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A Flexible Ligand for Multipurpose Complexation*

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The synthesis of the flexible ligand 2,6-bis-{(bis-(2-aminoethyl)amino(methyl}anisole (L) is reported. The basicity behaviour in aqueous solution was studied by potentiometry (25°C, $I = 0.15\,\mathrm{mol\,dm^{-3}}$, Me_4NCl). L behaves as pentaprotic base ($\log K_1 = 10.31(2)$, $\log K_2 = 9.65(2)$, $\log K_3 = 9.16(2)$, $\log K_4 = 8.39(2)$, $\log K_5 = 2.14(2)$). The stability constants for Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes were determined by potentiometry and all of these metal ions were found to form both mono and binuclear species: $\log K_{ML} = 9.39(3)$ for Co(II); 14.5(1) for Ni(II); 17.57(7) for Cu(II); 10.62(2) for Zn(II) and 9.83(3) for Cd(II). $\log K_{M2L} = 15.19(3)$ for Co(II); 19.57(5) for Ni(II); 28.44(3) for Cu(II); 16.77(6) for Zn(II) and 14.62(3) for Cd(II). The crystals of $[Cu_4L_2(N_3)_6](ClO_4)_2 \cdot H_2O$ are triclinic, space group P−1 $a = 13.770(6)$, $b = 14.043(2)$, $c = 16.800(3)$ Å, $\alpha = 105.700(1)$, $\beta = 102.790(3)$, $\gamma = 103.660(3)°$, $Z = 2$. L behaves as ditopic ligand and the crystal lattice consists of branched chains of Cu(II) ions.

Keywords: Synthesis; Complexes; Crystal structure; Equilibria

INTRODUCTION

In metal coordination chemistry, ligand topology and the nature of the donor atom are by far the most important characteristics influencing ligand binding capabilities. Synthetic control of the above properties was the unreachable goal of the present work. Herein we report the synthesis and ligational capabilities of a member of one (L in Fig. 1) series of very flexible ligands prone to form binuclear metal complexes. These species are of great interest because they can mimic biological sites and can be used to host small external molecules such as oxygen or nitric oxide to form supramolecular assemblies [1].

The synthesis of the new acyclic ligand 2,6-bis-{[bis-(2-aminoethyl)amino]methyl}-anisole (L), which contains two diethylentriamine subunits linked through the central nitrogen atom by a 2,6-dimethylanisolic group, is described.

RESULTS AND DISCUSSION

Synthesis

The synthetic pathway used to obtain ligand L is depicted in Scheme 1. The reaction of

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*Dedicated to Prof. Piero Paoletti, a mentor who has instilled his rigour and enthusiasm for the field of chemistry in his students.

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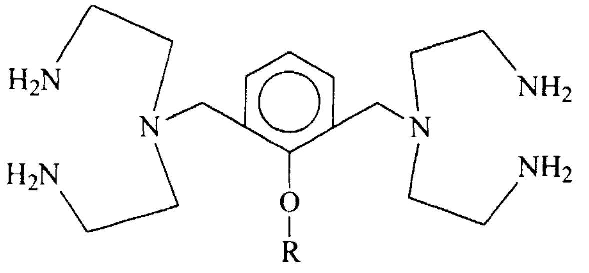
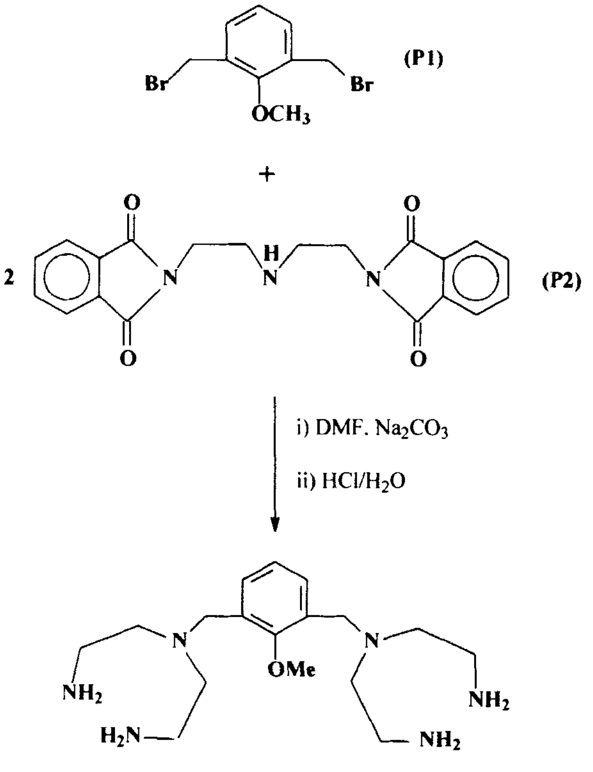


