Synthesis of triple cyclam (1,5,9,12,16,20,24,27-octaazatricyclo-[18.10.2.2^{5,16}]tetratriacontane) and its 36-membered analogue 1,5,9,13,17,21,25,29-octaazatricyclo[19.11.2.2^{5,17}]hexatriacontane and studies of their co-ordinating properties in solution and the solid state

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Reaction of cyclam (1,4,8,11-tetraazacyclotetradecane) with toluene-*p*-sulfonylazetidine has been shown to provide a means for appending a 3-toluene-*p*-sulfonylaminopropane unit to each of the four nitrogen atoms in high yield. The resulting compound has been used as a precursor for two new tricyclic macrocyclic ligands, 1,5,9,12,16,20,24,27-octaazatricyclo[18.10.2.2^{5,16}]tetratriacontane (tcoa-14) and 1,5,9,13,17,21,25,29-octa-azatricyclo[19.11.2.2^{5,17}]hexatriacontane (tcoa-15) which were synthesized under Richman–Atkins conditions using the appropriate tosylated diol. Potentiometric titrations show that both ligands form mono- and bi-metallic complexes in solution, but only the latter could be isolated in the solid state. These bimetallic complexes are not effective at retaining anions in a bridging position between the two metal ions, probably due to the intermetallic distance {measured by X-ray crystallography as 5.24 Å on [Cu$_2$Cl$_2$(tcoa-14)]Cl$_2$} being too great. Formation constants of complexes of both ligands with Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} were determined and indicate the sequential occupation of the two outer binding compartments of these tricycles.

Pendant aminoalkyl groups projecting from the nitrogen atoms of a polyazamacrocyclic ligand have been utilised in a number of situations as a basis for fusing a second and, sometimes, a third polyazamacrocycle to the pre-existing one.[1] Methods used for doing this have involved reaction of pairs of pendant 3-aminopropyl groups with glyoxal in the presence of a metal template,[2–5] tosylation (tosyl = toluene-*p*-sulfonyl) of pendant 3-aminopropyl groups and subsequent reaction of pairs of deprotonated sulfonamides with a tosylated diol (Richman–Atkins cyclisation),[6,7] or direct attachment of pendant tosylated 2-aminoethyl groups through the reaction of the macrocycle with tosylated aziridine, followed by a Richman–Atkins cyclisation.[8] Of these methods, the first is circuitous since the only established pathway to the 3-aminopropyl group is *via* the 2-cyanoethyl group which must undergo reduction, the second suffers from the same problem with the added requirement of successful monotosylation of the pendant amines and the third is more elegant but can only be used for syntheses in which an aminoethyl group is sought as the opening linkage to the new macrocycle. The third technique would become more versatile, however, if tosylated heterocyclic amines larger than the three-membered tosylaziridine could be used. Towards this end we now report conditions under which the generally recalcitrant four-membered heterocycle tosylazetidine can be used to directly attach four tosylated 3-aminopropyl groups to the nitrogen atoms of cyclam (1,4,8,11-tetraazacyclotetradecane) in high yield. These pendant groups are then available for cyclisation, using Richman–Atkins conditions, as we have been able to demonstrate in this work using ditosylated 1,2-dihydroxy-ethane or 1,3-dihydroxypropane (Scheme 1). The former synthesis leads to the interesting situation where three cyclam residues are fused together to form a 'triple cyclam' molecule and the latter to the fusing of a fifteen-membered tetraaza-macrocycle to either side of a cyclam residue. As a pair, these two ligands continue the series of ligands which began with the synthesis of tcoa (= 1,5,8,12,15,19,22,26-octaazatricyclo-[17.9.2.2^{5,15}]dotriacontane) from tetratosylated tetrakis(2-aminoethyl) cyclam (Scheme 2).[8] As tcoa contains thirteen-membered rings in the outer positions it is, now, better referred

to as tcoa-13, with the new ligands being tcoa-14 and -15. Preliminary studies of the co-ordination chemistry of tcoa-14 and -15 are described in this work, particularly with respect to their capacity for forming bimetallic complexes capable of trapping anions between the two metal ions in the manner previously demonstrated for tcoa-13,[8] taec-14,[9–14] -15 and -16,[14,15] and tpmc-14 (Scheme 2).[16,17]
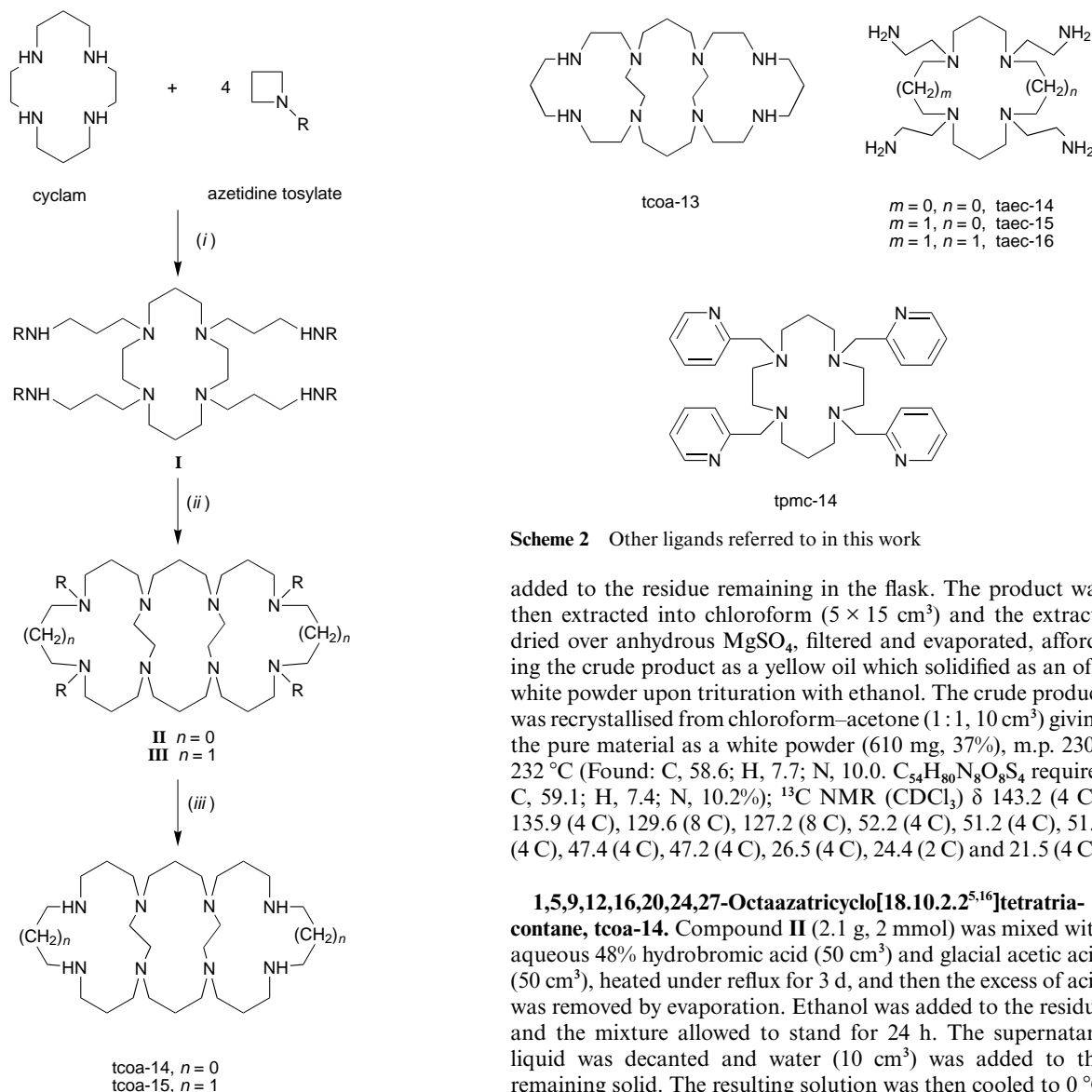
Experimental

