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FULL PAPER

Synthesis and characterisation of pendant-arm amino derivatives of 1,4,7-triazacyclononane and alkyl-bridged bis(1,4,7-triazacyclononane) macrocycles and complexation to Cu(II)

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The new pentadentate and bis(pentadentate) ligands 1-methyl-4,7-bis(3-aminopropyl)-1,4,7-triazacyclononane **6** and 1,2-bis[4,7-bis(3-aminopropyl)-1,4,7-triazacyclonon-1-yl]ethane **14** have been synthesised by reaction of acrylonitrile with the corresponding macrocyclic precursors and subsequent reduction of the nitrile groups with BH_3·THF. Cu(II) complexes of the two ligands having formulations [Cu(**6**)][BF$_4$]$_2$ and [Cu$_2$(**14**)][PF$_6$]$_4$·6MeCN, respectively, have been prepared and structurally characterised. Both complexes exhibit distorted square-based pyramidal geometries about the metal centres with the two primary amino groups belonging to the pendant arms occupying basal positions [Cu–N$_{ap}$ 2.257(6), Cu–N$_{eq}$ 2.026(6)–2.074(5) Å for [Cu(**6**)]$^{2+}$, and 2.337(2) and 2.038(3)–2.085(3) Å for [Cu$_2$(**14**)]$^{4+}$]. The binuclear complex [Cu$_2$(**14**)]$^{4+}$ is centrosymmetric about the ethane bridge with the two pentadentate compartments oriented away from one another to give a transoid *anti*-configuration with a MeCN molecule interacting with each Cu(II) centre at 2.710(4) Å. Both complexes have also been characterised by electronic and EPR spectroscopy and by cyclic voltammetry, and their properties compared to those of Cu(II) complexes of analogous macrocyclic ligands having 2-methylpyridyl pendant arms.

Introduction

The co-ordination chemistry of the nine-membered ring crown [9]aneN$_3$ (1,4,7-triazacyclononane) has been well studied over the last twenty years,[1–3] with sandwich complexes of general formula [M([9]aneN$_3$)$_2$]$^{x+}$ well known for their kinetic and thermodynamic stability. More recently, *N*-functionalisation of [9]aneN$_3$[4] *via* incorporation of three pendant N,[5] O,[6] S[7] and P-donor[8] groups has afforded a variety of hexadentate ligands which can confer remarkable stability upon metal centres, thereby controlling their co-ordination geometries and oxidation states. However, there have been fewer reports on selectively functionalised derivatives of [9]aneN$_3$ having only one or two pendant donors[9,10] or with "innocent" alkyl substituents,[11] reflecting the synthetic difficulties typically encountered for this type of ligand. In this context, functionalised pendant-arm derivatives of [9]aneN$_3$ leading to the formation of potentially five co-ordinate metal complexes are of particular interest since they offer the possibility of binding and activating small molecules at the co-ordinatively unsaturated metal centre, so providing the basis for models of the active sites of biological systems or catalytic reagents.[9,10] In this regard, ligands comprising two alkyl-bridged [9]aneN$_3$ moieties have attracted a great attention in the last few years as they can afford kinetically and thermodynamically stable polynuclear complexes having two or three co-ordination sites on each metal centre available for additional ligands or bridge formation.[12–15] A further development has been the attachment of functionalised pendant arms to the secondary nitrogen atoms of the bis(1,4,7-triazacyclonon-1-yl) ligands to give bis(pentadentate) systems capable of hosting separate metal centres, mostly Cu(II), within five-co-ordinating compartments lying in close proximity to one another.[16–19] However, bis(pentadentate) ligands of this type are quite rare and only alcohol,[16] acetate[17] and 2-pyridylmethyl[18,19] pendant arms have been incorporated into the alkyl-bridged bis([9]aneN$_3$) framework. We report herein the synthesis and characterization of two new pentadentate ligands **6** and **14** formally derived from 1-methyl-1,4,7-triazacyclononane **4** and 1,2-bis(1,4,7-triacyclonon-1-yl)ethane **12**, respectively, by attaching 3-aminopropyl pendant arms to the secondary nitrogen atoms. The complexation behaviour of these two ligands towards Cu(II) has been investigated and the complexes [Cu(**6**)][BF$_4$]$_2$ and [Cu$_2$(**14**)][PF$_6$]$_4$·6MeCN have been synthesised and characterised by X-ray diffraction studies, cyclic voltammetry and EPR spectroscopy.

Results and discussion

The preparation of 1-methyl-4,7-bis(3-aminopropyl)-1,4,7-triazacyclononane **6** is summarised in Scheme 1. Two alternative synthetic routes have been followed, both of which use 1,4,7-tris(*p*-tolylsulfonyl)-1,4,7-triazacyclononane **1**[20] as starting material. The first route consists of two main steps: selective mono-methylation of [9]aneN$_3$ to give 1-methyl-1,4,7-triazacyclononane **4** and subsequent functionalisation of the remaining two nitrogen centres. In particular, compound **4** has been prepared in 54% yield from 1,4-bis(*p*-tolylsulfonyl)-1,4,7-triazacyclononane **2** [obtained from **1** according to the procedure reported by Sessler *et al.*[21] (see Scheme 1)], by methylation with formic acid (98%) and paraformaldehyde (35 wt% aq)[22] and subsequent detosylation of the resulting compound **3** with concentrated H_2SO_4.[21] Michael addition of acrylonitrile[23] to **4** affords 1-methyl-4,7-bis(2-cyanoethyl)-1,4,7-triazacyclononane **5** in 74% yield; the conversion to the desired compound **6** is achieved in high yield by reduction of **5** with BH_3·THF in THF solution and subsequent purification of the hydrochloridic salt of **6** by using an ion-exchange resin (Dowex-1X8-200). The second synthetic route to **6** consists of conversion of [9]aneN$_3$ into its orthoamide derivative, 1,4,7-triazatricyclo-[5.2.1.0^{4,10}]decane **8**,[24] and subsequent hydrolysis in dilute hydrochloric acid to afford OHC[9]aneN$_3$ **9**.[11c] Reaction of **9** with acrylonitrile gives **10** in 80% yield which can be converted quantitatively to **6** by simultaneous reduction of the formyl and the two nitrile groups with BH_3·THF in THF solution. The two synthetic procedures used for the preparation of the new ligand