L, R = CH_3

FIGURE 1 Synthetic pathway followed to obtain compound L.



L

SCHEME 1 Schematic representation of the compound L.

2,6-dibromo-methyl-anisole (**P1**) with two equivalent of N,N′-imminodiethylenebisphthalimide (**P2**), in the presence of a base, gives the intermediate molecule 2,6-bis[[bis-(2-phthalimdoethyl)-amino]methyl]-anisole in high yield. The cleavage reaction of the *phthalic* groups was carried out with HCl 6 M, obtaining **L**, after the work up, as hydrochloride salt. The ligand is very flexible and belongs to a series of similar molecules: the anisolic group can be either removed [2] or transformed into a phenolic group [3]. Furthermore, while maintaining the same overall molecular framework the ligational properties can be varied considerably by changing both the length of the hydrocarbon chains connecting the nitrogen atoms and the substituent groups on the donor atoms. The synthesis and some results related to the similar compound containing a phenolic group rather than an anisolic group are reported in Ref. [3].

Equilibrium Studies

Under the experimental conditions employed, **L** can bind up to five hydrogen ions. The stepwise basicity constants are reported in Table I. The sequence of basicity constants of L can be easily interpreted in terms of positive charge repulsions. In the first four protonation steps there is only a slightly decrease in the basicity strength: from $\log K_1 = 10.31$ to $\log K_4 = 8.39$ (see Tab. I). The molecule is very flexible and the four positive charges can be located on the primary nitrogen atoms which are distant from each other, thus experiencing little repulsion. Only in the last protonation step should the proton be bound to tertiary nitrogen atoms experiencing a great charge repulsion due to the two protons already present on the secondary nitrogen atoms

TABLE I Equilibrium constants (298.15 K, I = 0.15 mol dm^{-3}, Me_4NCl) for the protonation equilibria of L in aqueous solution

Reaction	Log K
$L + H^+ = HL^+$	10.31(2)[a]
$HL^+ + H^+ = H_2L^{2+}$	9.65(2)
$H_2L^{2+} + H^+ = H_3L^{3+}$	9.16(2)
$H_3L^{3+} + H^+ = H_4L^{4+}$	8.39(2)
$H_4L^{4+} + H^+ = H_5L^{5+}$	2.14(2)

[a] Values in parentheses are the standard deviations in the last significant figure.

of the same unit. As a consequence of these strong charge repulsions, the basicity strength of **L** in the fifth protonation step drops by more than six log units from $\log K_4 = 8.39$ to $\log K_5 = 2.14$ (see Tab. I). Furthermore, the first four protonation constants of **L** are similar to the first two basicity constants of the linear triamine diethylenetriamine ($\log K_1 = 9.85$, $\log K_2 = 9.06$ from Ref. [4]), indicating that the two subunits behave independently and the influence of the anisolic group on the basicity behaviour of **L** is marginal or inexistent.