General

Carbon-13 and ^{1}H NMR spectra were recorded at 75.46 and 300.08 MHz, respectively, using a Varian Gemini 300 spectrometer, in CDCl$_3$ at 295 K; ^{13}C chemical shifts are quoted with respect to the central resonance of the CDCl$_3$ multiplet taken as δ 77.00, ^{1}H shifts with respect to internal SiMe$_4$ taken as δ 0.00. Elemental analyses were performed by Chemical and Microanalytical Services Pty Ltd. Mass spectra were recorded on a Kratos M25RF spectrometer operating at an ionising voltage of 70 eV (*ca.* 1.12 × 10^{-17} J). Molecular ions are reported as their mass to charge ratio (*m/z*) followed by their relative intensities as compared to that of the base fragment. Melting points were determined using a Reichert hot-stage apparatus and are uncorrected. Magnetic susceptibility measurements were made using a Sherwood Scientific magnetic susceptibility balance and corrected for ligand and inner-core diamagnetism using Pascal's constants.[18] Conductivity measurements were made on 10^{-3} mol dm^{-3} solutions in dmf at 293 K using a Phillips PW9504 conductivity bridge.

The di-(toluene-*p*-sulfonates) of 1,2-dihydroxyethane and 1,3-dihydroxypropane,[19] toluene-*p*-sulfonylazetidine[20] and cyclam[21] were prepared according to the literature procedures.
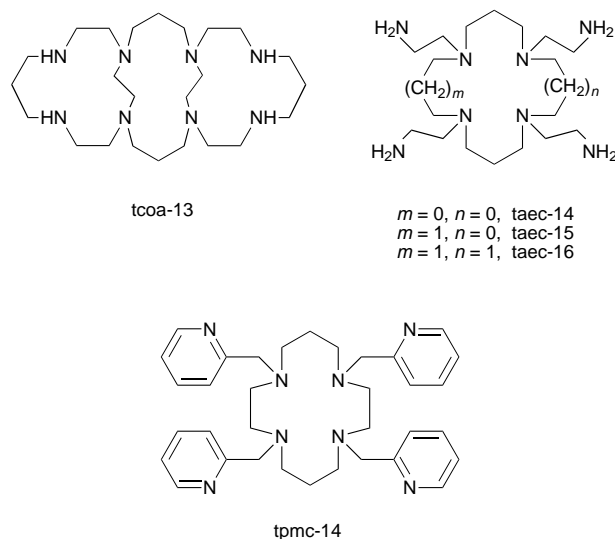
Syntheses

1,4,8,11-Tetrakis(3-toluene-*p*-sulfonylaminopropyl)-1,4,8,11-tetraazacyclotetradecane I. The compounds cyclam (10 g, 0.05 mol) and toluene-*p*-sulfonylazetidine (42.19 g, 0.2 mol) were mixed and ground together into a homogeneous powder. The

cyclam

azetidine tosylate

tcoa-13

$m = 0$, $n = 0$, taec-14
$m = 1$, $n = 0$, taec-15
$m = 1$, $n = 1$, taec-16

tpmc-14

Scheme 2 Other ligands referred to in this work

RNH

HNR

RNH

HNR

I

R

R

$(CH_2)_n$

$(CH_2)_n$

R

R

II $n = 0$
III $n = 1$

HN

NH

$(CH_2)_n$

$(CH_2)_n$

HN

NH

tcoa-14, $n = 0$
tcoa-15, $n = 1$

Scheme 1 (*i*) Fusion at 154 °C; (*ii*) Cs$_2$CO$_3$, ROCH$_2$(CH$_2$)$_n$CH$_2$OR (R = *p*-MeC$_6$H$_4$SO$_2$, $n = 0$ or 1), dmf; (*iii*) HBr–MeCO$_2$H

mixture was melted (150–154 °C), whereupon the flask containing it was stoppered and the mixture then maintained at its melting point for 4 h. The product was cooled, dissolved in hot thf (300 cm^3), cooled again and filtered to remove traces of insoluble materials. Addition of water (500 cm^3) to the stirred thf solution produced an oily layer of the crude product which solidified on standing. The mixture was left overnight and then the supernatant was decanted. The remaining water was drawn off the crude product by azeotropic distillation using benzene, which was then evaporated until a yellow oil remained. Trituration of the oil with dry ethanol produced the pure product as a white solid (40.8 g, 78%), m.p. 150–153 °C (Found: C, 58.2; H, 7.7; N, 10.9. C$_{50}$H$_{76}$N$_8$O$_8$S$_4$ requires C, 57.4; H, 7.3; N, 10.7%); ^{13}C NMR (CDCl$_3$) δ 142.8 (4 C), 137.6 (4 C), 129.5 (8 C), 126.9 (8 C), 50.8 (4 C), 49.5 (4 C), 49.1 (4 C), 40.7 (4 C), 25.5 (4 C), 23.2 (2 C) and 21.4 (4 C).

9,12,24,27-Tetrakis(toluene-*p*-sulfonyl)-1,5,9,12,16,20,24,27-octaazatricyclo[18.10.2.2^{5,16}]tetratriacontane II. Compound **I** (1.57 g, 1.5 mmol) in dmf (150 cm^3) was added at a stoichiometrically compatible rate with a solution of ditosylated 1,2-dihydroxyethane (1.12 g, 3 mmol) in dmf (150 cm^3) over 7 h to a suspension of Cs$_2$CO$_3$ (2.06 g, 6.3 mmol) in dmf (50 cm^3). On completion of the addition the mixture was stirred for 24 h. The dmf was evaporated under reduced pressure and water (25 cm^3)

added to the residue remaining in the flask. The product was then extracted into chloroform (5 × 15 cm^3) and the extracts dried over anhydrous MgSO$_4$, filtered and evaporated, affording the crude product as a yellow oil which solidified as an off-white powder upon trituration with ethanol. The crude product was recrystallised from chloroform–acetone (1 : 1, 10 cm^3) giving the pure material as a white powder (610 mg, 37%), m.p. 230–232 °C (Found: C, 58.6; H, 7.7; N, 10.0. C$_{54}$H$_{80}$N$_8$O$_8$S$_4$ requires C, 59.1; H, 7.4; N, 10.2%); ^{13}C NMR (CDCl$_3$) δ 143.2 (4 C), 135.9 (4 C), 129.6 (8 C), 127.2 (8 C), 52.2 (4 C), 51.2 (4 C), 51.0 (4 C), 47.4 (4 C), 47.2 (4 C), 26.5 (4 C), 24.4 (2 C) and 21.5 (4 C).

1,5,9,12,16,20,24,27-Octaazatricyclo[18.10.2.2^{5,16}]tetratriacontane, tcoa-14. Compound **II** (2.1 g, 2 mmol) was mixed with aqueous 48% hydrobromic acid (50 cm^3) and glacial acetic acid (50 cm^3), heated under reflux for 3 d, and then the excess of acid was removed by evaporation. Ethanol was added to the residue and the mixture allowed to stand for 24 h. The supernatant liquid was decanted and water (10 cm^3) was added to the remaining solid. The resulting solution was then cooled to 0 °C and adjusted to pH 14 with 10 M NaOH. From this the product was extracted into dichloromethane (3 × 25 cm^3). The extracts were dried over anhydrous MgSO$_4$, filtered and evaporated leaving the crude product which was recrystallised from acetonitrile–methanol (10 : 1, 10 cm^3) giving the pure product as an off-white solid (660 mg, 76%), m.p. 149–151 °C (Found: C, 64.4; H, 11.6; N, 22.9. C$_{26}$H$_{56}$N$_8$ requires C, 64.9; H, 11.7; N, 23.3%); ^{13}C NMR (CDCl$_3$) δ 51.6 (4 C), 50.8 (4 C), 50.4 (4 C), 45.5 (4 C), 43.7 (4 C), 24.6 (2 C) and 24.1 (4 C); ^{1}H NMR (CDCl$_3$) δ 2.71 (br s, 8 H), 2.66 (t, $J = 5.4$, 12 H), 2.41 (s, 8 H), 2.31 (t, $J = 5.4$, 16 H) and 1.63 (br quintet, $J = 6.0$ Hz, 12 H). m/z 480 (M^+, 31%).

