

Synthesis of a New Binucleating Ligand LH_4 : † Synthesis and X-Ray Structures of *anti*- $[Co_2(LH_4)(H_2O)_2](NO_3)_4 \cdot 5H_2O$, *anti*- $[Ni_2(LH_4)(NCMe)_2](PF_6)_4 \cdot 4H_2O$, *anti*- $[Zn_2(LH_4)(NO_3)_2](NO_3)_2$ and *syn*- $[Cu_2(LH_2)](BPh_4)_2$

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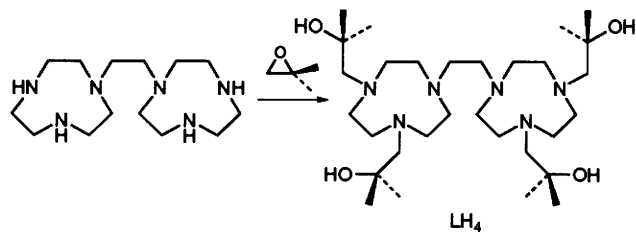
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The binuclear octahedral M^{II} complexes $[Co_2(LH_4)(H_2O)_2]^{4+}$, $[Ni_2(LH_4)(NCMe)_2]^{4+}$ and $[Zn_2(LH_4)(NO_3)_2]^{2+}$, incorporating the new 10 coordinate pendant arm ligand LH_4 , † all show an *anti*-configuration; in contrast the Cu^{II} complex $[Cu_2(LH_2)]^{2+}$ adopts a *syn*-configuration incorporating intramolecular H-bonding.

Metal macrocyclic complexes incorporating pendant arms offer a methodology by which the coordination geometry at the metal centre(s) can be controlled and manipulated for specific stereochemistries.¹ A variety of pendant arm N ,² O ,³ S^4 and P -donor⁵ derivatives of [9]aneN₃ have been prepared. We have embarked upon a programme to design and synthesise ligands to complex one, two or more metal centres in specific coordination geometries. The availability of vacant site(s) at the metal centre can be controlled by the number of pendant arms and the donicity of the cyclic core. We report herein the synthesis of the pendant arm alcohol ligand, LH_4 , and its complexation to Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} ions.

The potentially 10-coordinate ligand LH_4 is of interest since it would be expected to complex two metal ions leaving one vacant site at each octahedral metal centre. In principle, therefore, this ligand might form complexes in which five-coordinate metal ions are placed in close proximity to one another. LH_4 † was prepared by reaction of 1,2-bis(1,4,7-triazacyclo-1-nonyl)ethane⁶ with 2,2-dimethyl oxirane in ethanolic solution. ‡ (Scheme 1).

$[Co_2(LH_4)(H_2O)_2][NO_3]_4$ † is prepared in good yield from the reaction of LH_4 with $[Co(H_2O)_6][NO_3]_2$ in aqueous ethanol at room temperature. Pale lilac crystals suitable for X-ray diffraction were grown by the slow evaporation of an H_2O -EtOH solution of the complex. The single crystal X-ray structure of the cation $[Co_2(LH_4)(H_2O)_2]^{4+}$ (Fig. 1) shows § the ligand binding two metal centres in a transoid *anti*-configuration. The sixth coordination site of each metal centre is occupied by a water molecule. The cation in $[Co_2(LH_4)(H_2O)_2][NO_3]_4$ shows complex hydrogen bonding to the nitrate counter ions; this is not an uncommon feature in structures with nitrate ions. In the preparation of $[Co_2(LH_4)(H_2O)_2][NO_3]_4$ no oxidation to the corresponding Co^{III} species is observed in spite of the N_3O_3 donor set and the relatively small cavity size of the ligand at each coordination site. The oxidative stability of $[Co_2(LH_4)(H_2O)_2]^{4+}$ is of note as it is an example of a 9-membered N-donor ligand in which the Co^{II} state is stable in solution at neutral pH. In contrast, Co^{II} derivatives of [9]aneN₃ with three pendant-arm alcohol donors are very air sensitive and rapidly oxidise in air to afford the corresponding Co^{III} species.⁷ Normally, 10-membered or larger ring systems are required to stabilise Co^{II} in the presence of pendant arm OH donors.⁸ The air stability of $[Co_2(LH_4)(H_2O)_2][NO_3]_4$ is, however, only possible at neutral pH values, with the addition of base resulting in the formation of a brown solution which becomes an intense purple colour



Scheme 1

within a few minutes. This purple species has an absorption spectrum characteristic of a Co^{III} complex, potentially a μ -peroxo species.

