

Stacked Amido Macrocyclic Complexes: Synthesis and Single Crystal X-Ray Structure of $\text{Na}[\text{Cu}(\text{L})(\text{NCMe})](\text{BF}_4)_2(\text{NO}_3)$ [$\text{L} = 1\text{-formyl-4,7-bis(2-hydroxy-2-methylpropyl)-1,4,7-triazacyclononane}$]

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The synthesis of bi-functional derivatives of $[9]\text{aneN}_3$ is described; the structure of $\text{Na}[\text{Cu}(\text{L})(\text{NCMe})](\text{BF}_4)_2(\text{NO}_3)$ shows a central $[\text{Na}(\text{BF}_4)_2]^-$ core with the *O*-donor of the amide moiety of successive $[\text{Cu}(\text{L})(\text{NCMe})]^{2+}$ cations bound to Na^+ to give a stacked structure.

The synthesis of pendant arm derivatives of $[9]\text{aneN}_3$ (1,4,7-triazacyclononane) has led to the preparation of a range of highly stable metal complexes.^{1,2} Most of these complexes are based upon the functionalisation of all three *N*-donors of the macrocycle to afford trifunctionalised ligands incorporating octahedral recognition sites for metal ion coordination. We wished to investigate the specific formation of five-coordinate metal complexes based on the coordination to bi-functionalised $[9]\text{aneN}_3$ ligands.³ We report herein a general route to bi-functionalised derivatives of $[9]\text{aneN}_3$, and the structure of an unusual stacked Cu^{II} complex of the amido ligand **L**.

Our approach was based upon the synthesis of the orthoamide **1** of $[9]\text{aneN}_3$.^{4,5} Acid hydrolysis affords the formyl species **2** in which one *N*-donor is protected by an external formyl function.⁴ Derivatisation of **2** with 2,2-dimethyl oxirane affords the bi-functionalised ligand **L**.[†] Base hydrolysis of **L** affords **3** in high yield. Scheme 1 summarises these and related

synthetic routes to functionalised ligands. The single crystal X-ray structure of **3** confirms[‡] (Fig. 1) the formation of the bi-functionalised macrocycle with the two pendant arm alcohols H-bonded to a CHCl_3 molecule of crystallisation. The macrocyclic ring adopts a $[333]$ conformation.

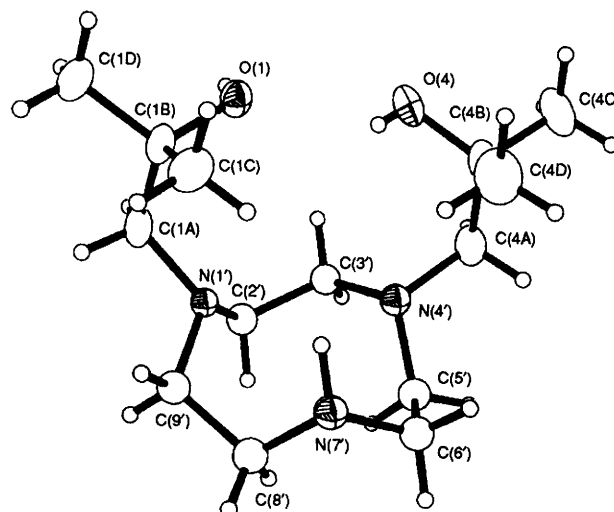
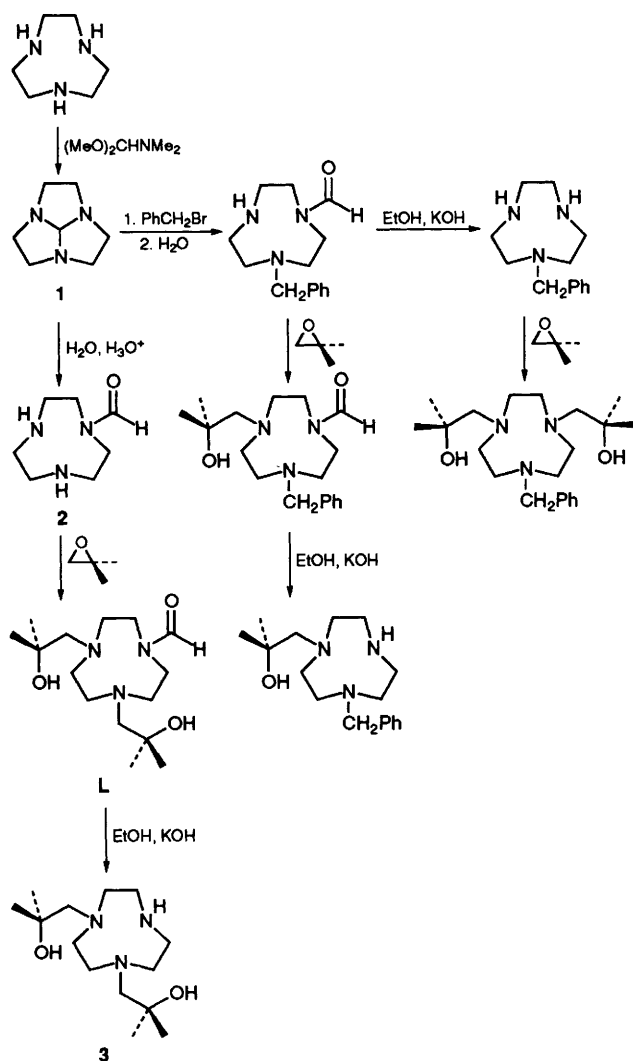