9,13,25,29-Tetrakis(toluene-*p*-sulfonyl)-1,5,9,13,17,21,25,29-octaazatricyclo[19.11.2.2^{5,17}]hexatriacontane III. A solution of ditosylated 1,3-dihydroxypropane (3.08 g, 8 mmol) in dry dmf (100 cm^3) was added dropwise over 7 h to a stirred mixture of compound **I** (4.18 g, 4 mmol) and Cs$_2$CO$_3$ (4.48 g, 16.8 mmol) in dry dmf (100 cm^3) at room temperature. The reaction mixture was allowed to stir for 24 h before evaporating off the solvent under reduced pressure. Water (50 cm^3) was then added to the residue and the mixture extracted with chloroform (5 × 25 cm^3). All chloroform portions were combined, dried (MgSO$_4$), filtered and then evaporated to yield a light yellow oil. A white solid was obtained from the oil by addition of acetonitrile (5 cm^3) and overnight refrigeration. This was filtered off and recrystallised from chloroform–methanol (1 : 1, 10 cm^3) giving the pure product as a white powder (1.8 g, 41%),

m.p. 207–209 °C (Found: C, 59.3; H, 7.5; N, 9.9. $C_{56}H_{84}N_8O_8S_4$ requires C, 59.8; H, 7.5; N, 10.0%); ^{13}C NMR (CDCl$_3$) δ 143.3 (4 C), 135.9 (4 C), 129.8 (8 C), 127.2 (8 C), 52.9 (4 C), 52.3 (4 C), 51.5 (4 C), 48.4 (4 C), 47.6 (4 C), 29.3 (2 C), 27.6 (4 C), 25.5 (2 C) and 21.5 (4 C).

1,5,9,13,17,21,25,29-Octaazatricyclo[19.11.2.2^{5,17}]hexatria-contane, tcoa-15. Compound **III** (4.52 g, 4 mmol) was heated at reflux for 4 d in a mixture of aqueous 48% hydrobromic acid (60 cm^3) and glacial acetic acid (60 cm^3). When the reaction was complete the acid was evaporated. Water (10 cm^3) was added to the remaining solid in the flask and then adjusted to pH 14 with 10 M NaOH. The product was extracted into chloroform (5 × 15 cm^3), dried (MgSO$_4$) and then evaporated to dryness. Recrystallisation from acetonitrile (10 cm^3) afforded the compound as white crystals (961 mg, 47%), m.p. 97–98 °C (Found: C, 66.0; H, 12.1; N, 22.0. $C_{28}H_{60}N_8$ requires C, 66.1; H, 11.9; N, 22.0%); ^{13}C NMR (CDCl$_3$) δ 53.3 (4 C), 52.4 (4 C), 51.6 (4 C), 48.9 (4 C), 48.0 (4 C), 28.5 (2 C), 26.6 (4 C) and 25.4 (2 C); ^{1}H NMR (CDCl$_3$) δ 2.71 (t, $J = 5.4$, 8 H), 2.65 (t, $J = 5.7$ Hz, 8 H), 2.39 (m, 28 H) and 1.58 (m, 16 H). m/z 508 (M^+, 18%).

Metal complexes. CAUTION: perchlorate salts of metal complexes are potentially explosive. Although we have had no incidents with any of the perchlorate salts described in this work suitable precautions should be taken.

The complexes of tcao-14 and -15 that were prepared are detailed in Table 1. They mostly fall into one of three groups according to the ratio of the weakly binding anion, perchlorate, to a potentially more strongly binding anion. General syntheses for members of each group were as follows.

Tetraperchlorates. A solution of the ligand (0.31 mmol) in dry ethanol (10 cm^3) was added dropwise over 15 min to a stirred solution of the hydrated metal perchlorate (0.68 mmol) in dry refluxing ethanol. When the addition was complete the reaction mixture was allowed to stir for 30 min and then cooled to room temperature. The product was collected and washed with dry ethanol (3 × 10 cm^3) and then dried *in vacuo*. Notes: for the cadmium complex anhydrous metal perchlorate was used to avoid formation of the monohydroxide triperchlorate; for the complexes of Hg^{II} and Pb^{II} the reaction was conducted at 273 K to avoid decomposition, which was observed as a pronounced darkening of the reaction mixture and may correspond to the deposition of elemental mercury or lead.

Triperchlorates. A solution of the ligand (0.31 mmol) in dry ethanol (10 cm^3) was added dropwise over 15 min to a stirred solution of a mixture of hydrated metal perchlorate (0.47 mmol) and hydrated metal chloride (0.16 mmol) in dry ethanol (10 cm^3), heating at a gentle reflux. Precipitation occurred immediately. When the addition was complete the stirring was continued for 30 min and then the mixture was cooled. The product was filtered off, washed with dry ethanol (3 × 10 cm^3) and dried *in vacuo*. Where the binding anion is hydroxide the complexes were obtained by the method described for the tetraperchlorates except that in the case of Cd^{II} the hydrated metal perchlorate was used. For the reason mentioned above, the mercury(II) reaction was conducted at 273 K to avoid decomposition. For the dicopper(II) complexes with Br$^-$, I$^-$, NCS$^-$ or N$_3^-$ the following method was used: an aqueous solution of 0.1 M NaX (X = Br$^-$, I$^-$, NCS$^-$ or N$_3^-$) (2 cm^3) was added dropwise to a stirred solution of [Cu$_2$L][ClO$_4$]$_4$ (L = tcoa-14 or -15) (0.2 mmol) in a mixture of methanol (4 cm^3) and water (4 cm^3) at reflux. On completion of the addition the mixture was allowed to stir for 30 min and then cooled to ambient temperature. The product was then filtered off, washed with methanol (3 × 10 cm^3) and dried *in vacuo*.

Diperchlorates. An aqueous solution of 0.1 M NaX (X = I$^-$ or NCS$^-$) (4 cm^3) was added dropwise to a stirred solution of [Cu$_2$L][ClO$_4$]$_4$ (L = tcoa-14) (0.2 mmol) in a mixture of methanol (4 cm^3) and water (4 cm^3) at reflux. On completion of the

addition the mixture was allowed to stir for 30 min and then cooled to ambient temperature. The product was filtered off, washed with methanol (3 × 10 cm^3) and dried *in vacuo*. For L = tcoa-15 and X = NCS$^-$ the diperchlorate formed when the reaction was conducted using the triperchlorate synthesis (above). For L = tcoa-14 and X = Cl$^-$ or Br$^-$ the following procedure was used: a solution of tcoa-14 (150 mg, 0.31 mmol) in dry ethanol (10 cm^3) was added dropwise over 15 min to a stirred refluxing mixture of Cu(ClO$_4$)$_2$·6H$_2$O (0.31 mmol) and CuX$_2$ (0.31 mmol). Precipitation occurred immediately. The reaction mixture was stirred for 30 min. The product was filtered off, washed with dry ethanol (3 × 10 cm^3) and then dried *in vacuo*.

