 6(18)
O(21)	0.481 7(38)	0.652 7(20)	0.136 3(22)	C(7)	0.279 0(15)	0.291 9(15)	−0.052 4(20)
O(22)	0.561 3(17)	0.776 9(20)	0.123 0(37)	C(8)	0.289 4(10)	0.252 7(12)	0.112 1(21)
O(23)	0.515 4(36)	0.702 8(25)	0.007 8(27)	C(9)	0.359 4(15)	0.183 3(14)	0.103 0(19)
O(24)	0.436 8(20)	0.793 4(25)	0.089 2(53)	C(10)	0.376 7(12)	0.129 9(14)	0.192 7(20)
O(31)	0.161 7(19)	0.613 8(23)	0.395 8(34)	C(11)	0.476 4(15)	0.055 2(16)	0.295 6(15)
O(32)	0.285 9(18)	0.614 3(18)	0.475 9(19)	C(12)	0.490 9(20)	0.132 0(20)	0.361 5(17)
O(33)	0.266 3(19)	0.712 8(16)	0.355 9(20)	C(13)	0.688 1(17)	0.116 9(21)	0.059 4(29)
O(34)	0.280 2(27)	0.563 7(28)	0.336 3(33)	C(14)	0.727 8(18)	0.175 0(32)	0.110 5(31)
N(1)	0.465 2(10)	0.091 2(10)	0.199 8(11)	C(15)	0.478 8(26)	0.408 6(26)	−0.149 3(25)
N(2)	0.594 7(10)	0.110 6(12)	0.069 2(12)	C(16)	0.511 0(25)	0.480 7(22)	−0.102 5(25)
N(3)	0.425 0(15)	0.342 1(12)	−0.093 8(12)	C(17)	0.227 9(15)	0.399 2(16)	0.059 4(22)
N(4)	0.291 6(10)	0.328 0(10)	0.041 6(14)	C(18)	0.258 4(17)	0.462 9(16)	0.134 3(21)
(*c*) $Ni_2(taec)(ClO_4)_4$							
Ni	0.190 2(1)	−0.094 3(1)	0.5000	O(6)	0.263 5(17)	0.110 8(15)	0.110 0(24)
Cl(1)	0.376 3(3)	0.145 0(2)	0.5000	N(1)	0.080 3(6)	−0.110 8(4)	0.350 3(7)
Cl(2)	0.200 1(4)	0.129 5(3)	0.0000	N(2)	0.305 9(7)	−0.089 2(7)	0.364 1(13)
O(1)	0.282 0(14)	0.090 8(10)	0.5000	C(1)	−0.018 8(8)	−0.047 8(6)	0.332 2(9)
O(2)	0.329 3(18)	0.227 5(12)	0.5000	C(2)	0.033 1(9)	−0.202 4(6)	0.370 0(12)
O(3)	0.441 8(12)	0.128 0(15)	0.611 9(18)	C(3)	−0.031 2(13)	−0.217 3(9)	0.5000
O(4)	0.100 0(12)	0.079 4(9)	0.0000	C(4)	0.148 0(12)	−0.108 0(8)	0.219 9(12)
O(5)	0.187 4(24)	0.215 4(16)	0.0000	C(5)	0.267 4(12)	−0.136 7(9)	0.242 7(13)