The equilibrium constants relative to metal complex equilibria in aqueous solution are reported in Table II. **L** forms stable mono- and binuclear complexes with all of the transition metal ions thus investigated (see Tab. II). The molecular topology with two symmetrical subunits facilitates the formation of binuclear species; however, because the subunits are close to each other and not independent, the addition of the second metal ion is affected by the presence of the first one and is less favoured. The addition of one hydrogen atom to the mononuclear species $[\mathrm{ML}]^{2+}$ to form the protonated species $[\mathrm{MLH}]^{3+}$ has a very high reaction constant (see Tab. II) very similar to that of ligand protonation. This is a clear indication that the protonated nitrogen donor atom is not bound to the metal ion. Even the addition value of a further proton to the $[\mathrm{MLH}]^{3+}$ species to obtain the $[\mathrm{MLH_2}]^{4+}$ species is very high, confirming that in the mononuclear species there are too many donor atoms for all of them to be involved in the complex formation. The situation changes in the case of binuclear $[\mathrm{M_2}\mathbf{L}]^{4+}$ species, which have a great tendency to form hydroxo species, indicating that for two metal ions the donor atoms present in the molecule are not enough to satisfy the coordination requirement of two metal ions. It is in fact the lack of donor atoms which makes the binuclear species especially important for binding substrates like water molecules or azide ions, as found in the reported crystal structure. While the influence of the anisolic group was found on the basicity behaviour of **L** to be marginal, the situation is completely different in the case of metal complex formation, where the bulky non-coordinating —O—$\mathrm{CH_3}$ group forces the molecule to behave in a completely ditopic manner. In this case, each metal ion must fulfil its coordination needs on each side of the molecule by using external donor atoms; indeed, all of the metal ions investigated form binuclear di-hydroxo species (see Tab. II).

TABLE II Equilibrium constants (298.15 K, $I = 0.15\ \mathrm{mol\ dm^{-3}}$, $\mathrm{Me_4NCl}$) for the metal complex equilibria of **L** in aqueous solution

Reaction	Log K				
	Co	Ni	Cu	Zn	Cd
$\mathrm{M} + \mathbf{L} = \mathrm{ML}$[a]	9.39(3)[b]	14.5(1)	17.56(7)	10.62	9.83(3)
$\mathrm{M} + \mathbf{L} + \mathrm{H} = \mathrm{MLH}$	18.46(5)	22.57(7)	26.62(7)	19.71(5)	18.75(3)
$\mathrm{M} + \mathbf{L} + 2\mathrm{H} = \mathrm{MLH_2}$	26.74(3)	29.04(3)	33.40(3)	27.74(3)	26.53(3)
$\mathrm{M} + \mathbf{L} + \mathrm{H_2O} = \mathrm{MLOH} + \mathrm{H}$	−0.88(5)		6.3(1)	0.63(5)	−1.24(5)
$2\mathrm{M} + \mathbf{L} = \mathrm{M_2L}$	15.19(3)	19.57(5)	28.44(3)	16.77(6)	14.62(3)
$2\mathrm{M} + \mathbf{L} + \mathrm{H_2O} = \mathrm{M_2LOH} + \mathrm{H}$	5.36(6)	9.25(7)	21.79(7)	9.44(6)	4.80(5)
$2\mathrm{M} + \mathbf{L} + 2\mathrm{H_2O} = \mathrm{M_2L(OH)_2} + 2\mathrm{H}$	−4.79(4)	−1.9(1)	11.71(8)	0.13(8)	−6.38(7)
$\mathrm{ML} + \mathrm{H} = \mathrm{MLH}$	9.1	8.1	9.1	9.1	8.9
$\mathrm{MLH} + \mathrm{H} = \mathrm{MLH_2}$	8.3	6.5	6.8	8.0	7.8
$\mathrm{ML} + \mathrm{OH} = \mathrm{MLOH}$	3.5	–	2.5	3.7	2.7
$\mathrm{M_2L} + \mathrm{OH} = \mathrm{M_2LOH}$	3.9	3.4	7.0	6.4	3.9

[a] Charges omitted for clarity.

[b] Values in parentheses are the standard deviations in the last significant figure.

