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# Dinuclear Cu(II) Complexes with Two Pyrazolate Bridging Groups Formed from 26 Membered Oxaimine and Polyamine Macrocycles of 3,5-Disubstituted 1H-Pyrazole

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**Abstract:** The deprotonation in basic ethanolic solution of the 26 membered pyrazole derived macrocyclic Schiff base **1** and polyamine **3** affords dipyrazolate salts (**1´**and **3´**) from which dinuclear Cu(II) complexes (**2** and **4**) have been obtained. The X-ray crystallographic analysis of **4** demonstrates that inside the macrocyclic cavity, the two pyrazolate rings are simultaneously acting as exobidentate ligands linking both metal cations, the Cu-Cu separation being 3.9 Å.

The interest in the study of macrocyclic receptors able to form Cu(II) dinuclear complexes has increased in the last few years owing to their resemblance to the active site of copper proteins and enzymes such as haemocyanin, tyrosinase and dopamine-β-hydroxylase.[1]

It has been suggested that at the active site of haemocyanin, different endogenous bridges act as mediators of antiferromagnetic spin-exchange interaction between a pair of copper(II) ions and can produce the magnetic properties characteristic of oxyhaemocyanin and methaemocyanin derivatives.[2] In view of these facts, much effort has been directed at the synthesis of dinucleating ligands containing an alcoholic or phenolic group as an endogenous bridge in order to achieve Cu-Cu separations of 3.4-4.0 Å.[3]

The pyrazole unit introduced into the cavity of an acyclic or a cyclic receptor, can be deprotonated in alkaline medium affording a pyrazolate anion which behaves as exobidentate ligand.[4]

Up to now, only the syntheses of dinuclear copper(II) complexes of acyclic ligands containing a pyrazolate group as endogenous bridge have been described.[5]

In this paper, we report by the first time new dinuclear copper(II) complexes derived from 26 membered macrocycles containing two pyrazolate rings simultaneously linking both metal cations.

Using $^{13}C$ NMR techniques, we have recently studied the formation of Zn(II) dinuclear complexes in DMSO-$d_6$-$D_2O$ solution, by treatment of dipyrazolate salts of 26-membered tetraester-polyether or polyaminic crowns of 3,5-disubstituted pyrazole with $ZnCl_2$.[6,7]

Now, we have synthesized two solid dinuclear Cu(II) complexes **2** and **4** (Figure 1), derived from macrocyclic Schiff base **1** and from polyamine **3**. The starting disodium dipyrazolate ligands **1´**and **3´** were previously prepared by deprotonation of **1** and **3** with NaOH (2 equiv.) in hot anhydrous methanol; the addition of copper(II) perchlorate (2 equiv.) at room temperature afforded the corresponding complexes as pure solids of dark green (**2**) and deep blue colour (**4**) in 88 and 87% yield respectively.[8]

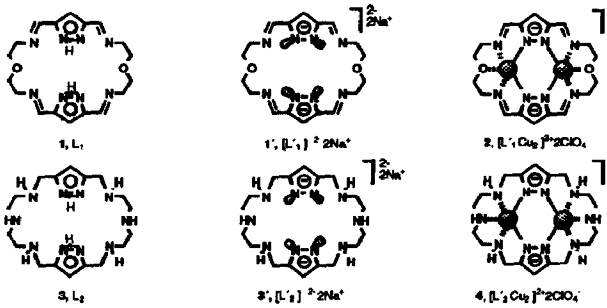

Figure 1

Their structures agree with their corresponding analytical and spectroscopical data (MS and IR). The FAB-MS showed in common four molecular ion peaks [$(M+2)^+$-ClO4], [$M^+$-ClO4], [$(M+2)^+$-2ClO4] and [$M^+$-2ClO4] at m/z 609 (20%), 607 (16%), 510 (27%) and 508 (30%) for **2**, and 615 (100%), 613 (90%), 516 (43%) and 514 (69%) for **4**. In the IR spectra (KBr), the C=N strong absorption band found at 1650 $cm^{-1}$ in **1** appears at 1605 $cm^{-1}$ in **2**, thus suggesting the presence of C=N···Cu interactions.The NH aliphatic groups of free ligand **3** are responsible of four sharp bands (3400/3300/3200/3100$cm^{-1}$). However in **4**, the complexed HN groups showed only two broad absortion bands at 3340 and 3240 $cm^{-1}$. Furthermore, both dinuclear complexes **2** and **4** showed in common a new group of strong C-N bands at 1140-1065 $cm^{-1}$. Crystallization of **4** from MeOH gave adequate crystals for X-ray analysis.[9]