Dichloro(1,5,9,12,16,20,24,27-*octaazatricyclo*[18.10.2.2^{5,16}]-*tetratriacontane*)*dicopper*(II) *dichloride,* [Cu$_2$Cl$_2$(tcoa-14)]Cl$_2$. A solution of tcoa-14 (150 mg, 0.31 mmol) in dry ethanol (10 cm^3) was added dropwise to a stirred refluxing solution of anhydrous copper(II) chloride (84 mg, 0.62 mmol) in ethanol (10 cm^3). On completion of the addition the suspension was stirred for 30 min, cooled to room temperature and the purple product filtered off. It was washed with ethanol (3 × 10 cm^3) and dried under vacuum (210 mg, 90%).

Spectroscopic methods

Analysis of solutions with varying co-ordinating anion: [Cu$_2$(tcoa-14)][ClO$_4$]$_4$ ratios. Aliquots (2 cm^3) of a 0.001 M aqueous solution of [Cu$_2$(tcoa-14)][ClO$_4$]$_4$ were mixed with NaX solutions (X = Cl$^-$, Br$^-$, I$^-$, SCN$^-$ or N$_3^-$) (0.25 cm^3) of varying concentration. In this way a series of solutions were made in which the ratio of X : [Cu$_2$(tcoa-14)][ClO$_4$]$_4$ varied from 0 : 1 to 20 : 1. Sufficient NaClO$_4$ was used to bring the ionic strength of all solutions to 0.02 M. The pH was adjusted to 4.7 ± 0.1, using HClO$_4$, to prevent competition with the hydroxo complex known from Fig. 3 to occur at higher pH. Each solution was stirred for 30 min and then allowed to stand in a water-bath at 25 ± 0.1 °C for 3 h before recording its UV/VIS spectrum on a Hewlett-Packard 8452A diode-array spectrophotometer equipped with cells thermostatted at 25 °C.

Job's method.[23] A 10^{-3} M solution of [Cu$_2$(tcoa-14)][ClO$_4$]$_4$ was mixed with an equimolar NaX (X = Cl$^-$, Br$^-$, I$^-$, SCN$^-$ or N$_3^-$) solution to make a series of solutions with mole fractions of NaX ranging from 0.3 to 0.9. The total concentration of NaX and [Cu$_2$(tcoa-14)][ClO$_4$]$_4$ in each solution was kept constant. The optical absorbances in each solution at 480, 500, 520, 540, 560, 580 and 600 nm were then measured. Each was corrected by subtracting the absorbance due to [Cu$_2$(tcoa-14)]-[ClO$_4$]$_4$ or [Cu$_2$X(tcoa-14)][ClO$_4$]$_3$. The corrected absorbances were plotted against the mole fraction of NaX.

Potentiometric titrations

The potentiometric titrations were carried out under an inert atmosphere of water-saturated nitrogen in a water-jacketed vessel maintained at 25 °C. Data were obtained from aliquots (10 cm^3) of solution containing 0.01 M HClO$_4$ or HNO$_3$, 0.100 M NEt$_4$ClO$_4$ or NaNO$_3$, and approximately 1.0×10^{-3} M ligand titrated with 0.10 M NEt$_4$OH or NaOH. Sodium nitrate was used as the background electrolyte for the tcoa-15 titrations owing to the precipitation of tcoa-15 hydroperchlorate salts when NEt$_4$ClO$_4$, which was used for tcoa-14, was used. A Metrohm E665 Dosimat autoburette equipped with a 5 cm^3 burette was used to deliver the titrant and the potential was measured by an Orion Ross Sure Flow 81-65BN combination electrode connected to an Orion 290A pH meter. The autoburette and pH meter were interfaced to an IBM-compatible personal computer which controlled the addition of titrant using a program written by Drs. A. P. Arnold and P. A. Duckworth so that successive additions of titrant caused a decrease of *ca.* 4 mV in the potential reading. The electrode was cali-

brated by a titration in the absence of ligand and fitting the resulting data from this strong acid–strong base titration using the Nernst equation to find correct values for E_o and pK_w. The pK_a and stability constants were determined using the program SUPERQUAD.[24] Stability constant data were gathered from solutions to which 0.1 M metal perchlorate solution was added so as to give a metal-to-ligand ratio in the range 0.5:1 to 2:1. At least three titrations, with different ratios, were performed for each metal ion. In the 2:1 titration involving copper(II) and tcoa-14 and in all the tcoa-15 titrations precipitation of a perchlorate salt occurred at an early stage. To avoid this problem the stability constants for these metal–ligand combinations were measured using 0.1 M NaNO₃, 0.01 M HNO₃ and 0.1 M NaOH.

Crystallography

Crystal data. [Cu₂Cl₂(tcoa-14)]Cl₂·2H₂O, C₂₆H₆₀Cl₄Cu₂N₈O₂, orthorhombic, space group *Pnma*, $a = 16.657(1)$, $b = 21.501(1)$, $c = 9.716(1)$ Å, $U = 3479.9(4)$ Å³, $Z = 4$, $D_c = 1.501$ Mg m³, $h = 0$–16, $k = 0$–21, $l = 0$–9, reflections measured = 1887, $\theta_{max} = 20.8°$, $T = 293$ K, reflections used in refinement [$|F_{obs}| > 2(|F_{obs}|)$] = 1312, parameters = 107, $R = 0.110$, $R' = 0.109$, $S = 4.4$. The highest peak in the final difference map was 2.06 e Å⁻³, 0.87 Å from Cu.

Data were collected on a Siemens SMART diffractometer using Mo-Kα X-radiation by Dr. L. Brammer at the University of Missouri, St. Louis.

Solution and refinement. The space group was determined, except for the center of symmetry ambiguity, by inspection of precession photographs. Refinement was based on F using the programs of the XTAL 3.5 system.[25] Heavy atoms were refined with anisotropic displacement parameters, and lighter atoms with isotropic displacement parameters. Hydrogen atoms, except for those on water molecules, were included at calculated positions but their coordinates were not refined. Eleven bond length and six angle constraints were introduced for C–C and C–N interactions during the refinement. There were no residual peaks greater than 1 e Å⁻³ in the 'cavity' between the Cu atoms.

The crystals of this compound were of extremely poor quality. They contained intergrowths and other imperfections and there was some twinning. The structure was solved by direct methods using SIR 92[26] on the complete data set. This program automatically identified all the non-hydrogen atoms in the structure. The atoms of the macrocycle were all correctly linked as expected and the co-ordination around copper was plausible. We therefore contend that, even though the R value is large by today's expectations, the molecular structure is essentially correct and shows the stereochemistry in the solid state. We are encouraged to make this claim by some of the details of the 'refined' structure, for example the geometry of the copper(II) co-ordination and the finer details of Cu^{II}–N bond lengths that reflect expected differences between copper(II)–secondary amine and C–tertiary amine distances. These unconstrained distances are 2.00(1) and 2.00(1) and 2.03(1) and 2.08(1) Å, respectively. Unconstrained C–C(N) bond lengths in this 'refined' structure range from 1.45 to 1.57 Å. Attempts to connect residual peaks in the difference map in a chemically sensible way proved fruitless.

The program SIR 92 produced an identical solution in the corresponding non-centrosymmetric space group. While this 'structure determination' is useful in the context of this paper the results should be treated with caution and details should not heedlessly be used to extrapolate to other conclusions.

