DALTON

Binuclear copper complexes of bis(1,4,7-triazacyclonon-1-yl) ligands incorporating acetate pendant arms†

Fiona H. Fry,[a] Bim Graham,[a] Leone Spiccia,*[,a] David C. R. Hockless[b] and Edward R. T. Tiekink[c]

[a] *Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia*
[b] *Research School of Chemistry, Australian National University, Canberra, ACT, 0200, Australia*
[c] *Department of Chemistry, University of Adelaide, South Australia, 5005, Australia*

Two new bis(pentadentate) compounds, 1,2-bis[4,7-bis(carboxymethyl)-1,4,7-triazacyclonon-1-yl]ethane (L^1) and 1,4-bis[4,7-bis(carboxymethyl)-1,4,7-triazacyclonon-1-yl]butane (L^2), have been prepared by functionalisation of the corresponding alkyl-bridged bis(macrocycles) with acetate pendant arms. Their binuclear copper(II) complexes have been prepared and characterised by X-ray crystallography. Both $[Cu_2L^1]\cdot 5H_2O$ and $[Cu_2L^2]\cdot 2H_2O$ are centrosymmetric about the alkyl bridge with the pentadentate compartments hosting the copper(II) centres oriented away from one another. Each Cu^{II} exhibits distorted square-pyramidal geometry with an N_2O_2 basal plane and an apical N atom.

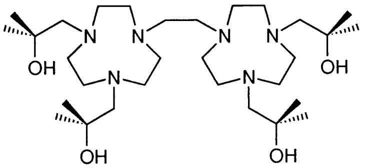
Interest in the synthesis and complexation properties of compounds comprising linked 1,4,7-triazacyclononane (tacn) macrocycles has expanded considerably over the last two decades.[1–10] It is well established that they are ideally suited to producing polynuclear complexes of high kinetic and thermodynamic stability, whilst leaving two or three co-ordination sites available per metal centre for the attachment of additional ligands or bridge formation. In some cases the resulting complexes find application as models for metallobiosites,[2,4,5] catalytic reagents,[9] and in the study of magnetic interactions between metal centres.[4,6,8,10]

An interesting recent development has been the structural elaboration of alkyl-bridged bis(tacn) compounds through attachment of potentially co-ordinating pendant arms to the secondary nitrogens of the tacn rings.[11,12] Such *N*-functionalisation produces bis(pentadentate) systems which are potentially binucleating, since the two linked pentadentate compartments may host separate metal centres. Variation in the types of pendant groups incorporated into the framework offers a potential means of controlling metal complex stability, selectivity for particular metal ions, as well as the redox potential and stereochemistry of co-ordinated metal ions.[13]

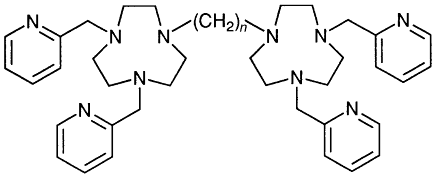
The first example of a pendant arm-bearing bis(tacn) compound, consisting of an ethane-linked bis(tacn) backbone functionalised with tertiary alcohol pendant arms, was reported by Schröder and co-workers[11] in 1994 (structure **A**). Binuclear complexes of Co^{II}, Ni^{II}, Zn^{II} and Cu^{II} with this bis(pentadentate) compound were prepared, with X-ray crystallography revealing a dependency of the overall geometry of the complexes on the extent of deprotonation of the alcohol pendant groups. The two pentadentate compartments of the copper(II) complex were found to adopt a *syn* conformation, due to intramolecular hydrogen bonding between protonated and deprotonated alcohol groups from different compartments of the ligand, whilst the other three binuclear complexes adopted *anti* conformations with all four alcohol groups remaining protonated.

Our group has recently reported the synthesis of three further *N*-functionalised bis(tacn) compounds (structure **B**), obtained by attachment of 2-pyridylmethyl pendant arms to ethane-, propane- and butane-bridged bis(tacn) backbones, and the characterisation of their binuclear copper(II) complexes.[12] The solid-state conformations of the complexes, as determined by X-ray crystallography,[12,14] parallel those found for the copper(II) complexes of the corresponding pendant arm-free bis(macrocycles),[7,15] with the ethane- and butane-bridged complexes both exhibiting *anti* conformations and the propane-bridged complex a *syn* conformation.

In this paper we describe two new polyaminocarboxylate bis(pentadentate) compounds (structure **C**) which have been prepared by the addition of acetate pendant arms to ethane- and butane-bridged bis(tacn) frameworks, respectively. The synthesis and structural characterisation of their binuclear copper(II) complexes are also reported.