Fig. 1 View of the structure of **3** with numbering scheme adopted



Scheme 1

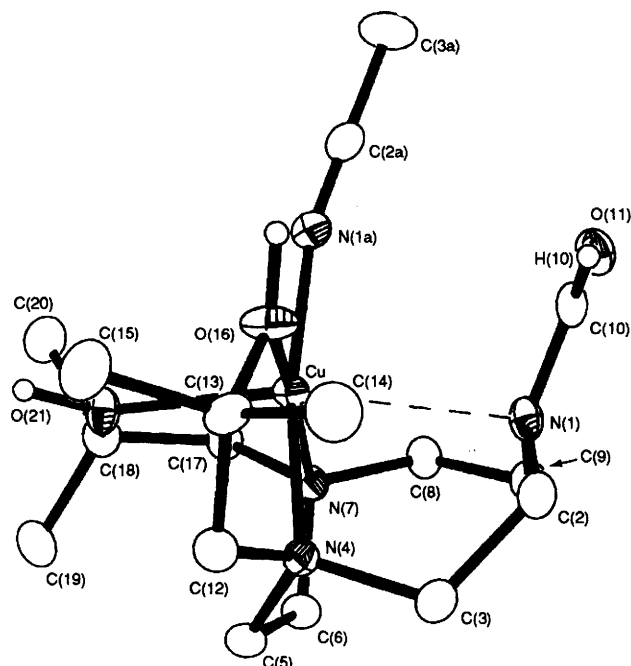


Fig. 2 View of the structure of $[\text{Cu}(\text{L})(\text{NCMe})]^{2+}$ with numbering adopted. $\text{Cu}-\text{N}(1) = 2.611(5)$, $\text{Cu}-\text{N}(4) = 2.002(3)$, $\text{Cu}-\text{N}(7) = 2.015(3)$, $\text{Cu}-\text{O}(16) = 1.963(3)$, $\text{Cu}-\text{O}(21) = 2.2518(25)$, $\text{Cu}-\text{N}(1a) = 1.984(3)$, $\text{N}(1)-\text{C}(2) = 1.481(5)$, $\text{N}(1)-\text{C}(9) = 1.472(5)$, $\text{N}(1)-\text{C}(10) = 1.357(5)$, $\text{C}(10)-\text{O}(11) = 1.218(4)$ Å. $\angle \text{N}(4)\text{CuN}(7) = 86.95(12)$, $\angle \text{N}(4)\text{CuO}(16) = 82.12(11)$, $\angle \text{N}(4)\text{CuO}(21) = 96.57(10)$, $\angle \text{N}(4)-\text{CuN}(1a) = 168.40(12)$, $\angle \text{N}(7)\text{CuO}(16) = 169.07(11)$, $\angle \text{N}(7)-\text{CuO}(21) = 77.66(10)$, $\angle \text{N}(7)\text{CuN}(1a) = 97.85(12)^\circ$.

