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Methanolysis of nitrile-functionalised pendant arm derivatives of 1,4,7-triazacyclononane upon coordination to Cu^{II} †

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The three ligands 1,4,7-tris(cyanomethyl)-1,4,7-triazacyclononane (**L**^{1}), 1,4,7-tris(2-cyanoethyl)-1,4,7-triazacyclononane (**L**^{2}) and 1,4-bis(2-cyanoethyl)-7-methyl-1,4,7-triazacyclononane (**L**^{3}) have been treated with $Cu(BF_4)_2\cdot 4H_2O$ in refluxing MeOH to afford complexes $[Cu(\mathbf{1})](BF_4)_2$, $[Cu(\mathbf{2})](BF_4)_2\cdot H_2O$ and $[Cu(\mathbf{3})](BF_4)_2$, respectively, where **1**, **2** and **3** have two nitrile groups of each starting **L**^{1}, **L**^{2} and **L**^{3} ligand transformed into imino-ether groups *via* nucleophilic attack of MeOH at the the CN triple bond. $[Cu(\mathbf{1})](BF_4)_2$ and $[Cu(\mathbf{2})](BF_4)_2$ have been structurally characterised and show distorted square-based pyramidal coordination at Cu^{II} with the N-donors from the imino-ether groups occupying two basal positions. Interestingly, one nitrile group does not undergo methanolysis and remains unbound to the metal centre in $[Cu(\mathbf{1})]^{2+}$ and $[Cu(\mathbf{2})]^{2+}$. **L**^{2} and **L**^{3} have also been treated with $CuCl_2\cdot 2H_2O$ in CH_3CN at room temperature to give the 1 : 1 complexes $[Cu(\mathbf{L}^2)Cl_2]$ and $[Cu(\mathbf{L}^3)Cl_2]\cdot \frac{1}{2}MeNO_2$. X-Ray diffraction studies confirm that in each case the two chloride anions and the three N-donors from the $[9]aneN_3$ framework coordinate to the metal centre in a distorted square-based pyramidal geometry. All the complexes have been characterised by electronic and EPR spectroscopy. The reaction of **L**^{2} with $CuCl_2\cdot 2H_2O$ has also been carried out in refluxing MeOH and followed by electronic spectroscopy in order to investigate whether the methanolysis of the two nitrile groups is effected by the presence of more strongly coordinating anions such as chloride. The complex $[Cu(\mathbf{4})Cl](BF_4)$ where **4** is derived from **L**^{2} by methanolysis of only one nitrile group, has been isolated after addition of an excess of Me_4NBF_4.

Introduction

Nitrile ligands, R–C≡N, can interact with metal centres in different ways but the most common mode of coordination is as a terminal η^1-NCR ($L_nM\longleftarrow:N\equiv C–R$) ligand *via* σ donation of the lone-pair on the N-centre.[1] Although macrocyclic ligands functionalised with nitrile pendant arms have been used as precursors in the synthesis of the corresponding amino derivatives,[2–4] their coordination chemistry has not been studied extensively. In principle, nitrile-functionalised macrocycles do not encapsulate the metal centre or form sandwich complexes, but promote the formation of multinuclear or polymeric compounds *via exo* coordination. Indeed, we have recently reported the use of nitrile-functionalised pendant arm derivatives of $[9]aneN_3$, $[9]aneN_2S$, $[9]aneNS_2$, $[12]aneNS_2O$ and $[15]aneN_3O_2$ for the construction of three-dimensional solid-state architectures.[5] These ligands are able to form polymeric Ag^I complexes, with the nitrile groups connecting two or more adjacent complex units in a multidimensional network.[5] The inability of the nitrile group to orient itself linearly to bind *via* a σ $M\longleftarrow:N\equiv C–R$ donation to a metal ion sitting within the macrocyclic cavity in an *endo* fashion is further demonstrated by the paucity of reported mononuclear complexes with cyanoalkyl pendant arm derivatives of macrocyclic ligands.[6,7] Chung and co-workers have reported[6] the synthesis of two tetraaza macrocycles functionalised with cyanoethyl pendant arms and the crystal structures of their square-planar Cu^{II} complexes. In these complexes the nitrile pendant arms are not coordinated to the Cu^{II} ion and point away from the metal centre in an *exo* manner without interacting with other complex units.[6] Similar behaviour has also been observed for the Cu^{II}, Ni^{II} and Cd^{II} complexes of the tris-cyanomethyl pendant arm derivative of $[15]aneN_3O_2$.[7]

Extensive studies on the coordination chemistry of the nitrile group R–C≡N (R = Me, Et, $CHCl_2$, ^{t}Bu and CH_2Ph) have been carried out with a range of substrates.[1,8,9] The nitrile group is often transformed into other organic functionalities *via* metal-catalysed reactions such as nucleophilic attack on the C≡N triple bond by alcohols, water and amines. These types of metal-catalysed reactions have been studied from a mechanistic viewpoint and the imino-ether and amidine products have proved extremely useful in the syntheses of pharmaceutical materials and interesting organic intermediates.[10] The coordination geometry at the metal centre catalysing the nucleophilic attack on the C≡N, generally Co^{III}, Rh^{III}, Ir^{III}, Ru^{III}, Pt^{II} or Pd^{II},[11] and the stabilisation of the product by complexation to the metal ion are important factors in deciding the course of these reactions. To our knowledge, only one example of Cu^{II}-promoted nucleophilic attack on nitrile groups has been reported. This work by Hubberstey and co-workers concerns[12] the alcoholysis of bis(2-cyanoguanidine) ligands with the formation of square-planar Cu^{II} complexes of the resulting bis(amidino-*O*-alkylurea) ligands. This reaction takes place with either MeOH or EtOH and with different Cu^{II} salts (BF_4^-, Cl^-, Br^- and SO_4^{2-}), indicating strong stabilisation for the resulting square-planar Cu^{II} complexes.[12]

We report herein studies on the complexation reactions of three different derivatives of 1,4,7-triazacyclononane ($[9]aneN_3$) bearing nitrile pendant arms (**L**^{1}, **L**^{2} and **L**^{3}) with $Cu(BF_4)_2\cdot 4H_2O$ in MeOH. Methanolysis of two nitrile groups is observed for **L**^{1}–**L**^{3} and complexes in which Cu^{II} is encapsulated by the resulting ligands **1**–**3** (Scheme 1), respectively, have been isolated and characterised. The complexation behaviour of **L**^{2} and **L**^{3} towards Cu^{II} has also been studied in MeCN using