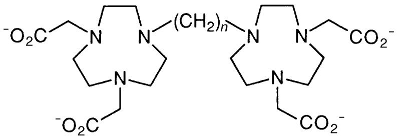


A



B

L^3 $n = 2$
L^4 $n = 3$
L^5 $n = 4$



C

L^1 $n = 2$
L^2 $n = 4$

---

† *Non-SI unit employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Cu–O(1)	1.937(4)	Cu–O(3)	1.936(4)
Cu–N(1)	2.203(4)	Cu–N(2)	2.014(4)
Cu–N(3)	2.000(4)	O(1)–C(7)	1.285(7)
O(2)–C(7)	1.225(7)	O(3)–C(9)	1.290(7)
O(4)–C(9)	1.209(7)	N(1)–C(1)	1.467(7)
N(1)–C(6)	1.484(7)	N(1)–C(11)	1.482(7)
N(2)–C(2)	1.483(7)	N(2)–C(3)	1.500(7)
N(2)–C(8)	1.473(7)	N(3)–C(4)	1.491(7)
N(3)–C(5)	1.482(7)	N(3)–C(10)	1.472(7)
C(11)–C(11′)	1.512(8)		
O(1)–Cu–O(3)	98.2(2)	O(1)–Cu–N(1)	103.5(2)
O(1)–Cu–N(2)	85.6(2)	O(1)–Cu–N(3)	168.9(2)
O(3)–Cu–N(1)	113.1(2)	O(3)–Cu–N(2)	159.6(2)
O(3)–Cu–N(3)	85.4(2)	N(1)–Cu–N(2)	85.2(2)
N(1)–Cu–N(3)	84.5(2)	N(2)–Cu–N(3)	87.5(2)
Cu–O(1)–C(7)	114.3(4)	Cu–O(3)–C(9)	113.0(4)
Cu–N(1)–C(1)	100.3(3)	Cu–N(1)–C(6)	105.9(3)
Cu–N(1)–C(11)	108.9(3)	C(1)–N(1)–C(6)	114.0(5)
C(1)–N(1)–C(11)	113.1(5)	Cu–N(2)–C(2)	110.1(3)
Cu–N(2)–C(3)	101.8(3)	Cu–N(2)–C(8)	104.9(3)
C(2)–N(2)–C(3)	111.4(4)	C(2)–N(2)–C(8)	113.9(5)
C(3)–N(2)–C(8)	113.8(5)	Cu–N(3)–C(4)	108.7(3)
Cu–N(3)–C(5)	105.6(3)	Cu–N(3)–C(10)	102.8(3)
C(4)–N(3)–C(5)	113.2(4)	C(4)–N(3)–C(10)	115.5(5)
C(5)–N(3)–C(10)	109.9(5)		

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Cu–O(1)	1.940(2)	Cu–O(3)	1.939(2)
Cu–N(1)	2.227(3)	Cu–N(2)	2.032(3)
Cu–N(3)	2.005(3)	O(1)–C(8)	1.270(4)
O(2)–C(8)	1.234(4)	O(3)–C(10)	1.295(4)
O(4)–C(10)	1.230(4)	N(1)–C(1)	1.495(4)
N(1)–C(6)	1.475(4)	N(1)–C(11)	1.478(4)
N(2)–C(2)	1.474(4)	N(2)–C(3)	1.509(4)
N(2)–C(7)	1.483(4)	N(3)–C(4)	1.481(4)
N(3)–C(5)	1.517(4)	N(3)–C(9)	1.474(4)
C(12)–C(12′)	1.530(6)		
O(1)–Cu–O(3)	98.9(1)	O(1)–Cu–N(1)	102.7(1)
O(1)–Cu–N(2)	86.0(1)	O(1)–Cu–N(3)	168.2(1)
O(3)–Cu–N(1)	115.5(1)	O(3)–Cu–N(2)	157.4(1)
O(3)–Cu–N(3)	85.0(1)	N(1)–Cu–N(2)	84.5(1)
N(1)–Cu–N(3)	85.3(1)	N(2)–Cu–N(3)	86.2(1)
Cu–O(1)–C(8)	114.2(2)	Cu–O(3)–C(10)	113.9(2)
Cu–N(1)–C(1)	100.2(2)	Cu–N(1)–C(6)	105.3(2)
Cu–N(1)–C(11)	116.4(2)	C(1)–N(1)–C(6)	111.2(3)
C(1)–N(1)–C(11)	110.0(3)	Cu–N(2)–C(2)	110.7(2)
Cu–N(2)–C(3)	100.8(2)	Cu–N(2)–C(7)	104.9(2)
C(2)–N(2)–C(3)	112.0(3)	C(2)–N(2)–C(7)	113.0(3)
C(3)–N(2)–C(7)	114.4(3)	Cu–N(3)–C(4)	109.2(2)
Cu–N(3)–C(5)	104.9(2)	Cu–N(3)–C(9)	104.2(2)
C(4)–N(3)–C(5)	113.5(3)	C(4)–N(3)–C(9)	114.0(3)
C(5)–N(3)–C(9)	110.2(3)	C(11)–C(12)–C(12′)	112.4(4)