Results and Discussion

Ligand synthesis

The syntheses for tcoa-14 and -15, outlined in Scheme 1, rely
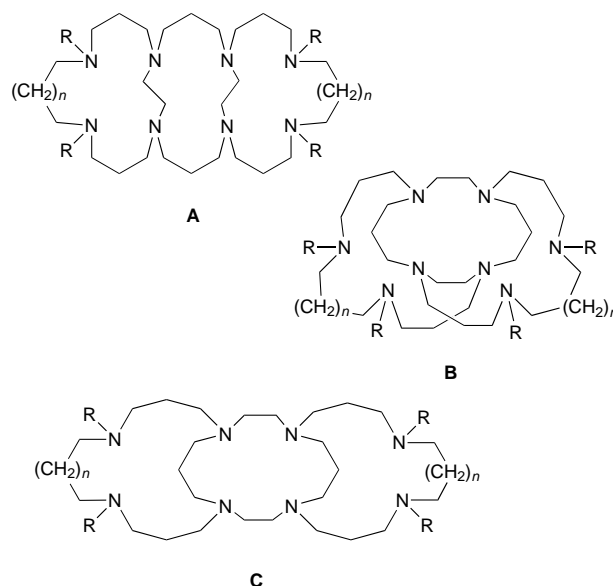
Scheme 3 Possible structural isomers that could derive from the Richman–Atkins cyclisation of compound **I**. R = *p*-MeC₆H₄SO₂

initially on the ring opening of azetidine tosylate to give compound **I**. When this reaction was attempted in refluxing acetonitrile, thf, dmf or dmso, at atmospheric pressure, which are typical of the conditions used previously with aziridine tosylate,[9] only starting materials were recovered. On the other hand, when the two reactants were ground together and then fused it was found that by keeping the mixture at its melting point for 4 h the required reaction proceeds to completion giving **I** in *ca*. 80% yield. This compound was then cyclised with two different tosylated diols, using Richman–Atkins conditions[6] and caesium carbonate as the base. In each case a single product in *ca*. 40% yield was isolated.

During ring closure there is the possibility of the reaction producing any combination of the three structural isomers **A**, **B** or **C** shown in Scheme 3. From ¹³C NMR spectroscopy it was possible to ascertain that with either tosylated diol the isolated product consisted of only a single isomer, but spectroscopic methods alone were insufficient to deduce its identity. In the case where ring closure was completed using ditosylated 1,2-dihydroxyethane it became clear from X-ray crystallographic work to be discussed below that the isomer isolated has structure **A**, that is, it is tcoa-14 as shown in Scheme 1. This corresponds to the same sense of ring closure as seen previously in the formation of tcoa-13.[8] The general properties and similarity of both the ¹³C and ¹H NMR spectra originating from the product arising from the use of ditosylated 1,3-dihydroxypropane gave us no reason to believe that the sense of ring closure had changed in this case, and accordingly we formulate the reaction product as tcoa-15 with the structure shown in Scheme 1. Use of sodium ethoxide as base in either cyclisation resulted in substantially lower yields of the same isomer as that obtained with caesium carbonate.

The protonation constants for tcoa-14 and -15 were determined by potentiometric titration and are given in Table 2, together with the data for taec-14 for comparison. The first protonation of both tricyclic ligands occurs slightly more readily than with taec-14. This suggests that one of the secondary amino sites, which are absent in taec-14, and where the proton can be stabilised by intramolecular hydrogen bonds within the macrocyclic framework is the site of the first protonation. With tcoa-14 and taec-14 a significant drop in value of the protonation constants occurs between K_{a4} and K_{a5}, showing the point at which a proton must be added to a nitrogen atom that is a part of an already protonated 1,2-diaminoethane ring. With tcoa-15 the corresponding drop occurs between K_{a6} and K_{a7}.

Table 1 Some properties of the synthesized compounds

Compound	Colour	Analysis (%)[a]			Visible spectrum[b] (λ/nm)	Magnetic moment[b] (μ_{eff}/μ_B)	Conductivity[d] ($\Omega^{-1}\,cm^2\,mol^{-1}$)
		C	H	N			
$[Cu_2(tcoa\text{-}14)][ClO_4]_4$	Purple	31.1 (31.1)	5.8 (5.6)	10.9 (11.1)	502 (245)	1.84	261
$[Cu_2(tcoa\text{-}14)]Cl[ClO_4]_3\cdot3H_2O$	Purple	31.5 (31.4)	5.9 (6.3)	10.9 (11.2)	522 (269)	1.92	288
$[Cu_2(tcoa\text{-}14)]Br[ClO_4]_3$	Red	31.6 (31.7)	5.9 (5.7)	11.2 (11.4)	504 (294)	1.89	231
$[Cu_2(tcoa\text{-}14)]I[ClO_4]_3\cdot2H_2O$	Orange	29.1 (29.2)	5.2 (5.7)	10.5 (10.5)	498 (360)	2.23	200
$[Cu_2(tcoa\text{-}14)][SCN][ClO_4]_3\cdot H_2O$	Purple	33.0 (33.0)	5.8 (5.9)	13.0 (12.8)	504 (291)	2.23	236
$[Cu_2(tcoa\text{-}14)][N_3][ClO_4]_3$	Purple	33.0 (32.9)	6.1 (6.0)	16.2 (16.2)	506 (296)	1.84	245
$[Cu_2Cl_2(tcoa\text{-}14)][ClO_4]_2$	Purple	35.4 (35.6)	6.6 (6.4)	12.8 (12.8)	536 (288)	1.88	238
$[Cu_2Br_2(tcoa\text{-}14)][ClO_4]_2$	Red	32.0 (32.3)	6.0 (5.8)	11.7 (11.6)	498 (301)	1.82	221
$[Cu_2I_2(tcoa\text{-}14)][ClO_4]_2$	Orange	29.3 (29.4)	5.4 (5.3)	10.4 (10.6)	498 (414)	1.92	236
$[Cu_2(SCN)_2(tcoa\text{-}14)][ClO_4]_2\cdot H_2O$	Purple	35.7 (35.7)	6.1 (6.2)	14.5 (14.9)	504 (266)	1.82	215
$[Cu_2Cl_2(tcoa\text{-}14)]Cl_2$	Purple	41.8 (41.7)	7.5 (7.5)	15.2 (15.0)	558 (345)	1.94	245
$[Ni_2(tcoa\text{-}14)][ClO_4]_4$	Yellow	31.4 (31.4)	5.6 (5.7)	11.0 (11.2)	460 (183)	Diamagnetic	282
$[Co_2(tcoa\text{-}14)][ClO_4]_4$	Pink	31.4 (31.3)	5.6 (5.7)	11.2 (11.2)	482 (73), 538 (73)	3.84	270
$[Zn_2(tcoa\text{-}14)]OH[ClO_4]_3\cdot H_2O$	White	33.2 (33.0)	6.4 (6.3)	11.6 (11.9)	—	Diamagnetic	246
$[Cd_2(tcoa\text{-}14)][ClO_4]_4$	White	27.9 (28.3)	4.8 (5.1)	10.2 (10.1)	—	Diamagnetic	262
$[Cd_2(tcoa\text{-}14)]Cl[ClO_4]_3$	White	30.0 (30.0)	5.5 (5.4)	10.6 (10.8)	—	Diamagnetic	209
$[Cd_2(tcoa\text{-}14)]OH[ClO_4]_3\cdot H_2O$	White	30.2 (30.6)	5.5 (5.6)	10.7 (11.0)	—	Diamagnetic	262
$[Hg_2(tcoa\text{-}14)][ClO_4]_4$	White	24.3 (24.4)	4.5 (4.4)	8.6 (8.8)	—	Diamagnetic	325
$[Hg_2(tcoa\text{-}14)]Cl[ClO_4]_3$	White	25.8 (25.7)	4.6 (4.6)	8.9 (9.2)	—	Diamagnetic	265
$[Pb_2(tcoa\text{-}15)][ClO_4]_4$	White	24.3 (24.2)	4.5 (4.4)	8.9 (8.7)	—	Diamagnetic	309
$[Cu_2(tcoa\text{-}15)][ClO_4]_4$	Blue	32.7 (32.5)	5.7 (5.9)	10.6 (10.8)	608 (416)	1.80	285
$[Cu_2(tcoa\text{-}15)]Cl[ClO_4]_3$	Blue	34.7 (34.7)	6.3 (6.2)	11.6 (11.6)	602 (452)	1.80	301
$[Cu_2(tcoa\text{-}15)]Br[ClO_4]_3$	Blue	33.0 (33.2)	6.0 (6.0)	10.9 (11.0)	600 (453)	2.13	257
$[Cu_2(tcoa\text{-}15)]I[ClO_4]_3$	Blue	32.2 (31.7)	5.8 (5.7)	10.9 (10.6)	602 (421)	1.98	293
$[Cu_2(NCS)_2(tcoa\text{-}15)][ClO_4]_2\cdot H_2O$	Blue-green	36.9 (37.2)	6.2 (6.4)	14.1 (14.5)	636 (470)	2.00	198
$[Zn_2(tcoa\text{-}15)][ClO_4]_4$	White	32.4 (32.4)	5.9 (5.8)	10.6 (10.8)	—	Diamagnetic	284
$[Pb_2(tcoa\text{-}15)][ClO_4]_4$	White	25.5 (25.5)	4.6 (4.6)	8.3 (8.5)	—	Diamagnetic	290

