

Copper(II) and Nickel(II) Complexes of *N,N',N'',N'''*-Tetrakis(2-aminoethyl)-1,4,7,11-tetra-azacyclotetradecane (taei), -1,4,8,12-tetra-azacyclopentadecane (taep), and -1,5,9,13-tetra-azacyclohexadecane (taeh). Crystal Structures of $[\text{Cu}_2(\text{taep})][\text{ClO}_4]_4$, $[\text{Cu}_2(\text{taeh})][\text{ClO}_4]_4$, and $[\text{Cu}_2(\text{N}_3)(\text{taeh})][\text{ClO}_4]_3$ †

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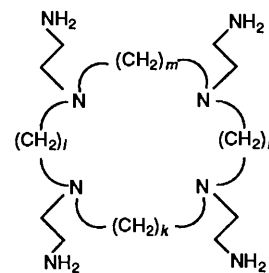
New octaamine dinucleating ligands, *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,7,11-tetra-azacyclopentadecane (taei), -1,4,8,12-tetra-azacyclopentadecane (taep), and -1,5,9,13-tetra-azacyclohexadecane (taeh) and their complexes with Cu^{II} and Ni^{II} were synthesized. Of the 19 complexes isolated, the structures of $[\text{Cu}_2(\text{taep})][\text{ClO}_4]_4$, $[\text{Cu}_2(\text{taeh})][\text{ClO}_4]_4$, and $[\text{Cu}_2(\text{N}_3)(\text{taeh})][\text{ClO}_4]_3$ were determined by X-ray crystal analysis. In all these complexes each copper is co-ordinated by two ring nitrogens and two pendant amino nitrogens, and the two CuN_4 co-ordination sets face each other. In the azido complex the N_3^- is bonded to both coppers in an end-to-end fashion. The dinuclear complexes $[\text{Cu}_2\text{L}][\text{ClO}_4]_4$ (L = taei or taep) further incorporate various anions between the two coppers to form $[\text{Cu}_2\text{X(L)}][\text{ClO}_4]_3$. However, only the azido complex was obtained with taeh. The results are discussed in terms of the ring-size effect.

Murase and co-workers¹ reported the synthesis and characterization of a number of $3d$ -metal complexes of *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane (taec) which exhibit interesting structures and chemical properties. The most prominent features are (1) non-incorporation of metal ions into the macrocyclic ring and facile formation of dinuclear complexes, and (2) strong affinities toward various anions, forming anion-bridged complexes.

In order to see how the characteristic properties of taec complexes depend on the ring size of the macrocycle, in this study we have synthesized three analogous octaamine ligands, *i.e.* *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,7,11-tetra-azacyclopentadecane, *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,12-tetra-azacyclopentadecane, and *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,5,9,13-tetra-azacyclohexadecane (taei, taep, and taeh, respectively). These ligands formed metal complexes principally similar to those of taec. However, substantial variations were observed in the co-ordination modes and the ability to bind anions. The results are discussed in terms of the binding abilities for anions.

Experimental

taei·7HBr·2H₂O.—1,4,7,11-Tetra-azacyclotetradecane (= isocyclam)² (10.8 g, 54 mmol) was dissolved in acetonitrile (500 cm³). To this solution was added with stirring under reflux an acetonitrile solution (400 cm³) of *N*-tosylaziridine (43 g, 220 mmol) in 4 h. The mixture was further refluxed for 4 h, and filtered to remove a small amount of insoluble material. The filtrate was evaporated to dryness under reduced pressure to obtain crude *N,N',N'',N'''*-tetrakis(2-*N*-tosylaminoethyl)-1,4,7,11-tetra-azacyclotetradecane as a pale brown oily residue (50 g). The product was refluxed with 47% hydrobromic acid-acetic acid (1:1, 800 cm³) for 70 h. The reaction mixture was evaporated almost to dryness in a rotary evaporator. The



k	l	m	n	
3	2	3	2	taec
3	3	2	2	taei
3	3	3	2	taep
3	3	3	3	taeh

residue was dissolved in water (500 cm³), treated with charcoal, and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was treated repeatedly with hot methanol and dried in a vacuum desiccator; yield 40 g (78%). The sample was purified by dissolving in the minimum amount of water followed by the addition of methanol, yielding colourless crystals (Found: C, 22.15; H, 5.50; N, 11.05. C₁₈H₄₄N₈·7HBr·2H₂O requires C, 22.15; H, 5.70; N, 11.50%).

The free amine was obtained as a sticky oil by passing the hydrobromide solution through an ion-exchange resin (Dowex 1 × 8, OH form) and evaporating the eluate to dryness under reduced pressure.

The hydrochloride was obtained from the free amine as a

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

colourless crystalline powder (Found: C, 31.35; H, 7.55; N, 16.35. $C_{18}H_{44}N_8 \cdot 8HCl \cdot H_2O$ requires C, 31.70; H, 8.00; N, 16.45%).

$[Cu_2(taei)][ClO_4]_4 \cdot H_2O$.—Free taei (370 mg, 1 mmol) was dissolved in water (20 cm³). To this solution was added copper(II) perchlorate hexahydrate (700 mg, 2 mmol) dissolved in the minimum amount of water and the mixture was heated on a water-bath for 20 min. After standing overnight at room temperature the deep blue solution was filtered. The filtrate was concentrated to 20 cm³ on a water-bath. Addition of sodium perchlorate and methanol resulted in the separation of blue-violet crystals, which were dissolved in hot water (5 cm³) and filtered while hot. A dark violet crystalline powder was obtained when methanol (20 cm³) was added to the hot filtrate. The recrystallization was repeated to obtain pure crystals; yield 632 mg (47%) (Found: C, 23.75; H, 5.10; Cu, 13.35; N, 12.45. $C_{18}H_{46}Cl_4Cu_2N_8O_{17}$ requires C, 23.60; H, 5.05; Cu, 13.90; N, 12.25%).

$[Cu_2Cl(taei)][ClO_4]_3$.—To an aqueous solution of $[Cu_2(taei)][ClO_4]_4 \cdot H_2O$ was added an excess of lithium chloride (*ca.* twice the stoichiometric amount). The mixture was heated for 30 min, and filtered. The filtrate was evaporated on a water-bath to obtain a dark blue oily product, to which methanol was added and heated for several minutes. A blue crystalline powder was obtained. Recrystallization from water-methanol solution gave pure fine blue crystals (Found: C, 25.95; H, 5.85; Cu, 14.80; N, 13.40. $C_{18}H_{44}Cl_4Cu_2N_8O_{12}$ requires C, 25.95; H, 5.30; Cu, 15.25; N, 13.45).