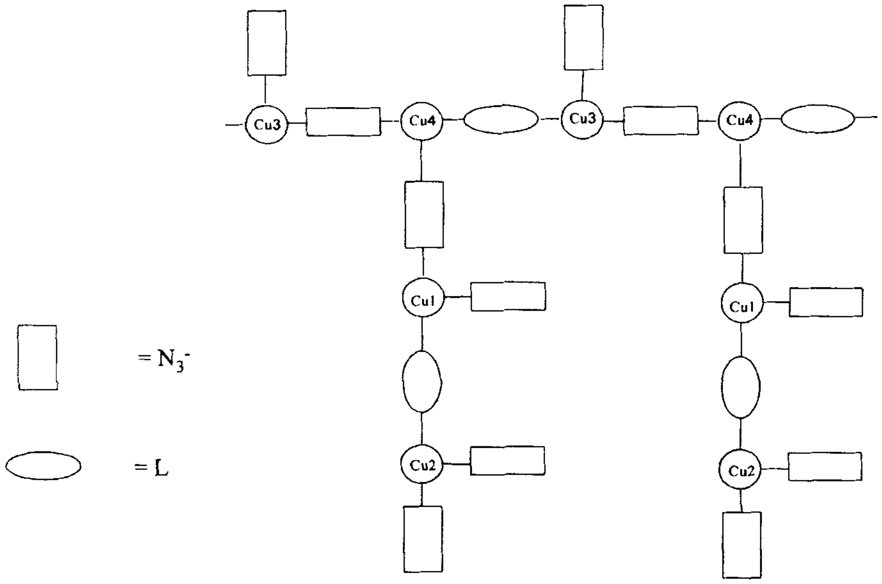
Crystal Structure

The crystal lattice consists of branched chains of Cu(II) ions bearing an overall bipositive charge, perchlorate anions and water molecules. The $[Cu_4L_2(N_3)_6]^{2+}$ moiety constitutes the repeating unit which propagates along the *y*-axis (Scheme 2).

The mean linear chain is made up of binuclear $[Cu_2L]^{4+}$ complexes linked by a single end-to-end azide group. In the same fashion, a second azide group bridges a copper ion of the main chain and the $[Cu_2L(N_3)]^{3+}$ unit of the ramification. Finally, with the exception of the branched copper, the other three metal ions each bear one terminally bound azide group. The tendency of the azide grouping to act as bridging unit between Cu(II) ions is well documented in several structures [5] retrieved from the Cambridge Structural Database [6].

Because **L** acts as a ditopic ligand providing three nitrogen donor atoms to each copper ion, the four independent metal ions reach an overall coordination number of five (Fig. 2). In all cases the arrangement of the nitrogen donor atoms around the metal ion results in a square pyramid with the nitrogen atoms supplied by the chelate ligand always positioned at the vertices of the basal plane. The azide group bridging the repeating unit in the *y*-propagating chain occupies the apical position in the Cu3 environment and an equatorial one in the Cu4 coordination sphere, while both of the terminal nitrogen atoms of the N_3^- moiety connecting the $[Cu_2L(N_3)]^{3+}$ side chain are at the apex of the square pyramid about Cu1 and Cu4 (Fig. 3). Given this disposition of the azide donors, the apexes of the square pyramids about Cu3 and Cu4 are pointing in opposite directions with respect to the mean plane of the ligand, while the apical azide donors are on the same side in the branched binuclear complex. As a consequence, the two $[Cu_2L]^{4+}$ moieties are intrinsically different, although the conformation adopted by the ligand is very similar.

The equatorial set of atoms of the square pyramid about each metal ion exhibits rather small deviations from planarity (largest deviation 0.07(2) Å), with the exception of the donors defining the basal plane of Cu4, where N22 shows the largest deviation from the



SCHEME 2 Block scheme of the branched Cu(II) chain.