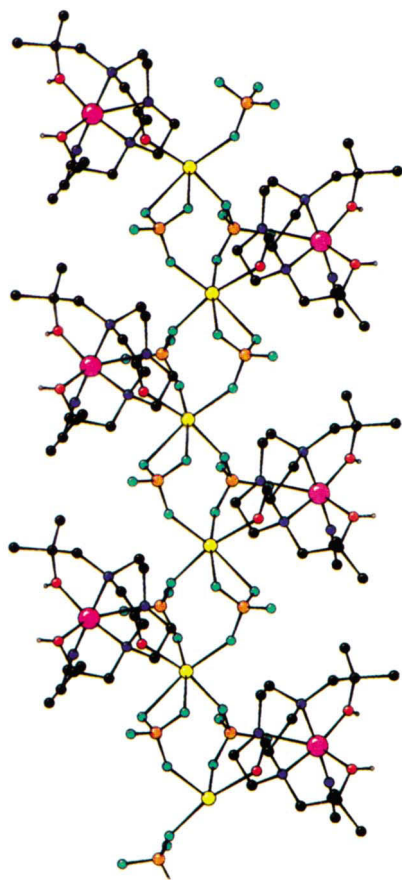


Fig. 3 Packing diagram of $\text{Na}[\text{Cu}(\text{L})(\text{NCMe})](\text{BF}_4)_2(\text{NO}_3)$. NO_3^- ions have been omitted for clarity; Na: yellow, Cu: magenta, C: black, B: brown, F: green, N: blue, O: red.

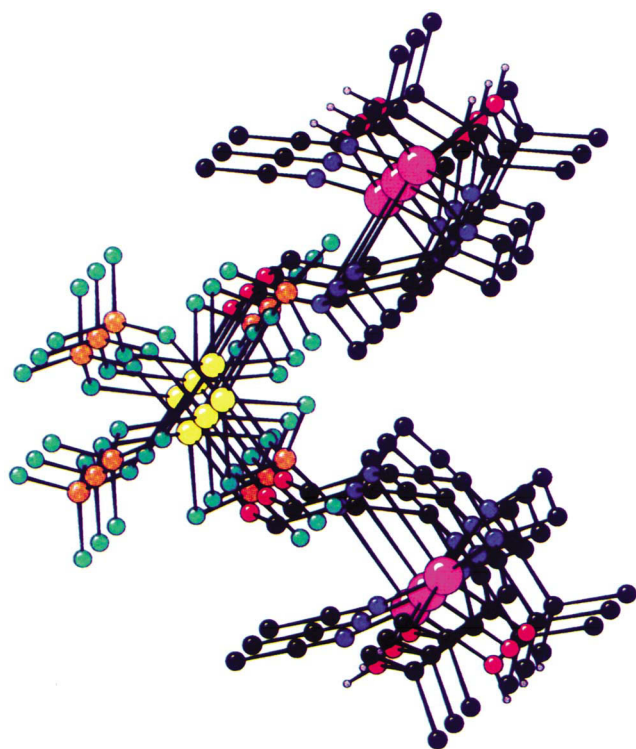


Fig. 4 Packing diagram of $\text{Na}[\text{Cu}(\text{L})(\text{NCMe})](\text{BF}_4)_2(\text{NO}_3)$. NO_3^- ions have been omitted for clarity; Na: yellow, Cu: magenta, C: black, B: brown, F: green, N: blue, O: red.

We were interested in determining the coordination characteristics of **L**. The presence of an amido function in **L** raised questions as to whether this moiety would bind to a metal centre or whether it would act as a dangling group available for intermolecular H-bonding. The formation of supramolecular arrays utilising H-bonding to amide functions has been reported previously.⁶ Additionally, although the binding of deprotonated amido macrocyclic ligands is well established,⁷ there are few examples of *N*-donors of tertiary amides binding to metal centres.⁸

Reaction of $[\text{Cu}(\text{NO}_3)_2]$ with **L** in MeCN affords a blue solution. Addition of an excess of NaBF_4 leads to the formation of deep-blue crystals containing the $[\text{Cu}(\text{L})(\text{NCMe})]^{2+}$ cation. The single crystal structure confirms the stoichiometry of the product to be $\text{Na}[\text{Cu}(\text{L})(\text{NCMe})](\text{BF}_4)_2(\text{NO}_3)$. The Cu^{II} centre is bound to both pendant arm alcohols and two *N*-donors of **L** and one MeCN molecule (Fig. 2). In addition, the complex cation shows an additional long-range interaction to the amido *N*-donor [N(1)] at 2.611(5) Å, with N(1) pointing directly to the sixth coordination site of the Cu^{II} ion. Interaction of N(1) with the Cu centre is confirmed further by the observed loss of planarity of the C(2)C(9)N(1)C(10)O(11)H(10) fragment. Thus, the dihedral angle between the planes defined by C(2)C(9)N(1) and N(1)C(10)O(11)H(10) (deviation 0.001 Å) is 27.1(4)°. The solid-state structure of $\text{Na}[\text{Cu}(\text{L})(\text{NCMe})](\text{BF}_4)_2(\text{NO}_3)$ is further complicated by the presence of an aggregate of $[\text{Na}(\text{BF}_4)_2]^-$ ions which forms a polymeric chain. $[\text{Cu}(\text{L})(\text{NCMe})]^{2+}$ cations are bound through the amide *O*-donor [O(11)] to Na^+ ions within this chain. Thus, each Na^+ ion is six coordinate with five interactions to F^- ions of BF_4^- at 2.242(3)–2.424(3) Å, and a sixth interaction with the amide *O*-donor at 2.321(3) Å. Figs. 3 and 4 illustrate the packing of successive $[\text{Cu}(\text{L})(\text{NCMe})]^{2+}$ cations along the $[\text{Na}(\text{BF}_4)_2]^-$ chain. Thus, the amide function in **L** not only interacts with the Cu^{II} centre *via* the N-atom, but also binds to an external Na^+ ion *via* the O-atom to afford a supramolecular array of cation–anion interactions.