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† Electronic supplementary information (ESI) available: frozen solution EPR (77 K) spectra for $[Cu(\mathbf{1})](BF_4)_2$ and $[Cu(\mathbf{2})](BF_4)_2\cdot H_2O$ (Fig. S1) and $[Cu(\mathbf{L}^2)Cl_2]$ (Fig. S2) in CH_3CN–DMF (9 : 1) solutions. Modelling of the disorder in $[Cu(\mathbf{1})](BF_4)_2$ and $[Cu(\mathbf{2})](BF_4)_2\cdot H_2O$. See http://www.rsc.org/suppdata/dt/b2/b209091k/

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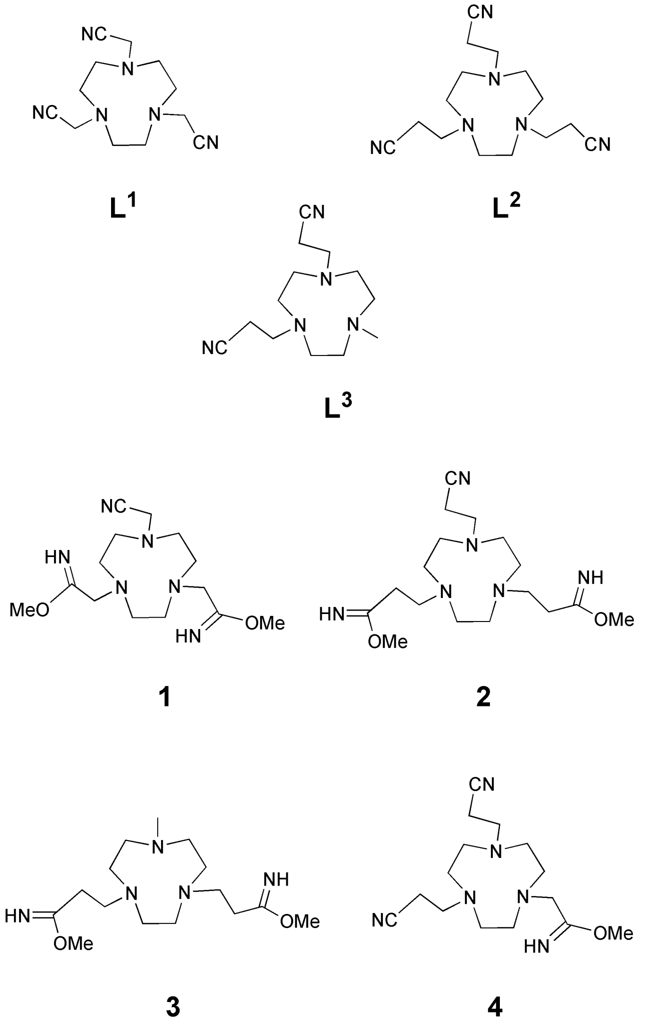


Scheme 1 Summary of ligands.

$CuCl_2·2H_2O$ as starting material and the results compared to those obtained using MeOH and $Cu(BF_4)_2·4H_2O$. X-Ray crystallographic, electronic and EPR spectroscopic studies have been carried out on the isolated complexes.

Results and discussion

The three ligands L^1, L^2 and L^3 were synthesised according to literature procedures.[2–4] Single crystals of L^1 suitable for X-ray diffraction studies were grown by diffusion of Et_2O vapour into a CH_3CN solution. The crystal structure (Fig. 1) shows the nitrile-functionalised pendant arms pointing away from the cavity of the [9]aneN_3 framework. The intramolecular distances and angles are typical of this type of organic compound and the approximate linearity of the C–C≡N fragments [175.8(2)–177.9(2)°] suggests that it is unlikely that the nitrile groups can participate in efficient σ M⟵:N≡C–R *endo*-binding to a metal ion sited within the macrocyclic cavity.

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

Cu–N(1)	2.044(5)	N(4)–Cu–N(7)	83.1(2)
Cu–N(4)	2.030(5)	N(1)–Cu–N(3A)	82.8(2)
Cu–N(7)	2.249(5)	N(1)–Cu–N(3B)	161.3(2)
Cu–N(3A)	1.942(5)	N(4)–Cu–N(3A)	165.2(2)
Cu–N(3B)	1.947(5)	N(4)–Cu–N(3B)	83.8(2)
		N(7)–Cu–N(3A)	105.3(2)
N(1)–Cu–N(4)	86.1(2)	N(7)–Cu–N(3B)	110.7(2)
N(1)–Cu–N(7)	83.5(2)	N(3A)–Cu–N(3B)	104.1(2)

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu(\mathbf{2})](BF_4)_2·H_2O$[a]

Cu(1)–N(1)	2.050(3)	N(4)–Cu(1)–N(7)	84.2(1)
Cu(1)–N(4)	2.031(3)	N(1)–Cu(1)–N(4A)	90.7(1)
Cu(1)–N(7)	2.280(3)	N(1)–Cu(1)–N(4B)	177.6(1)
Cu(1)–N(4A)	1.979(3)	N(4)–Cu(1)–N(4A)	170.9(1)
Cu(1)–N(4B)	2.003(3)	N(4)–Cu(1)–N(4B)	92.3(1)
		N(7)–Cu(1)–N(4A)	103.5(1)
N(1)–Cu(1)–N(4)	81.6(1)	N(7)–Cu(1)–N(4B)	99.1(1)
N(1)–Cu(1)–N(7)	85.6(1)	N(4A)–Cu(1)–N(4B)	91.2(1)

[a] Four independent $[Cu(\mathbf{2})]^{2+}$ cations are present in the asymmetric unit, but among them there are no significant differences in bond lengths and angles. Here selected structural data for only one of them are reported.

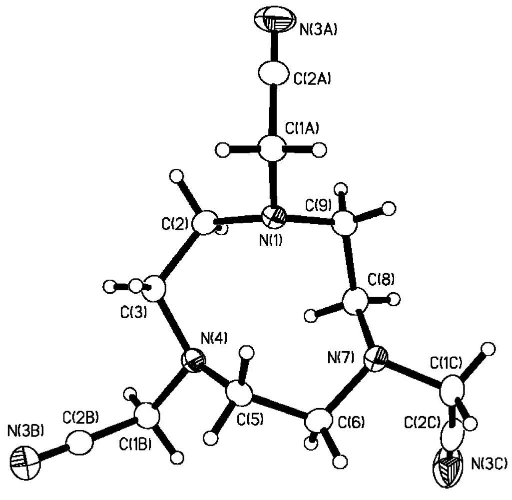


Fig. 1 Crystal structure of the ligand L^1 with numbering scheme adopted. Displacement ellipsoids are drawn at 50% probability.