Results and Discussion

Preparation of bis(macrocycles)

The acetate pendant arm-bearing bis(macrocycles) **C** were prepared using adaptions of the method described by Wieghardt *et al.*[16] for the synthesis of 1,4,7-tris(carboxymethyl)-1,4,7-triazacyclononane. The hexahydrobromide salts of 1,2-bis(1,4,7-triazacyclonon-1-yl)ethane and 1,4-bis(1,4,7-triazacyclonon-1-yl)butane were treated with an excess of bromoacetic acid in water at 80 °C while maintaining the pH at 11 through periodic addition of base. This facilitated the functionalisation process which was complete after 3–4 d. Attempts to extract the compounds into non-aqueous solvents or to precipitate their sodium or hydrobromide salts were unsuccessful. Thus, the reaction mixtures were used directly in the preparation of the copper(II) complexes.

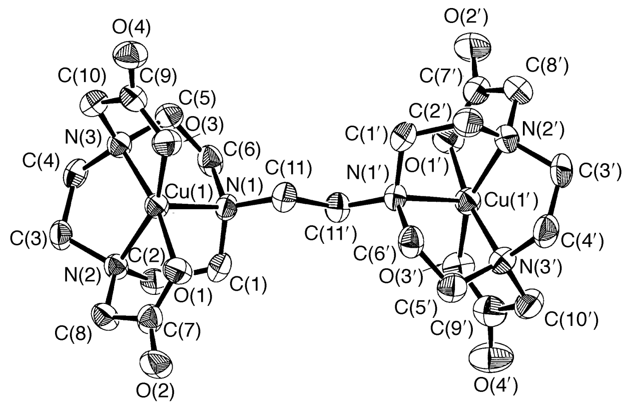


Fig. 1 An ORTEP[17] plot of complex **1** with the atomic labelling scheme

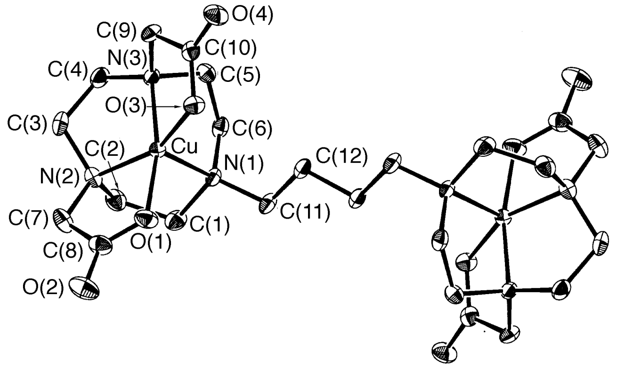


Fig. 2 An ORTEP[17] plot of complex **2** with the atomic labelling scheme

The formation of the bis(macrocycles) was confirmed by recording the ^1H and ^{13}C NMR spectra of the residue obtained on evaporation of reaction mixtures to dryness (in D_2O). The spectra show all the necessary signals and, in addition, those assignable to the conjugate base of glycolic acid (formed by hydrolysis of the excess of bromoacetic acid in alkaline solution). The absence of any other signals indicates that the compounds form cleanly. For example, the ^{13}C NMR spectrum of the L^1 reaction mixture shows signals corresponding to the methylene carbons of the tacn ring and the ethane bridge at δ 50.36, 50.67, 50.86 and 53.18. The methylene carbons of each acetate pendant arm appear further downfield at δ 61.23 due to the deshielding effect of the adjacent carboxyl groups, while a signal at δ 178.45 is attributed to the carboxyl carbons of the acetate arms. The ^{13}C NMR spectrum of the L^2 reaction mixture is similar except that it displays an extra signal at δ 22.35 representing the extra carbons of the butane bridging unit.