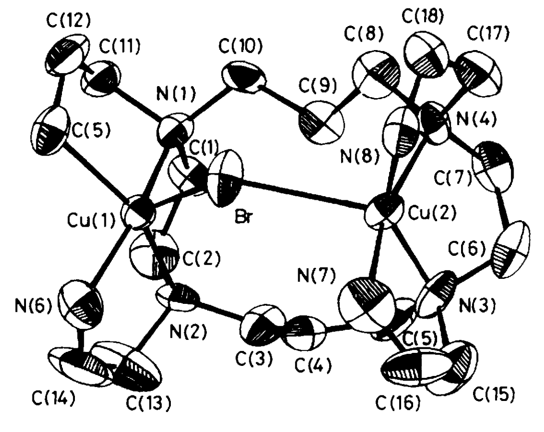


Figure 2. ORTEP diagram of $Cu_2(taec)Br(ClO_4)_3$

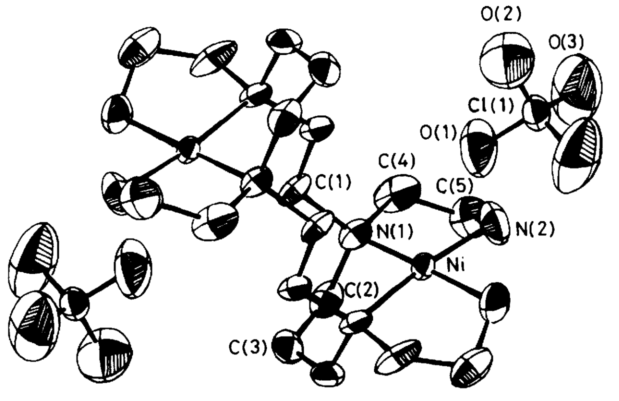


Figure 3. ORTEP diagram of $Ni_2(taec)(ClO_4)_4$

elongated square pyramid with a perchlorate oxygen at the top [Cu–O 2.562(7) Å]. The basal plane is formed by two aza-nitrogen and two terminal nitrogen atoms, and is perfectly planar as required from the symmetry (C_{2h}) of the molecule. The deviation of the copper atom from the plane is 0.193 Å. Bond lengths and angles are in Table 3.

Cu$_2$(taec)Br(ClO$_4$)$_3$. The asymmetric unit (Figure 2) consists of a discrete [Cu$_2$(taec)Br]$^{3+}$ cation and three perchlorate ions. The complex adopts the (**B2**) structure (Figure 1), different from the tetraperchlorate complexes. The co-ordination geometry of each copper atom is a distorted square pyramid. The bromide ion weakly co-ordinates to both copper atoms at the apical positions with Cu–Br distances [2.730(3) and 2.688(4) Å] which are considerably longer than the sum of the covalent radii (2.46 Å).[14] The deviations of the basal atoms from the mean plane are within ±0.2 Å, and Cu(1) and Cu(2) are displaced by 0.44 and 0.42 Å, respectively, from the mean plane towards Br.

Table 3. Interatomic distances (Å) and angles (°) in the co-ordination spheres with their estimated standard deviations in parentheses*

(*a*) Cu$_2$(taec)(ClO$_4$)$_4$			
Cu–N(1)	2.066(4)	Cu–O(1)	2.562(7)
Cu–N(2)	2.000(6)	Cu ··· Cu^{i}	5.479(1)
N(1)–Cu–N(2)	85.3(2)	N(1)–Cu–O(1)	107.0(1)
N(1)–Cu–N(1^{ii})	94.6(1)	N(2)–Cu–O(1)	83.4(2)
N(2)–Cu–N(2^{ii})	92.6(2)		
(*b*) Cu$_2$(taec)Br(ClO$_4$)$_3$			
Cu(1)–N(1)	2.069(15)	Cu(2)–N(3)	2.056(18)
Cu(1)–N(2)	2.070(17)	Cu(2)–N(4)	2.089(15)
Cu(1)–N(5)	2.063(19)	Cu(2)–N(7)	1.988(27)
Cu(1)–N(6)	2.010(19)	Cu(2)–N(8)	2.053(20)
Cu(1)–Br	2.730(3)	Cu(2)–Br	2.688(4)
Cu(1) ··· Cu(2)	4.656(3)		
Cu(1)–Br–Cu(2)	118.5(1)	Br–Cu(2)–N(3)	122.5(6)
Br–Cu(1)–N(1)	105.5(4)	Br–Cu(2)–N(4)	103.7(5)
Br–Cu(1)–N(2)	121.6(5)	Br–Cu(2)–N(7)	91.2(9)
Br–Cu(1)–N(5)	90.8(5)	Br–Cu(2)–N(8)	90.4(6)
Br–Cu(1)–N(6)	92.9(6)	N(3)–Cu(2)–N(4)	87.7(8)
N(1)–Cu(1)–N(2)	85.0(6)	N(3)–Cu(2)–N(7)	83.9(11)
N(1)–Cu(1)–N(5)	86.3(7)	N(3)–Cu(2)–N(8)	147.1(8)
N(1)–Cu(1)–N(6)	161.6(7)	N(4)–Cu(2)–N(7)	165.1(10)
N(2)–Cu(1)–N(5)	147.5(7)	N(4)–Cu(2)–N(8)	85.7(8)
N(2)–Cu(1)–N(6)	85.1(9)	N(7)–Cu(2)–N(8)	94.6(10)
N(5)–Cu(1)–N(6)	93.9(10)		
(*c*) Ni$_2$(taec)(ClO$_4$)$_4$			
Ni–N(1)	1.971(7)	Ni–O(1)	2.988(16)
Ni–N(2)	1.904(11)	Ni ··· Ni^{i}	5.267(2)
N(1)–Ni–N(2)	86.4(4)	N(1)–Ni–O(1)	110.5(3)
N(1)–Ni–N(1^{ii})	97.1(3)	N(2)–Ni–O(1)	73.1(4)
N(2)–Ni–N(2^{ii})	89.6(5)		

* Superscripts i and ii refer to the equivalent positions $-x, -y, z$ and $x, y, 1-z$ respectively.