Reaction of Ni^{II} and Zn^{II} salts with LH_4 affords the corresponding complexes *anti*- $[Ni_2(LH_4)(NCMe)_2](PF_6)_4 \cdot 4H_2O$ and *anti*- $[Zn_2(LH_4)(NO_3)_2](NO_3)_2$ respectively. ‡ These species have been characterised by single crystal X-ray diffraction, which confirms § the *anti*-configuration for both complexes.

Reaction of $[Cu(OAc)_2]$ with LH_4 affords a dark blue complex $[Cu_2(LH_2)]^{2+}$. ‡ The single crystal X-ray structure

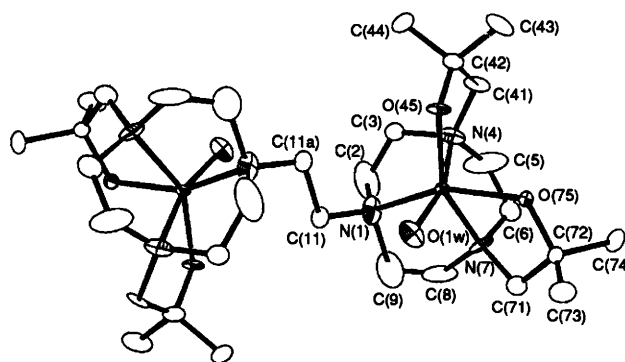


Fig. 1 View of structure of $[Co_2(LH_4)(H_2O)_2]^{4+}$ with numbering scheme adopted. H atoms omitted for clarity. $Co-N(1)$ 2.166(6), $Co-N(4)$ 2.133(6), $Co-N(7)$ 2.123(6), $Co-O(45)$ 2.065(4), $Co-O(75)$ 2.157(4), $Co-O(1W)$ 2.091(5) Å. For $[Ni_2(LH_4)(NCMe)_2]^{4+}$: $Ni-N(1)$ 2.057(4), $Ni-N(4)$ 2.046(4), $Ni-N(7)$ 2.137(4), $Ni-O(14)$ 2.150(3), $Ni-O(19)$ 2.036(3), $Ni-N(1s)$ 2.028(4) Å. For $[Zn_2(LH_4)(NO_3)_2]^{2+}$: $Zn-O(5N)$ 2.055(5), $Zn-O(20)$ 2.114(5), $Zn-O(15)$ 2.123(5), $Zn-N(4)$ 2.157(6), $Zn-N(7)$ 2.175(6), $Zn-N(1)$ 2.231(6) Å.

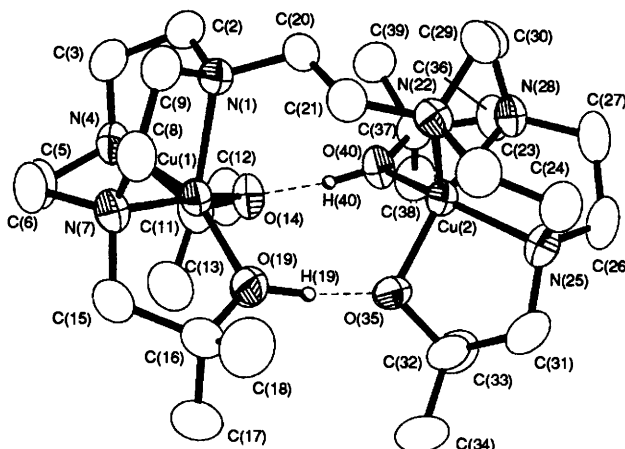


Fig. 2 View of structure of *syn*- $[Cu_2(LH_2)]^{2+}$ with numbering scheme adopted. H atoms not involved in intramolecular H-bonding have been omitted for clarity. $Cu(1)-N(1)$ 2.245(3), $Cu(1)-N(4)$ 2.039(3), $Cu(1)-N(7)$ 2.013(3), $Cu(1)-O(14)$ 1.9079(24), $Cu(1)-O(19)$ 1.964(3), $Cu(2)-N(22)$ 2.215(3), $Cu(2)-N(25)$ 2.029(3), $Cu(2)-N(28)$ 2.012(3), $Cu(2)-O(35)$ 1.9191(23), $Cu(2)-O(40)$ 1.9454(23) Å.