[a] Calculated values in parentheses. [b] In aqueous solution, ε ($M^{-1}\,cm^{-1}$) given in parentheses. [c] Measured at ambient temperatures; $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}. [d] For 10^{-3} M solutions in dmf at 293 K; established conductivity ranges for electrolytes in dmf are 200–240 (3:1) and *ca.* 300 $\Omega^{-1}\,cm^2$ mol^{-1} (4:1).[22]
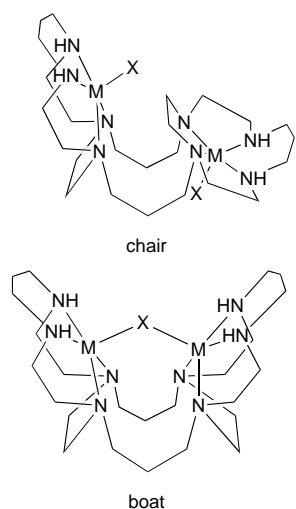
Metal-ion binding studies

Experience with the octaaza macrocycles taec-14, -15 and -16 and with tpmc and tcoa-13 has shown that their dominant tendency is to bind two metal ions, one in each outer compartment.[8–17,27] The binding of a single metal ion (Ni^{2+}, Cu^{2+}, Zn^{2+} or Cd^{2+}) has, however, been noted with taec-14 in aqueous solution, and with ions of large radius (Cd^{2+} and Hg^{2+}) it has been possible to isolate such complexes in the solid state.[13] To examine the situation with tcoa-14 and -15 a large number of syntheses (detailed in Table 1) were conducted in which metal ion:ligand ratios of both 1:1 and 2:1 were used. In all cases only a 2:1 complex could be isolated from the reaction conducted in ethanol.

2:1 Complexes formed from this type of octaaza ligand have been shown to exist in two structural arrangements; the ligand can be arranged in the chair configuration, with the metal ions on opposite sides of the central macrocycle, or in the boat structure, in which the metal ions are on the same side.[8–17,27] For complexes of tcoa-13 these two arrangements are shown schematically in Fig. 1. In cases where the boat form occurs it has generally been the case that there is a bridging anion covalently bound to both metal ions,[8–17] although there are exceptions to this.[10,15] The chair configuration tends to occur when only weakly co-ordinating anions such as perchlorate or tosylate, which bind in terminal positions, are available, but, again, there are exceptions.[11,27] The former situation is of considerable interest because of the

Table 2 Ligand protonation constants at 298.2 K [a]

Ligand	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$	$\log K_{7+8}$ [b]
tcoa-14 [c]	10.30(1)	9.61(2)	8.34(3)	7.19(3)	3.44(5)	2.08(7)	3.97(8)
tcoa-15 [c]	10.22(1)	9.80(2)	8.40(2)	7.61(2)	5.95(2)	5.01(2)	4.8(1)
taec-14 [d]	10.14	9.67	9.12	8.59	5.48	4.16	4.15

[a] Determined by glass-electrode potentiometry in water at $I = 0.1$ M NEt$_4$ClO$_4$ (tcoa-14) or NaNO$_3$ (tcoa-15). The stepwise equilibrium constants K_1, K_2, *etc.* refer to the equations $L + H^+ \rightleftharpoons HL^+$, $HL^+ + H^+ \rightleftharpoons H_2L^{2+} + H^+$, *etc.*, $pK_a = -\log_{10} K_a$. [b] This constant refers to the reaction $H_6L^{6+} + 2H^+ \rightleftharpoons H_8L^{8+}$. [c] This work. These constants are averaged from three separate titrations; the numbers in parentheses refer to the maximum variation found in the least significant figure exhibited by different titrations. [d] From ref. 13.
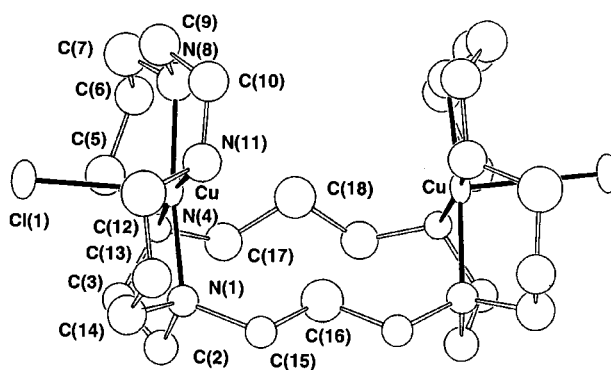

Fig. 1 The chair and boat forms of bimetallic complexes of tcoa-13 (ref. 8)

Fig. 2 An ORTEP [28] diagram of the cation in [Cu$_2$Cl$_2$(tcoa-14)]Cl$_2$·2H$_2$O with outlines of the displacement ellipsoids and spheres drawn at the 50% probability level. Only the Cu and Cl atoms were refined with anisotropic displacement parameters. A crystallographic mirror plane passing through C(16) and C(18) relates the two halves of the molecule
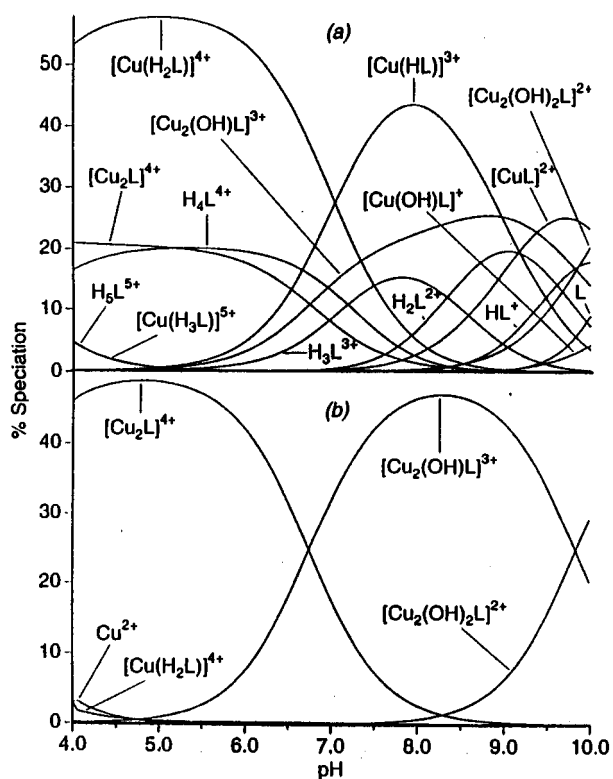
exceptionally high stability with which the anion is bound and the possibility of using these complexes as anion sequestering agents.[14,16] It is easily recognised by the ease with which complexes having a single co-ordinating anion, for example a halide, and three non-co-ordinating anions, for example perchlorates, may be isolated, and also by the fact that if a co-ordinating anion is titrated into a solution of, for example, [Cu$_2$L][ClO$_4$]$_4$ (L = octaaza ligand) a smooth change in the visible spectrum, usually proceeding through a single isosbestic point, is seen.[12,14]