Ni$_2$(taec)(ClO$_4$)$_4$. The ORTEP diagram is shown in Figure 3. The structure is similar to that of the copper analogue except that the perchlorate co-ordination can no longer be detected [the shortest Ni–O distance being 2.988(16) Å]. In each co-ordination unit the donor atoms are strictly coplanar from the requirement of crystallographic symmetry, and the nickel atom deviates from this plane towards the oxygen atom of a perchlorate ion by 0.089 Å. The perchlorate ions are hydrogen bonded to the primary amino nitrogens, *e.g.* O(1) ··· N(2) and O(3) ··· N(2) $(1-x, 1-y, 1-z)$ are 3.040(18) and 3.008(17) Å, respectively.

Discussion

For all the compounds so far isolated the metal : ligand ratio is 2 : 1, and all attempts to obtain 1 : 1 complexes were unsuccessful. The molecular model study has revealed that (**B1**) and (**B2**) are much more favourable than (**C**) (Figure 1). In fact, no (**C**)-type complexes have been found thus far.

Copper(II) *Complexes*.—It is to be noted that the addition of a large excess of sodium perchlorate into the aqueous Cu$_2$(taec)Br$_4$ solution readily yields Cu$_2$(taec)Br(ClO$_4$)$_3$, but not Cu$_2$(taec)(ClO$_4$)$_4$, which can only be isolated by adding excess sodium perchlorate after removal of bromide ion by adding silver perchlorate. The visible spectra of the tetrabromide and bromide triperchlorate complexes closely resemble each other in Nujol mull and are practically the same in aqueous solution, whereas the *d–d* band of the tetraperchlorate is substantially shifted to a higher frequency relative to those of the bromide-containing complexes in both aqueous solution and Nujol mull (Table 4). The aqueous solution spectrum of the tetrabromide complex obeys Beer's law in the concentration range examined (2×10^{-3} to 1×10^{-4} mol dm^{-3}). All the above facts suggest an unusually high stability for the Cu–Br

Table 4. Electronic spectroscopic and magnetic data

Complex	$10^{-3}\ \tilde{\nu}_{max.}$/cm^{-1} ($\varepsilon$/dm^3 mol^{-1} cm^{-1})	μ_B/Metal atom [a]	θ/K [a]
Cu$_2$(taec)Br$_4$	[b] 16.3 (235) [c] 16.2	1.82	−20
Cu$_2$(taec)Br(ClO$_4$)$_3$	[b] 16.3 (235) [c] 16.3	1.98	−24
Cu$_2$(taec)(ClO$_4$)$_4$	[b] 17.7 (165) [c] 19.2	1.81	−20
Ni$_2$(taec)(ClO$_4$)$_4$	[b] 22.2 (55), 25.8 (sh) [c] 22.1	diamagnetic	
Ni$_2$(taec)Br$_4$	[b] 16.4 (13), 22.5 (22), 25.8 (34) [c] 22.3	diamagnetic	
Ni$_2$(taec)Cl$_4$·H$_2$O	[b] 16.4 (14), 22.5 (27), 25.6 (37) [c] 15.8, 21.9, 25.1	2.35	−24
Co$_2$(taec)Cl$_2$(BPh$_4$)$_2$	[d] 12.4 (8), 17.3 (48), 19.6 (39) [c] 11.6, 17.1, 19.6	4.51	−25
Co$_2$(taec)(OH)(ClO$_4$)$_3$	[d] 12.5 (9), 17.8 (50), 20.0 (40) [c] 12.9, 17.8, 20.1	4.17	
Co$_2$(taec)(OH)(PF$_6$)$_3$	[d] 12.5 (8), 17.9 (51), 20.1 (41) [c] 13.2, 17.9, 20.2	4.04	

[a] For all the complexes $N\alpha = 0$ was assumed. [b] H$_2$O solution. [c] Nujol mull. [d] dmf solution.

bond in aqueous solution, in spite of the generally accepted view that the Cu^{II}–Br bond is readily hydrolysed in aqueous solution.[15] These facts are due to thermodynamic stability, and not kinetic, because the aqueous solution of the tetraperchlorate complex and potassium bromide in 1:1 mole ratio gave the same spectrum as that of the bromide triperchlorate complex of the same concentration. Thus, in order to explain the unusual behaviour we proposed a structure in which the bromide ion is bound by both copper ions.[7] In fact the present *X*-ray analysis has shown that the structure is consistent with our assumption as described in the Results section of this paper. It is also interesting to note that this compound adopts the (**B2**) structure, in contrast with the (**B1**) structure of the tetraperchlorate complex (Figure 1).