The reaction of L^1 with one equivalent of $Cu(BF_4)_2·4H_2O$ in MeOH at room temperature yielded a dark-green oil which could not be recrystallised. Interestingly, warming the same reaction mixture to 65 °C for 2 h led to the formation of an intense blue solution from which a blue crystalline powder was isolated. Elemental analysis and spectroscopic data suggested the formation of the complex $[Cu(\mathbf{1})](BF_4)_2$ derived from methanolysis of two nitrile groups of L^1. The strong bands in the ranges 3350–3120 cm^{-1} ($\nu_{N\text{–}H}$) and 1660–1630 cm^{-1} ($\nu_{C=N}$), in the IR spectrum are clearly indicative of the presence of the NH=C(OMe)R moiety in the complex. The same reaction was also carried out with L^2 and L^3 to see whether, despite their longer nitrile pendant arms, they behave similarly to L^1. Indeed, the reaction of L^2 or L^3 with one equivalent of $Cu(BF_4)_2·4H_2O$ in refluxing MeOH formed an intense blue solution from which blue crystalline powders were obtained. Again, analytical and spectroscopic data confirmed the methanolysis of two nitrile groups in each starting ligand to give complexes $[Cu(\mathbf{2})](BF_4)_2$ and $[Cu(\mathbf{3})](BF_4)_2$.

Blue single crystals suitable for X-ray diffraction studies could be grown only for the complexes $[Cu(\mathbf{1})](BF_4)_2$ and $[Cu(\mathbf{2})](BF_4)_2·H_2O$. Both crystal structures (Fig. 2, Tables 1 and 2) confirm the formation in each ligand of two imino-ether groups by methanolysis of two nitrile groups. The coordination geometry at Cu^{II} ions is square-based pyramidal with two imine donors {N(3A) and N(3B) for $[Cu(\mathbf{1})]^{2+}$ and N(4A) and N(4B) for $[Cu(\mathbf{2})]^{2+}$} from the pendant arms, and two tertiary amines [N(1) and N(4)] from the macrocyclic framework occupying the basal positions. The r.m.s. deviations of the N atoms from the N_4 basal planes are 0.046 Å for $[Cu(\mathbf{1})]^{2+}$ and 0.063 Å for $[Cu(\mathbf{2})]^{2+}$. The Cu^{II} ion in $[Cu(\mathbf{1})]^{2+}$ lies 0.242 Å above the N_4 mean plane in the direction of the apical tertiary amine donor N(7); the corresponding distance in $[Cu(\mathbf{2})]^{2+}$ is 0.082 Å. The Cu–N(7) vector forms an angle with the normal to the N_4 basal plane of 18.6° in $[Cu(\mathbf{1})]^{2+}$ and of 12.9° in $[Cu(\mathbf{2})]^{2+}$. The basal Cu–N bond lengths lie in the ranges 1.942(5)–2.044(5) and 1.979(3)–2.050(3) Å for $[Cu(\mathbf{1})]^{2+}$ and $[Cu(\mathbf{2})]^{2+}$, respectively,

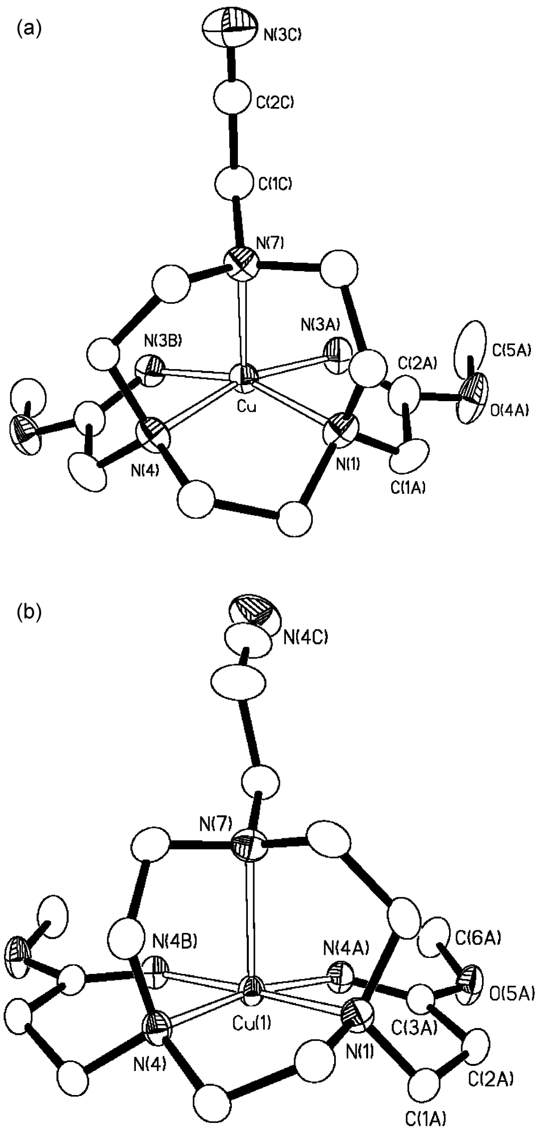


Fig. 2 Crystal structures of the complex cations (a) $[Cu(\mathbf{1})]^{2+}$ and (b) $[Cu(\mathbf{2})]^{2+}$ with numbering schemes adopted. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at 50% probability.

Table 3 Selected bond lengths (Å) and angles (°) for $[Cu(\mathbf{L}^2)Cl_2]$ and $[Cu(\mathbf{L}^3)Cl_2]\cdot½MeNO_2$

	$[Cu(\mathbf{L}^2)Cl_2]$	$[Cu(\mathbf{L}^2)Cl_2]\cdot½MeNO_2$
Cu–N(1)	2.2368(16)	2.265(4)
Cu–N(4)	2.1290(16)	2.154(5)
Cu–N(7)	2.1203(17)	2.081(6)
Cu–Cl(1)	2.2871(6)	2.277(2)
Cu–Cl(2)	2.2624(6)	2.288(2)
N(1)–Cu–N(4)	83.28(6)	81.59(16)
N(1)–Cu–N(7)	82.59(6)	83.0(2)
N(4)–Cu–N(7)	83.02(6)	82.8(2)
N(1)–Cu–Cl(1)	98.97(4)	102.50(15)
N(1)–Cu–Cl(2)	111.00(4)	101.27(13)
N(4)–Cu–Cl(1)	93.92(5)	92.55(15)
N(4)–Cu–Cl(2)	163.99(5)	175.18(16)
N(7)–Cu–Cl(1)	176.40(5)	172.27(16)
N(7)–Cu–Cl(2)	91.46(5)	93.74(18)
Cl(1)–Cu–Cl(2)	91.00(2)	90.61(7)