The compounds $[Cu_2Br(taei)][ClO_4]_3 \cdot H_2O$, $[Cu_2(NO_2)(taei)][ClO_4]_3$, and $[Cu_2(N_3)(taei)][ClO_4]_3$ were obtained by similar methods using NaBr, NaNO₂, or NaN₃ instead of LiCl (Found: C, 24.10; H, 5.10; Cu, 15.15; N, 12.60. $C_{18}H_{46}BrCl_3Cu_2N_8O_{13}$ requires C, 24.15; H, 5.15; Cu, 14.20; N, 12.50. Found: C, 26.45; H, 5.65; Cu, 14.85; N, 15.90. $C_{18}H_{44}Cl_3Cu_2N_9O_{14}$ requires C, 25.60; H, 5.25; Cu, 15.05; N, 14.95. Found: C, 25.75; H, 5.45; Cu, 14.80; N, 18.10. $C_{18}H_{46}Cl_3Cu_2N_{11}O_{12}$ requires C, 25.65; H, 5.50; Cu, 15.10; N, 18.30%).

$[Ni_2(taei)][ClO_4]_4$.—To an acetonitrile solution (3 cm³) of nickel(II) perchlorate hexahydrate (800 mg, 2.2 mmol) was added dropwise a methanol solution (3 cm³) of taei (370 mmol, 1 mmol) with stirring. The mixture was heated with stirring to dissolve a white amorphous precipitate, and filtered. The filtrate was evaporated to *ca.* 2 cm³. The orange crystals formed were collected by filtration, washed with a small amount of methanol, and dried in a vacuum desiccator. Yield 130 mg (15%) (Found: C, 24.05; H, 5.10; N, 12.40; Ni, 12.40. $C_{18}H_{44}Cl_4N_8Ni_2O_{16}$ requires C, 24.35; H, 5.00; N, 12.40; Ni, 13.20%).

taep·8HBr.—1,4,8,12-Tetra-azacyclopentadecane³ (12 g, 50 mmol) was dissolved in hot acetonitrile (500 cm³). To this solution was added dropwise an acetonitrile solution (350 cm³) of *N*-tosylaziridine (50 g, 250 mmol) with stirring under reflux in 3 h. The mixture was refluxed overnight and filtered to remove insoluble material. The pale yellow filtrate was concentrated to 70 cm³ under reduced pressure. To this solution was added hot methanol (300 cm³). The resulting precipitate was removed by filtration, and the filtrate was evaporated by a rotary evaporator to give crude *N,N',N'',N'''*-(2-*N*-tosylaminoethyl)-1,4,8,12-tetra-azacyclopentadecane as a yellowish brown sticky mass (55 g), which was refluxed for 70 h with hydrobromic acid (47%) acetic acid (1:1). The reaction mixture was evaporated almost to dryness in a rotary evaporator. The residue was dissolved in hot water, treated with active charcoal, and filtered. The pale yellow filtrate was concentrated almost to dryness, and the residue was treated with hot methanol to obtain a pale yellow

crystalline powder. Yield 60 g. This was used for the preparation of the free amine without further purification.

To obtain a pure sample for elemental analysis a small portion of the crude product was dissolved in the minimum amount of dilute hydrobromic acid, and an equal volume of acetic acid was added. The resulting crystalline solid was collected, treated with methanol, and dried in a vacuum desiccator over P₂O₅. The product was a very hygroscopic pale yellow crystalline powder (Found: C, 22.05; H, 5.35; N, 10.25. $C_{19}H_{54}Br_8N_8$ requires C, 22.05; H, 5.25; N, 10.85%).

Free taep was obtained by passing the hydrobromide through anion-exchange resin (Dowex 1 × 8, OH form) and evaporating the eluate to dryness under vacuum.

$[Cu_2(taep)][ClO_4]_4$.—Free taep (0.4 g, 1 mmol) was dissolved in hot water (10 cm³). To this solution was added an aqueous solution of copper(II) perchlorate hexahydrate (1 g, 2.6 mmol), and the mixture was heated on a water-bath for 10 min. After adding an excess of sodium perchlorate, the mixture was cooled to room temperature. Deep violet crystals yielded were collected by filtration and recrystallized from water. Yield 0.3 g (37%) (Found: C, 24.85; H, 5.00; Cu, 14.05; N, 12.25. $C_{19}H_{46}Cl_4Cu_2N_8O_{16}$ requires C, 25.05; H, 5.10; Cu, 13.95; N, 12.30%).

$[Cu_2Br(taep)][ClO_4]_3$.—To an aqueous solution of $[Cu_2(taep)][ClO_4]_4$ was added about twice the stoichiometric amount of sodium bromide. The mixture was heated on a water-bath for 10 min and filtered. The filtrate was concentrated on a water-bath until crystals began to deposit and then allowed to cool to room temperature. The deep blue crystals were collected by filtration, washed with methanol, and dried over P₂O₅ in a vacuum desiccator (Found: C, 25.50; H, 5.25; Cu, 14.45; N, 12.50. $C_{19}H_{46}BrCl_3Cu_2N_8O_{12}$ requires C, 25.60; H, 5.20; Cu, 14.25; N, 12.60%).

$[Cu_2Cl_2(taep)][ClO_4]_2$.—To an aqueous solution (5 cm³) of $[Cu_2(taep)][ClO_4]_4$ (200 mg, 0.22 mmol) was added sodium chloride (130 mg, 2.2 mmol). The mixture was heated for 30 min. Ethanol (15 cm³) was added and a blue crystalline powder was deposited upon cooling. The product was collected by filtration, washed with methanol, and dried in a vacuum desiccator. Yield: 86 mg (46%) (Found: C, 29.65; H, 6.30; Cu, 15.70; N, 14.15. $C_{19}H_{46}Cl_4Cu_2N_8O_8$ requires C, 29.15; H, 5.90; Cu, 16.20; N, 14.30%).

$[Cu_2(N_3)(taep)][ClO_4]_3$.—Fine crystals of $[Cu_2(taep)][ClO_4]_4$ (0.2 g, 2.2 mmol) were suspended in water (2 cm³) and an aqueous solution of sodium azide (30 mg, 4.6 mmol) was added. The mixture was treated in a similar way to that of the bromo complex described above. The deep blue crystals thus obtained were hydrolyzed when heated in a dilute aqueous solution (Found: C, 26.60; H, 5.45; Cu, 14.85; N, 18.30. $C_{19}H_{46}Cl_3Cu_2N_{11}O_{12}$ requires C, 26.70; H, 5.45; Cu, 14.90; N, 18.05%).

$[Ni_2(taep)][ClO_4]_4 \cdot H_2O$.—Crude free taep (0.3 g, 0.7 mmol) and nickel(II) perchlorate hexahydrate (1 g, 2.7 mmol) were mixed in water (30 cm³). The mixture was heated on a water-bath and filtered to remove insoluble material. The filtrate was evaporated to half volume on a water-bath, and an excess of sodium perchlorate was added. The solution was allowed to stand at room temperature. The yellow crystals deposited were collected by filtration, washed with methanol, and dried over P₂O₅ in a vacuum desiccator. Yield 0.2 g (31%) (Found: C, 24.65; H, 5.05; N, 12.20; Ni, 12.55. $C_{19}H_{48}Cl_4N_8Ni_2O_{17}$ requires C, 24.80; H, 5.25; N, 12.20; Ni, 12.75%).