Preparation and crystal structures of copper complexes

Addition of 2 molar equivalents of $Cu(NO_3)_2 \cdot 3H_2O$ to the L^1 and L^2 reaction mixtures (adjusted to pH 7) produced dark blue solutions of the copper(II) complexes. Single crystals of the pentahydrate $[Cu_2L^1] \cdot 5H_2O$ **1** and the dihydrate $[Cu_2L^2] \cdot 2H_2O$ **2** were slowly grown from the respective solutions following addition of ethanol and subsequent refrigeration. Details of the solution and refinement of the structures are given in the Experimental section, selected bond lengths and angles in Tables 1 and 2 and views of the molecular structures in Figs. 1 and 2. Both complexes feature two pentadentate compartments which are linked *via* an alkyl bridge between N(1) and N(1′) atoms. In each case these compartments are oriented away from one another so that the complexes display *anti* conformations and are centrosymmetric about the alkyl bridges. This

Table 3 Electronic spectroscopic data for copper(II) complexes

Complex	Solvent	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Chromophore
1	Water	648 (282)	$CuN_3(O_2CR)_2$
2	Water	654 (286)	$CuN_3(O_2CR)_2$
$[CuL^6]$ [a]	Water	640 (155)	$CuN_2S(O_2CR)_2$
$[CuL^7(O_2CPh)(OH_2)]ClO_4$ [b]	MeOH	649 (75)	$CuN_3(O_2CR)(OH_2)$
$[\{CuL^7(OH_2)\}_2(CuL^7)_2(\mu\text{-tftp})_3][ClO_4]_2\cdot 6H_2O$ [c]	MeOH	666 (282)	$CuN_3(O_2CR)(OH_2)$, $CuN_3(O_2CR)_2$
$[\{CuL^7(\mu\text{-bpdc})_n(OH_2)_2\}_n]$ [d]	MeOH	647 (89)	$CuN_3(O_2CR)_2$
$[Cu_2L^3][ClO_4]_4\cdot 2H_2O$ [e]	MeCN	598 (398)	CuN_5
$[Cu_2L^5][ClO_4]_4$ [e]	MeCN	600 (420)	CuN_5

[a] Ref. 20, L^6 = 4,7-bis(carboxymethyl)-1-thia-4,7-diazacyclononane. [b] Ref. 21, L^7 = 1,4,7-trimethyl-1,4,7-triazacyclononane. [c] Ref. 21, tftp = tetrafluoroterephthalate. [d] Ref. 21, bpdc = biphenyl-4,4′-dicarboxylate. [e] Ref. 12.

conformation is probably favoured by steric, electrostatic and electronic factors. It has been observed in the complexes of Co^{II}, Ni^{II} and Zn^{II} with the alcohol pendant arm-bearing analogue of L^1 (ref. 11) and the copper(II) complexes of **B** ($n = 2$ or 4),[12,14] the 2-pyridylmethyl pendant arm-bearing analogues of L^1 and L^2 respectively. As a result of the open structures adopted the intramolecular $Cu\cdots Cu'$ separations for **1** and **2** are 7.511(1) and 8.2962(9) Å, while the shortest intermolecular $Cu\cdots Cu$ distances in the lattices are 6.815(2) and 6.7844(2) Å, respectively.

In both complexes the copper(II) centres are in distorted square-pyramidal environments with basal planes defined by two O atoms, derived from two monodentate carboxylate residues, and two tertiary amine N atoms; the apical position, in each case, is occupied by the bridgehead N(1) amine atom. The mean deviation of the basal atoms from their least-squares plane is 0.084(5) Å for **1** and 0.099(3) Å for **2**, with the Cu^{II} displaced 0.252 and 0.273 Å, respectively, from the plane in the direction of N(1). For both complexes the two Cu–O separations are experimentally equivalent, averaging 1.937(4) Å for **1** and 1.940(2) Å for **2**, whereas the Cu–N distances in the basal plane are, on average, 0.196(8) and 0.209(6) Å shorter than the Cu–N (apical) distances of 2.203(4) and 2.227(3) Å for **1** and **2**, respectively. The pentadentate mode of co-ordination about each Cu^{II} leads to the formation of two CuOCCN and three CuNCCN five-membered rings, each of which is puckered. The N_{cis}–Cu–N_{cis} bond angles for **1** and **2** are all below the 90° expected for an idealised orthogonal square-pyramidal structure, ranging between 83.9(2) and 87.7(2)° for **1** and 84.5(1) and 86.2(1)° for **2**, due to the constraints imposed by the tacn ring in forming three edge-sharing, five-membered chelate rings. The O(3)–Cu(1)–N(3) and O(1)–Cu(1)–N(2) angles are likewise reduced below 90°, averaging 85.5(2) Å for both structures, as a result of the nitrogen- and oxygen-donor atoms forming part of the same five-membered chelate ring.