From Table 1 it can be seen that with tcoa-14 and -15, as well as a variety of monohalide (or pseudo-halide) triperchlorate species, dihalide diperchlorate species could also be isolated, suggesting that terminal anion binding is occurring. This theory was supported by the nature of the spectral changes seen when titration of solutions of [Cu$_2$(tcoa-14)][ClO$_4$]$_4$ or [Cu$_2$-(tcoa-15)][ClO$_4$]$_4$ with Cl$^-$, Br$^-$, I$^-$, SCN$^-$ or N$_3^-$ was carried out in the manner described in the Experimental section. Not only did the titrations fail to give sharp isosbestic points in the spectral overlay, suggesting that more than one anion-containing species was forming, but it was also noted that substantial absorbance increases were still occurring at the point in the titration where the anion:complex ratio had reached 20:1, suggestive of anion binding constants of much lower value than those associated with bridging anions.[14,16] Construction of Job's plots[23] for each combination of dicopper(II) complex and anion indicated that monoanion- and dianion-containing species are formed in aqueous solution. The combination of these data points to the fact that neither dicopper(II) complex is well suited for anion bridging and that the introduction of two weakly binding anions, as observed, probably represents the sequential filling of the two terminal binding sites on each co-ordinated metal ion.

The occurrence of terminal anion binding was surprising since carbonate bridging has been noted for tcoa-13 in [Co$_2$(CO$_3$)(tcoa-13)][ClO$_4$]$_2$.[8] The intermetallic separation in

Fig. 3 Speciation diagrams for the copper(II)–L system (10^{-3} M), where L = tcoa-14, in 0.1 M NaNO$_3$: (*a*) 1:1, (*b*) 2:1 Cu^{2+}:L. Percentage abundances are relative to the number of moles of copper(II) present

this compound is 4.20 Å and although it had been anticipated that the intermetallic separation in tcoa-14 and -15 complexes would be larger it was not expected to exceed 5.16 Å, which is the largest intermetallic distance in this class of compounds yet seen to accommodate anion bridging.[15] This occurs in the com-

Table 3 Formation constants and pK_a values for complexes of tcoa-14, -15 and taec-14 in aqueous solution[a]

		log K					
Reaction[c]	Ligand[d]	Co^{2+}	Ni^{2+}	Cu^{2+b}	Zn^{2+}	Cd^{2+}	Pb^{2+}
M + H$_4$L ⇌ M(H$_4$L)	tcoa-14	e	f	e	e	2.4(1)	e
	tcoa-15	f	f	6.8(1)	e	e	f
	taec-14	e	e	6.7(2)	e	e	f
M + H$_3$L ⇌ M(H$_3$L)	tcoa-14	2.9(1)	f	8.6(1)	e	e	3.3(1)
	tcoa-15	f	f	9.9(1)	3.4(1)	3.2(1)	f
	taec-14	e	4.8(2)	12.5(2)	5.8(1)	<5.6	f
M + H$_2$L ⇌ M(H$_2$L)	tcoa-14	e	f	14.0(1)	e	e	e
	tcoa-15	f	f	13.5(1)	4.9(1)	5.3(1)	f
	taec-14	e	8.2(1)	16.9(3)	e	10.1(2)	f
M + HL ⇌ M(HL)	tcoa-14	e	f	16.51(4)	e	8.8(1)	e
	tcoa-15	f	f	e	7.7(1)	7.9(1)	f
	taec-14	e	9.6(2)	18.0(5)	e	12.0(1)	f
M + L ⇌ ML	tcoa-14	10.01(2)	f	17.64(2)	10.84(4)	9.5(1)	8.75(8)
	tcoa-15	f	f	16.2(2)	8.5(1)	10.6(1)	f
	taec-14	e	10.8(1)	19.9(2)	e	13.4(1)	f
M + ML ⇌ M$_2$L	tcoa-14	<2.9[g]	f	13.75(5)	6.65(7)	5.6(2)	4.9(1)
	tcoa-15	f	f	9.8(3)	5.1(1)	3.5(1)	f
	taec-14	h	4.7(2)	11.8(4)	h	<4.1	f
ML ⇌ ML(OH) + H$^+$	tcoa-14	e	f	6.8(1)	e	e	e
	tcoa-15	f	f	e	e	e	f
	taec-14	e	e	e	e	e	f
M$_2$L ⇌ M$_2$L(OH) + H$^+$	tcoa-14	<6.6	f	6.8(1)	5.43(4)	5.8(1)	8.3(1)
	tcoa-15	f	f	7.7(1)	7.5(1)	7.6(2)	f
	taec-14	7.3(1)	9.0(1)	7.65(5)	<5.3	<6.6	f
M$_2$L(OH) ⇌ M$_2$L(OH)$_2$ + H$^+$	tcoa-14	10.22(5)	f	9.8(2)	9.9(1)	10.5(1)	8.9(2)
	tcoa-15	f	f	8.9(2)	9.0(2)	9.8(2)	f
	taec-14	e	e	e	e	e	f

[a] Determined by glass-electrode potentiometry at 25 °C in water at constant ionic strength (I = 0.1 M NEt$_4$ClO$_4$). A value of 13.7(1) was obtained for the apparent pK_w under these conditions. [b] With tcoa-14 the background electrolyte was changed to 0.1 M NaNO$_3$ to avoid precipitation. [c] Charges are omitted for clarity. [d] Data for taec-14 are taken from ref. 13. [e] Reaction not observed. [f] Not measured. [g] This upper bound was determined on the basis that if the stability constant was greater than, or equal to, this value then, under the conditions of the titration (ca. 10^{-3} M concentrations of reactants), the corresponding metal complex would become 5% or more of the total metal concentration at some stage during the titration. At these concentrations it would have been necessary to include the constant in our model to achieve a satisfactory correlation between the experimental and theoretical titration curves. [h] Stepwise constant cannot be given as the ML species was not observed; log$_{10}$ β values are 13.9(1) for Co^{2+} and <19.6 for Zn^{2+}.
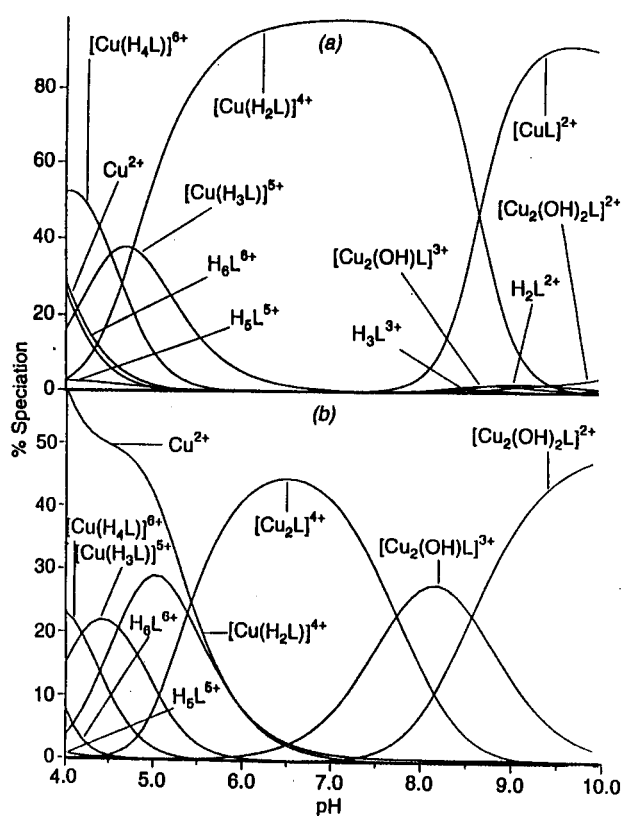