with Cu–N apical distances of 2.249(5) and 2.280(3) Å, respectively. The Cu–N(imine) bond lengths are the shortest in both structures and are comparable to the Cu–N(imine) bond lengths reported for the Cu^{II} complexes with bis(amidino-*O*-alkylurea) ligands.[12] The Cu–N(macrocycle) bond distances, both Cu–N(basal) and Cu–N(apical), are comparable to those reported for other Cu^{II} complexes of pentadentate [9]aneN_3 derivatives showing the same type of coordination geometry, for example 1-methyl-4,7-bis(3-aminopropyl)-1,4,7-triazacyclononane,[3] 4,7-bis(3-aminopropyl)-1,4,7-triazacyclononane,[13] or 4,7-bis(2-methylpyridyl)-1,4,7-triazacyclononane.[14] However, for the latter ligand the Cu–N apical bond is significantly shorter at 2.162(8) Å. In both our structures the *trans*-basal angles [N(1)–Cu–N(3B) 161.3(2)° and N(4)–Cu–N(3A) 165.2(2)° in $[Cu(\mathbf{1})]^{2+}$; N(1)–Cu–N(4B) 177.6(1)° and N(4)–Cu–N(4A) 170.9(1)° in $[Cu(\mathbf{2})]^{2+}$] are in good agreement with the values expected for a square-based pyramidal geometry around d^9 Cu^{II} centres.[15] In $[Cu(\mathbf{1})]^{2+}$ three five-membered chelate rings are formed in the basal plane with very similar angles [82.8(2)–86.1(2)°] subtended at the metal centre. However, since there is a high degree of planarity in the imino-ether moieties, the torsion angles about the central C–C bonds for the chelate rings involving the pendant arms [16.9(8) and 21.8(8)°] are significantly different from the corresponding torsion angle in the chelate ring involving the [9]aneN_3 framework [46.7(11)°]. In $[Cu(\mathbf{2})]^{2+}$, because of the longer pendant arms, one five- and two six-membered chelate rings are formed in the basal coordination plane, with angles subtended at the metal centre of 81.6(1)° for the former and of 90.7(1) and 92.3(1)° for the latter. While the five-membered ring adopts a *gauche* conformation with a torsion angle about the central C–C bond of 47.3(4)°, the two six-membered chelate rings show pseudo-boat conformations due to the planarity of the imino-ether fragment. Significantly, a chair conformation has been observed for the six-membered chelate rings in square-based pyramidal Cu^{II} complexes with bis-aminopropyl pendant arm derivatives of [9]aneN_3.[3,13] Remarkably, in neither $[Cu(\mathbf{1})]^{2+}$ nor $[Cu(\mathbf{2})]^{2+}$ did the nitrile group on the pendant arm attached to the apical N-donor undergo nucleophilic attack by MeOH and this group is therefore oriented away from the square-based pyramidal coordination sphere of the metal centre.

$\mathbf{L}^2$ and $\mathbf{L}^3$ were also treated with $CuCl_2\cdot 2H_2O$ in CH_3CN at room temperature. Under these conditions the nitrile groups cannot undergo solvolysis and will remain unable to coordinate in an *endo* manner to the metal centre located within the macrocyclic cavity. Elemental analysis and FAB mass spectra for the isolated green powders confirmed the formulations $[Cu(\mathbf{L}^2)Cl_2]$ and $[Cu(\mathbf{L}^3)Cl_2]$, with the chloride anions coordinated to the metal centre. Pale green single crystals suitable for X-ray diffraction studies were grown for both complexes by diffusion of Et_2O vapour into MeCN or $MeNO_2$ solution. The crystal structures of $[Cu(\mathbf{L}^2)Cl_2]$ and of $[Cu(\mathbf{L}^3)Cl_2]\cdot½MeNO_2$ (Fig. 3, Table 3) confirm a distorted square-based pyramidal geometry around each metal centre. In both structures, the basal positions are occupied by two tertiary amines from the [9]aneN_3 framework [N(4) and N(7)] and by two chloride ions, while the nitrile-functionalised pendant arms are oriented away from the metal centres. In $[Cu(\mathbf{L}^2)Cl_2]$ and $[Cu(\mathbf{L}^3)Cl_2]\cdot½MeNO_2$ the Cu^{II} ion is displaced by 0.166 and 0.093 Å, respectively, from the mean plane defined by N(4), N(7), Cl(1) and Cl(2), in the direction of the apical position occupied by the remaining tertiary amine donor N(1). The Cu–N(1) vector shows a slight deviation from perpendicularity with the basal plane [16.1° in $[Cu(\mathbf{L}^2)Cl_2]$ and 13.7° in $[Cu(\mathbf{L}^3)Cl_2]\cdot½MeNO_2$], which seems to be in agreement with a common inability of tridentate nonane rings to fully encapsulate the axial site(s) of a square pyramidal or a distorted octahedral geometry.[3,13,14,16] The Cu–N(basal) bond distances [2.120(2)–2.154(5) Å] are significantly longer than those observed for $[Cu(\mathbf{1})]^{2+}$ and $[Cu(\mathbf{2})]^{2+}$while the Cu–N(apical) bond lengths (2.237(2) and 2.265(4) Å in $[Cu(\mathbf{L}^2)Cl_2]$ and $[Cu(\mathbf{L}^3)Cl_2]\cdot½MeNO_2$, respectively) are similar to those reported for other square-based pyramidal Cu^{II} complexes with [9]aneN_3 derivatives.[3,13,14]

Table 4 Spin Hamiltonian parameters for the simulated spectra of [Cu(**1**)](BF_4)$_2$, [Cu(**2**)](BF_4)$_2$·H_2O, [Cu(**3**)](BF_4)$_2$, [Cu(**L**^{2})Cl_2] and [Cu(**L**^{3})Cl_2]·½$MeNO_2$[a]

	g_{33}	g_{22}	g_{11}	A_{33}/G	A_{22}/G	A_{11}/G	A_N[b]/G
[Cu(**1**)](BF_4)$_2$	2.215	2.055	2.045	181.6	15.0	15.0	12.0
[Cu(**2**)](BF_4)$_2$·H_2O	2.216	2.065	2.041	185.6	21.0	—	12.0
[Cu(**3**)](BF_4)$_2$	2.216	2.063	2.042	185.1	22.0	—	12.0
[Cu(**L**^{2})Cl_2]	2.296	2.074	2.055	135.3	15.0	10.0	10.0
[Cu(**L**^{3})Cl_2]·½$MeNO_2$	2.291	2.074	2.049	138.0	10.0	10.0	10.0

[a] Accurate simulations were not achieved because of the small rhombicity of the spectrum. [b] Simulated superhyperfine coupling constant.