N,N',N'',N'''-Tetrakis(2-*N*-tosylaminoethyl)-1,5,9,13-tetra-azacyclohexadecane.—To a refluxing acetonitrile solution (360

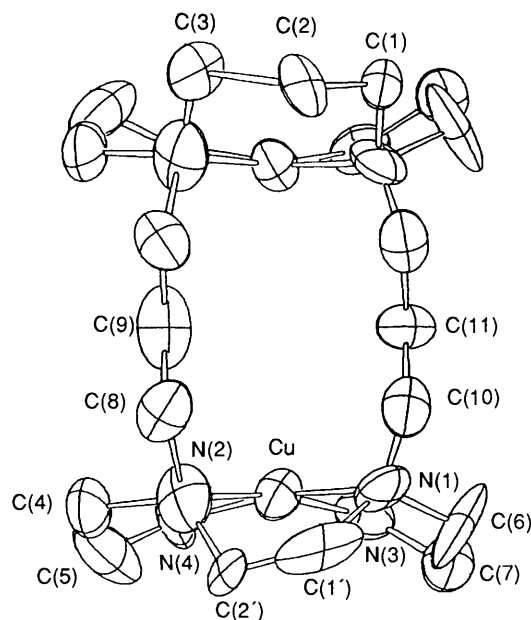


Figure 1. ORTEP representation of the complex cation in $[\text{Cu}_2(\text{taep})][\text{ClO}_4]_4$

cm^3) of 1,5,9,13-tetra-azacyclohexadecane⁴ (4.6 g, 20 mmol) was added dropwise an acetonitrile solution (200 cm^3) of *N*-tosylaziridine (14.5 g, 80 mmol) during 2 h. The mixture was further refluxed for 2 h and filtered. The filtrate was evaporated to dryness by a rotary evaporator. The pale yellow residue was treated with hot ethanol (300 cm^3) and allowed to stand at room temperature. The crystalline product precipitated was collected by filtration. The crude yield was almost quantitative (20 g), and the product was used for the syntheses of metal complexes without further purification. To obtain a pure sample the crude product was recrystallized from a large amount of ethanol. The crystals sintered at *ca.* 110 °C and melted 114–115 °C (Found: C, 56.25; H, 7.00; N, 10.75. $\text{C}_{48}\text{H}_{72}\text{N}_8\text{O}_8\text{S}_4$ requires C, 56.65; H, 7.15; N, 11.00%).

taeh·8HBr.—The crude *N*-tosylate obtained by the above procedure was dissolved in hydrobromic acid (47%, 300 cm^3)–acetic acid (300 cm^3) and refluxed for 70 h. The solution was concentrated nearly to dryness in a rotary evaporator. When the residue was treated with a large amount of hot ethanol a crystalline product was obtained. The crude yield was almost quantitative. Pure crystals were obtained by recrystallization from dilute ethanol; m.p. 276 °C (decomp.) (Found: C, 23.20; H, 5.35; N, 10.90. $\text{C}_{20}\text{H}_{56}\text{Br}_8\text{N}_8$ requires C, 22.90; H, 5.40; N, 10.70%).

Free taeh was obtained from the hydrobromide as a sticky solid by a similar method to those for taei and taep.

$[\text{Cu}_2(\text{taeh})][\text{ClO}_4]_4$.—To an aqueous solution (10 cm^3) of taeh (430 mg, 1 mmol) was added copper(II) perchlorate hexahydrate (1.4 g, 3.8 mmol) dissolved in the minimum amount of water. The mixture was heated in a water-bath for 10 min, and then allowed to stand overnight at room temperature. The resulting deep purple crystals were recrystallized from hot water. Yield 70% (Found: C, 25.60; H, 5.25; Cu, 13.50; N, 12.05. $\text{C}_{20}\text{H}_{48}\text{Cl}_4\text{Cu}_2\text{N}_8\text{O}_{16}$ requires C, 25.95; H, 5.25; Cu, 13.75; N, 12.10%).

The complexes $[\text{Cu}_2(\text{taeh})][\text{BF}_4]_4$ and $[\text{Cu}_2(\text{taeh})][\text{NO}_3]_4$ were obtained by similar methods to that for the perchlorate described above using copper(II) tetrafluoroborate hexahydrate or nitrate trihydrate instead of the perchlorate (Found: C, 27.35;

H, 5.65; Cu, 14.30; N, 12.70. $\text{C}_{20}\text{H}_{48}\text{B}_4\text{Cu}_2\text{F}_{16}\text{N}_8$ requires C, 27.45; H, 5.55; Cu, 14.55; N, 12.80. Found: C, 30.70; H, 6.25; Cu, 16.05; N, 21.55. $\text{C}_{20}\text{H}_{48}\text{Cu}_2\text{N}_{12}\text{O}_{12}$ requires C, 30.95; H, 6.25; Cu, 16.40; N, 21.65%).

$[\text{Cu}_2(\text{N}_3)(\text{taeh})][\text{ClO}_4]_3$.—This compound was obtained in a similar procedure to that for the corresponding taep complex using $[\text{Cu}_2(\text{taeh})][\text{ClO}_4]_4$ instead of $[\text{Cu}_2(\text{taep})][\text{ClO}_4]_4$ (Found: C, 27.75; H, 5.65; Cu, 14.70; N, 18.15. $\text{C}_{20}\text{H}_{48}\text{Cl}_3\text{Cu}_2\text{N}_{11}\text{O}_{12}$ requires C, 27.65; H, 5.55; Cu, 14.65; N, 17.75%).

$[\text{Ni}_2(\text{taeh})][\text{ClO}_4]_4$.—Nickel perchlorate hexahydrate (0.18 g, 0.5 mmol) and taeh (0.1 g, 0.25 mmol) were mixed in water (20 cm^3), and heated on a water-bath for 10 min. The resulting orange-yellow solution was filtered, and the filtrate allowed to stand overnight at room temperature. The yellowish orange crystals were collected, washed with methanol and dried in a vacuum desiccator (Found: C, 26.00; H, 5.40; N, 12.15; Ni, 12.55. $\text{C}_{20}\text{H}_{48}\text{Cl}_4\text{N}_8\text{Ni}_2\text{O}_{16}$ requires C, 26.25; H, 5.30; N, 12.25; Ni, 12.80%).