In the lattices of complexes **1** and **2** there are some significant interactions involving water molecules of crystallisation but not involving the Cu atoms; the closest $Cu\cdots OH_2$ interactions are 3.38 (1) (symmetry operation: $x, y + 1, z$) and 4.455 (4) Å ($x, y, z - 1$) for **1** and **2**, respectively.

Physicochemical characterisation of copper complexes

The molar conductivities of complexes **1** and **2** in water are well below that expected for a 1:1 electrolyte,[18] consistent with their formulation as neutral species. The IR spectra of the complexes both show strong broad bands centred at *ca.* 1620 and 1360 cm^{-1}, which are assigned to the asymmetric and symmetric stretching modes of the carboxylate groups, respectively. The large difference between these stretching frequencies is indicative of unidentate co-ordination of the acetate pendant arms to the Cu^{II}.[19]

Electronic spectroscopic data for complexes **1** and **2** are summarised in Table 3 together with those for related five-co-ordinate square-pyramidal copper(II) complexes. The spectra of **1** and **2** both exhibit a d–d transition centred at *ca.* 650 nm similar to that found for the copper(II) complex of 4,7-bis(carboxymethyl)-1-thia-4,7-diazacyclononane,[20] which contains an $N_2S(O_2CR)_2$ donor set, and a number of copper(II) complexes derived from 1,4,7-trimethyl-1,4,7-triazacyclononane and carboxylic or dicarboxylic acids which contain $CuN_3(O_2CR)(OH_2)^+$ and/or $CuN_3(O_2CR)_2$ chromophores with a $(d_{x^2-y^2})^1$ electronic ground-state configuration.[21] The d–d bands of **1** and **2** are red shifted relative to those of the copper(II) complexes of L^3 and L^5 (ref. 12) due to the weaker ligand field of the carboxylate residues. Intense bands centred at *ca.* 265 nm are also observed in the spectra of complexes **1** and **2**.

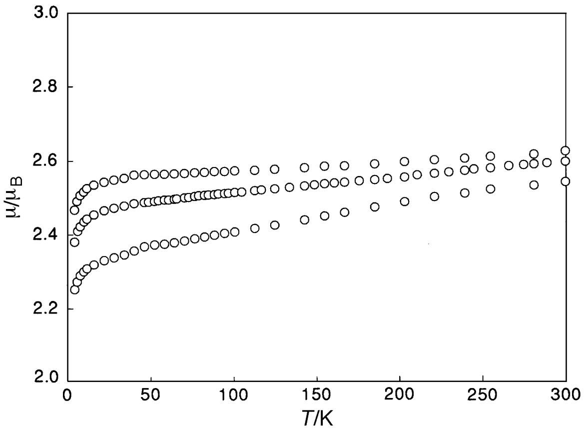


Fig. 3 Temperature dependence of the magnetic moment of three samples of complex **1**

The room-temperature magnetic moments for complexes **1** and **2** are typical of d^9 Cu^{II}. The solid-state magnetic susceptibility plot for **2** over the temperature range 300–4.2 K shows Curie-like behaviour, indicating the absence of any inter- or intra-molecular coupling between copper(II) centres. Susceptibility data for **1** give an indication of weak antiferromagnetic exchange, probably inter- rather than intra-molecular, involving $Cu(RCO_2)\cdots H_2O\cdots (O_2CR)Cu$ pathways. However, attempts to quantify this interaction have been frustrated by irreproducibility in the μ *vs.* *T* data, probably because of the occurrence of variable amounts of a magnetic impurity and/or dehydration effects. Three crystalline bulk samples have been studied, all with rather similar gradual decreases in μ over the range 300–4.2 K (Fig. 3). The room-temperature μ values, however, varied between 2.62 and 2.53 μ_B per Cu_2, whilst corresponding values at 4.2 K varied between 2.47 and 2.25 μ_B. The crystal-structure sample showed $\mu = 2.59$ μ_B per Cu_2 at 300 K and 2.38 μ_B at 4.2 K. Neither binuclear nor chain models would fit the μ *vs.* *T* data but *J* values of *ca.* -0.5 cm^{-1} can be roughly estimated. We note that Wieghardt and co-workers[21] have recently compared intra- and inter-molecular long-range coupling in μ-carboxylato copper(II) systems with emphasis on the effects of intramolecular $O\text{–}H\cdots O$ hydrogen-bonded pathways deriving from $Cu\text{–}OH_2$ and $Cu\text{–}O_2CR$ bonds.