Fig. 4 Speciation diagrams for the copper(II)–L system (10^{-3} M), where L = tcoa-15. Details as in Fig. 3

plex [Cu$_2$(taec-16)][ClO$_4$]$_4$, which is unusual in having a boat structure without a bridging anion. The separation increases to 5.54 Å when N$_3^-$ bridges, in the 1,3 orientation, giving [Cu$_2$(N$_3$)(taec-16)[ClO$_4$]$_3$.[15]

To establish the intermetallic separation in the tcoa-14 and/or -15 dicopper complexes attempts were made to grow crystals suitable for structural analysis by X-ray diffraction. These attempts were only partially successful and because of disorder in all the crystals examined led only to a less than optimum solution of the crystal and molecular structures of [Cu$_2$Cl$_2$(tcoa-14)]Cl$_2$. Whilst this structure cannot be reported in full, it was sufficiently well refined to establish the atom connectivity, gross structure, and interatomic distances to ± 0.1 Å. An ORTEP[28] diagram is shown in Fig. 2. The complex cation occurs in the boat configuration with an intermetallic separation of 5.24 ± 0.1 Å. The long Cu···Cu separation and the probable greater rigidity of the complex, compared to comparable monocyclic structures, appear to explain the inability of the complex to accommodate bridging anions with high stability.

The location of the chloride ions in the structure is quite different to anything observed previously in complexes of this type: the two chloride ions are located at external apical sites of square-pyramidal copper(II) ions and have Cu–Cl separations of 2.7 ± 0.1 Å. These distances are within the limits of Cu–Cl separations (2.4–3.2 Å) listed in the Cambridge Crystallographic Data Base[29] that are identified with apical chloride bonding in square-pyramidal copper(II) complexes having a tetraazamacrocycle at the base. Each copper(II) ion lies significantly out of the least-squares plane of its four nitrogen donors towards the Cl atom.
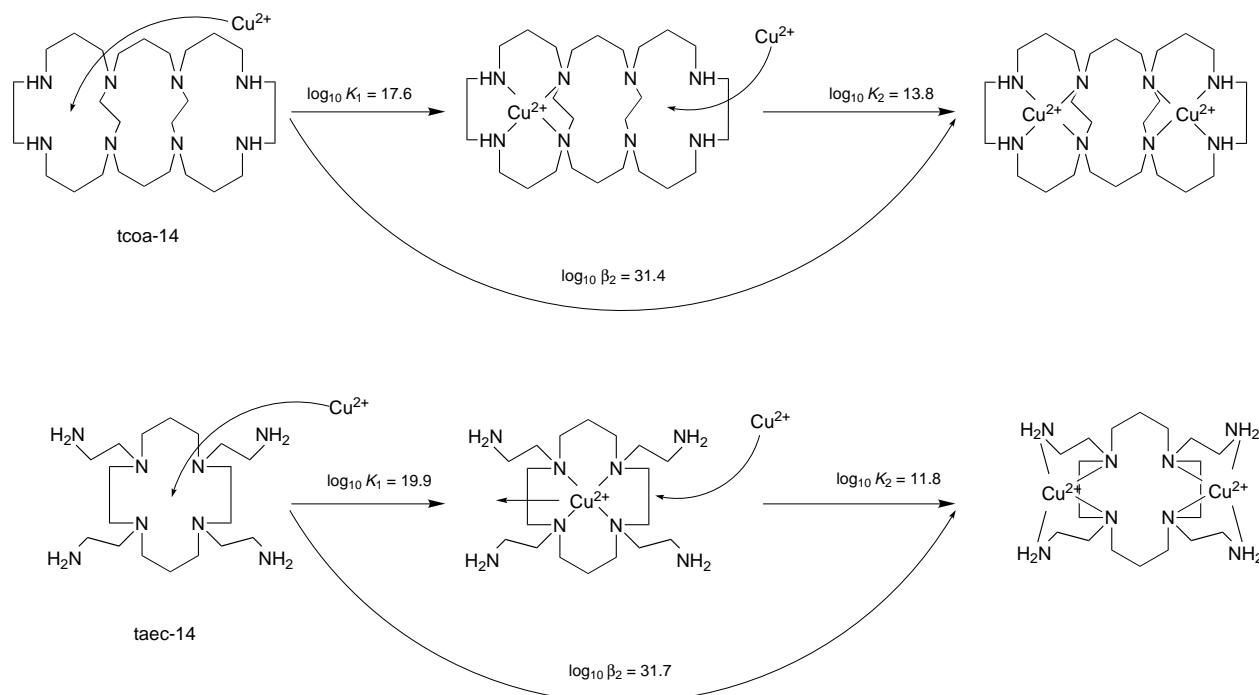
Scheme 4 Sequence of metal ion ingress into tcoa-14 and taec-14 that is suggested by the formation constant measurements

Formation constant measurements

Glass-electrode potentiometric titration of protonated tcoa-14 or -15 with NEt_4OH or NaOH, respectively, in the presence of an M^{2+} cation (M = Co, Cu, Zn, Cd or Pb)† revealed the occurrence, in aqueous solution at differing pH, of both mono- and bi-metallic species. The full set of species observed for each metal ion can be seen in Table 3, together with the corresponding stepwise formation constants. For copper(II) the speciation is displayed diagrammatically in Figs. 3 and 4.

All the bimetallic complexes undergo two stages of hydrolysis forming first the mono- and then the di-hydroxo species. This contrasts with the situation with taec-14 where only the monohydroxo species is seen,[13] and parallels the behaviour, noted above, whereby the tcoa-14 and -15 complexes bind up to two anions in terminal positions while bimetallic taec-14 complexes bind just one, in the intramolecular bridging position.

When comparing the stepwise formation constant for the ML species with the stepwise constant for M_2L, within our data set shown in Table 3, two situations can be seen: the constant either undergoes a large decrease, of between 6.1 and 9.3 orders of magnitude (six cases), or a smaller decrease of between 4.2 and 3.4 orders of magnitude (five cases). The first situation occurs with all the taec-14 complexes, strongly suggesting that the first metal ion enters the central compartment of the ligand, as it is the only cyclic cavity available, and that entry of the second metal ion, which must be into an outer compartment, causes displacement of the first into the other outer compartment. The second situation occurs only with tcoa-14 or -15 complexes and suggests that when confronted with these ligands the first metal ion usually enters one of the outer compartments, presumably to take advantage of the secondary amino donors, leaving the second metal ion to enter the other equivalent cavity (Co^{2+} with tcoa-14 and Cu^{2+} and Cd^{2+} with tcoa-15 appear to be exceptions to this). This is shown in Scheme 4. The net result is that the overall formation constants for the M_2L species are quite similar, irrespective of whether the ligand is tri- or mono-cyclic.

Conclusion

The findings presented here indicate that octaazamacrocycles consisting of three fused macrocyclic rings have the ability to form bimetallic complexes in which the two outer compartments are occupied by the metal ions. Although they can adopt a boat conformation, their rigidity may result in the intermetallic distance being too long for intramolecular binding of anions between the two metal ions. This appears to be the case when the outer rings are 14- or 15-membered. The overall formation constants for the bimetallic complexes of tcoa-14 and -15 are not substantially different to those displayed by taec-14, which is a comparable monocyclic octaaza ligand.

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† Equilibration times for Ni^{2+} with both tcoa-14 and -15 and with Co^{2+} and tcoa-15 were too long to allow the acquisition of useful data by this method, and tcoa-15 with Pb^{2+} led to precipitation early in the titration, irrespective of whether a perchlorate- or nitrate-containing background electrolyte was used.

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