The compounds $[\text{Ni}_2(\text{taeh})][\text{NO}_3]_4\cdot\text{H}_2\text{O}$, $[\text{Ni}_2(\text{taeh})]\text{Cl}_4\cdot\text{H}_2\text{O}$, and $[\text{Ni}_2(\text{taeh})]\text{Br}_4\cdot 2\text{H}_2\text{O}$ were obtained in similar procedures to that for the perchlorate described above using nickel(II) nitrate, chloride, or bromide instead of perchlorate (Found: C, 30.65; H, 6.45; N, 21.45; Ni, 15.00. $\text{C}_{20}\text{H}_{50}\text{N}_{12}\text{Ni}_2\text{O}_{13}$ requires C, 30.65; H, 6.45; N, 21.45; Ni, 14.95. Found: C, 35.20; H, 7.30; N, 16.15; Ni, 17.45. $\text{C}_{20}\text{H}_{50}\text{Cl}_4\text{N}_8\text{Ni}_2\text{O}$ requires C, 35.45; H, 7.45; N, 16.55; Ni, 17.30. Found: C, 27.05; H, 5.90; N, 12.30; Ni, 13.85. $\text{C}_{20}\text{H}_{52}\text{Br}_4\text{N}_8\text{Ni}_2\text{O}_2$ requires C, 27.50; H, 6.00; N, 12.85; Ni, 13.45%).

Structure Determinations.—Three dimensional *X*-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $\text{Cu-K}\alpha$ radiation using an ω – 2θ scan mode. The calculation was carried out using the Enraf-Nonius structure determining package.⁵ The structures were solved by direct methods in the case of $[\text{Cu}_2(\text{N}_3)(\text{taeh})][\text{ClO}_4]_3$ and the heavy-atom method in the other cases, and Fourier difference syntheses. The positional and thermal parameters of all non-hydrogen atoms were determined and refined by successive block-diagonal least-squares and Fourier methods. Hydrogen-atom positions were calculated but not included in the refinement. The atomic scattering factors for all atoms and the anomalous dispersion corrections for non-hydrogen atoms were taken from ref. 6.

Details of the crystal data, intensity measurements, and refinements are given in Table 1, final atomic fractional coordinates in Table 2, and selected bond distances and angles in Table 3.

In the case of $[\text{Cu}_2(\text{taep})][\text{ClO}_4]_4$, only the space group $P\bar{6}c2$ is compatible with the observed diffraction data; all efforts to interpret the data in terms of alternative space groups such as $P3c1$, *etc.*, which appeared to be compatible with the molecular structure of this compound, were in vain. This result can be interpreted in terms of disorder of the complex cation between two positions so that the average molecular structure has a mirror plane. Many cases like the present one in which the molecule does not have the symmetry required by the crystallographic symmetry have been reported.⁷

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results

Description of Structures.— $[\text{Cu}_2(\text{taep})][\text{ClO}_4]_4$. The crystal consists of dinuclear cations $[\text{Cu}_2(\text{taep})]^{4+}$ and perchlorate ions. A perspective view of the complex cation is shown in

Table 1. Crystal data and data collection details

Compound	[Cu ₂ (taep)][ClO ₄] ₄	[Cu ₂ (taeh)][ClO ₄] ₄	[Cu ₂ (N ₃)(taeh)][ClO ₄] ₃
<i>M</i>	911.55	925.58	868.11
Crystal system	Hexagonal	Hexagonal	Monoclinic
Space group	<i>P</i> 6̄ <i>c</i> 2	<i>P</i> 6̄ <i>c</i> 2	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> /Å	16.022(9)	16.042(3)	25.909(2)
<i>b</i> /Å			14.093(1)
<i>c</i> /Å	24.400(11)	24.591(3)	9.418(2)
β/°			94.28(2)
<i>U</i> /Å ³	5 424(5)	5 480(2)	3 429(2)
<i>Z</i>	6	6	4
<i>D_c</i> /g cm ⁻³	1.674	1.682	1.699
μ(Cu- <i>K</i> _α)/cm ⁻¹	48.93	48.51	43.42
Crystal dimensions	<i>r</i> = 0.143 ^a	<i>r</i> = 0.158 ^a	0.3 × 0.2 × 0.1 ^b
2θ range/°	0–120	0–120	0–120
Total no. of observed reflections	8 579	3 128	5 708
No. of unique reflections [<i>I</i> > 2.33σ(<i>I</i>)]	1 439	1 288	4 089
Variables	474	456	734
<i>R</i>	0.079	0.058	0.039
<i>R'</i>	0.089	0.066	<i>c</i>

^a The crystal was ground to a sphere of diameter *r*. ^b The absorption correction was made by the PSJ scan method (A. C. T. North, D. C. Phillip, and P. S. Mathews, *Acta Crystallogr., Sect. A.*, 1968, **24**, 351). ^c Unit weight.

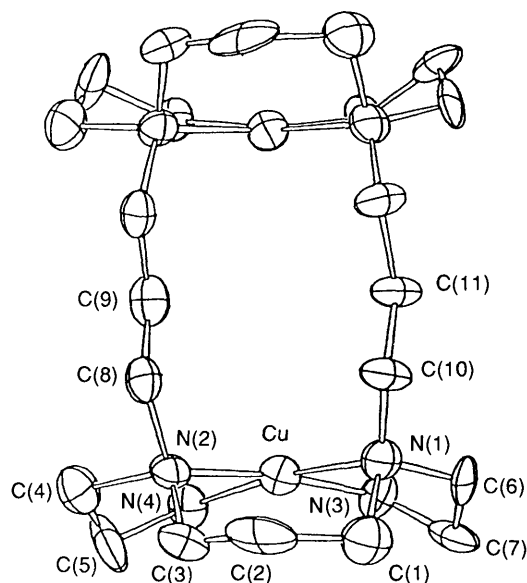
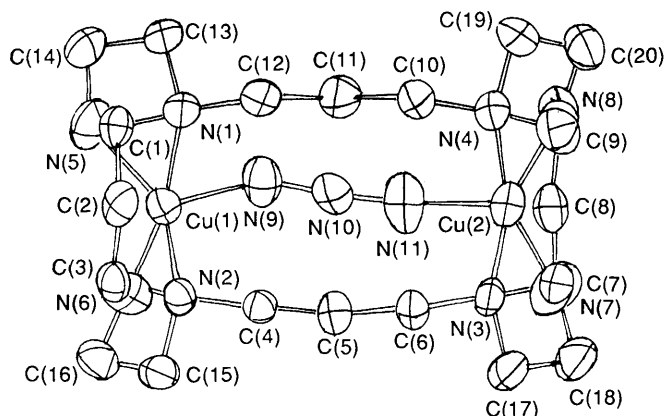
**Figure 2.** ORTEP representation of the complex cation in [Cu₂(taeh)]⁴⁺.**Figure 3.** ORTEP representation of the complex cation in [Cu₂(N₃)(taeh)]⁴⁺.