X-Band ESR spectra of complexes **1** and **2**, recorded as frozen ethylene glycol–water solutions, are typical of those found for mononuclear copper(II) complexes with nuclear spin $\frac{3}{2}$, suggesting the absence of any interaction between the copper centres in dilute solution: three of the four expected hyperfine signals are displayed with the fourth being hidden under the $g_\perp$ line. The parameters obtained from the ESR spectra ($g_\parallel = 2.209$, $A_\parallel = 175 \times 10^{-4}$ cm^{-1} and $g_\perp = 2.020$ for **1**; $g_\parallel = 2.232$, $A_\parallel = 177 \times 10^{-4}$ cm^{-1} and $g_\perp = 2.023$ for **2**) are typical of square-pyramidal copper(II) complexes, for which $g_\parallel > g_\perp > 2$, consistent with the geometry found in the crystal structures. Interestingly, the behaviour of **1** is in contrast to that of the binuclear copper(II) complex of L^3.[12] This showed some hyperfine splitting in its ESR spectrum but no deviation in magnetic moment from the spin-only value for Cu^{II} over the range 4.2–300 K, suggestive of a dipolar interaction between the copper(II) centres.

Experimental

Materials and reagents

Reagent or analytical grade materials were obtained from commercial suppliers and used without further purification. Hexahydrobromide salts of 1,2-bis(1,4,7-triazacyclonon-1-yl)ethane[2] and 1,4-bis(1,4,7-triazacyclonon-1-yl)butane[5] were prepared by published methods.

Physical measurements

Proton and carbon NMR spectra were recorded for D_2O solutions on a Bruker AC200 spectrometer, infrared spectra on a Perkin-Elmer 1600 FTIR spectrophotometer as KBr pellets and electronic spectra on a Cary 3 spectrophotometer. Electron microprobe analyses were made with a JEOL JSM-1 scanning electron microscope through an NEC X-ray detector and pulse-processing system connected to a Packard multichannel analyser. Microanalyses were performed by Chemical and Micro-Analytical Services (CMAS), Melbourne, Australia. X-Band ESR spectra were measured on a Bruker ECS 106 spectrometer as frozen (99 K) ethylene glycol–water solutions. Conductivity measurements were made for aqueous solutions using a Crison 522 conductimeter with platinum-black electrodes. Standard KCl (0.020 mol dm^{-3}) with a conductivity of 2.77 mS cm^{-1} was used as a calibrant. Room-temperature magnetic moments were determined by the Faraday method. Diamagnetic corrections were made using Pascal's constants. Variable-temperature magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID magnetometer as described in ref. 22.

Preparations

1,2-Bis[4,7-bis(carboxymethyl)-1,4,7-triazacyclonon-1-yl]ethane L^1. A solution of 1,2-bis(1,4,7-triazacyclonon-1-yl)ethane hexahydrobromide (4.35 g, 5.66 mmol) and bromoacetic acid (4.70 g, 33.8 mmol) dissolved in water (10 cm^{-3}) was heated to 80 °C and solid sodium hydroxide pellets added until the pH was ≈11. Sodium hydroxide solution (2 mol dm^{-3}) was then added to adjust the pH to 11 and to maintain it at this level during functionalisation. After 3 d the pH remained constant over a 12 h period without addition of further base, and the reaction was judged to be complete. A series of attempts to extract the product into chloroform or diethyl ether from the reaction mixture at pH 2, 4, 7 and 11 were unsuccessful, as were attempts to isolate a crystalline sodium or hydrobromide salt by addition of concentrated sodium hydroxide solution or hydrobromic acid to evaporated portions of the reaction mixture. A portion of the reaction mixture was evaporated to dryness *in vacuo* and dried over phosphorus pentaoxide for several days so that NMR analysis could be undertaken of the reaction products. δ_H(200.13 MHz, D_2O) 2.83 (8 H, s, tacn ring CH_2), 2.88 (16 H, br, tacn ring CH_2), 3.03 (4 H, s, bridge CH_2) and 3.40 (8 H, s, acetate CH_2); δ_C(50.32 MHz, D_2O) 50.36, 50.67, 50.86, 53.18 (tacn ring and bridge CH_2), 61.23 (acetate CH_2) and 178.45 (acetate CO_2).

1,4-Bis[4,7-bis(carboxymethyl)-1,4,7-triazacyclonon-1-yl]butane L^2. The method outlined for the preparation of L^1 was employed except that 1,4-bis(1,4,7-triazacyclonon-1-yl)butane hexahydrobromide (3.00 g, 3.76 mmol) and bromoacetic acid (3.15 g, 22.7 mmol) were used as the starting materials. δ_H(200.13 MHz, D_2O) 1.74 (4 H, br, centre of bridge CH_2), 2.82 (8 H, s, tacn ring CH_2), 2.99 (8 H, t, tacn ring CH_2), 3.08 (12 H, br, tacn ring and bridge CH_2) and 3.39 (8 H, s, acetate CH_2); δ_C(50.32 MHz, D_2O) 22.35 (centre of bridge CH_2), 48.88, 50.41, 51.06, 55.41 (tacn ring and bridge CH_2), 61.46 (acetate CH_2) and 179.07 (acetate CO_2).