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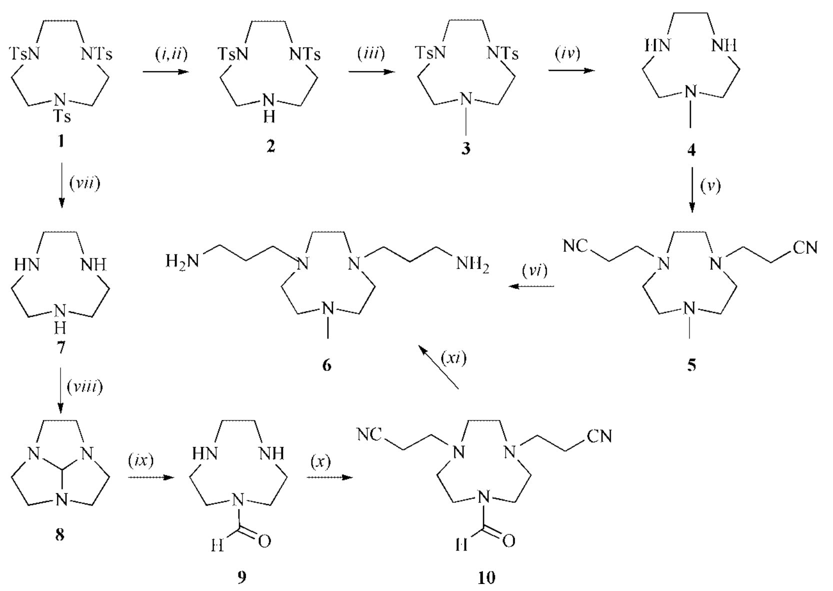
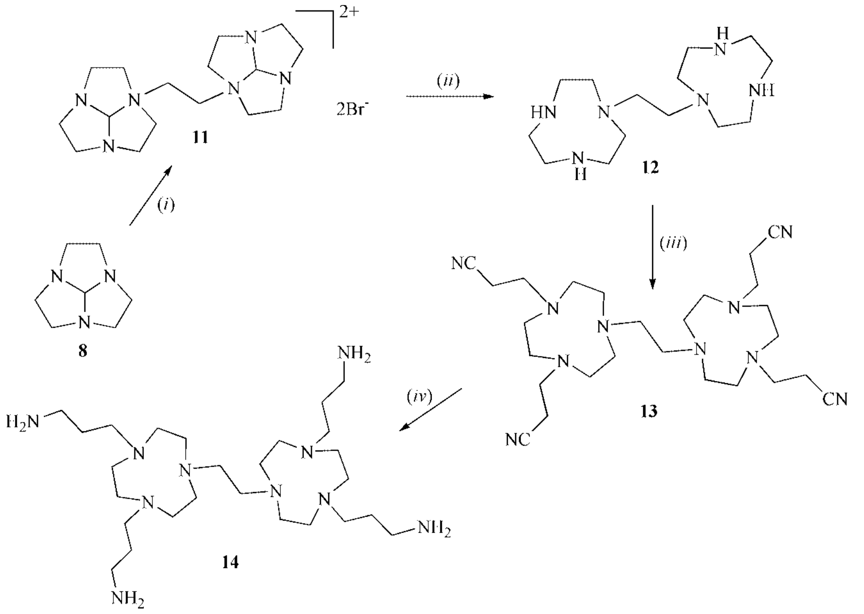


Scheme 1 *Reagents and conditions*: (*i*) HBr–MeCO$_2$H, phenol, 90 °C, 36 h (30% yield); (*ii*) NaOH (7.5 M)/TsCl, Et$_2$O, r.t., 3 h (100% yield); (*iii*) HCO$_2$H (98%)–HCOH (35 wt% aq), reflux, 24 h (100% yield); (*iv*) H$_2$SO$_4$ conc., 90 °C, 48 h (54% yield); (*v*) acrylonitrile, reflux, 24 h (74% yield); (*vi*) 1) BH$_3$·THF (THF solution), reflux, 48 h; 2) HCl (2 M), reflux, 24 h (97% yield); (*vii*) 1) H$_2$SO$_4$ conc., 90 °C, 48 h, HBr; 2) NaOH, toluene, reflux, 24 h (61% yield); (*viii*) (MeO)$_2$CHNMe$_2$, reflux, 5 h (85% yield); (*ix*) HCl, r.t., 8 h (45% yield); (*x*) acrylonitrile, reflux, 24 h (80% yield); (*xi*) 1) BH$_3$·THF (THF solution), reflux, 48 h; 2) HCL (2 M), reflux, 24 h (100% yield).



Scheme 2 *Reagents and conditions*: (*i*) 1,2-dibromoethane, MeCN, r.t., 12 h (80% yield); (*ii*) 1) water, reflux, 3 h; 2) EtOH–KOH, reflux, 2 days (74% yield); (*iii*) acrylonitrile, reflux, 12 h, (100% yield); (*iv*) 1) BH$_3$·THF (THF solution), reflux, 48 h; 2) HCl (2 M), reflux, 24 h (99% yield).

6 are characterised by the same number of reaction steps, and they involve the synthesis as intermediates of two new compounds **5** and **10** which could offer interesting co-ordinating properties. However, the second procedure discussed has a higher overall yield starting from **1** (18.5 *vs.* 11.5% for the first procedure).

The method used for the synthesis of 1,2-bis[4,7-bis(3-aminopropyl)-1,4,7-triazacyclonon-1-yl]ethane **14** is summarised in Scheme 2. The ethylene-bridged bis([9]aneN$_3$) **12** was prepared according to the method described by Zompa and co-workers[25] and subsequently adapted by Spiccia and co-workers for the synthesis of xylylene-bridged bis([9]aneN$_3$) ligands.[14] In particular, the reaction of two equivalents of 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane **8** with 1,2-dibromoethane in MeCN affords the bis(amidinium) salt intermediate **11** which is converted 59% yield into the target compound **12** by base hydrolysis. The addition of acrylonitrile to **12** affords quantitatively the nitrile pendant arm derivative **13** which is subsequently transformed in high yield into the desired bis(pentadentate) ligand **14** by reduction with BH$_3$·THF in THF solution followed by acid hydrolysis.