Figure 1. The ethylene group [C(1'), C(2')] and trimethylene group [C(1), C(2), C(3)] are located in an unsymmetrical arrangement as shown in Figure 1 with a half-occupancy. Thus, the average structure possesses a mirror plane containing C(9) and C(11), as required from the crystallographic symmetry. Each copper is co-ordinated with two ring nitrogens and two amino nitrogens of pendant groups. Their co-ordination geometry is nearly square planar. The largest deviation from the best plane formed by N(1), N(2), N(3), and N(4) is 0.011 Å. The copper atom is displaced from the plane by 0.178 Å towards the centre of the complex cation. All the perchlorate ions are separated from the copper ions by more than the van der Waals contact. The distance between two copper ions is 5.048(2) Å, shorter than that [5.479(1) Å] of [Cu₂(taec)(ClO₄)₂][ClO₄]₂.^{1b}

[Cu₂(taeh)][ClO₄]₄. This crystal is isomorphous to that of [Cu₂(taep)][ClO₄]₄. It consists of the complex cation [Cu₂(taeh)]⁴⁺ and perchlorate ions. A perspective view of the complex cation is shown in Figure 2. It has a mirror plane containing C(9) and C(11) as required from the crystallographic symmetry. The co-ordination geometry is nearly square planar. The largest deviation of nitrogen atoms from the best plane formed by the donor nitrogens is 0.014 Å. The copper atom is displaced by 0.126 Å from the plane towards the centre of the complex ion. The Cu...Cu distance is 5.160(2) Å, slightly longer than in the taep analogue, and substantially shorter than that of the taec analogue.

[Cu₂(N₃)(taeh)][ClO₄]₃. The crystal consists of discrete dinuclear complex cations and perchlorate ions. A perspective view of the complex cation is shown in Figure 3. The co-ordination geometry of the coppers can be described by a square pyramid, whose basal plane is formed by the two ring nitrogens and two pendant nitrogens. The azide ion is linear (the NNN angle is 178.55°), and co-ordinates to both copper ions at the apices of the square pyramid in an end-to-end fashion with CuNN angles of 132.0(3) and 138.9(4)°. In the co-ordination unit of Cu(2) the four nitrogens form an almost perfect plane, the maximum deviation being less than 0.004 Å. Atom Cu(2) is displaced from the plane by 0.320 Å towards the centre of the complex cation. In the co-ordination unit of Cu(1), however, a significant deviation from the mean N₄ plane was observed for the nitrogen atoms, the maximum being 0.184 Å. Atom Cu(1) is displaced from the basal plane by 0.358 Å towards the centre of the complex cation.