determination of $[\text{Cu}_2(\text{LH}_2)](\text{BPh}_4)_2$ confirms§ (Fig. 2) that deprotonation of two of the pendant alcohol groups has occurred to form two $\text{O}\cdots\text{H}\cdots\text{O}$ bridges between the two halves of the binucleating ligand. Moreover, the complex cation $[\text{Cu}_2(\text{LH}_2)]^{2+}$ adopts a *syn* conformation in which the two encapsulated Cu^{II} centres lie on the same side of the binucleating ligand. Thus, double deprotonation of LH_4 affords a binuclear complex which is held in a *syn* configuration via intramolecular H-bonding. The Cu^{II} centres show a distorted square-based pyramidal stereochemistry. The loss of one proton from each coordination centre to form a coordinated alkoxide is unusual for a 2+ cation given that the product was crystallised at neutral pH. Normally, at least a 3+ cation is required to render coordinated alcohols sufficiently acidic.⁷

Current work is aimed at studying further potential *syn-anti* interconversion via variation of pH, metal oxidation state and by incorporation of bridging ligand(s).

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Footnotes

† L = 4,7,4',7'-tetrakis-(2-methyl-2-hydroxypropyl)-bis-1,1',1,4,7-triazacyclononylethane.

‡ All ligands and complexes were characterised by FAB mass spectrometry, electronic and IR spectroscopy and elemental analysis.

§ *Crystal data*. $\text{C}_{30}\text{H}_{78}\text{Co}_2\text{N}_{10}\text{O}_{23}$ (1), lilac column, $M = 1064.9$, triclinic, space group $P\bar{1}$, $a = 9.326(5)$, $b = 9.813(6)$, $c = 15.512(11)$ Å, $\alpha = 73.07(3)$, $\beta = 87.36(4)$, $\gamma = 62.99^\circ$, $V = 1207$ Å³ [from 2θ values of 23 reflections measured at $\pm\omega$ ($2\theta = 30\text{--}32^\circ$), $T = 150$ K], $Z = 1$, $D_c = 1.465$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.775$ mm⁻¹. $\text{C}_{34}\text{H}_{78}\text{F}_{24}\text{N}_8\text{Ni}_2\text{O}_6\text{P}_4$ (2), purple block, $M = 1312.0$, orthorhombic, space group $Pcab$, $a = 15.1656(15)$, $b = 18.353(3)$, $c = 20.539(3)$ Å, $V = 5716$ Å³ [from 2θ values of 35 reflections measured at $\pm\omega$ ($2\theta = 30\text{--}32^\circ$), $T = 150$ K], $Z = 4$, $D_c = 1.524$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.888$ mm⁻¹. $\text{C}_{30}\text{H}_{64}\text{N}_{10}\text{O}_{16}\text{Zn}_2$ (3), colourless column, $M = 951.7$, monoclinic, space group $P2_1/n$, $a = 8.387(4)$, $b = 13.053(3)$, $c = 18.607(5)$ Å, $\beta = 91.78(8)^\circ$, $V = 2036$ Å³ [from 2θ values of 20 reflections measured at $\pm\omega$ ($2\theta = 18\text{--}30^\circ$), $T = 150$ K], $Z = 2$, $D_c = 1.552$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.259$ mm⁻¹. $\text{C}_{78}\text{H}_{102}\text{Cu}_2\text{B}_2\text{N}_6\text{O}_4$ (4), royal blue plate, $M = 1336.5$, monoclinic, space group $P2_1/n$, $a = 14.2427(14)$, $b = 12.8965(11)$, $c = 38.652(3)$ Å, $\beta = 91.564(7)^\circ$, $V = 7097$ Å³ [from 2θ values of 37 reflections measured at $\pm\omega$ ($2\theta = 30\text{--}32^\circ$), $T = 298$ K], $Z = 4$, $D_c = 1.251$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.651$ mm⁻¹.