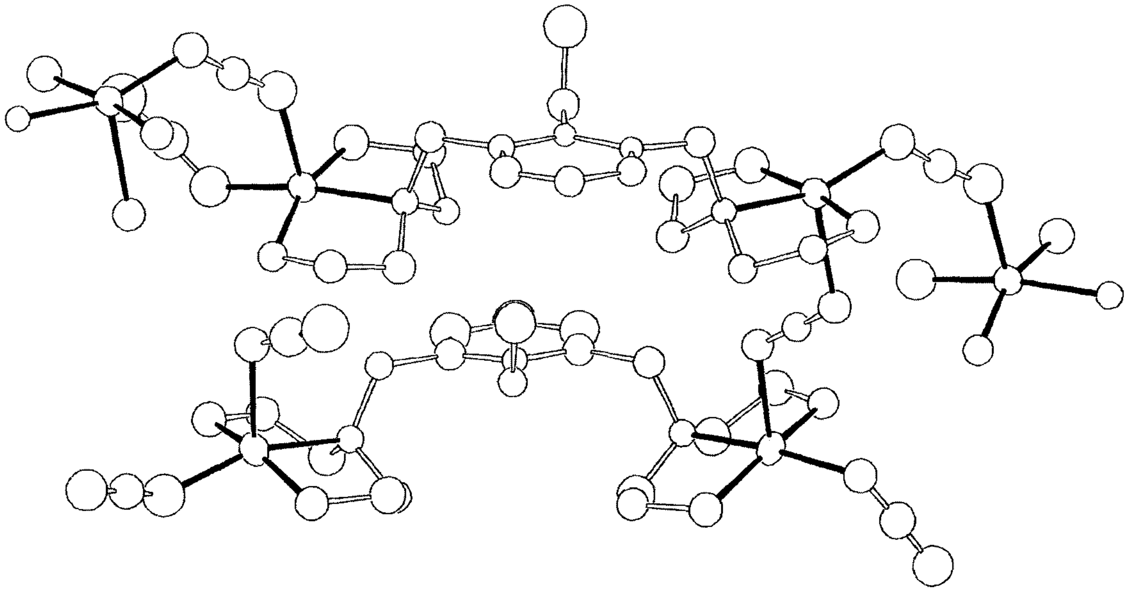


FIGURE 2 ORTEP view of the two binuclear complexes with atom numbering.

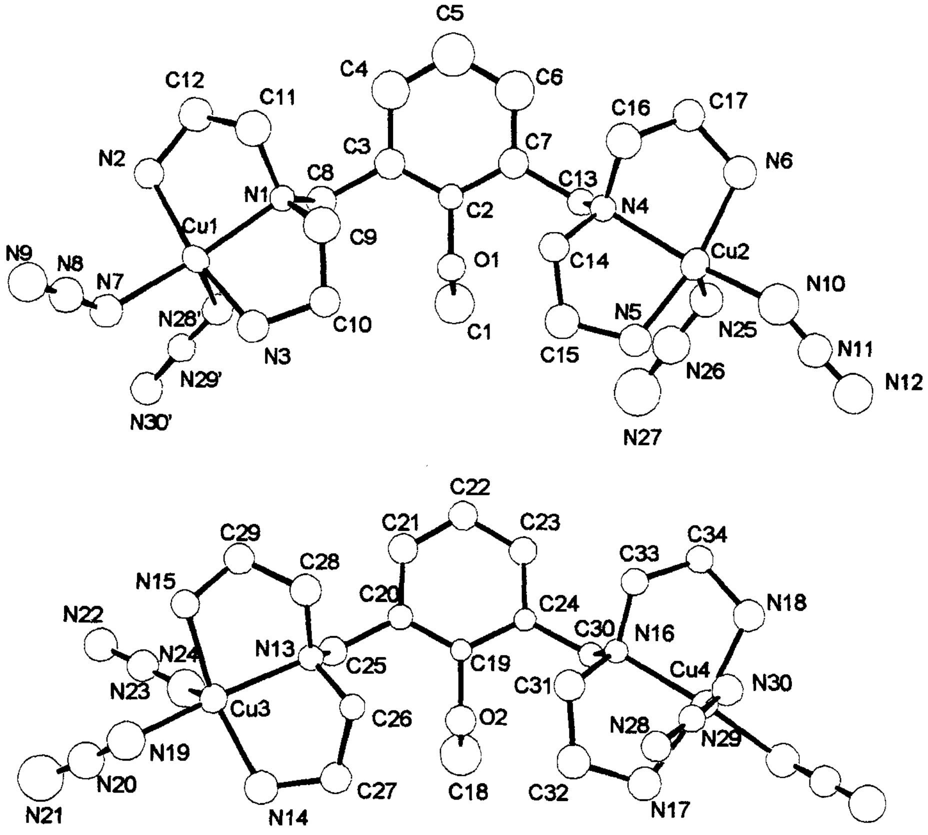


FIGURE 3 Drawing of the cation $[Cu_2L(N_3)_6]_n^{2+}$.