Table 2. Positional parameters and occupancy factors

Atom	X/a	Y/b	Z/c	AI	Atom	X/a	Y/b	Z/c	AI
[Cu ₂ (taep)][ClO ₄] ₄ (parameters × 10 ⁴)					(parameters × 10 ³)				
Cu	6 316(1)	-2(2)	1 474(1)	1.0	O(11)	523(1)	-7(2)	1/4	0.49
N(1)	7 715(9)	1 091(9)	1 452(5)	1.0	O(12)	420(1)	35(2)	295(1)	0.55
N(2)	6 724(10)	-1 033(8)	1 502(4)	1.0	O(13)	373(2)	-110(2)	1/4	0.17
N(3)	6 043(10)	1 066(7)	1 317(5)	1.0	O(14)	454(3)	100(2)	269(1)	0.28
N(4)	4 967(8)	-1 042(9)	1 341(4)	1.0	O(15)	503(9)	-35(9)	233(5)	0.07
C(1)	8 247(38)	965(25)	975(13)	0.5	O(16)	384(4)	-66(4)	204(2)	0.15
C(2)	8 193(19)	-130(27)	1 091(10)	0.5	O(17)	423(6)	30(5)	191(3)	0.10
C(3)	7 164(17)	-1 023(16)	1 053(10)	0.5	O(21)	605(1)	8(2)	27(0)	0.76
C(4)	5 837(14)	-1 911(12)	1 271(8)	1.0	O(22)	559(2)	-64(2)	-52(0)	0.41
C(5)	5 029(14)	-1 892(11)	1 036(6)	1.0	O(23)	715(1)	-3(2)	-31(1)	0.61
C(6)	7 651(16)	2 073(11)	1 401(6)	1.0	O(24)	645(2)	103(1)	-39(1)	0.55
C(7)	6 857(17)	1 848(14)	1 125(7)	1.0	O(25)	603(2)	12(3)	-72(1)	0.29
C(8)	7 056(10)	-1 250(9)	1 996(6)	1.0	O(26)	647(3)	48(3)	-23(2)	0.19
C(9)	6 391(13)	-1 334(14)	1/4	0.5	O(27)	628(2)	-31(2)	-23(1)	0.28
C(10)	8 306(9)	1 324(10)	1 985(5)	1.0	O(28)	532(3)	-103(3)	-54(1)	0.24
C(11)	7 837(15)	1 285(16)	1/4	0.5	O(29)	741(3)	46(3)	-23(1)	0.21
C(1')	8 224(17)	697(15)	1 006(9)	0.5	O(210)	607(3)	58(3)	-65(2)	0.21
C(2')	7 715(29)	-291(31)	1 147(11)	0.5	O(211)	720(3)	23(3)	-53(2)	0.18
Cl(1)	4 345(4)	-34(6)	1/4	0.5	O(212)	563(4)	-122(4)	-21(2)	0.18
Cl(2)	6 288(4)	37(6)	-271(1)	0.79	O(213)	625(4)	-11(6)	33(2)	0.17
Cl(3)	2/3	1/3	1/4	0.17	O(31)	618(2)	231(2)	241(3)	0.40
Cl(4)	0	0	1/4	0.16	O(32)	671(13)	313(9)	200(2)	0.20
Cl(5)	1/3	-1/3	1/4	0.16	O(33)	720(9)	394(9)	206(0)	0.08
					O(34)	668(0)	238(0)	238(4)	0.11
					O(41)	-86(2)	-92(3)	268(8)	0.43
					O(42)	-96(4)	-62(4)	1/4	0.09
					O(43)	0	0	183(2)	0.07
					O(44)	0	0	226(3)	0.05
					O(45)	-48(18)	138(19)	1/4	0.03
					O(46)	-55(5)	-68(6)	197(0)	0.16
					O(53)	390(3)	-263(3)	281(2)	0.26
					O(54)	283(3)	-354(4)	191(2)	0.23
					O(55)	241(3)	-336(3)	1/4	0.16
[Cu ₂ (taeh)][ClO ₄] ₄ (parameters × 10 ⁴)					(parameters × 10 ³)				
Cu	6 310(2)	-4(3)	1 451.2(0.3)	1.0	O(31)	628(1)	232(1)	238(1)	0.5
N(1)	7 690(7)	1 093(6)	1 471(3)	1.0	O(32)	2/3	1/3	291(3)	0.11
N(2)	6 639(8)	-1 118(7)	1 499(3)	1.0	O(41)	0	0	187(3)	0.06
N(3)	6 037(6)	1 068(7)	1 297(4)	1.0	O(42)	-84(3)	-84(3)	273(1)	0.40
N(4)	4 939(8)	-992(7)	1 332(4)	1.0	O(51)	341(3)	-397(3)	283(1)	0.25
C(1)	8 252(11)	929(10)	1 027(4)	1.0	O(52)	277(3)	-361(4)	198(2)	0.21
C(2)	8 269(14)	85(26)	1 042(4)	1.0	O(11')	448(3)	91(3)	268(1)	0.21
C(3)	7 230(10)	-955(10)	1 007(5)	1.0	O(14')	376(10)	-88(10)	214(5)	0.08
C(4)	5 741(10)	-1 972(8)	1 366(5)	1.0	O(12')	401(9)	-25(9)	209(5)	0.06
C(5)	4 988(9)	-1 816(10)	1 051(4)	1.0	O(21')	606(3)	21(4)	-73(2)	0.20
C(6)	7 735(11)	2 111(9)	1 391(5)	1.0	O(24')	690(8)	128(8)	-32(4)	0.09
C(7)	6 914(12)	1 891(9)	1 074(6)	1.0	O(22')	560(6)	-133(6)	-35(3)	0.12
C(8)	7 086(9)	-1 214(9)	1 989(4)	1.0	O(22'')	598(6)	-40(6)	-29(3)	0.14
C(9)	6 450(14)	-1 329(13)	1/4	0.5	O(31')	680(5)	246(5)	1/4	0.08
C(10)	8 272(8)	1 297(8)	2 007(4)	1.0	O(32')	685(6)	309(6)	191(2)	0.14
C(11)	7 757(14)	1 248(12)	1/4	0.5	O(41')	0	0	218(3)	0.07
Cl(1)	4 347(4)	5(8)	1/4	0.5	O(42')	-76(3)	-100(3)	1/4	0.16
Cl(2)	6 307(4)	23(7)	-252(1)	1.0	O(42'')	-78(8)	-62(8)	195(4)	0.10
Cl(3)	2/3	1/3	1/4	0.17	O(51')	241(6)	-336(6)	1/4	0.08
Cl(3')	2/3	1/3	156(11)	0.01					
Cl(4)	0	0	1/4	0.17					
Cl(5)	1/3	-1/3	1/4	0.17					
[Cu ₂ (N ₃)(taeh)][ClO ₄] ₃ (parameters × 10 ⁴)									
Cu(1)	7 449.1(0.2)	1 379.3(0.4)	1 620.8(0.6)	1.0	N(10)	8 288(2)	2 738(2)	625(4)	1.0
Cu(2)	9 441.0(0.2)	2 835.6(0.4)	2 099.3(0.7)	1.0	N(11)	8 726(2)	2 935(3)	637(5)	1.0
N(1)	7 457(1)	1 806(2)	3 745(4)	1.0	Cl(1)	8 778(0)	452(1)	7 618(1)	1.0
N(2)	7 831(1)	85(2)	2 060(4)	1.0	O[(1)Cl(1)]	8 812(2)	170(3)	6 191(4)	1.0
N(3)	9 640(1)	1 410(2)	2 458(4)	1.0	O[(2)Cl(1)]	8 899(1)	-297(3)	8 592(4)	1.0
N(4)	9 275(1)	3 101(3)	4 217(4)	1.0	O[(3)Cl(1)]	8 218(3)	610(8)	7 647(9)	0.5
N(5)	6 777(1)	2 161(3)	1 385(5)	1.0	O[(4)Cl(1)]	9 221(3)	1 128(5)	7 848(7)	0.7
N(6)	7 327(2)	845(3)	-342(4)	1.0	O[(5)Cl(1)]	8 385(3)	1 005(7)	7 944(10)	0.5
N(7)	9 827(2)	2 669(4)	299(5)	1.0	O[(6)Cl(1)]	8 902(7)	1 330(11)	8 069(18)	0.3
N(8)	9 484(2)	4 269(3)	1 989(5)	1.0	Cl(2)	10 859(0)	4 854(1)	1 697(1)	1.0

Table 2. (continued)

Atom	X/a	Y/b	Z/c	AI	Atom	X/a	Y/b	Z/c	AI
[Cu ₂ (N ₃)(taeh)][ClO ₄] ₃ (parameters × 10 ⁴)									
C(1)	7 171(2)	1 024(3)	4 433(5)	1.0	O[(1)Cl(2)]	10 440(2)	5 472(3)	1 399(5)	1.0
C(2)	7 428(2)	61(3)	4 457(5)	1.0	O[(2)Cl(2)]	11 248(3)	5 266(8)	2 536(10)	0.5
C(3)	7 484(2)	-412(3)	3 030(5)	1.0	O[(3)Cl(2)]	10 757(3)	4 220(6)	2 766(9)	0.5
C(4)	8 371(1)	54(3)	2 723(4)	1.0	O[(4)Cl(2)]	11 167(3)	4 714(6)	511(8)	0.6
C(5)	8 758(2)	638(3)	1 989(5)	1.0	O[(5)Cl(2)]	10 825(8)	4 183(13)	565(17)	0.3
C(6)	9 261(2)	697(3)	2 907(5)	1.0	O[(6)Cl(2)]	10 690(4)	3 941(8)	2 129(16)	0.4
C(7)	10 080(2)	1 467(3)	3 588(5)	1.0	O[(7)Cl(2)]	11 101(10)	5 645(20)	2 561(29)	0.2
C(8)	9 939(2)	1 829(4)	5 019(5)	1.0	O[(8)Cl(2)]	10 466(13)	4 658(34)	534(45)	0.2
C(9)	9 774(2)	2 863(3)	5 093(5)	1.0	O[(9)Cl(2)]	10 478(9)	4 713(20)	559(28)	0.1
C(10)	8 841(2)	2 626(3)	4 888(5)	1.0	Cl(3)	6 244(1)	2 097(1)	-2 653(1)	1.0
C(11)	8 329(2)	2 636(3)	4 006(5)	1.0	O[(1)Cl(3)]	6 197(3)	2 544(7)	-3 968(8)	0.5
C(12)	7 942(2)	2 003(3)	4 651(5)	1.0	O[(2)Cl(3)]	6 776(3)	2 473(5)	-2 430(9)	0.5
C(13)	7 135(2)	2 687(3)	3 701(6)	1.0	O[(3)Cl(3)]	6 408(2)	1 076(5)	-2 633(7)	0.5
C(14)	6 646(2)	2 574(3)	2 740(6)	1.0	O[(4)Cl(3)]	5 749(5)	2 096(8)	-1 956(13)	0.4
C(15)	7 818(2)	-448(3)	678(5)	1.0	O[(5)Cl(3)]	6 485(6)	2 573(10)	-1 551(15)	0.3
C(16)	7 348(2)	-188(3)	-277(5)	1.0	O[(6)Cl(3)]	5 989(10)	3 096(13)	-2 052(31)	0.2
C(17)	9 846(2)	1 064(4)	1 107(5)	1.0	O[(7)Cl(3)]	6 297(5)	1 256(9)	-1 948(14)	0.3
C(18)	10 145(2)	1 818(4)	410(6)	1.0	O[(8)Cl(3)]	6 079(3)	2 008(7)	-4 094(9)	0.4
C(19)	9 195(2)	4 142(2)	4 305(6)	1.0	O[(9)Cl(3)]	5 662(6)	1 847(12)	-2 409(19)	0.4
C(20)	9 551(2)	4 681(4)	3 416(7)	1.0	O[(10)Cl(3)]	6 046(5)	2 511(10)	-1 895(17)	0.1
N(9)	7 852(1)	2 552(3)	639(5)	1.0					