The co-ordination behaviour of the two new pendant arm amino ligands **6** and **14** towards Cu(II) has been studied and the structural and electrochemical properties of the resulting complexes have been compared to those of analogous systems. The complex [Cu(**6**)][BF$_4$]$_2$ can be prepared in good yield from the reaction of **6** with one equivalent of Cu(BF$_4$)$_2$·xH$_2$O in MeCN at room temperature. Green columnar crystals suitable for X-ray diffraction were grown by diffusion of Et$_2$O vapour into a solution of the complex in MeCN. The single crystal X-ray structure of the cation [Cu(**6**)]$^{2+}$ (Fig. 1, Table 1) shows the ligand encapsulating the metal ion in a distorted square-based pyramidal geometry, with the two primary amino groups of the pendant arms occupying basal positions and the apical position taken up by the tertiary amino N(7) atom. The Cu(1)–N(7) vector shows a slight deviation from perpendicularity with the

Table 1 Selected bond distances (Å) and angles (°) for $[Cu(\mathbf{6})][BF_4]_2$

Cu(1)–N(1)	2.074(5)	Cu(1)–N(14)	2.026(6)
Cu(1)–N(4)	2.064(6)	Cu(1)–N(44)	2.044(6)
Cu(1)–N(7)	2.257(6)		
N(1)–Cu(1)–N(4)	85.2(3)	N(4)–Cu(1)–N(14)	171.0(2)
N(1)–Cu(1)–N(7)	81.9(2)	N(4)–Cu(1)–N(44)	94.1(3)
N(1)–Cu(1)–N(14)	90.6(3)	N(7)–Cu(1)–N(14)	103.6(2)
N(1)–Cu(1)–N(44)	175.1(3)	N(7)–Cu(1)–N(44)	102.9(3)
N(4)–Cu(1)–N(7)	83.8(2)	N(14)–Cu(1)–N(44)	89.4(3)

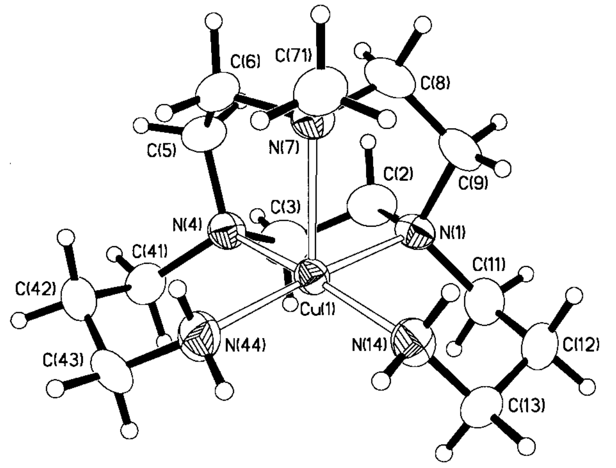


Fig. 1 View of the $[Cu(\mathbf{6})]^{2+}$ cation with the numbering scheme adopted. Displacement ellipsoids are drawn at 50% probability.

basal N_4 plane and the *trans*-basal angles [N(4)–Cu(1)–N(14) 171.0(2), N(1)–Cu(1)–N(44) 175.1(3)°] are in good agreement with the values expected for a square-pyramidal geometry around d^9 Cu(II) complexes.[26] The Cu centre is displaced 0.117 Å out of the mean plane defined by the atoms N(1), N(4), N(14) and N(44) towards the apical nitrogen atom N(7). The Cu(1)–N(7) bond distance [2.257(6) Å] is considerably longer than the other Cu–N bond lengths [2.026(6)–2.074(5) Å], as expected for a square-based pyramidal geometry at Cu(II). Moreover, the Cu–N bond distances in the basal plane involving the tertiary amine N atoms of the $[9]aneN_3$ framework are slightly longer than those involving the primary amine N atoms of the pendant arms in part because of increased steric repulsion at the tertiary amines. However, the Cu–N bond distances in the present complex are comparable with those reported for the Cu(II) complexes of the pentadentate ligands 4,7-bis(2-methylpyridyl)-1,4,7-triazacyclononane [$Cu–N_{ap}$ 2.162(8), $Cu–N_{eq}$ 2.000(8)–2.071(8) Å],[18] 15-thia-1,5,8,12-tetraazabicyclo[10.5.2]-nonadecane [$Cu–N_{eq}$ 2.021(7)–2.064(7) Å][23] and 4,7-bis(2-methylpyridyl)-1-thia-4,7-diazacyclononane [$Cu–N_{eq}$ 2.005(8)–2.037(8) Å][27] which show the same type of co-ordination geometry around the metal centre, although for the last two ligands a sulfur atom occupies the apical position of the distorted square-based pyramid. However, in the case of the 4,7-bis(2-methylpyridyl)-1,4,7-triazacyclononane the apical Cu–N bond is significantly shorter than that observed in $[Cu(\mathbf{6})]^{2+}$. As a consequence of this mode of co-ordination of **6** to Cu(II), one five- and two six-membered chelate rings are formed at the metal centre involving the donor atoms in the basal plane: the five-membered ring adopts a *gauche* conformation with a torsion angle at the central C–C bond of 47.6(10)°, while the six-membered rings adopt chair conformations.

Table 2 Selected bond distances (Å) and angles (°) for $[Cu_2(\mathbf{14})][PF_6]_4·6MeCN$

Cu(1)–N(1)	2.337(2)	Cu(1)–N(44)	2.038(3)
Cu(1)–N(4)	2.066(3)	Cu(1)–N(74)	2.039(3)
Cu(1)–N(7)	2.085(3)	Cu(1)···N(2S)	2.710(4)
N(1)–Cu(1)–N(4)	83.20(10)	N(7)–Cu(1)–N(74)	89.83(11)
N(1)–Cu(1)–N(7)	80.54(9)	N(44)–Cu(1)–N(74)	91.25(11)
N(1)–Cu(1)–N(44)	100.09(10)	N(2S)–Cu(1)–N(4)	86.95(11)
N(1)–Cu(1)–N(74)	100.93(10)	N(2S)–Cu(1)–N(1)	169.66(10)
N(4)–Cu(1)–N(7)	85.18(11)	N(2S)–Cu(1)–N(7)	95.53(11)
N(4)–Cu(1)–N(44)	93.67(12)	N(2S)–Cu(1)–N(44)	83.64(12)
N(4)–Cu(1)–N(74)	172.93(10)	N(2S)–Cu(1)–N(74)	88.56(11)
N(7)–Cu(1)–N(44)	178.62(10)		

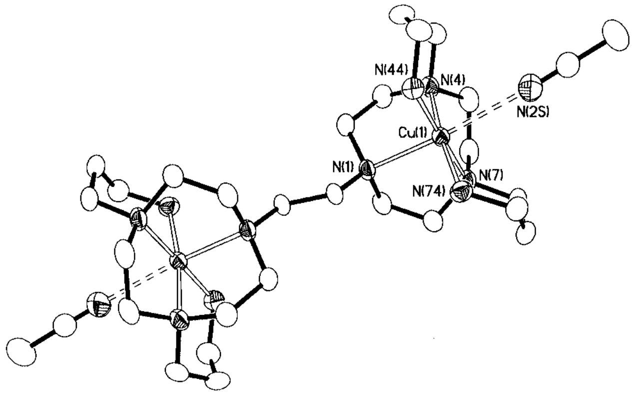


Fig. 2 View of the $[Cu_2(\mathbf{14})]^{4+}$ cation with the numbering scheme adopted. Hydrogen atoms and unco-ordinated acetonitrile molecules are omitted for clarity. Displacement ellipsoids are drawn at 50% probability.