TABLE III Selected bond lengths [Å] and angles [°] for **1**

Cu(1)—N(1)	2.07(1)
Cu(1)—N(2)	2.01(1)
Cu(1)—N(3)	2.01(1)
Cu(1)—N(7)	2.02(1)
Cu(1)—N(28)′	2.35(1)
Cu(2)—N(4)	2.11(1)
Cu(2)—N(5)	2.00(1)
Cu(2)—N(6)	2.00(1)
Cu(2)—N(10)	2.01(2)
Cu(2)—N(25)	2.21(1)
Cu(3)—N(13)	2.10(1)
Cu(3)—N(14)	1.99(1)
Cu(3)—N(15)	1.99(1)
Cu(3)—N(19)	1.98(2)
Cu(3)—N(24)″	2.27(2)
Cu(4)—N(16)	2.05(1)
Cu(4)—N(17)	2.00(1)
Cu(4)—N(18)	1.99(1)
Cu(4)—N(22)	1.97(1)
Cu(4)—N(30)	2.35(1)
N(2)—Cu(1)—N(7)	93.4(5)
N(2)—Cu(1)—N(3)	163.3(5)
N(7)—Cu(1)—N(3)	96.0(5)
N(2)—Cu(1)—N(1)	84.2(5)
N(7)—Cu(1)—N(1)	171.1(5)
N(3)—Cu(1)—N(1)	84.5(5)
N(2)—Cu(1)—N(28)′	99.0(5)
N(7)—Cu(1)—N(28)′	91.6(5)
N(3)—Cu(1)—N(28)′	94.5(5)
N(1)—Cu(1)—N(28)′	97.2(5)
N(6)—Cu(2)—N(5)	161.2(5)
N(6)—Cu(2)—N(10)	91.8(6)
N(5)—Cu(2)—N(10)	92.3(6)
N(6)—Cu(2)—N(4)	84.2(5)
N(5)—Cu(2)—N(4)	85.0(5)
N(10)—Cu(2)—N(4)	157.4(6)
N(6)—Cu(2)—N(25)	99.0(5)
N(5)—Cu(2)—N(25)	98.0(5)
N(10)—Cu(2)—N(25)	102.4(6)
N(4)—Cu(2)—N(25)	100.2(5)
N(19)—Cu(3)—N(14)	92.6(6)
N(19)—Cu(3)—N(15)	94.9(5)
N(14)—Cu(3)—N(15)	162.0(5)
N(19)—Cu(3)—N(13)	170.2(6)
N(14)—Cu(3)—N(13)	84.4(5)
N(15)—Cu(3)—N(13)	85.5(5)
N(19)—Cu(3)—N(24)″	94.2(6)
N(14)—Cu(3)—N(24)″	102.5(5)
N(15)—Cu(3)—N(24)″	93.3(5)
N(13)—Cu(3)—N(24)″	95.5(5)
N(22)—Cu(4)—N(18)	95.9(5)
N(22)—Cu(4)—N(17)	94.2(5)
N(18)—Cu(4)—N(17)	169.7(5)
N(22)—Cu(4)—N(16)	159.9(5)
N(18)—Cu(4)—N(16)	84.8(5)
N(17)—Cu(4)—N(16)	84.9(5)
N(22)—Cu(4)—N(30)	99.0(5)
N(18)—Cu(4)—N(30)	88.7(5)
N(17)—Cu(4)—N(30)	91.8(5)
N(16)—Cu(4)—N(30)	101.2(4)

′: x − 1, y, z.
″: x, y + 1, z.