Table 3. Selected interatomic distances (Å) and angles (°)

[Cu ₂ (taep)][ClO ₄] ₄			
Cu...Cu	5.048(2)	Cu-N(3)	2.007(16)
Cu-N(1)	2.044(10)	Cu-N(4)	1.989(10)
Cu-N(2)	2.062(17)		
N(1)-Cu-N(2)	92.1(6)	N(2)-Cu-N(4)	88.9(6)
N(1)-Cu-N(3)	82.9(6)	N(3)-Cu-N(4)	94.3(6)
[Cu ₂ (taeh)][ClO ₄] ₄			
Cu...Cu	5.160(2)	Cu-N(3)	2.011(13)
Cu-N(1)	2.027(8)	Cu-N(4)	1.987(10)
Cu-N(2)	2.104(14)		
N(1)-Cu-N(2)	96.1(5)	N(2)-Cu-N(4)	88.8(5)
N(1)-Cu-N(3)	82.7(5)	N(3)-Cu-N(4)	91.5(5)
[Cu ₂ (N ₃)(taeh)][ClO ₄] ₃			
Cu(1)...Cu(2)	5.541(1)	Cu(1)-N(1)	2.088(4)
Cu(1)-N(2)	2.102(3)	Cu(1)-N(5)	2.059(4)
Cu(1)-N(6)	2.000(4)	Cu(1)-N(9)	2.195(4)
Cu(2)-N(3)	2.095(4)	Cu(2)-N(4)	2.105(4)
Cu(2)-N(7)	2.045(5)	Cu(2)-N(8)	2.026(4)
Cu(2)-N(11)	2.229(4)	N(9)-N(10)	1.161(5)
N(10)-N(11)	1.167(6)		
N(1)-Cu(1)-N(2)	95.2(1)	N(1)-Cu(1)-N(5)	84.1(2)
N(2)-Cu(1)-N(6)	83.9(2)	N(5)-Cu(1)-N(6)	91.6(2)
N(9)-Cu(1)-N(1)	102.5(1)	N(9)-Cu(1)-N(2)	120.3(1)
N(9)-Cu(1)-N(5)	88.7(2)	N(9)-Cu(1)-N(6)	86.7(2)
Cu(1)-N(9)-N(10)	132.0(3)	N(3)-Cu(2)-N(4)	94.8(1)
N(3)-Cu(2)-N(7)	83.9(2)	N(4)-Cu(2)-N(8)	83.5(2)
N(7)-Cu(2)-N(8)	92.3(2)	N(11)-Cu(2)-N(3)	110.1(2)
N(11)-Cu(2)-N(4)	110.8(2)	N(11)-Cu(2)-N(7)	86.0(2)
N(11)-Cu(2)-N(8)	87.2(2)	Cu(2)-N(11)-N(10)	138.9(4)
N(9)-N(10)-N(11)	178.6(5)		

Discussion

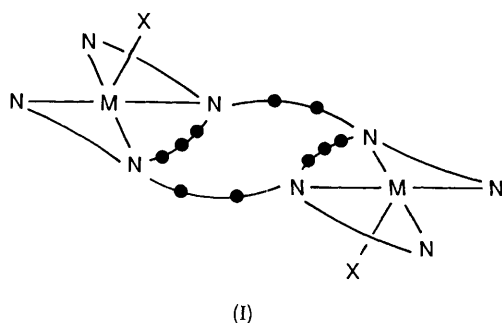
The synthesis of the new ligands taep and taeh was verified by the X-ray structural analyses of their complexes. There is also no doubt of the synthesis of taei according to the elemental analysis, use of a synthetic method similar to those for taec,¹ taeh, and taep, and the formation of metal complexes analogous to those of the other octaamine ligands.

The elemental analyses of the complexes revealed that the metal/L(octaamine ligand) molar ratio is 2:1 for all the complexes obtained, as observed for taec complexes.^{1b} Hence, they are all supposed to be dinuclear by analogy with the taec complexes for which a dinuclear structure was demonstrated by X-ray structure analyses. This was exemplified by X-ray structure determinations for [Cu₂(taep)][ClO₄]₄, [Cu₂(N₃)(taeh)][ClO₄]₃, and [Cu₂(taeh)][ClO₄]₄. Although no single crystal was obtained for taei complexes, a dinuclear structure is implied by analogy with other homologous octaamine complexes.

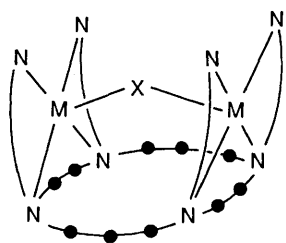
The major difference in molecular structure between taec and taeh complexes is that there are two modes of co-ordination for the former (I) and (II), but no such choice for the latter ones. In the case of [Cu₂(taec)][ClO₄]₄ the complex adopts co-ordination mode (I) and a chair conformation in which the two co-ordination units are connected by two -(CH₂)₂- chains and each copper is co-ordinated by a perchlorate ion at the apical site,^{1a} whereas the taep and taeh analogues adopt a boat (or crown) conformation (II), in which the co-ordination planes face each other with no perchlorate co-ordination and are connected by the -(CH₂)₃- chains (*cf.* Figures 1 and 2).

A prominent feature of the taec copper(II) complexes was the strong binding of an anion as a bridge between two copper atoms.¹ Similar features were found in the taei and taep complexes; *i.e.* complexes with the general formula [Cu₂X(L)]-[ClO₄]₃ (L = taei or taep; X = Cl, Br, or N₃) were isolated. However, in the case of taeh no halogeno complex but only an azido complex was isolated. According to the results of our previous study,⁸ the formation constants for the reaction [Cu(L)]⁴⁺ + X⁻ ⇌ [Cu₂X(L)]³⁺ remarkably decrease in the order taec > taep > taeh. This trend is quite consistent with the present results.