$[Cu_2L^1]\cdot 5H_2O$ 1. To a portion of the aqueous L^1 reaction mixture (1.9 mmol, assuming quantitative yield), adjusted to pH 7, was added $Cu(NO_3)_2\cdot 3H_2O$ (0.91 g, 3.8 mmol) with stirring. The solution turned deep blue immediately, suggestive of complex formation. The pH was readjusted to 7 using sodium hydroxide solution (1 mol dm^{-3}) and the volume reduced to approximately 10 cm^{-3}. Absolute ethanol (80 cm^{-3}) was then added and the solution cooled to 4 °C. After 1 week the dark blue crystals of complex **1** which formed were collected, washed with ethanol and ether and left to air-dry (0.73 g, 61%) (Found: C, 36.1; H, 6.7; N, 11.6. $C_{22}H_{46}Cu_2N_6O_{13}$ requires C, 36.2; H, 6.4; N, 11.5%); $\tilde{\nu}_{max}$/cm^{-1} 3417s (OH), 1625s (CO_2) and 1358m (CO_2); λ_{max}/nm (water) 266 and 648 (ε/dm^3 mol^{-1} cm^{-1} 5910 and 282); electron microprobe Cu present, Br absent; μ_{eff}(294 K) = 1.79–1.85 μ_B per Cu^{II}; Λ_M (water) = 25 S cm^2 mol^{-1}.

$[Cu_2L^2]\cdot 2H_2O$ 2. The method used to prepare compound **1** was followed except that $Cu(NO_3)_2\cdot 3H_2O$ (0.62 g, 2.6 mmol) and a portion of the L^2 reaction mixture (1.3 mmol, assuming quantitative yield) were used. Dark blue crystals of **2** were obtained (0.59 g, 65%) (Found: C, 40.0; H, 6.4; N, 11.6. $C_{24}H_{44}Cu_2N_6O_{10}$ requires C, 40.1; H, 6.3; N, 11.9%); $\tilde{\nu}_{max}$/cm^{-1} 3427s (OH), 1618s (CO_2) and 1366m (CO_2); λ_{max}/nm (water) 267 and 654 (ε/dm^3 mol^{-1} cm^{-1} 7320 and 286); electron microprobe Cu present, Br absent; μ_{eff}(294 K) = 1.92 μ_B per Cu^{II}; Λ_M (water) = 21 S cm^2 mol^{-1}.

Crystallography

Intensity data for deep blue plate crystals of complex **1** (dimensions 0.32 × 0.20 × 0.06 mm) and **2** (0.45 × 0.24 × 0.07 mm) were measured at 296 K on a Rigaku AFC6R diffractometer fitted with graphic-monochromated Cu-Kα radiation for **1** and Mo-Kα radiation for **2**. Cell constants were obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections. For both complexes the data were collected using the ω–2θ scan technique. No decomposition of the crystals occurred during data collection (three standard reflections showed no significant variation in intensity) and only absorption-corrected data[23] which satisfied the criterion $I \geqslant 3.0\sigma(I)$ were used in the subsequent analyses. Crystal parameters and details of the data collection and refinement for **1** and **2** are summarised in Table 4.

The structures were solved by direct methods (SIR 92 for **1**,[24] SHELXS 86 for **2**[25]) and refined by a conventional full-matrix least-squares procedure based on *F*.[26] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the models at their calculated positions (C−H 0.97 Å). For complex **1** the hydrogen atoms of the O(04) and O(05) water molecules could not be located, while for **2**, none of the water-bound hydrogens were located. Scattering

Table 4 Crystallographic data for complexes **1** and **2**

	1	**2**
Formula	$C_{22}H_{46}Cu_2N_6O_{13}$	$C_{24}H_{44}Cu_2N_6O_{10}$
M	729.73	703.74
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	13.578(2)	7.559(1)
b/Å	15.023(2)	14.734(2)
c/Å	14.800(3)	6.7844(7)
α/°		91.53(1)
β/°	104.34(2)	102.82(1)
γ/°		99.92(1)
U/Å^3	2924.7(9)	724.1(2)
Z	4	1
D_c/g cm^{-3}	1.657	1.614
λ/Å	1.541 78 (Cu-Kα)	0.710 73 (Mo-Kα)
F(000)	1528	368
μ/cm^{-1}	24.55	15.34
Transmission factor range	0.6146–1.0000	0.947–1.025
$2\theta_{max}$/°; *hkl* data collected	120.7; $\pm h, +k, -l$	55.0; $+h, \pm k, \pm l$
No. data measured	4767	3597
No. unique data	4573	3343
No. observed data [$I \geqslant 3.0\sigma(I)$]	3275	2588
No. parameters refined	389	190
R[a]	0.047	0.038
R'[b]	0.055	0.039
Goodness of fit	2.85	2.00
Maximum Δ/σ	<0.01	<0.001
Maximum Δρ/e Å^{-3}	0.58	0.45