least-squares plane (0.19(2) Å). In all cases the copper ion is shifted ca. 0.2 Å towards the apical donor. The values of the Cu—N(**L**) bonds (mean 2.03 Å) are very close to those observed in previously reported Cu(II) complexes with chelating ligands and amine nitrogen donors (Tab. III) [6]. Concerning the values of the azido-copper bonds, the equatorial distances (ranging from 1.97(1) to 2.02(1) Å) are shorter than the axial ones (range 2.21(1) - 2.35(1) Å), and both are in agreement with those shown by other azido-Cu(II) complexes [6]. Finally, about the azido groupings, these are nearly linear (maximum deviation 5°) with the intra azide N—N bond distances equal within 3σ; in addition all the angles at the bound azide-nitrogen atoms are compatible with an sp^2 hybridization, thus their electronic structure can be represented in valence bond theory as $(\langle N{=}N{=}N\rangle)^{-}$. The Cu—Cu interatomic distances are ca. 9.7 Å in the binuclear $[Cu_2\mathbf{L}]^{4+}$ cations (Cu3—Cu4 9.725(4) and Cu1—Cu2 9.789(4) Å), while the shortest intra-chain distance is 5.341(4) between Cu3 and Cu4′(x, y + 1, z). Concerning the inter-chain distances Cu1 is 6.252(5) Å apart from Cu4 and Cu2 is 6.601(5) Å far from Cu3.

Finally, the water molecule interacts, *via* H-bond, with an azide-nitrogen (O11…N25 2.90(3) Å) and many contacts below 3 Å exist between the perchlorate oxygen atoms and the hydrogen atoms of the terminal —NH_2 groups.

Conclusions

The compound studied shows a great capability to form binuclear metal complexes, both in solution and in the solid state. The presence of two subunits separated by the anisolic group which enhance the compartmental behaviour of **L**, greatly influences its binding properties towards metal ions. The crystal structures of the Cu(II) complex are chain-like, with azide groups acting as bridging groups between different binuclear $[Cu_2L]^{4+}$ units (see Fig. 2). In the case of the similar ligand, where the anisolic group is replaced by a phenolic group, the crystal structures of Cu(II) binuclear complexes show either —OH (see Ref. [2]) or N_3^- (see Ref. [3]) as bridging groups within the same binuclear species. These results once again support the importance of the role played by the anisolic group.

EXPERIMENTAL

Synthesis

The synthesis of ligands **L** was obtained following the procedure reported in Scheme 1. 2,6-Dibromo-methyl-anisole (**1**) [7] and N,N′-imminodiethylenebisphthalimide (**2**) [8] were prepared as previously described. Solvents and starting materials were used as purchased.

2,6-bis{[bis-(2-phthalimidoethyl)-amino]methyl}-anisole

Over a period of 3 h, a solution of **P1** (2.9 g, 0.01 mol) in 200 cm^3 of dimethylformamide was added to a refluxing suspension of **P2** (7.3 g, 0.02 mol) and of Na_2CO_3 (5.3 g, 0.05 mol) in 250 cm^3 of dimethylformamide. The reaction mixture was maintained under reflux for a further 3 hours. Subsequently, the mixture was cooled to room temperature and the resulting suspension was filtered. The solution was concentrated to 100 cm^3 under reduced pressure and poured into cold water (500 cm^3), obtaining the product as a white solid. Yield: 7.8 g (91%). Anal. Calcd. For $C_{49}H_{42}N_6O_9$: C 68.52; H 4.93; N 9.78. Found: C 68.3; H 4.8; N 9.7. ^{1}H NMR ($CDCl_3$, 25°C): 2.79 (t, 8H), 3.59 (s, 3H), 3.66 (s, 4H), 3.76 (t, 8H), 6.16 (t, 1H), 6.86 (d, 2H), 7.70 (m, 16H) ppm.