The structure of [Cu₂(N₃)(taeh)][ClO₄]₃ is to be noted in this context. The azide ion is bonded to the two copper ions in end-to-end fashion (Figure 3), whereas azide ion bridges the two copper ions in end-on fashion in the case of the corresponding taec complex.^{1d} These results are explainable in terms of the longer Cu...Cu distance [5.160(2) Å] in the case of the taeh complex compared with that of the taec complex [4.312 Å (1)]. The elongation of Cu...Cu distance in going from taec to taeh



(I)



(II)

complexes must be the main factor for the above-mentioned trend in decreasing formation constants for $[\text{CuX}(\text{L})]^{3+}$.

The i.r. bands due to the N_3^- stretching vibration were observed at 2 040, 2 050, 2 020, and 2 068 cm^{-1} for the taec, taei, taep, and taeh azido complexes, respectively. The $\nu(\text{N}_3^-)$ values for the taei and taep complexes are close to that of the taec complex rather than that of the taeh complex, hence the azido ion seems to be bound in an end-on fashion in these complexes, though a final conclusion cannot be drawn from this data only.

All the copper complexes show a broad band due to $d-d$ transitions, ν_{max} , of which are summarized in Table 4. Judging from the high ν_{max} values, the tetraperchlorate complexes of taep and taeh [also (tetrakis)tetrafluoroborate] and tetranitrate in the case of taeh] appear to assume square-planar co-ordination in solid state, whereas $[\text{Cu}_2(\text{taei})][\text{ClO}_4]_4$ seems to adopt square-pyramidal co-ordination (lower ν_{max} value). The anion-bridged complexes, such as $[\text{Cu}_2\text{Br}(\text{taep})][\text{ClO}_4]_3$, show much lower frequencies, implying stronger axial co-ordination. When dissolved in water the spectra of the non-bridged complexes undergo substantial red shift due to aquation at the axial sites. In contrast, a blue shift is observed for the anion-bridged complexes, and ν_{max} becomes close to that of the non-bridged complex. This indicates that the bridging anion is dissociated to some extent in aqueous solution.

All the nickel complexes obtained here are orange-yellow and diamagnetic at room temperature, indicating square-planar co-ordination as was already demonstrated for $[\text{Ni}_2(\text{taec})][\text{ClO}_4]_4$ by X-ray analysis.^{1b} However, when these complexes were dissolved in water their colour turned to blue except for the taeh complexes, indicating that the complexes became six- or five-co-ordinated (except for the taeh complexes). This conclusion is clearly supported by the electronic spectral data summarized in Table 4. In the cases of $\text{Ni}_2(\text{taeh})\text{X}_4$ ($\text{X} = \text{ClO}_4, \text{NO}_3, \text{Cl}$, or Br) the aqueous solution is yellow, implying that square-planar co-ordination is maintained. These complexes show electronic spectra typical of square-planar co-ordinated nickel(II) in both solid and aqueous solution with practically the same ν_{max} as shown in Table 4.

Table 4. Spectral and magnetic data

Complex	Band maxima ($\times 10^3 \text{ cm}^{-1}$)		μ_{eff}^a
	powder	solution (water)	
$[\text{Cu}_2(\text{taei})][\text{ClO}_4]_4 \cdot \text{H}_2\text{O}$	17.2	16.2 (148 ^b)	1.79
$[\text{Cu}_2\text{Cl}(\text{taei})][\text{ClO}_4]_3 \cdot \text{H}_2\text{O}$	15.9	16.4 (100)	1.80
$[\text{Cu}_2\text{Br}(\text{taei})][\text{ClO}_4]_3 \cdot \text{H}_2\text{O}$	15.9	16.8 (158)	1.78
$[\text{Cu}_2(\text{NO}_2)(\text{taei})][\text{ClO}_4]_3$	16.0	16.6 (140)	1.87
$[\text{Cu}_2(\text{N}_3)(\text{taei})][\text{ClO}_4]_3$	15.4	16.6 (143)	1.84
$[\text{Ni}_2(\text{taei})][\text{ClO}_4]_4$	21.6	17.2, 21.6 (sh), 27.4 ^c	<i>d</i>
$[\text{Cu}_2(\text{taep})][\text{ClO}_4]_4$	19.3	17.4 (124)	1.80
$[\text{Cu}_2\text{Cl}_2(\text{taep})][\text{ClO}_4]_2$	15.9	16.8 (183)	1.76
$[\text{Cu}_2\text{Br}(\text{taep})][\text{ClO}_4]_3$	16.3	16.6 (179)	1.78
$[\text{Cu}_2(\text{N}_3)(\text{taep})][\text{ClO}_4]_3$	16.1	16.4 (109)	1.85
$[\text{Ni}_2(\text{taep})][\text{ClO}_4]_4$	21.4	<i>c</i>	<i>d</i>
$[\text{Cu}_2(\text{taeh})][\text{ClO}_4]_4$	19.9	18.5 (109)	1.78
$[\text{Cu}_2(\text{taeh})][\text{BF}_4]_4$	19.7	18.5 (111)	1.76
$[\text{Cu}_2(\text{taeh})][\text{NO}_3]_4$	20.0	18.6 (109)	1.78
$[\text{Cu}_2(\text{N}_3)(\text{taeh})][\text{ClO}_4]_3$	16.1	17.2 (130)	1.88
$[\text{Ni}_2(\text{taeh})][\text{ClO}_4]_4$	21.4	21.4 (83)	<i>d</i>
$[\text{Ni}_2(\text{taeh})][\text{NO}_3]_4 \cdot \text{H}_2\text{O}$	21.4	21.4 (83)	<i>d</i>
$[\text{Ni}_2(\text{taeh})]\text{Cl}_4 \cdot \text{H}_2\text{O}$	21.6	21.5 (89)	<i>d</i>
$[\text{Ni}_2(\text{taeh})]\text{Br}_4 \cdot 2\text{H}_2\text{O}$	21.4	21.5 (88)	<i>d</i>

^a Effective magnetic moment per atom. ^b ϵ in $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ per metal atom. ^c Absorption decreases with time due to decomposition of the complex. ^d Diamagnetic.

The persistency of the square-planar co-ordination of the nickel taeh complex can be ascribed to steric conditions favourable for this co-ordination mode (*cf.* Figure 2).

The magnetic moments of the copper complexes all fall in the range of 1.77–1.88 μ_B as shown in Table 4, and obey the Curie–Weiss law with small Weiss constants (less than 10 cm^{-1}), indicating little or no spin coupling between copper ions. This is explainable in that in the present anion-bridged complexes the two co-ordination units are connected with the anion at the apices of square pyramids so that the unpaired electrons which localize in the basal planes cannot effectively couple with each other.

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