

Design, synthesis and metal binding properties of a mixed-donor macrobicyclic

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A cryptand is resolved into its three independent macrocyclic components leading to novel, dynamic metal ion complexation.

Chelating agents which operate with the benefit of the macrocyclic effect possess an exceptional complexation potential which has facilitated the study of metals in unusual circumstances, *e.g.* uncommon coordination numbers, coordination geometries, donor atoms and/or oxidation states.¹ We describe below a case where, through innovative ligand design, Cu^I and Ag^I ions are guests in a novel and dynamic environment.

Macrobicyclic L¹ was conceptualised as a logical extension of an earlier study on the conformational preferences of [*n.n*]cyclophanes.² The molecule lies in a potential energy minimum where the aromatic rings are face to face and the three heteroatoms are in fixed equatorial positions.³ An important design consideration of this ligand system is that sandwich-type complexation involving η⁶-bonding to the benzene rings is disfavoured by the large Ar...Ar separation (*ca.* 5.0 Å), and no assistance from the nitrogens can be expected owing to the distance between these atoms and the centre of the trigonal plane (*ca.* 3.0 Å) which they define. This means that L¹, formally a cryptand, is reduced conceptually to three independent, 16-membered azamacrocycles (Fig. 1) each capable of complexing a metal, especially if some contribution from the aromatic systems was forthcoming. Since only one of these three equivalent 'facets' can be occupied at any one time, it should be possible to promote spontaneous migration of the guest from nitrogen to nitrogen within the perimeter of the benzene rings above a characteristic temperature, effectively constituting 'dynamic' sandwich complexation with the centre of gravity of the metal coinciding with the molecular C₃ axis.

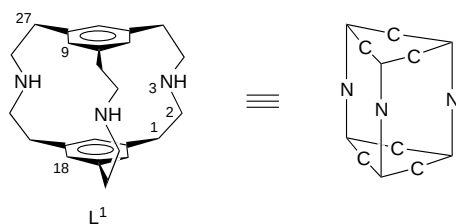
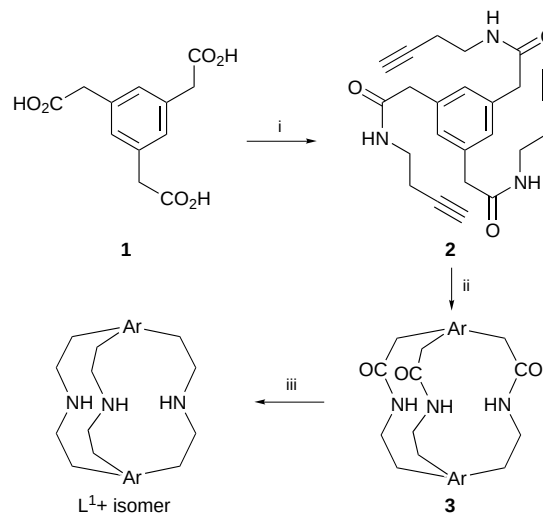


Fig. 1 Structure of L¹ and representation in terms of ligand sets

Compound L¹ can be conveniently synthesised by the cyclotrimerisation method shown in Scheme 1.⁴ Thus benzene 1,3,5-triacetic acid **1**, available by Willgerodt–Kindler reaction on commercial triacetylbenzene, is condensed with 4-aminobut-1-yne to give triyne **2** in 94% yield. Reaction of **2** with catalytic [CoCp(CO)₂] provides the bicyclic amide **3** as an inseparable mixture of 1,2,4- and 1,3,5-isomers (1.3:1, ratio) in 54% overall yield. The mixture is finally reduced with borane, whereupon L¹ can be isolated by column chromatography.

A stable complex is formed between L¹ and Cu^I by simply adding a solution of [Cu(MeCN)₄]BF₄ in acetonitrile to an equimolar quantity of the macrocycle in dichloromethane at room temp. The ¹H and ¹³C NMR spectra of this material show a desymmetrisation of the ligand resonances consistent with the expected mode of inclusion. In particular, the aromatic CH