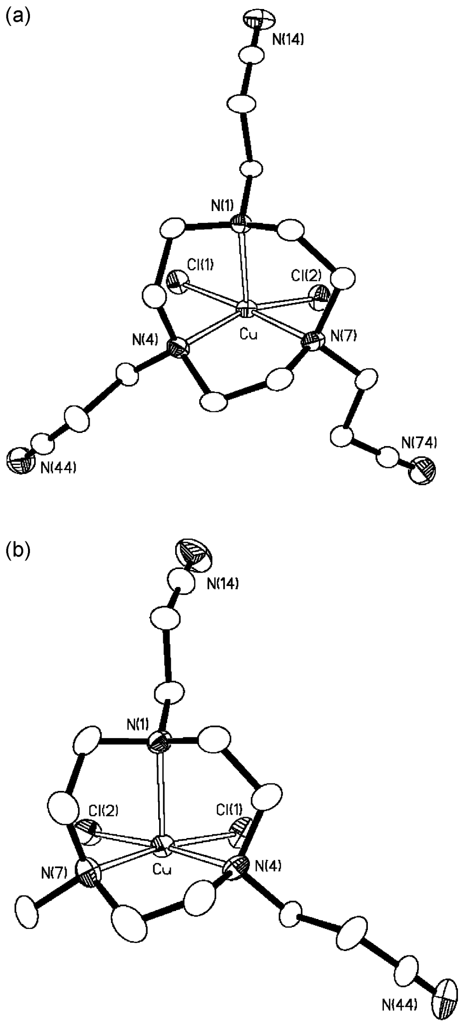


Fig. 3 Crystal structures of (a) [Cu(**L**^{2})Cl_2] and (b) [Cu(**L**^{3})Cl_2]·½$MeNO_2$ with numbering scheme adopted. Hydrogen atoms and solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at 50% probability.

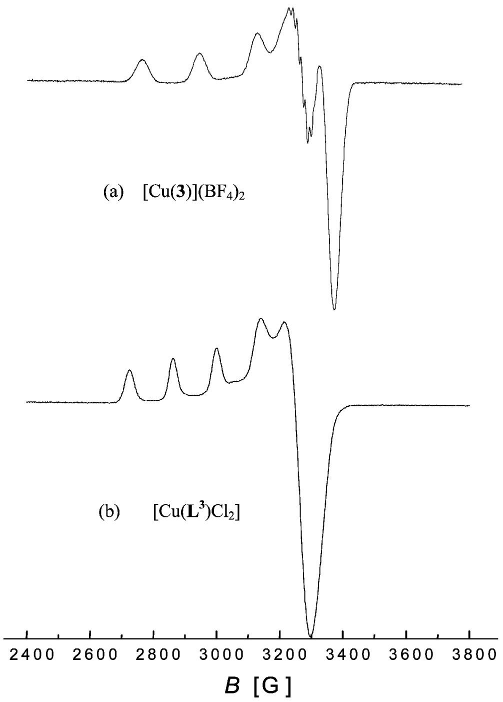
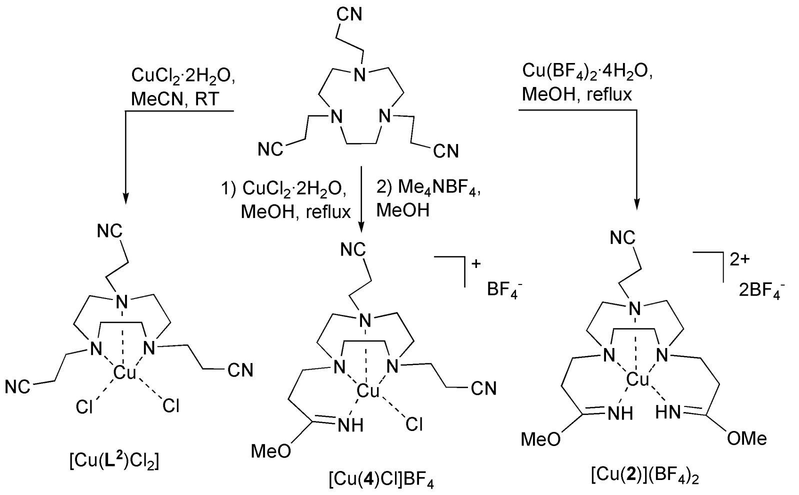


Fig. 4 CH_3CN–DMF (9 : 1) frozen glass solution X-band EPR spectra recorded at 77 K of two of the Cu^{II} complexes discussed in this paper: (a) [Cu(**3**)](BF_4)$_2$ and (b) [Cu(**L**^{3})Cl_2]·½$MeNO_2$. The EPR spectra of the other structurally characterised complexes have been deposited as electronic supplementary information (ESI†).

The electronic spectra of all the isolated complexes recorded in MeOH at room temperature show only one broad band in the visible region at about 580 nm (λ_{max}) for [Cu(**1**)]$^{2+}$ and [Cu(**2**)]$^{2+}$, at 625 nm for [Cu(**3**)]$^{2+}$, at 669 nm for [Cu(**L**^{2})Cl_2] and at 630 nm for [Cu(**L**^{3})Cl_2]·½$MeNO_2$, with molar extinction coefficients (ε) between 80 and 100 dm^3 mol^{-1} cm^{-1}. These spectral features are typical for a d_{xz}, $d_{yz} \longrightarrow d_{x^2-y^2}$ transition in a Cu^{II} ion having square-based pyramidal or distorted square-based pyramidal coordination geometry.[3,13,14]

The X-band EPR spectra of [Cu(**1**)](BF_4)$_2$, [Cu(**2**)](BF_4)$_2$·H_2O, [Cu(**3**)](BF_4)$_2$, [Cu(**L**^{2})Cl_2] and [Cu(**L**^{3})Cl_2]·½$MeNO_2$ were recorded as frozen (77 K) MeCN–DMF (9 : 1, v/v ratio) glasses (see Table 4 and Fig. 4). All spectra are typical of mononuclear $^{63,65}Cu^{II}$ (I = 3/2) complexes with square-based pyramidal coordination geometries possessing $d_{x^2-y^2}$ ground states. The spin Hamiltonian parameters for the simulated spectra of [Cu(**1**)](BF_4)$_2$, [Cu(**2**)](BF_4)$_2$·H_2O and [Cu(**3**)](BF_4)$_2$ are comparable (Table 4), reflecting the similarities in the coordination sphere about the Cu centre in these complexes. For [Cu(**2**)](BF_4)$_2$·H_2O and [Cu(**3**)](BF_4)$_2$, a superhyperfine coupling can be resolved in the perpendicular region of the spectra consistent with the coupling of four nitrogen atoms (probably the basal N-donors) to the metal centre (Fig. 4(a)). For [Cu(**L**^{2})Cl_2] and [Cu(**L**^{3})Cl_2]·½$MeNO_2$ the parameters g_{33} and A_{33} obtained from simulation of the experimental spectra are respectively higher and lower (Table 4) than the corresponding parameters obtained for [Cu(**1**)](BF_4)$_2$, [Cu(**2**)](BF_4)$_2$·H_2O and [Cu(**3**)](BF_4)$_2$. This is consistent with greater covalent contributions from the chloride donors in [Cu(**L**^{2})Cl_2] and [Cu(**L**^{3})Cl_2]·½$MeNO_2$ to the Cu $d_{x^2-y^2}$ ground state. These contributions are absent in [Cu(**1**)](BF_4)$_2$, [Cu(**2**)](BF_4)$_2$·H_2O and [Cu(**3**)](BF_4)$_2$.