In order to ascertain whether the potentially 10-co-ordinate ligand **14** would bind two Cu(II) ions into the two adjacent five co-ordinating compartments, we treated **14** with 2 equivalents of $Cu(NO_3)_2·6H_2O$ in EtOH at room temperature. The resultant precipitate was dissolved in water and upon addition of an excess of NH_4PF_6 a purple solid was formed. Crystallization from MeCN–Et_2O gave tabular crystals suitable for X-ray diffraction studies. The binuclear cation $[Cu_2(\mathbf{14})]^{4+}$ (Fig. 2, Table 2) lies across a crystallographic inversion centre and can be considered the dimeric form of the complex $[Cu(\mathbf{6})]^{2+}$. In fact, for both pentadentate halves of the ligand the Cu(II) centres are in distorted square-based pyramidal environments with basal planes defined by two tertiary amine N atoms from the $[9]aneN_3$ frameworks and two primary amine N atoms from the pendant arms [$Cu(1)–N_{eq}$ 2.038(3)–2.085(3) Å]. In each half the apical position is occupied by the bridgehead N amine atom N(1) or its symmetric equivalent $N(1^i)$ [Cu(1)–N(1) 2.337(2) Å, i = $-x, -y, -z$]. The Cu centre is displaced by only 0.052 Å out of the mean plane defined by the atoms N(4), N(7), N(44) and N(74), towards the apical nitrogen atom N(1). Considering the basal angles [N(4)–Cu(1)–N(74) 172.93(10), N(7)–Cu(1)–N(44) 178.62(10)°] a value of 9.5% can be calculated for the geometrical parameter τ [$\tau = \{(\theta - \varphi)/60\} \times 100$ where θ and φ are the largest and second largest basal angles, respectively] which, according to Addison *et al.*,[28] should have a value of 0% for a perfect square pyramid and 100% for a perfect trigonal bipyramid structure. The same parameter for $[Cu(\mathbf{6})]^{2+}$ has a value of 6.8% indicating a slightly more regular square-pyramidal geometry for this complex than for its dimeric form. The Cu–N bond distances observed in the $[Cu_2(\mathbf{14})]^{4+}$ complex cation are comparable with those in $[Cu(\mathbf{6})]^{2+}$ but on average are significantly longer than those imposed by the N_5 donor sets derived from bis-(pentadentate) ligands featuring alkyl-bridged bis($[9]aneN_3$) macrocycles with 2-methylpyridyl pendant arms [$Cu–N_{ap}$ 2.18(1)–2.242(5); $Cu–N_{eq}$ 1.97(1)–2.039(5) Å];[18,19] this seems to be in agreement with the 2-methylpyridyl pendant arms preventing the Cu–N bonds from lengthening to the extent shown in $[Cu(\mathbf{6})]^{2+}$ and $[Cu_2(\mathbf{14})]^{4+}$. The same also occurs for the mononuclear complex of Cu(II) with 4,7-bis(2-methylpyridyl)-1,4,7-triazacyclononane for which the $Cu–N_{ap}$ and the $Cu–N_{eq}$

bond distances are significantly shorter than those observed in $[Cu(\mathbf{6})]^{2+}$ (see above). The two pentadentate compartments of **14** bind the Cu(II) centres in an open *anti*-configuration with a Cu···Cu distance of 7.817(2) Å; this seems to be a feature common to most of the binuclear transition-metal complexes reported so far where the ligands are functionalised pendant arm derivatives of alkyl-bridged bis([9]aneN$_3$) macrocycles.[17–19] A *syn*-configuration has been observed in very few cases such as the binuclear Cu(II) complex of the ethane-bridged bis([9]aneN$_3$) with alcohol pendant arms.[16] However, the orientation of the two pentadentate compartments in such compounds is the result of the deprotonation of two of the pendant alcohol groups to form two intramolecular O···H–O bridges between the halves of the binucleating ligand. A similar situation has been observed by Tolman and co-workers[15] in the bis(μ-oxo)dicopper complex of 1,2-bis(4,7-diisopropyl-1,4,7-triazacyclonon-1-yl)ethane in which two oxo groups bridge between the metal centres, forcing the two co-ordinating compartments of the ligand into a *syn*-configuration. In this case the ligand does not have functionalised pendant arms. The *anti*-configuration adopted by the two pentadentate compartments in $[Cu_2(\mathbf{14})]^{4+}$ favours the long-range interaction of a molecule of MeCN at each metal centre (Fig. 2) [Cu(1)–N(2S) 2.710(4) Å N(1)–Cu(1)–N(2S) 169.66(10)°].

The electronic spectra of $[Cu(\mathbf{6})]^{2+}$ and $[Cu_2(\mathbf{14})]^{4+}$ recorded in MeCN at room temperature show only one band in the visible region, at around 570 nm (see Experimental section) with molar extinction coefficients in the range 60–110 dm^3 mol^{-1} cm^{-1} which are typical for a d_{xy}, $d_{yz} \longrightarrow d_{x^2-y^2}$ transition in a Cu(II) ion having square-based pyramidal or distorted square-based pyramidal co-ordinating geometry.[18]

The X-band EPR spectra of the complexes $[Cu(\mathbf{6})]^{2+}$ and $[Cu_2(\mathbf{14})]^{4+}$ were recorded as solid powders and as frozen (77 K) MeCN, MeNO$_2$ and dmf glasses. The EPR spectrum of $[Cu(\mathbf{6})]^{2+}$ measured as a powder shows a rhombic signal with $g_1 = 2.1516$, $g_2 = 2.1023$, $g_3 = 2.0430$ and no hyperfine coupling to the metal centre is observed. In contrast the EPR spectrum recorded for $[Cu_2(\mathbf{14})]^{4+}$ in the solid state shows an isotropic signal with $g_{iso} = 2.0784$. For both complexes the EPR spectra measured as frozen MeCN glasses show isotropic signals with very similar g_{iso} values (2.0712 and 2.0723 for $[Cu(\mathbf{6})]^{2+}$ and $[Cu_2(\mathbf{14})]^{4+}$, respectively). However, in frozen dmf, the EPR spectrum of $[Cu(\mathbf{6})]^{2+}$ is typical of a mononuclear Cu(II) complex with nuclear spin 3/2 and tetragonally distorted or square-based pyramidal co-ordinating geometry with $d^1_{x^2-y^2}$ ground state ($g_\parallel = 2.2101$, $A_\parallel = 182$G, $g_\perp = 2.0534$); a very similar spectrum is observed in frozen MeNO$_2$ and only three of the four hyperfine signals are always observed with the fourth being hidden under the $g_\perp$ line (Fig. 3). The EPR spectrum of $[Cu_2(\mathbf{14})]^{4+}$ recorded in frozen dmf presents additional hyperfine lines in the parallel region (Fig. 3) which, according to Spiccia and co-workers,[18] can be attributed to a weak dipole–dipole interaction between the metal centres in the binuclear complex. Indeed the EPR spectrum does not change on using the non-co-ordinating MeNO$_2$ as solvent, thus excluding the possibility that dmf co-ordination to one of the Cu(II) centres is creating two different environments around the metal centres.