Scheme 1 Reagents and conditions: i, carbonyldiimidazole, 4-aminobut-1-yne, THF; ii, [CoCp(CO)₂], *o*-xylene, heat; iii, BH₃·SMe₂, THF, heat then MeOH, heat

signal associated with the Cu is shifted 0.59 ppm downfield of the other two protons, indicative of electron withdrawal to the metal bond. Mass spectral data are also consistent with the formation of a 1:1 complex. Colourless crystals of [CuL¹]BF₄·H₂O suitable for X-ray diffraction were obtained from dichloromethane/ether solution, and determination of the structure† (Fig. 2) served to confirm our model. The Cu sits in a general position with Cu–N bond lengths of 2.01 Å. The closing of the N...N distance in **1** in order to achieve these bond lengths is made possible by a puckering inwards of the chains

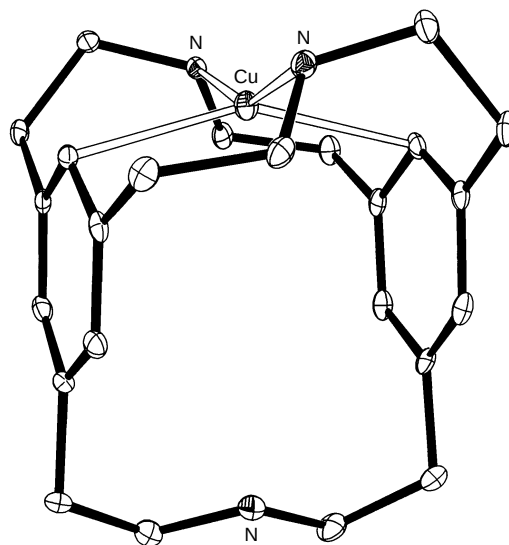


Fig. 2 Crystal structure of [CuL¹]BF₄·H₂O. Displacement ellipsoids are represented at the 30% probability level. The H-atoms, counter-ion and water of crystallization are omitted for clarity.

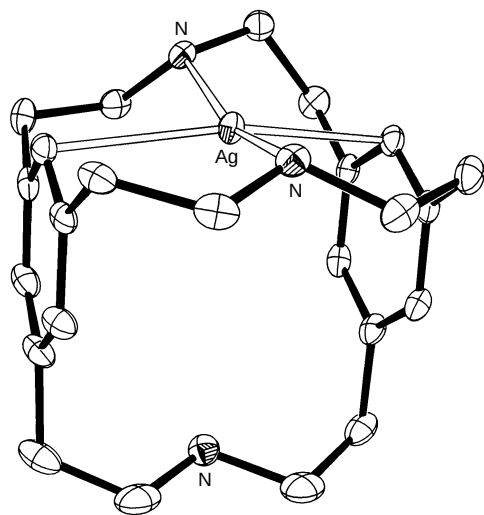


Fig. 3 Crystal structure of $[\text{AgL}^1]\text{OTf}$. Displacement ellipsoids are represented at the 20% probability level and the H-atoms and counter-ion are omitted for clarity. Only the major component of disorder affecting the free nitrogen [N3] is shown.

between which the metal is located. An interesting feature of this structure is the relationship of Cu to the benzene rings. This may involve either the metal acting as an electron acceptor in η^1 bonds to C,⁵ or three-centre, two-electron σ complexation to the aromatic C–H bonds.⁶ The $\text{Cu}\cdots\text{C}$ distances are 2.38 and 2.40 Å, and the 0.57 Å displacement of the metal away from C(9)–C(18) axis puts the contacts to the midpoint of the C–H bonds at 2.37 and 2.39 Å. The downfield shift in the NMR of the protons involved argues in favour of this type of interaction and against agostic bonding to the H, which would normally result in an upfield shift.⁷ It is noted that interactions between copper(I) and aryl rings are somewhat of a novelty in any case, with only five other structurally characterised examples appearing in the literature.⁸ All of these show exclusively η interactions to carbon, most with the Cu located over a π bond in an η^2 fashion.⁹

We then examined the dynamics of ligand exchange in $[\text{CuL}^1]$. The ^1H NMR spectrum ($\text{CDCl}_2\text{CDCl}_2$) shows temperature dependent fluxional behaviour, with collapse of the two aromatic signals to a single, broad peak occurring around 95 °C. Migration of the copper nominally involves breaking away from one of the nitrogens and both carbons [or C–H(σ) $\rightarrow$ Cu bonds] of a C_2N_2 ligand set before regaining the same from another set, although progression from site to site would take place under the continuous influence of the π system.