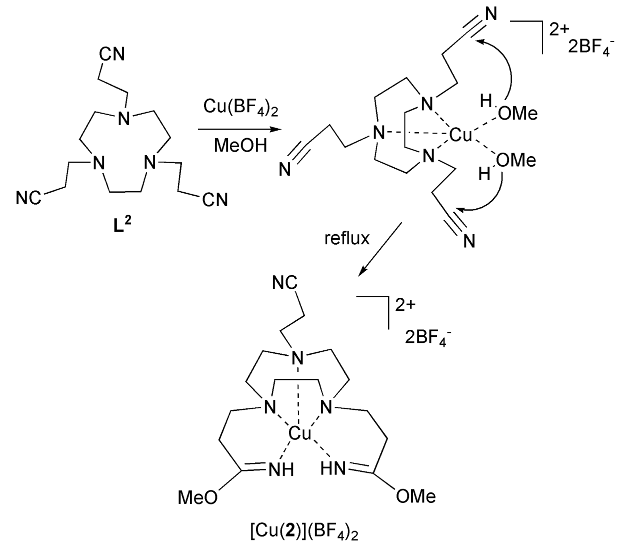
In order to evaluate whether methanolysis of nitrile groups in **L**^{1}, **L**^{2} and **L**^{3} could be effected by the presence of coordinating counter-anions, we carried out the reaction of **L**^{2} with $CuCl_2$·$2H_2O$ in refluxing MeOH and followed the course of the reaction by electronic spectroscopy. On mixing the reagents, a band at 669 nm appeared in the electronic spectrum; given the similarity to the electronic spectrum of [Cu(**L**^{2})Cl_2], this is taken to indicate the formation of the 1 : 1 complex between **L**^{2} and $CuCl_2$. The maximum of this broad band moved towards lower wavelengths on warming the reaction mixture to 65 °C. After



Scheme 2 Products obtained from the reaction of L^2 with $CuCl_2·2H_2O$ and $Cu(BF_4)_2·4H_2O$ under different experimental conditions.

5 h under reflux a stable band was established near 630 nm, intermediate between the value for the starting complex (669 nm) and that expected for $[Cu(\mathbf{2})]^{2+}$ (580 nm) following methanolysis of two arms after 2 h reflux in MeOH. Slow diffusion of Et_2O vapour into the reaction mixture gave first a small amount of $[Cu(\mathbf{L}^2)Cl_2]$ as a green microcrystalline powder, then a blue oil the electronic spectrum of which exhibited a broad band at 632 nm. The IR spectrum showed a band at *ca.* 1630 cm^{-1} typical for the ν(C=N) stretching vibration of an imino group. These data suggest the formation of an intermediate species during the methanolysis of $[Cu(\mathbf{L}^2)Cl_2]$ which contains at least one imino group but does not give $[Cu(\mathbf{2})]^{2+}$ on prolonged heating under these conditions. In order to identify the blue oil we treated it with excess of Me_4NBF_4 in MeOH and isolated a very hygroscopic blue solid by diffusion of Et_2O vapour into the resulting solution. The fast-atom bombardment (FAB) mass spectrum of this solid exhibited a molecular ion peak with the correct isotopic distribution for $[^{63}Cu(\mathbf{4})Cl]^+$ (m/z = 418), and elemental analysis agreed with the formulation $[Cu(\mathbf{4})Cl]BF_4$. This suggests that when $CuCl_2·2H_2O$ is used instead of $Cu(BF_4)_2·4H_2O$ only one nitrile group of $\mathbf{L}^2$ undergoes methanolysis to give **4** (Scheme 1). Scheme 2 shows the different complexes isolated from the reaction of $\mathbf{L}^2$ with $CuCl_2·2H_2O$ and $Cu(BF_4)_2·4H_2O$ as a function of the solvent and the reaction conditions.

On the basis of data reported in the literature for similar reactions performed on different substrates,[17] two general mechanisms for the Cu^{II}-promoted methanolysis of the nitrile groups in $\mathbf{L}^1$, $\mathbf{L}^2$ and $\mathbf{L}^3$ can be proposed: (a) nucleophilic attack by coordinated MeOH molecules on the nitrile groups of the ligands coordinated solely through the donor atoms of the [9]aneN_3 framework; and (b) nucleophilic attack on the free nitrile groups by uncoordinated MeOH molecules with subsequent coordination of the resulting imino-ether groups to the metal centre. Since methanolysis does not appear to take place in the absence of Cu^{II}, our results in the presence of a poorly coordinating anion BF_4^- appear to agree with the first mechanism. This implies the formation of intermediate Cu^{II} complexes of $\mathbf{L}^1$, $\mathbf{L}^2$ or $\mathbf{L}^3$ having basal positions occupied by MeOH (Scheme 3). For geometric reasons related to the length of the pendant arms, the cyano groups in these ligands cannot coordinate in an *endo* manner *via* a σ $M\leftarrow:N\equiv C–R$ donation to the metal centre if the latter is encapsulated within the macrocyclic cavity. Completion of the coordination sphere at Cu^{II} is therefore completed with MeOH, which is activated *via* metal-assisted deprotonation leading to nucleophilic attack on the nitrile centre(s). The roles of the metal centre are, therefore, to template and activate the reaction of MeOH with nitrile groups of the ligands, and to bind and protect the imino-ether groups of the resulting pentacoordinate ligands **1**, **2** and **3**. In contrast, the methanolysis of only one nitrile group during the reaction of $\mathbf{L}^2$ with $CuCl_2·2H_2O$ in MeOH (Scheme 3) clearly highlights how the final product of the Cu^{II}-promoted methanolysis can be effected by the presence of the more strongly coordinating chloride anion. Therefore, selective methanolysis of one or two nitrile groups in $\mathbf{L}^1$–$\mathbf{L}^3$ can be readily achieved *via* control of choice of anion in the starting Cu^{II} salt.



Scheme 3 Possible reaction pathway for the Cu^{II}-catalysed methanolysis of cyano groups in nitrile pendant arm derivatives of [9]aneN_3: case of $\mathbf{L}^2$.