The redox properties of the Cu(II) complexes were monitored by cyclic voltammetry in MeCN solutions (0.1 mol dm^{-1} NBu$^n_4$PF$_6$, 100 mV s^{-1}) at room temperature. Two irreversible reductions were observed at −1.35 and −1.95 V *vs.* Fc/Fc$^+$ for $[Cu(\mathbf{6})]^{2+}$, together with a desorption peak at −0.55 V. Coulometric measurements in MeCN at 298 K under N$_2$ at controlled potential confirm each of the reduction processes to be single-electron transfers with the formation of colourless solutions. Furthermore, a black layer of copper metal is formed on the platinum working electrode after reductive electrolysis at the potential corresponding to the second reduction process in the cyclic voltammogram. For $[Cu_2(\mathbf{14})]^{4+}$ two broad reduction peaks at −1.17 and −2.16 V *vs.* Fc/Fc$^+$ and a desorption peak at −0.61 V are observed in the cyclic voltammogram. Coulometric measurements at controlled potential under the same conditions as for $[Cu(\mathbf{6})]^{2+}$ showed the two reduction processes each to be two-electron transfers with formation of an EPR-silent colourless solution after reductive electrolysis at the potential corresponding to the first reduction process, and a black deposit of Cu(0) metal on the working electrode after reductive electrolysis at the potential corresponding to the second reduction process in the cyclic voltammogram. These data suggest that the two reductions for $[Cu_2(\mathbf{14})]^{4+}$ each involve two one-electron processes at very similar potentials to form Cu(I)Cu(I) and Cu(0)Cu(0), respectively, resulting in complete demetallation of the complex. An analogous hypothesis has been suggested by Spiccia and co-workers[19] to explain the redox behaviour observed for a series of binuclear Cu(II) complexes with differently alkyl-bridged bis([9]aneN$_3$) ligands bearing 2-methylpyridyl pendant arms. However, for each of these complexes only one reversible two-electron reductions process was observed by cyclic voltammetry, in the range −0.71 to −0.80 V *vs.* Fc/Fc$^+$. Moreover, reduction of $[Cu_2(\mathbf{14})]^{4+}$ to the corresponding Cu(I)Cu(I) species occurs less easily than in the systems studied by Spiccia and co-workers;[19] this could indicate either a significant destabilising effect exerted by the amino-functionalised pendant arms on the reduced Cu(I)Cu(I) form of the $[Cu_2(\mathbf{14})]^{4+}$ complex or a stabilising effect of the ligand on the Cu(II) state. The same effect is observed for the mononuclear complex $[Cu(\mathbf{6})]^{2+}$ with respect to its analogues with 2-methylpyridyl pendant arms for which only one reversible reduction peak was observed at −0.81 V *vs.* Fc/Fc$^+$.[19] It is important to note that the reduced binuclear Cu(I)Cu(I) complex $[Cu_2(\mathbf{14})]^{2+}$ is more stable than the reduced mononuclear Cu(I) species $[Cu(\mathbf{6})]^{+}$ indicating, as was suggested by Spiccia and co-workers,[19] that there exists an electrostatic destabilising repulsion between the two Cu(II) centres in this type of binuclear complex which is dependent on the Cu(II)···Cu(II) separation.

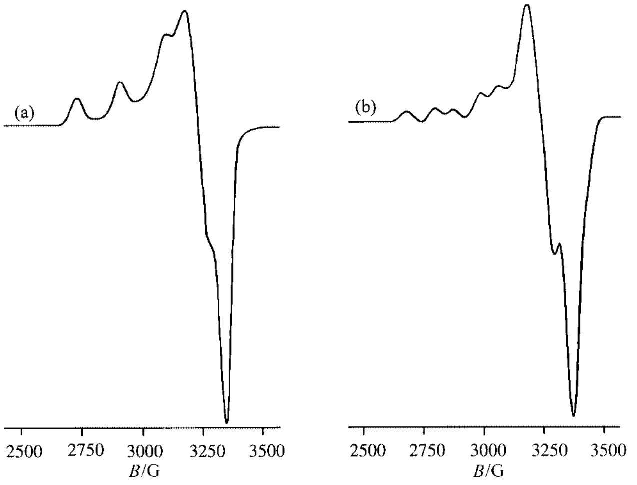


Fig. 3 X-band EPR spectra of the complexes $[Cu(\mathbf{6})]^{2+}$ (a) and $[Cu_2(\mathbf{14})]^{4+}$ (b) as frozen dmf solutions (77 K).

Experimental

Melting points are uncorrected. Microanalyses were performed by the University of Nottingham School of Chemistry Microanalytical Service. IR spectra were recorded as KBr discs using a Perkin-Elmer 598 spectrometer over the range 400–4000 cm^{-1}. NMR spectra (^{1}H and ^{13}C) were recorded at 298 K on a Bruker DPX300 instrument. Fast atom bombardment (FAB) and electron impact mass spectra were run on VG Autospec VG7070E and Kratos MS 50TC spectrometers. UV–VIS spectra were measured in quartz cells using a Perkin-Elmer Lambda 9 spectrophotometer. Electrochemical measurements were performed on a Bruker E310 Universal Modular Polarograph. All readings were taken using a three-electrode potentiostatic system in MeCN freshly distilled from CaH_2 and containing $NBu^n_4PF_6$ as supporting electrolyte (0.1 M). Cyclic voltammetric measurements were carried out using a double platinum electrode and an Ag/AgCl reference electrode in a solution of 0.1 M $NBu^n_4PF_6$ in MeCN with ferrocene as internal standard. Scan rates ranged from 50 to 400 mV s^{-1}. EPR spectra were recorded on a Bruker ER-200D spectrometer. Reagents were obtained from commercial suppliers and used without further purification. All solvents were dried by conventional methods, freshly distilled and degassed. 1,4,7-Tris(*p*-tolylsulfonyl)-1,4,7-triazacyclononane **1**,[20] 1,4,7-triazacyclononane **7**,[20] 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane **8**,[24] 1-formyl-1,4,7-triazacyclononane **9**[11c] and 1,4-bis(*p*-tolylsulfonyl)-1,4,7-triazacyclonanone **2**[21] were prepared by published methods.