Magnetic moments of the copper complexes are all slightly higher than the spin-only value (Table 4) as in other copper(II) complexes. Cryomagnetic measurements down to liquid nitrogen temperature revealed that the magnetic susceptibilities obey the Curie-Weiss law with negative Weiss constants (Table 4), suggesting weak antiferromagnetic interaction between the copper(II) ions.

Electron spin resonance spectra of the tetrabromide and bromide triperchlorate complexes were measured in frozen solution at liquid nitrogen temperature. In acetonitrile the tetraperchlorate complex showed a symmetrical signal at g = 2.08 with no hyperfine splitting. In contrast to this, in dimethylformamide (dmf) solution several hyperfine lines were observed as shown in Figure 4. The existence of more than four hyperfine lines is an indication of the coupling of unpaired electrons between the two copper ions in a molecule. In the spectra of $Cu_2(taec)Br(ClO_4)_3$ and $Cu_2(taec)Br_4$ in dmf and methanol a weak signal was observed at g = 4.07 and 4.02, respectively. This is also evidence for the spin coupling between the two copper ions. In the case of the tetraperchlorate complex, however, no signal was detected around g = 4, though the binuclear structure is evident from the crystal structure and the hyperfine splitting.

Nickel(II) *Complexes*.—The yellow nickel(II) complexes, $Ni_2(taec)(ClO_4)_4$ and $Ni_2(taec)Br_4$, are diamagnetic and their Nujol mull spectra are typical of N_4-donor square-planar nickel(II) complexes, *i.e.* showing a band at *ca.* 22 × 10^3 cm^{-1} with no absorption in the near-i.r. region. All these facts are consistent with the structure revealed by *X*-ray analysis.

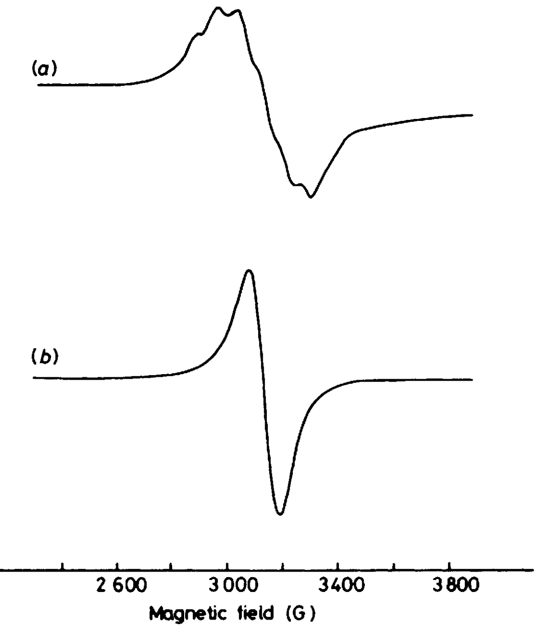


Figure 4. E.s.r. spectra of copper(II) complexes: (*a*) $Cu_2(taec)Br(ClO_4)_3$ (frozen dmf solution) and (*b*) $Cu_2(taec)(ClO_4)_4$ (frozen MeCN solution)

In contrast to this, $Ni_2(taec)Cl_4{\cdot}H_2O$ is green and paramagnetic. The Nujol mull spectrum showed bands at 16 × 10^3 cm^{-1} in addition to the 22 × 10^3 cm^{-1} band, suggesting the presence of both square-planar and six- or five-co-ordinate species in the solid state. The magnetic moment at room temperature is 2.35 μ_B per atom and obeys the Curie-Weiss law in the range 300—80 K with $\theta = -24$ K. These facts suggest a binuclear structure in which one of the nickel ions is square planar and diamagnetic, and the other is six- or five-co-ordinate and paramagnetic (S = 1).

The aqueous solutions of the yellow complexes display a strange behaviour. As shown in Figure 5, a 0.01 mol dm^{-3} solution shows a spectrum similar to that of the Nujol mull, and no appreciable change was detected after the solution was allowed to stand several days at room temperature. However, more dilute solutions (<2 × 10^{-3} mol dm^{-3}) showed complicated spectra which changed with time. As an example, the spectral change of a 1.5 × 10^{-3} mol dm^{-3} solution of $Ni_2(taec)(ClO_4)_4$ is shown in Figure 5.