Experimental

Spectra were recorded on a Bruker ER-200D spectrometer (EPR, frozen solutions), on a Perkin-Elmer 1600 spectrometer (FTIR, KBr disks) and on a Cary 5 spectrophotometer (UV-vis). Elemental analytical data were obtained by the Microanalytical Service (Perkin-Elmer 240B analyser) at the University of Nottingham. FAB (Fast Atom Bombardment) mass spectra were obtained by the EPSRC National Mass Spectrometry Service at the University of Swansea. EPR spectra were simulated using the Bruker Symphonia software suite. 1,4,7-tris(cyanomethyl)-1,4,7-triazacyclononane ($\mathbf{L}^1$)[2] 1,4,7-tris(2-cyanoethyl)-1,4,7-triazacyclononane ($\mathbf{L}^2$)[4] and 1,4-bis(2-cyanoethyl)-7-methyl-1,4,7-triazacyclononane ($\mathbf{L}^3$)[3] were prepared as described in the literature. All starting materials were obtained from Aldrich Chemical Co. and were used without further purification.

Table 5 Selected crystal data for the single crystal structures of **L**^{1}, [Cu(**1**)](BF$_4$)$_2$ and of [Cu(**2**)](BF$_4$)$_2$·H$_2$O, [Cu(**L**^{2})Cl$_2$] and [Cu(**L**^{3})Cl$_2$]·½MeNO$_2$

Compound	**L**^{1}	[Cu(**1**)](BF$_4$)$_2$	[Cu(**2**)](BF$_4$)$_2$·H$_2$O	[Cu(**L**^{2})Cl$_2$]	[Cu(**L**^{3})Cl$_2$]·½MeNO$_2$
Formula	$C_{12}H_{18}N_6$	$C_{14}H_{26}B_2CuF_8N_6O_2\cdot$	$C_{17}H_{34}B_2CuF_8N_6O_3$	$C_{15}H_{24}Cl_2CuN_6$	$C_{13.5}H_{24.5}Cl_2CuN_{5.5}O$
M/g mol^{-1}	246.32	547.57	607.66	422.84	414.833
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	P-1	$P2_1/n$	$P2_1$
a/Å	9.892(2)	9.710(3)	10.1492(8)	10.9750(11)	8.325(2)
b/Å	15.726(3)	16.466(5)	16.5575(14)	11.1671(11)	8.090(2)
c/Å	9.972(2)	13.784(5)	31.057(3)	14.9887(15)	15.219(3)
α/°	90	90	100.735(1)	90	90
β/°	114.84(2)	95.52(3)	97.780(1)	96.183(2)	105.87(3)
γ/°	90	90	91.402(1)	90	90
U/Å^3	1407.7(5)	2193.6(12)	5073.8(8)	1826.3(3)	985.9(4)
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
Z	4	4	8	4	2
D_c/g cm^{-3}	1.162	1.658	1.591	1.538	1.396
μ/mm^{-1}	0.076	1.088	0.952	1.498	1.389
Unique reflections, R_{int}[a]	2487, 0.0433	3852, —	23282, 0.034	4452, 0.023	3856, 0.042
Observed reflections	2056 [$F_o \geq 4\sigma(F_o)$]	3029 [$F_o \geq 4\sigma(F_o)$]	14322 [$F_o \geq 4\sigma(F_o)$]	3420 [$F_o \geq 4\sigma(F_o)$]	2980 [$F_o \geq 4\sigma(F_o)$]
R_1, wR_2	0.0422, 0.0875	0.0639, 0.1430	0.0498, 0.1167	0.0310, 0.0819	0.0601, 0.1246

[a] Following absorption corrections (except for **L**^{1}).

Synthesis of [Cu(1)](BF$_4$)$_2$

A mixture of 1,4,7-tris(cyanomethyl)-1,4,7-triazacyclononane (**L**^{1}) (20.0 mg, 0.081 mmol) and Cu(BF$_4$)$_2$·4H$_2$O (25.0 mg, 0.081 mmol) in MeOH (30 cm^3) was stirred at 65 °C for 2 h until an intense blue colour appeared. 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$_2$O vapour into this solution (yield 28.0 mg, 0.051 mmol, 63.0%). FAB mass spectrum (3-NOBA matrix): m/z = 460 ([^{63}Cu(**1**)(BF$_4$)]$^+$) and 373 ([^{63}Cu(**1**)]$^+$). Electronic spectrum (MeOH): λ_{max} = 588 nm (ε_{max} = 102 dm^3 mol^{-1} cm^{-1}). Elemental analysis: found (calc. for $C_{14}H_{26}B_2CuF_8N_6O_2$): C, 31.10 (30.71); H, 4.88 (4.79); N, 15.58 (15.35%). IR spectrum (KBr disk): 3353s, 3332s, 3125s, 2930m, 2877m, 2242w, 1655s, 1639s, 1458m, 1409m, 1314m, 1217m, 1084s, 879m cm^{-1}.

Synthesis of [Cu(2)](BF$_4$)$_2$·H$_2$O

A mixture of 1,4,7-tris(2-cyanoethyl)-1,4,7-triazacyclononane (**L**^{2}) (20.0 mg, 0.069 mmol) and Cu(BF$_4$)$_2$·4H$_2$O (21.3 mg, 0.069 mmol) in MeOH (30 cm^3) was stirred under reflux for 2 h until an intense blue colour appeared. The solvent was removed under reduced pressure and the residue dissolved in MeCN. Blue crystals of diffraction quality were obtained by slow diffusion of Et$_2$O vapour into this solution (yield 26.5 mg, 0.045 mmol, 65.2%). FAB mass spectrum (3-NOBA matrix): m/z = 502 ([^{63}Cu(**2**)(BF$_4$)]$^+$) and 415 ([^{63}Cu(**2**)]$^+$). Electronic spectrum (MeOH): λ_{max} = 581 nm (ε_{max} = 97 dm^3 mol^{-1} cm^{-1}). Elemental analysis: found (calc. for $C_{17}H_{34}B_2CuF_8N_6O_3$): C, 34.08 (33.60); H, 5.27 (5.64); N, 14.14 (13.83%). IR spectrum (KBr disk): 3349s, 3328s, 3125s, 2955m, 2868m, 2249w, 1637s, 1466m, 1414m, 1221m, 1084s, 1035s, 841m, 772m cm^{-1}.