Data collection and processing. Crystals of (1)–(4) were transferred to a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device [J. Cosier & A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105] and graphite-monochromated Mo-Kα X-radiation ($\lambda = 0.71073$ Å). Data were collected at 150 K for (1)–(3) and at 298 K for (4).

For (1): 3467 absorption-corrected reflections to $2\theta_{\text{max}} 45^\circ$, 3139 unique ($R_{\text{int}} 0.018$), of which 2990 with $F \geq 4\sigma(F)$ were used in all calculations. The structure was solved by automatic direct methods [SHELXTL/PC: G. M. Sheldrick, Univ. of Göttingen, Germany 1990; Siemens Analytical X-ray Instrumentation, Inc., Madison, WI, USA] and refined by full-matrix least squares analysis (on F) with anisotropic thermal parameters for all non-H atoms [SHELX76: G. M. Sheldrick, Univ. of Cambridge, England, 1976]. Disorder in the nitrate anions and in one of the water molecules required modelling. H atoms on C were included in fixed, calculated positions while those on O were omitted. At final convergence, $R = 0.0794$, $R_w = 0.1239$, $S = 4.14$ for 292 parameters and the final ΔF synthesis showed no feature above 1.94 eÅ⁻³.

For (2): 5390 reflections to $2\theta_{\text{max}} 45^\circ$, 3421 unique ($R_{\text{int}} 0.010$), of which 2729 with $F \geq 4\sigma(F)$ were used in all calculations. Following

solution by heavy atom methods the structure was refined by full-matrix least squares (on F) with anisotropic thermal parameters for all non-H atoms. With the exception of the hydroxyl H(14), H(19), H(1 wa), H(1 wb), H(2 wa) and H(2 wb), which were located in a ΔF synthesis and restrained to lie $0.96(1)$ Å from their respective O atoms, H atoms were included in calculated positions [SHELX 76: as above]. At final convergence, $R = 0.0392$, $R_w = 0.0441$, $S = 1.249$ for 382 parameters and the final ΔF synthesis showed no feature above 0.73 eÅ⁻³.

For (3): 5045 reflections to $2\theta_{\text{max}} 40^\circ$, 1910 unique ($R_{\text{int}} 0.074$), of which 1903 were used in all calculations. The Zn was located from a Patterson synthesis and the remaining non-H atoms in subsequent ΔF syntheses. All non-H atoms were allowed anisotropic motion, and all H atoms except that on O(20) were located. After refinement of 263 parameters on F^2 [SHELXL-93: G. M. Sheldrick, Univ. of Göttingen, Germany, 1993], convergence gave $R[F \geq 4\sigma(F)] = 0.0397$ for 1207 data and $wR[F^2] = 0.1037$, $S[F^2] = 1.081$ for all 1910 data and the final ΔF synthesis showed no feature above ± 0.39 eÅ⁻³.

For (4): 14826 absorption-corrected reflections to $2\theta_{\text{max}} 50^\circ$, 11417 unique ($R_{\text{int}} 0.036$) of which 9097 with $F \geq 4\sigma(F)$ were used in all calculations. Following solution by heavy atom methods [SHELXS-86: G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467] the structure was refined by full-matrix least-squares (on F). Anisotropic thermal parameters were allowed for non-H atoms and H atoms were included in calculated positions, excepting the hydroxylic H(19) and H(40) which were located from a ΔF synthesis and subsequently refined [SHELX-76: as above]. At final convergence, $R = 0.0473$, $R_w = 0.0509$, $S = 1.204$ for 741 parameters and the final ΔF synthesis showed no feature above 0.50 eÅ⁻³.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited with the Cambridge Crystallography Data Centre. See Information for Authors, Issue No. 1.

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