These facts appear to imply that the square-planar complex gradually changes into a six- or five-co-ordinate species. However, the process does not seem simple, since the absorption at 26 × 10^3 cm^{-1} first increased and then later decreased. Therefore, at least one intermediate species appeared before reaching the final state. The spectral change with time was studied under various conditions, and it was found that the rate and mechanism of the reaction are highly dependent on the concentration and pH of the solution. The reaction is so complicated that we have not yet reached a conclusion for the mechanism. Detailed analysis of the reaction will be an interesting subject for successive investigations.

Cobalt(II) *Complexes*.—The magnetic moment of $Co_2(taec)Cl_2(BPh_4)_2$ is 4.51 μ_B per atom at room temperature. It obeys the Curie-Weiss law in the range 300—88 K with θ = −25 K, indicating that the cobalt(II) is in the high-spin state with a very weak antiferromagnetic interaction. The magnetic moments of $Co_2(taec)(OH)(ClO_4)_3$ and $Co_2(taec)(OH)(PF_6)_3$

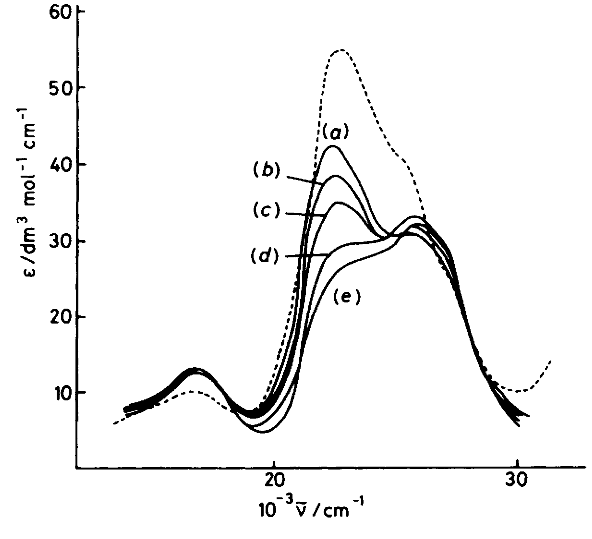


Figure 5. Time dependence of the spectrum of $Ni_2(taec)(ClO_4)_4$ (1.5 × 10^{-3} mol dm^{-3}): after (*a*) 12, (*b*) 30, (*c*) 60, (*d*) 170, and (*e*) 470 min. (- - - -) Spectrum of 1.0 × 10^{-2} mol dm^{-3} $Ni_2(taec)(ClO_4)_4$

are 4.17 and 4.04 μ_B per atom respectively which are slightly lower than the lowest limit for high-spin cobalt(II) complexes. They obey the Curie-Weiss law in the range 300—150 K with $\theta = -150$ K and -130 K, respectively, indicating the presence of substantial antiferromagnetic interactions. Thus, in these complexes, the cobalt ions are likely to be bridged by the hydroxide ion.

The OH stretching vibration can be observed at 3 550 cm^{-1} for the perchlorate complex, and at 3 610 and 3 705 cm^{-1} as sharp bands for the hexafluorophosphate complex. The presence of two OH bands for the latter complex may be attributed to the two different OH sites in the crystal probably caused by the perturbation of the PF_6^- ions.

In spite of the considerable difference in magnetic behaviour between the chloro and hydroxo complexes, all the cobalt complexes showed similar spectra in the visible region in Nujol mull and in dmf solution with peaks at 12.5×10^3, 17.5×10^3, and 20.0×10^3 cm^{-1} compatible with the five-co-ordinate structure.

Attempts to obtain cobalt(III) complexes with taec were all unsuccessful. This must be due to the fact that the cobalt ions are incorporated into the ligand so that six-co-ordination is sterically difficult. As a consequence, cobalt(II) taec complexes are very stable towards oxidizing agents.

It should be noted that there is a remarkable difference in the co-ordination mode between *N,N′,N″,N‴*-tetrakis(3-aminopropyl)-1,4,8,11-tetra-azacyclotetradecane and taec. The former only afforded mononuclear complexes in which the metal ion was incorporated into the centre of the macrocyclic ring, whereas the latter exclusively formed binuclear chelates outside of the ring. This difference cannot be due to the steric hindrance by the pendant aminoalkyl groups, because the environment of the macrocyclic ring is more crowded in the former. The reason is not clear at present.

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