1-Formyl-4,7-bis(2-cyanoethyl)-1,4,7-triazacyclononane 10

A mixture of 1-formyl-1,4,7-triazacyclononane **9** (672 mg, 4.27 mmol) and acrylonitrile (30 cm^3) was stirred at 77 °C under an N_2 atmosphere for 12 h. The solvent was removed under reduced pressure to give a yellow oil which solidified on standing at −20 °C. This oil was purified by flash-chromatography on silica gel using THF as eluent to give a white solid (0.90 g, 80% yield). Mp = 84–86 °C. Found (calc. for $C_{13}H_{21}N_5O$): C, 58.90 (59.29); H, 7.80 (7.98); N, 26.50 (26.61%). EI^+ mass spectrum: *m*/*z* = 263 (M^+), 223 ($M^+ - CH_2CN$). δ_H($CDCl_3$, 300 MHz); 2.38–2.47 (4H, m), 2.57–2.63 (2H, m), 2.67–2.73 (2H, m), 2.80–2.91 (6H, m), 3.15–3.20 (2H, m), 3.29–3.34 (2H, m), 3.54–3.60 (2H, m), 8.09 (1H, s, HCO). δ_C($CDCl_3$, 75.5 MHz): 17.09, 17.33, 30.24, 46.72, 50.61, 52.55, 53.47, 54.47, 55.91, 58.73, 118.96, 119.31, 163.70. IR spectrum (KBr disc): ν/cm^{-1} 2933s, 2844s, 2800s, 2244s, 1650s, 1461s, 1422s, 1378s, 1350s, 1322s, 1211m, 1128s, 1055m, 1028s, 978m, 883w, 822w, 728w, 639m, 589w, 539s.

1,4-Bis(*p*-tolylsulfonyl)-7-methyl-1,4,7-triazacyclononane 3

1,4-Bis(*p*-tolylsulfonyl)-1,4,7-triazacyclononane **2** (5 g, 0.0114 mol) was refluxed under N_2 for 24 h with 98% formic acid (30 cm^3) and aqueous paraformaldehyde (45 cm^3, 35% w/w). The mixture was cooled and basified to pH >12 with 15 M aqueous NaOH solution, then extracted with chloroform (5 × 100 cm^3). The combined extracts were dried over $MgSO_4$ and the solvent removed *in vacuo* to yield the product as a white powder (5.14 g, 100% yield). Mp = 206 °C. Found (calc. for $C_{21}H_{29}N_3O_4S_2$): C, 55.35 (55.85); H, 5.98 (6.47); N, 8.78 (9.30%). EI^+ mass spectrum: *m*/*z* = 296 ($M^+ - C_7H_7SO_2$. δ_H(300 MHz, $CDCl_3$): 2.41 (9H, br s, NCH_3, $ArCH_3$), 2.88 (4H, t, *J* = 4.79 Hz, CH_3NCH_2), 3.18 (4H, t, *J* = 4.40 Hz, $CH_3NCH_2CH_2N$), 3.46 (s, 4H, NCH_2CH_2N), 7.30 (4H, d, *J* = 8.0 Hz, $CH_3Ar(H)$), 7.65 (4H, d, *J* = 8.3 Hz, $CH_3Ar(H)$). δ_C(75.5 MHz, $CDCl_3$): 21.42 ($ArCH_3$), 44.75 (CH_3N), 50.66, 52.31, 56.60 (CH_2 ring), 127.16, 129.70 (Ar(CH)), 135.66, 143.36 (Ar(C)). IR spectrum (KBr disc): ν/cm^{-1} 3067w, 2933w, 2844w, 2800w, 1594m, 1494m, 1450s, 1328s, 1155s, 1083s, 1022s, 950s, 883m, 844m, 817m, 750m, 714s, 689s, 638s, 550s, 511m, 472m.

1-Methyl-1,4,7-triazacyclononane 4

A mixture of 1,4-bis(*p*-tolylsulfonyl)-7-methyl-1,4,7-triazacyclononane **3** (5 g, 0.011 mol) and H_2SO_4 (50 cm^3) was stirred at 90 °C under a nitrogen atmosphere for 48 h. The resulting brown solution was cooled in an ice-bath and basified to pH >12 by the cautious addition of a 15 M aqueous solution of NaOH. Extraction with $CHCl_3$ (4 × 250 cm^3) yielded organic layers which were combined and dried over $MgSO_4$. Following removal of solvent, the desired compound was obtained as a white solid (0.85 mg, 54% yield). Found (calc. for $C_7H_{17}N_3$): C, 58.55 (58.62), H, 12.73 (12.98), N, 31.95 (32.06%). EI^+ mass spectrum: *m*/*z* = 144 (MH^+ = 144). δ_H($CDCl_3$, 300 MHz): 2.40 (3H, s, NCH_3), 2.60 (4H, m, CH_2 ring), 2.91 (8H, m, CH_2 ring), 5.71 (2H, br s, NH). δ_C(75.5 MHz, $CDCl_3$, π/2, 3π/4 DEPT): 44.01 (CH_2 ring), 44.23 (NCH_3), 44.86 (CH_2 ring), 52.81 (CH_2 ring).

1-Methyl-4,7-bis(2-cyanoethyl)-1,4,7-triazacyclononane 5

A solution of 1-methyl-1,4,7-triazacyclononane **4** (0.452 g, 3.16 mmol) in acrylonitrile (15 cm^3) was refluxed under nitrogen overnight. The solvent was removed under reduced pressure and the residue treated with charcoal in hot CH_2Cl_2 to give the desired product as a yellow solid (580 mg, 74% yield). Mp 158–160 °C. Found (calc. for $C_{13}H_{23}N_5$): C, 62.55 (62.62); H, 9.15 (9.30); N, 27.85 (28.09%). EI^+ mass spectrum: *m*/*z* = 249 (M^+), 223 ($M^+ - CN$), 195 ($M^+ - C_2H_4CN$), 180 ($M^+ - (CH_3 + C_2H_4CN)$). δ_H($CDCl_3$, 300 MHz): 2.57 (4H, t, *J* = 6.3 Hz), 2.66 (4H, s, NCH_2CH_2N), 2.67 (3H, s, NCH_3), 2.85–2.93 (8H, m), 3.27 (4H, m). δ_C($CDCl_3$, 755 MHz): 17.10, 43.68 (NCH_3), 51.84, 53.96, 54.76, 54.96, 120.63 (CN). IR spectrum (KBr disc): ν/cm^{-1} 2906m, 2826s, 2753m, 2238m, 1501m, 1467s, 1425w, 1360s, 1343m, 1293s, 1245w, 1186s, 1139m, 1089m, 1040m, 1003m, 980w, 897w, 775w, 724w, 605w, 572w.