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, where $w = [\sigma^2(F_o)]^{-1}$.

factors for all atoms were those incorporated in the TEXSAN program.[26] Molecular plots were generated using the ORTEP program[17] with 50 and 35% probability ellipsoids, respectively.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/369.

Acknowledgements

We are grateful to Drs. B. Moubaraki and K. S. Murray for their assistance with magnetic susceptibility measurements. This work was supported by the Australian Research Council. B. G. and F. H. F. are both recipients of an Australian Postgraduate Award.

References

1 N. Tanaka, Y. Kobayashi and S. Takamoto, *Chem. Lett.*, 1977, 107.
2 K. Wieghardt, I. Tolksdorf and W. Herrmann, *Inorg. Chem.*, 1985, **24**, 1230.
3 G. R. Weisman, D. J. Vachon, V. B. Johnson and D. A. Gronbeck, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 886.
4 H. Chang, H. Diril, M. J. Nilges, X. Zhang, J. A. Potenza, H. J. Schugar, D. N. Hendrickson and S. S. Isied, *J. Am. Chem. Soc.*, 1988, **110**, 625.
5 J. L. Sessler, J. W. Sibert and V. Lynch, *Inorg. Chem.*, 1990, **29**, 4143.
6 J. L. Sessler, J. W. Sibert, A. K. Burrell, V. Lynch, J. T. Markert and C. L. Wooten, *Inorg. Chem.*, 1993, **32**, 4277.
7 X. Zhang, W.-Y. Hsieh, T. N. Margulis and L. J. Zompa, *Inorg. Chem.*, 1995, **34**, 2883.
8 L. Behle, M. Neuburger, M. Zehnder and T. A. Kaden, *Helv. Chim. Acta*, 1995, **78**, 693.
9 M. J. Young and J. Chin, *J. Am. Chem. Soc.*, 1995, **117**, 10577.
10 P. D. Beer, M. G. B. Drew, P. B. Leeson, K. Lyssenko and M. I. Ogden, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 929.
11 A. J. Blake, T. M. Donlevy, P. A. England, I. A. Fallis, S. Parsons and M. Schröder, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1981.
12 S. J. Brudenell, L. Spiccia and E. R. T. Tiekink, *Inorg. Chem.*, 1996, **35**, 1974.
13 P. Chaudhuri and K. Wieghardt, *Prog. Inorg. Chem.*, 1987, **35**, 329; R. Bhula, P. Osvath and D. C. Weatherburn, *Coord. Chem. Rev.*, 1988, **91**, 89; P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.
14 S. J. Brudenell, L. Spiccia and D. C. R. Hockless, unpublished work.
15 G. D. Fallon, B. Graham and L. Spiccia, unpublished work.
16 K. Wieghardt, U. Bossek, P. Chaudhuri, W. Herrmann, B. C. Menke and J. Weiss, *Inorg. Chem.*, 1982, **21**, 4308.
17 C. K. Johnson, ORTEP II, Report ORNL-5136, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
18 W. J. Moore, *Physical Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 4th edn., 1972.
19 G. B. Deacon and F. Huber, *Inorg. Chim. Acta*, 1985, **104**, 41.
20 D. M. Wambeke, W. Lippens, G. G. Herman and A. M. Goeminne, *J. Chem. Soc.*, *Dalton Trans*, 1993, 2017.
21 K.-S. Bürger, P. Chaudhuri, K. Wieghardt and B. Nuber, *Chem. Eur. J.*, 1995, **1**, 583.
22 G. A. McLachlan, G. D. Fallon, R. L. Martin, B. Moubaraki, K. S. Murray and L. Spiccia, *Inorg. Chem.*, 1994, **33**, 4663.
23 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.
24 A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, SIR 92, *J. Appl. Crystallogr.*, 1993, **26**, 343.
25 G. M. Sheldrick, SHELXS 86, Program for the Automatic Solution of Crystal Structure, University of Göttingen, 1986.
26 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

Received 2nd *September* 1996; *Paper* 6/06021H