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Footnotes

† All ligands have been characterised by NMR spectroscopy, mass spectrometry and elemental analysis.

‡ *Crystal data* for $\text{C}_{15}\text{H}_{31}\text{N}_3\text{O}_2\text{CHCl}_3$: $M = 404.8$, orthorhombic, space group $Pna2_1$, $a = 11.813(6)$, $b = 11.300(6)$, $c = 15.231(9)$ Å, $V = 2033$ Å³ [from 2θ values of 32 reflections measured at $\pm\omega$ ($25 \leq 2\theta \leq 27^\circ$), $\lambda = 0.71073$ Å, $T = 150$ K], $Z = 4$, $D_c = 1.322$ g cm⁻³, colourless plate, $\mu = 0.465$ mm⁻¹. 1858 Data ($5 \leq 2\theta \leq 45^\circ$) were collected using a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low temperature device [J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105] and Mo-Kα X-radiation. The structure was solved by direct methods using SHELXS-86 [G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467] and refined on F^2 using SHELXL-93 [G. M. Sheldrick, Univ. of Göttingen, Germany, 1993]. Substantial disorder was modelled by allowing isotropic refinement of two interpenetrant rings with constrained values of C–C and C–N bonds which converged at 1.515(7) and 1.472(3) Å, respectively. The major and minor conformers have occupancies of 0.663(8) and 0.337(8), respectively. Other non-H atoms were refined with anisotropic thermal parameters, H atoms bound to N and O atoms were refined positionally and other H atoms were included in calculated positions. At final convergence, $R[F \geq 4\sigma(F)] = 0.047$, $wR[F^2, \text{all data}] = 0.104$, $S[F^2] = 1.11$ for 217 parameters. The final ΔF synthesis contained no feature beyond ± 0.30 e Å⁻³.

§ *Crystal data* for $\text{C}_{17}\text{H}_{34}\text{B}_2\text{F}_8\text{N}_5\text{NaO}_6\text{Cu}$: $M = 664.52$, monoclinic, space group $P2_1/a$, $a = 9.6373(22)$, $b = 30.814(12)$, $c = 10.1042(22)$ Å, $\beta = 114.433(22)^\circ$, $V = 2732$ Å³ [from 2θ values of 25 reflections measured at $\pm\omega$ ($30 \leq 2\theta \leq 32^\circ$), $\lambda = 0.71073$ Å, $T = 150$ K], $Z = 4$,

$D_c = 1.615 \text{ g cm}^{-3}$, deep-blue triangular prism, $\mu = 0.909 \text{ mm}^{-1}$, 3449 Unique data were collected as above and the structure solved and developed using heavy-atom methods. All non-H atoms were refined anisotropically on F ; H atoms bonded to O were constrained to lie at distances of 0.96 Å; the methyl group of MeCN was allowed to rotate about the CCN axis as a rigid entity and all other H atoms were included at calculated positions [SHELX76: G. M. Sheldrick, Univ. of Cambridge, 1976]. At final convergence, R , $R_w = 0.034$, 0.045, respectively, $S = 1.037$ for 376 parameters and 3239 data with $F \geq 4\sigma$ (F). The final ΔF synthesis exhibited no feature beyond $\pm 0.45 \text{ e Å}^{-3}$.

Crystal packings (CAMERON, L. J. Pearce and D. J. Watkin, Chemical Crystallography Laboratory, University of Oxford, 1993) are illustrated in Figs. 3 and 4. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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