2,6-bis{[bis-(2-aminoethyl)-amino]methyl}-anisole (L)

2,6-bis{[bis-(2-phthalimidoethyl)-amino]methyl}-anisole (4.3 g, 5.0 mmol) was suspended in HCl 6 M (50 cm^3). The reaction mixture was maintained under reflux for one day. Subsequently, the mixture was cooled to room temperature and the resulting suspension was filtered to eliminate the phthalic acid. The solution was evaporated under reduced pressure to give a white solid, which was recrystallized with hot ethanol achieving **L** as hexa-hydrochloride salt. Yield: 2.4 g (86%). Anal. Calcd. For $C_{17}H_{40}N_6Cl_6O$: C 36.64; H 7.23; N 15.08. Found: C 36.9; H 7.1; N 15.2. ^{1}H NMR D_2O, (pH 3, 25°C): 3.07 (t, 8H), 3.24 (t, 8H), 3.74 (s, 3H), 4.04 (s, 4H), 7.25 (t, 1H), 7.48 (d, 2H) ppm. ^{13}C NMR 36.5, 51.4, 53.6, 64.0, 127.1, 128.0, 134.6, 158.5 ppm.

$[Cu_4L_2(N_3)_6](ClO_4)_2 \cdot H_2O$

A sample of $Cu(ClO_4)_2 \cdot 6H_2O$ (22.2 mg, 0.06 mmol) in water (10 cm^3) was slowly added to 10 cm^3 of an aqueous solution of **L** (10.1 mg, 0.03 mmol). The resulting solution was stirred for 10 min at room temperature and the evaporation of the solvent led to crystallization of the complex as blue crystals. Anal. Calcd. for $C_{34}H_{70}Cl_2Cu_4N_{30}O_{11}$: C 29.17; H 5.04; N 30.01. Found: C 29.0; H 4.9; N 30.2.

Crystal Data

$C_{34}H_{70}Cl_2Cu_4N_{30}O_{11}$ (**1**). M = 1400.3, colourless crystals of 0.35 × 0.40 × 0.50 mm size, T = 298 K, triclinic, space group P−1, a = 13.770(6), b = 14.043(2), c = 16.800(3) Å, $\alpha = 105.700(1)$, $\beta; = 102.790(3)$, $\gamma = 103.660(3)°$, V = 2894(1) Å^3, Z = 2, $D_c = 1.607$ g/cm^3, graphite monochromated Cu- Kα radiation $\lambda = 1.5418$ Å,

$\mu = 3.179\,\text{mm}^{-1}$; data were collected on a Siemens P4 diffractometer, $\theta-2\theta$ scan, $5.8 < 2\theta < 90^\circ$, 3499 reflections, 2295 observed $[I > 2\sigma(I)]$ data. Intensities were corrected for Lorentz and polarization effects; an absorption correction was applied once the structure was solved by using the Walker and Stuart method [9]. The structure was solved by direct methods, using the SIR-97 program [10] and subsequently refined by the full-matrix least-squares program SHELXL-97 [11]. The hydrogen atoms of the macrocycle were introduced in calculated positions, and their coordinates refined in agreement with those of the linked atoms. Their overall isotropic thermal displacement parameters converged to U values of 0.0063(3) Å^2. Carbon and nitrogen atoms were refined isotropically; the four copper atoms, the two chlorine atoms and the eight oxygen atoms of the two perchlorate anions were refined anisotropically. Atomic scattering factors and anomalous dispersion corrections for all the atoms were taken from Ref. [12]. Geometrical calculations were performed using PARST97 [13]. The molecular plots were produced with the ORTEP program [14]. Table III reports selected bond distances (Å) and angles (°) for **1**.

EMF Measurements

Equilibrium constants for complexation reactions were determined by pH-metric measurements ($pH = -\log [H^+]$) in 0.15 mol dm^{-3} Me_4NCl at 298.1 ± 0.1 K, using the fully automatic equipment that has already been described; the EMF data were acquired with the PASAT computer program [15]. The combined glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free Me_4NOH solutions and determining the equivalent point by Gran's method [16], which gives the standard potential E° and the ionic product of water ($pK_w = 13.73(1)$ at 298.1 K in 0.15 mol dm^{-3} Me_4NCl, $K_w = [H^+][OH^-]$). Ligand and metal ion concentrations of $1 \times 10^{-3}-2 \times 10^{-3}$ were employed in the potentiometric measurements, performing at least three measurements in the pH range 2–11. The HYPERQUAD [17] computer program was used to process the potentiometric data. All titrations were treated either as single sets or as separate entities, for each system, without significant variation in the values of the determined constants.

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