1-Methyl-4,7-bis(3-aminopropyl)-1,4,7-triazacyclononane 6

This compound was prepared using two different starting materials according to the two procedures outlined below. Procedure (a): a mixture of 1-methyl-4,7-bis(2-cyanoethyl)-1,4,7-triazacyclononane **5** (0.579 g, 2.32 mmol) and BH_3·THF (THF solution, 1 M, 25 cm^3) was refluxed under nitrogen for 48 h. The mixture was cooled and water (40 cm^3) added to destroy excess BH_3. The solvent was removed under reduced pressure and the solid residue was treated with 2 M HCl (75 cm^3) under reflux for 2 h. The solvent was removed under reduced pressure and the residue dried *in vacuo*. The white solid obtained was dissolved in water and the solution passed through ion-exchange resin (Dowex-1X8-200) to give, after removal of solvent, a colourless oil (0.570 g, 97% yield).

Procedure (b): a mixture of 1-formyl-4,7-bis(2-cyanoethyl)-1,4,7-triazacyclononane **10** (850 mg, 3.23 mmol) and BH_3·THF (THF solution, 1 M, 50 cm^3) was refluxed under nitrogen for 48 h. The mixture was cooled and water added to destroy excess BH_3. The solvent was removed under reduced pressure and the solid white residue was treated with 2 M HCl (75 cm^3) under reflux for 2 h. The solvent was removed under reduced pressure and the residue dried *in vacuo*. The white solid obtained was dissolved in water and the solution passed through ion-exchange resin (Dowex-1X8-200) to give, after removal of solvent, a colourless oil (827 mg, 100% yield). EI^+ mass spectrum: *m*/*z* = 144 ($M^+ - 2(CH_2CH_2CH_2NH_2) = 141$), 127 ($M^+ - 2(CH_2CH_2CH_2NH_2) - Me = 126$). δ_H(300 MHz, $CDCl_3$): 1.34 (4H, qnt, *J* = 7.03 Hz, $NCH_2CH_2CH_2NH_2$), 2.10 (3H, s, NCH_3), 2.27 (4H, t, *J* = 7.02 Hz), 2.39 (4H, s, NCH_2CH_2N), 2.43–2.60 (12H, m), 3.33 (br s, NH_2). δ_C(75.5 MHz, $CDCl_3$): 29.56, 31.29, 39.84, 45.63 (NCH_3), 55.41, 56.23, 61.19. IR spectrum (film between KCl discs): ν/cm^{-1} 3333 br s, 2933s, 2811s, 1655m, 1600m, 1455m, 1361m, 1311m, 1100m, 1055m, 989w, 878w.

1,2-Bis[1,4,7-triazacyclonon-1-yl]ethane 12

A solution of 1,2-dibromoethane (3.44 g, 17.5 mmol) in dry MeCN (50 cm^3) was added dropwise to a solution of 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane **8** (5 g, 35 mmol) in dry MeCN (50 cm^3) and the resulting mixture stirred overnight at room temperature. The white precipitate which formed was filtered off, washed with dry acetonitrile and dried under reduced pressure (6.58 g). A portion of this solid (3.8 g) was dissolved

Table 3 Crystallographic data

Compound	[Cu(**6**)](BF_4)$_2$	[Cu_2(**14**)](PF_6)$_4$·6MeCN
Formula	$C_{13}H_{31}B_2CuF_8N_5$	$C_{38}H_{78}Cu_2F_{24}N_{16}P_4$
M	494.59	1466.12
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)
a/Å	9.767(4)	11.786(2)
b/Å	13.341(6)	12.189(2)
c/Å	15.612(5)	12.849(2)
α/°	90	107.220(10)
β/°	90	90.88(2)
γ/°	90	118.530(10)
V/Å^3	2034.3(14)	1521.8(4)
Z	4	1
T/K	150(2)	150(2)
μ(Mo-Kα) mm^{-1}	1.155	0.922
Reflections collected	2428	5904
Unique reflections, R_{int}	2189, 0.010	5364, 0.039
Absorption correction:		
T_{min}, T_{max}	0.522, 0.685	0.493, 0.542
R_1	0.0364 [2095 $F \geq 4\sigma(F)$]	0.0417 [4738 $F \geq 4\sigma(F)$]
wR_2 [all data]	0.0849	0.1108

in water (30 cm^3) and the solution refluxed for 3 h. The solvent was removed *in vacuo* and the resulting white solid dissolved in EtOH (25 cm^3). KOH (6 g, 0.11 mol) was added and the mixture obtained was refluxed for 2 days. After cooling to room temperature, water (25 cm^3) was added to the solution. Extraction with $CHCl_3$ (5 × 30 cm^3), drying of the combined extracts over $MgSO_4$ and removal of the solvent *in vacuo* yielded the product as an oil which crystallised on standing (1.7 g, 74% yield). Found (calc. for $C_{14}H_{32}N_6$): C, 58.85 (59.11); H, 10.88 (11.34); N, 29.35 (29.54%). EI$^+$ mass spectrum: *m*/*z* 284 (M$^+$). δ_H(300 MHz, $CDCl_3$): 2.32 (4H, br s, NH), 2.60 (8H, t, $J = 65$ Hz, ring CH_2), 2.69 (4H, s, bridge CH_2), 2.72 (8H, t, $J = 6$ Hz, ring CH_2), 2.74 (8H, s, ring CH_2). δ_C(75.5 MHz, $CDCl_3$): 47.06, 53.75, 56.23 (ring and bridge CH_2); 47.06 is an accidental equivalence. IR spectrum (KBr disc): ν/cm^{-1} 3442 (NH stretch).

1,2-Bis[4,7-bis(2-cyanoethyl)-1,4,7-triazacyclonon-1-yl]ethane 13

A solution of 1,2-bis(1,4,7-triazacyclonon-1-yl)ethane **12** (1.0 g, 3.5 mmol) in acrylonitrile (5 cm^3) was refluxed under nitrogen for 12 h; the solvent was removed *in vacuo* to give the product as a white solid (1.75 g, 100% yield). Found (calc. for $C_{26}H_{44}N_{10}$): C, 61.98 (62.87); H, 8.45 (8.93); N, 27.88 (28.20%). EI$^+$ mass spectrum: *m*/*z* 497 (M$^+$). δ_H(300 MHz, $CDCl_3$): 2.46 (8H, t, $J = 6.7$ Hz, NCH_2CH_2CN), 2.64 (4H, s, bridging CH_2), 2.80 (24H, m, ring CH_2), 2.88 (8H, t, $J = 6.7$ Hz, NCH_2CH_2CN). δ_C(75.5 MHz, $CDCl_3$): 17.01 (NCH_2CH_2CN), 54.23, 55.81, 55.93, 56.24 (ring and bridging CH_2), 57.14 (NCH_2CH_2CN), 119.28 (CN). IR spectrum (KBr disc): ν/cm^{-1} 2245 (CN stretch).