The structure consists of $[C_{18}H_{32}N_{10}Cu_2]^{2+}$ cations and $ClO_4^-$ anions held together by electrostatic interactions. The binuclear cation is represented in Figure 2 which also contains the more significant bond-lengths and angles.

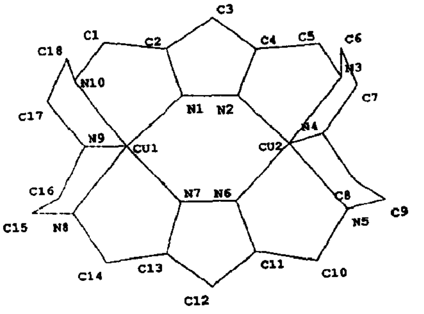

Figure 2: Representation of the $[C_{18}H_{32}N_{10}Cu_2]^{2+}$ cation showing its accesible plane. Selected bond lengths (Å) : Cu(1)-N(1) 1.92 (1), Cu(1)-N(7) 1.92(1), Cu(2)-N(2) 1.96, Cu(2)-N(6) 1.94(1), Cu(1)-N(8) 2.14(1), Cu(1)-N(10) 2.06(1), Cu(2)-N(5) 2.17(1), Cu(2)-N(3) 2.09(1), Cu(1)-N(9) 2.23(1), Cu(2)-N(4) 2.26(1), Contact length Cu(1)-Cu(2): 3.924(3) Å. Selected angles (°): N(1)-Cu(1)-N(7) 93.3(5), N(7)-Cu(1)-N(8) 81.3(4), N(8)-Cu(1)-N(10) 103.8(4), N(10)-Cu(1)-N(1) 81.1(5), N(2)-Cu(2)-N(3) 79.8(4), N(3)-Cu(2)-N(5), 104.1(5), N(5)-Cu(2)-N(6) 80.4(5), N(6)-Cu(2)-N(2) 93.5(4).

The two Cu atoms appear pentacoordinated by five N atoms forming very distorted square pyramids. The bases are formed by N(1), N(7), N(8) and N(10) around Cu(1), and by N(2), N(3), N(5) and N(6) around Cu(2). They are also very irregular, with two shorter Cu-N distances: 1.92Å and 1.95Å (mean value) involving the four N atoms of the pyrazolate rings and two longer ones: 2.07 Å and 2.15Å (mean values) corresponding to the four NH neighbour to the pyrazolate rings. In both polyhedra, the four N atoms of the basal planes deviate significantly from planarity, the greatest deviations being of 0.23 and 0.19Å for N(1) and N(2) respectively. The angle between both planes is 6.7(2)°. On the contrary, the two pyrazolate rings acting as exobidentate ligands are completely planar, but they are not parallel, the angle between them being 29.8(5)°. The macrocycle is conformed in such a way that N(9) and N(4) are situated at the apical positions of the pyramids (see Figure 3), completing the five-fold coordination around Cu(1) and Cu(2) respectively at distances significantly longer (2.23-2.26 Å) than those of the basal plane.