Reaction of the macrobicycle with AgOTf in THF gave the corresponding complex $[\text{AgL}^1]\text{OTf}$. Unlike $[\text{CuL}^1]\text{BF}_4$, the proton NMR (CD_2Cl_2) of this material showed a single resonance in the aromatic region at room temperature, and only on cooling below –50 °C did the signal split analogously to the copper(I) system into two sharp peaks (1:2), separated in this case by 0.27 ppm. This indicated a much greater degree of mobility for the silver ion than for Cu^I. The X-ray crystal structure of $[\text{AgL}^1]\text{OTf}$ † (Fig. 3) was comparable to that of $[\text{CuL}^1]\text{BF}_4$, the major difference being that only one of the two CCNCC chains needed to distort from the ideal all-*trans* conformation to accommodate the larger silver ion (Ag–N 2.32 Å). The outward displacement of the silver from the C9–C18 axis (0.40 Å) is slightly less than that for copper(I), but the same general NMR and structural arguments apply and either η^1 complexation or two electron donation from the C–H bonds can be invoked. A longer range contact to one of the oxygens of the

triflate ion (2.92 Å) is also observed normal to the (approximate) C_2N_2 plane.

Future work in this area will address the behaviour of other metal ions in the presence of L^1 , as well as structural modifications to the macrocycle (O, S analogues) which should further expand its scope as a novel ligand.

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Notes and References

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† *Single crystal structure determinations*: $[\text{CuL}^1]\text{BF}_4\cdot\text{H}_2\text{O}$: $\text{C}_{24}\text{H}_{33}\text{BCuF}_4\text{N}_3\cdot\text{H}_2\text{O}$, $M_r = 531.90$, colourless irregular plate $0.39 \times 0.39 \times 0.10$ mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.937(12)$, $b = 10.094(6)$, $c = 13.656(15)$ Å, $\alpha = 83.23(7)^\circ$, $\beta = 81.19(12)^\circ$, $\gamma = 61.24(6)^\circ$, $U = 1185.0(17)$ Å³, $Z = 2$, $D_c = 1.491$ g cm^{–3}, $\mu(\text{Mo-K}\alpha) = 0.976$ mm^{–1}, $T = 150$ K. Stoe Stadi-4 four-circle diffractometer, Mo-K α radiation ($\lambda = 0.71073$ Å) $2\theta_{\text{max}} = 50^\circ$. Numerical absorption corrections ($T = 0.756\text{--}0.908$). The structure was solved by automatic direct methods (G. M. Sheldrick, SHELXS-96, *Acta Crystallogr., Sect. A*, 1990, **46**, 467) and refined by full-matrix least squares on F^2 (G. M. Sheldrick, SHELXL-96, University of Göttingen, Germany, 1996) with all non-H atoms assigned anisotropic displacement parameters. Methylene H atoms were placed geometrically, others being located from ΔF syntheses; thereafter those of H_2O were refined freely with others constrained to ride on their parent atoms. Final R_1 [$F_o > 4\sigma(F_o)$] = 0.0551, wR_2 (all data) = 0.1264 for 4150 unique reflections and 328 refined parameters.

$[\text{AgL}^1]\text{OTf}$: $\text{C}_{25}\text{H}_{33}\text{AgF}_3\text{N}_3\text{O}_3\text{S}$, $M_r = 620.5$, colourless plate $0.53 \times 0.48 \times 0.11$ mm, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.152(5)$, $b = 10.655(5)$, $c = 19.306(4)$ Å, $\beta = 106.50(2)^\circ$, $U = 2594.0(9)$ Å³, $Z = 4$, $D_c = 1.589$ g cm^{–3}, $\mu(\text{Mo-K}\alpha) = 0.911$ mm^{–1}, $T = 220$ K. Data were collected as for $[\text{CuL}^1]\text{BF}_4\cdot\text{H}_2\text{O}$ and absorption corrections ($T = 0.582\text{--}0.775$) based on azimuthal scans were applied. The structure was solved and refined as for $[\text{CuL}^1]\text{BF}_4\cdot\text{H}_2\text{O}$. Static disorder was modelled in the region of the non-coordinating N, with major (0.76) and minor (0.24) components and with restraints applied to C–C and C–N distances. The H atom on the minor component was omitted, that on the major was restrained during refinement and all others were riding on their parent atoms. Final R_1 [$F_o > 4\sigma(F_o)$] = 0.0414, wR_2 (all data) = 0.1071 for 4561 unique reflections and 328 refined parameters. CCDC 182/710.

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