1,2-Bis[4,7-bis(3-aminopropyl)-1,4,7-triazacyclonon-1-yl]ethane 14

A mixture of 1,2-bis[4,7-bis(2-cyanoethyl)-1,4,7-triazacyclonon-1-yl]ethane **13** (1.0 g, 2.0 mmol) and BH_3·THF (THF solution 1 M, 40 cm^3) was refluxed under N_2 for 24 h. The mixture was cooled and water (80 cm^3) was carefully added to destroy excess BH_3. The solvent was removed under reduced pressure and the resulting solid refluxed for 6 h in 6 M HCl (50 cm^3). The solvent was removed and the residue dried *in vacuo*. The white solid obtained was dissolved in water and the solution passed through ion-exchange resin (Dowex-1X8-200) to give, after removal of the solvent, a colourless oil (1.0 g, 99% yield). EI$^+$ mass spectrum: *m*/*z* 513 (M$^+$). δ_H(300 MHz, $CDCl_3$): 1.64 (8H, qnt, $J = 7.1$ Hz, $NCH_2CH_2CH_2NH_2$), 2.51 (8H, t, $J = 7.2$ Hz, $NCH_2CH_2CH_2NH_2$), 2.54 (4H, s, bridging CH_2), 2.70 (32H, m, ring CH_2, $NCH_2CH_2CH_2NH_2$). δ_C(75.5 MHz, $CDCl_3$): 32.21, ($NCH_2CH_2CH_2NH_2$), 43.76, ($NCH_2CH_2CH_2NH_2$) 53.86, 56.47, 56.84, 56.97 (ring and bridging CH_2), 63.18 ($NCH_2CH_2CH_2NH_2$). IR spectrum (film between KCl discs): ν/cm^{-1} 3382 (NH stretch).

[Cu(6)][BF$_4$]$_2$

A mixture of 1-methyl-4,7-bis(3-aminopropyl)-1,4,7-triazacyclononane **6** (20 mg, 0.078 mmol) and $Cu(BF_4)_2 \cdot xH_2O$ (18.5 mg, 0.078 mmol) in MeCN (6 cm^3) was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue dissolved in the minimum amount of MeCN. Deep blue crystals of diffraction quality were obtained by slow diffusion of Et_2O vapour (20 mg, 52% yield). Mp 220–222 °C. Found (calc. for $C_{13}H_{31}B_2CuF_8N_5$): C, 31.10 (31.57); H, 5.88 (6.31); N, 14.28 (14.16%). FAB mass spectrum (3-nitrobenzyl alcohol (3-NOBA) matrix): *m*/*z* 407, 320; calc. for [^{63}Cu(**6**)(BF_4)]$^+$ and [^{63}Cu(**6**)]$^+$ 407 and 320, respectively. Electronic spectrum: (MeCN) $\lambda_{max} = 574$ nm ($\varepsilon_{max} = 68$ dm^3 mol^{-1} cm^{-1}). IR spectrum (KBr disc): ν/cm^{-1} 3416s, 3332s, 3290s, 3205s, 3125s, 2938m, 2877m, 1614m, 1485m, 1457m, 1302m, 1067s, 908w, 778m, 734m, 578w, 521m.

[Cu$_2$(14)][PF$_6$]$_4$·6MeCN

A mixture of 1,2-bis[4,7-bis(3-aminopropyl)-1,4,7-triazacyclonon-1-yl]ethane **14** (200 mg, 0.39 mmol) and $Cu(NO_3)_2 \cdot 6H_2O$ (115 mg, 0.39 mmol) in EtOH (10 cm^3) was stirred overnight at room temperature. The resulting purple precipitate was collected by filtration and dissolved in H_2O (4 cm^3) and an excess of NH_4PF_6 was added to the resulting solution. The purple precipitate formed was collected by filtration, dried under reduced pressure and recrystallised from MeCN–Et_2O to give purple tabular crystals (137 mg, 27%). Mp 190–192 °C. Found (calc. for $C_{19}H_{39}CuF_{12}N_8P_2$) C, 30.95 (31.13); H, 4.98 (5.36); N, 14.88 (15.29%). FAB mass spectrum (3-NOBA matrix) *m*/*z*: 460; calc. for [^{63}Cu(**14**) − 2($CH_2CH_2CH_2NH_2$)]$^+$ 459. Electronic spectrum: (MeCN) $\lambda_{max} = 570$ nm (ε_{max} 110 dm^3 mol^{-1} cm^{-1}). IR spectrum (KBr pellet): ν/cm^{-1} 3346m, 3200m, 2968w, 2840w, 1659m, 1400m, 1166w, 1064w, 1032w, 1011w, 832s, 559s cm^{-1}.

Crystallography

Crystal data for the two structure determinations appear in Table 3. Crystals were cooled to 150(2) K on a Stoë Stadi-4 four circle diffractometer using an Oxford Cryosystems open-flow nitrogen cryostat.[29] Only special features of the analyses are noted here.

[Cu(6)][BF$_4$]$_2$. Data were acquired as ω–θ scans using on-line profile fitting.[30] Numerical absorption corrections were applied and the structure was solved by a combination of direct and Fourier methods.[31,32] All non-H atoms were refined anisotropically and H atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms.[32] During refinement, both BF_4^- ions in the asymmetric unit were found to be disordered. The disorder was modelled by a partial occupancy model over two sites with all F atoms having an occupancy factor of 0.50. Similarity restraints[32] were applied to B–F distances and F–B–F angles.

[Cu$_2$(14)][PF$_6$]$_4$·6MeCN. Data were corrected for the effects of absorption by means of ψ-scans. The structure was solved and refined as for [Cu(**6**)][BF$_4$]$_2$ above.[31,32] During refinement, both PF_6^- ions in the asymmetric unit were found to be disordered. The disorder in both ions was modelled by partial occupancy models over two sites for the F atoms to give for each PF_6^- two coincident octahedra at the phosphorus atoms with occupancy factors of 0.77 and 0.61 for the major components and 0.23 and 0.39 for the minor. Similarity restraints[32] were applied to P–F bond distances and F–P–F angles.

CCDC reference number 186/2064.

See http://www.rsc.org/suppdata/dt/b0/b002626n/ for crystallographic files in .cif format.

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