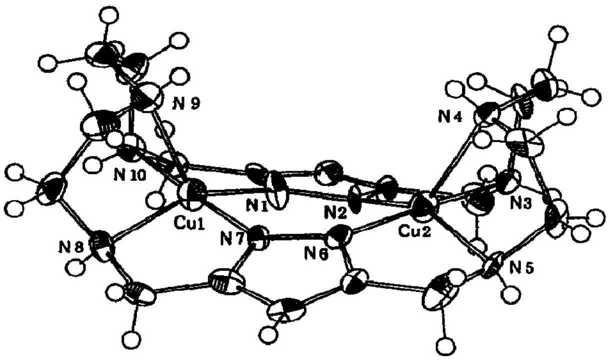

Figure 3: View of the cation $[C_{18}H_{32}N_{10}Cu_2]^{2+}$

The angles between normal to basal planes and the lines from Cu atoms to apical positions of the pyramids are 23.8(4)° and 29.2(4)° for Cu(1) and Cu(2) respectively. The whole binuclear complex cation could be also regarded as a saddle with a central hexagonal pseudo-ring [N(1)-N(2)-Cu(2)-N(6)-N(7)-Cu(1)] surrounded by 10 five member pseudoheterocycles, of which only the pyrazolate rings are planar. In the central pseudoring, the Cu atoms are separated by a distance of 3.92 Å, comparable to the value (< 4 Å) reported for the active site of haemocyanin.[10] The dinuclear cation presents an accessible surface (just the plane represented in Figure 2) through which additional ligands could bond to the Cu atoms, increasing their coordination number.

In accordance with our earlier experiences in formation of Zn(II) dinuclear complexes by $^{13}C$ NMR spectroscopy[7], the above X-ray crystallographic analysis of **4** confirms that, inside its polyaza macrocyclic cavity, each of the metal cations belonging to the [Cu(II) Cu(II)] center are linked stronger by the four pyrazolate nitrogens than by the four aliphatic NH ones neighbour to the heteroaromatic rings. The interaction of copper cations with the two NH nitrogens located in the middle of the flexible chains is even weaker.

Work is now in progress in order to study the magnetic and electrochemical properties of these new dinuclear complexes (**2** and **4**) as well as those corresponding to other acyclic analogues of related structure.[11]

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8. *General Procedure*: NaOH (0.2 mmol) was dissolved with stirring and warming in about 2 mL of MeOH. To this solution the crown **1** or **3** (0.1 mmol) was added portionwise. The ligand became soluble after a few minutes. $Cu(ClO_4)_2.6H_2O$ (0.2 mmol) was dissolved in MeOH (2 mL) and added to the above dipyrazolate salt (**1'** or **3'**) solution. A green (or blue) colour developed and a precipitate was immediately formed. *Dinuclear complex* **2**, mp >350°C. Analysis: Calculated for $C_{18}H_{22}N_8O_2Cu_2\ (ClO_4)_2.4H_2O$: C, 27.69; H, 3.84; N; 14.35 Cl, 9.09; Found: C, 27.34; H, 3.53; N, 14.12; Cl, 9.18. *Dinuclear complex* **4**, mp >350°C. Analysis: Calculated for $C_{18}\ H_{32}\ N_{10}Cu_2(ClO_4)_2$: C, 30.25; H, 4.48; N, 19.61; Cl, 9.93; Found: C, 30.04; H, 4.46; N, 19.51; Cl, 10.04.
9. *Crystal data* of **4** for $C_{18}H_{32}N_{10}O_8Cl_2Cu_2$, M= 714.55, triclinic, space group P1, a = 10.416 (1), b = 11.633 (1), c = 13.227 (2) Å, $\alpha$ = 109.52 (2)°, $\beta$ = 72.49 (2)°, $\gamma$ = 78.80(2)°, V = 1360.9 (3) Å$^3$, Z = 2, Dc = 1.7436 g/cm$^3$. Intensity data were collected with graphite monochromated Cu-K$\alpha$ radiation, ($\lambda$ = 1.5418 Å) on a Seifert XRD300-S four-circle diffractometer . 2830 reflections were measured in $\omega/2\theta$ scan mode (3° < $\theta$ < 50°), leading to 2670 unique reflections. Of them 2015 with $I < \sigma\ (I)$ were considered as observed and used for the structure solution refinement. Structure solved by heavy-atom method and further Fourier synthesis, allowing the location of all non-hydrogen atoms. A total of 457 variables (non-hydrogen atom coordinates and anisotropic thermal parameters) were refined by least-square procedures leading to R = 0.065, $R_w$ = 0.071. H-atoms were fixed at the calculated positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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