Synthesis of [Cu(3)](BF$_4$)$_2$

A solution of Cu(BF$_4$)$_2$·4H$_2$O (37.0 mg, 0.12 mmol) in MeOH (5 cm^3) was added to a solution of 1,4-bis(2-cyanoethyl)-7-methyl-1,4,7-triazacyclononane (**L**^{3}, 30.0 mg, 0.12 mmol) in MeOH (25 cm^3). The resulting mixture was refluxed for 3 h until the solution turned blue. The solvent was removed under reduced pressure and blue crystals were obtained by diffusion of Et$_2$O vapour into a MeOH solution of the complex (yield 49.2 mg, 0.095 mmol, 79.0%). FAB mass spectrum (3-NOBA matrix): m/z = 432 ([^{63}Cu(**3**)(BF$_4$)]$^+$) and 345 ([^{63}Cu(**3**)]$^+$). Electronic spectrum (MeOH): λ_{max} = 625 nm (ε_{max} = 91 dm^3 mol^{-1} cm^{-1}). Elemental analysis: found (calc. for $C_{15}H_{31}B_2CuF_8N_5O_2$): C, 32.28 (32.72); H, 5.27 (5.67); N, 12.54 (12.72%). IR spectrum (KBr disk): 3350s, 3320s, 3131s, 2950m, 2878m, 1641s, 1448m, 1410m, 1310m, 1210m, 1084s, 1025s, 840m, 770m cm^{-1}.

Synthesis of [Cu(4)Cl]BF$_4$

A mixture of 1,4,7-tris(2-cyanoethyl)-1,4,7-triazacyclononane (**L**^{2}) (10.0 mg, 0.035 mmol) and CuCl$_2$·2H$_2$O (5.9 mg, 0.035 mmol) in MeOH (30 cm^3) was stirred under reflux for 5 h until a blue colour appeared. Slow diffusion of Et$_2$O vapour into the reaction mixture gave first a green microcrystalline solid corresponding to [Cu(**L**^{2})Cl$_2$] then a blue oil. This oil was then dissolved in MeOH and excess Me$_4$NBF$_4$ was added. Slow diffusion of Et$_2$O vapour into this solution gave [Cu(**4**)Cl]BF$_4$ (yield 8.0 mg, 0.016 mmol, 45.7%). FAB mass spectrum (3-NOBA matrix): m/z = 418 ([^{63}Cu(**4**)Cl]$^+$). Electronic spectrum (MeOH): λ_{max} = 632 nm (ε_{max} = 85 dm^3 mol^{-1} cm^{-1}). Elemental analysis: found (calc. for $C_{16}H_{28}BClCuF_4N_6O$): C, 37.20 (37.96); H, 5.98 (5.57); N, 16.14 (16.60%). IR spectrum (KBr disk): 3330m, 3130m, 2970m, 2870m, 2261w, 1640s, 1485m, 1460m, 1405m, 1330w, 1305w, 1215w, 1105s, 1080s, 950m, 780m cm^{-1}.

Synthesis of [Cu(L^2)Cl$_2$]

1,4,7-Tris(2-cyanoethyl)-1,4,7-triazacyclononane (**L**^{2}) (20.0 mg, 0.069 mmol) and CuCl$_2$·2H$_2$O (11.8 mg, 0.069 mmol) were stirred in MeCN (30 cm^3) at room temperature for 3 h. The solvent volume was reduced and green blocky crystals of diffraction quality were obtained by slow diffusion of Et$_2$O vapour (yield 21.2 mg, 0.050 mmol, 72.7%). FAB mass spectrum (3-NOBA matrix): m/z = 388 ([^{63}Cu(**L**^{2})Cl]$^+$). Electronic spectrum (MeOH): λ_{max} = 669 nm (ε_{max} = 83 dm^3 mol^{-1} cm^{-1}). Elemental analysis: found (calc. for $C_{15}H_{24}Cl_2CuN_6$): C, 42.91 (42.59); H, 6.10 (5.72); N, 20.03 (19.87%). IR spectrum (KBr disk): 2978w, 2930w, 2880w, 2238m, 1448s, 1409m, 1345m, 1304s, 1210m, 1084s, 1030s, 980s, 731m cm^{-1}.

Synthesis of [Cu(L^3)Cl$_2$]·½MeNO$_2$

1,4-Bis(2-cyanoethyl)-7-methyl-1,4,7-triazacyclononane (**L**^{3}, 25.0 mg, 0.10 mmol) and CuCl$_2$·2H$_2$O (17.1 mg, 0.10 mmol) were stirred in MeCN (20 cm^3) at room temperature for 3 h. The solvent volume was reduced and green crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of Et$_2$O vapour (yield 31.0 mg, 0.08 mmol, 80.7%). FAB mass spectrum (3-NOBA matrix): m/z = 349 ([^{63}Cu(**L**^{3})Cl]$^+$). Electronic spectrum (MeOH): λ_{max} = 630 nm (ε_{max} = 88 dm^3 mol^{-1} cm^{-1}). Elemental analysis: found (calc. for $C_{13.5}H_{24.5}$-

$Cl_2CuN_{5.5}O$): C, 38.31 (39.09); H, 6.09 (5.95); N, 19.11 (18.57%). IR spectrum (KBr disc): 2940w, 2905w, 2880w, 2225m, 1458s, 1410m, 1351m, 1305s, 1210m, 1081s, 1028s, 980s, 710m cm^{-1}.

Crystal structure determinations

A summary of the crystal data and refinement details for the crystal structures reported in this paper is given in Table 5. Data for **L**^{1} and [Cu(**1**)]$(BF_4)_2$ were collected on a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems open-flow cryostat and using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Numerical absorption corrections based on face-indexing were applied to the data for [Cu(**1**)]$(BF_4)_2$. Data for [Cu(**L**^{3})Cl_2]·½$MeNO_2$ were collected on a Enraf Nonius kappaCCD area detector; semi-empirical absorption corrections based on equivalent reflections were applied. Data for [Cu(**2**)]$(BF_4)_2$·H_2O and [Cu(**L**^{2})Cl_2] were collected on a Bruker SMART CCD area detector diffractometer equipped with an Oxford Cryosystems open-flow cryostat and using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Semi-empirical absorption corrections based on equivalent reflections were applied.

The structures of [Cu(**1**)]$(BF_4)_2$ and [Cu(**L**^{3})Cl_2]·½$MeNO_2$ were solved by the heavy atom method and subsequent difference-Fourier syntheses.[18] All the other structures were solved by direct methods[18] and completed by iterative cycles of full-matrix least squares refinement and ΔF syntheses. All non-H atoms, except for those in disordered groups, were refined anisotropically. All the H atoms were placed in calculated positions and refined using a riding model,[17] except those on methyl groups and on solvent molecules (MeOH or MeCN) which were located from difference maps and refined as a rigid body. Disorder was identified in [Cu(**1**)]$(BF_4)_2$ and [Cu(**2**)]$(BF_4)_2$·H_2O, and the description and modelling of this disorder is reported as electronic supplementary information (ESI †).

CCDC reference numbers 193874–193878.

See http://www.rsc.org/suppdata/dt/b2/b209091k/ for crystallographic data in CIF or other electronic format.

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