212. Bonding Capabilities of the Biochemical Buffer TRIS toward Copper(II) Ion. Structure and Magnetic Properties of Binuclear and Tetranuclear Systems

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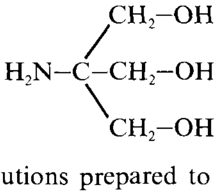
Summary

Following X-ray crystal structure studies, the products of the reaction between Cu(II) halides and tris(hydroxymethyl)methylamine (TRIS) can be formulated as $[Cu(TRISH_{-1})(TRIS)]_2X_2$ and $[Cu(TRISH_{-1})X]_4$ ($X = Cl$, Br). $TRISH_{-1}$ is the deprotonated ligand. Initial metal-ligand stoichiometric ratios of 1:2 and 1:1 are required to obtain the former and the latter species, respectively. Relevant crystal data for the dimeric compound with $X = Br$ are: monoclinic, $a = 11.394(2)$, $b = 10.049(2)$, $c = 12.149(2)$ Å, $\beta = 95.83(2)°$, space group $P2_1/c$, $Z = 2$. The tetramer with $X = Cl$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.182(1)$, $b = 9.120(2)$, $c = 8.817(1)$ Å, $\alpha = 88.95(1)$, $\beta = 87.01(1)$, $\gamma = 84.13(1)$, $Z = 1$. In the dimer, two square planar Cu(II)-units are held together by two H-bonds of the type $O{-}H\cdots O$, which involve the O-atoms coordinated to the metals. The formation of an eight-membered cycle containing two metal ions ensues. The tetramer contains two dinuclear units formed by two metal centers, square planar in first approximation, which share one O——O edge; the arrangement is significantly puckered at this vector. One of these bridging O-atoms has μ_3 character as it serves as a weak apical donor for a Cu-atom of another binuclear unit. Thus a step-like geometry of the central core is obtained. Both compounds have constant magnetic moments at least down to the liquid N_2 temperature. In this respect, they differ from other complexes of Cu(II) having comparable geometries, but temperature-dependent magnetic moments.

Introduction. – The compound tris(hydroxymethyl)methylamine (TRIS)



$$H_2N{-}C(CH_2{-}OH)_3$$

is often added as a buffer to solutions prepared to investigate biochemical reactions involving transition metal ions. Although inhibitory effects (higher than those of other common buffers) are known to be due to the complexing capabilities of TRIS [1], the latter have been not sufficiently documented. On the other hand, a detailed study for the chemical-physical characterization of important bio-inorganic substances should properly take into account all the collateral effects, even those induced by reagents alien to the process under consideration.

As a ligand, TRIS forms complexes with transition metal ions usually through deprotonation of one of the OH-groups, hence the abbreviation used in this paper, $TRISH_{-1}$ for the deprotonated species.

The behavior of the complexes in solution has been studied and in several cases the equilibrium constants have been determined [2] [3]. Preparation and stereochemistry in solid state of the TRIS complexes with metal ions of the first transition series have been also reported [4] [5]. In reaction with $CuCl_2$, two different compounds were isolated and on the basis of IR and electronic spectra as well as magnetic and conductivity measurements they were assumed to be a monomeric species $[Cu(TRISH_{-1})(TRIS)]Cl$ (**1**) and a dimer $[Cu(TRISH_{-1})Cl]_2$ (**2**).

In this communication, we report detailed results of the X-ray structure analysis performed for **2** and the Br analog of **1**, namely $[Cu(TRISH_{-1})(TRIS)]Br$ (**3**). The relationship between the X-ray results and the magnetic properties of the compounds will also be discussed in terms of the recent findings for similar polynuclear systems [6] [7].

Table 1. *Crystallographic Experimental Data for* $[Cu(TRISH_{-1})Cl]_4$ (**2**) *and* $[Cu(TRISH_{-1})(TRIS)]_2Br_2$ (**3**)

	2	**3**
Crystal Data		
Molecular Formula	$C_{16}H_{40}Cl_4Cu_4N_4O_{12}$	$C_{16}H_{42}Br_2Cu_2N_4O_{12}$
M.W.	876.51	769.43
Crystal System	triclinic	monoclinic
a [Å]	9.182(1)	11.394(2)
b [Å]	9.120(2)	10.049(2)
c [Å]	8.817(1)	12.149(2)
α [deg]	88.95(1)	90.0
β [deg]	87.01(1)	95.83(2)
γ [deg]	84.13(1)	90.0
V [Å^3]	733.4	1383.8
Space group	$P\bar{1}$	$P2_1/c$
Z	1	2
d(calcd) [g cm^{-3}]	1.984	1.846
μ(Mo$K\alpha$) [cm^{-1}]	33.0	44.6
Data Collection		
2^{θ} range [deg]	5–50	6–48
Scan speed [deg sec^{-1}]	0.05	0.04
Scan width [deg]	0.9	0.8
Total data	2576	2406
Unique reflections used in calculations	1429 with $I > 3\sigma(I)$	955 with $I > 2.5\sigma(I)$
Refinement		
Number of parameters	182	119
Weight	$1/\sigma^2(F) + 0.001F^2)$	
R	0.041	0.062
R_w	0.042	0.060

Experimental. – *Reagents and Physical Measurements.* Analytical grade tris-(hydroxymethyl)methylamine (*Merck*) was used without further purification. The Cu(II) complexes have been prepared according to [4] and recrystallized twice from MeOH: [Cu(TRISH$_{-1}$)(TRIS)]Br, blue crystalline solid (Anal. calc. for $C_{18}H_{21}BrCuN_2O_6$: C 24.98, H 5.50, Br 20.77, N 7.28; found: C 25.4, H 5.6, Br 20.3, N 7.6); Cu(TRISH$_{-1}$)Cl, green crystalline solid (Anal calc. for $C_4H_{10}ClCuNO_3$: C 21.92, H 4.60, Cl 16.18, Cu 29.00; found: C 22.0, H 4.5, Cl 16.4, Cu 28.8).

The magnetic susceptibilities of the complexes were measured in the temp. range 100–300 K on a *Gouy* balance. The diamagnetic corrections were made by using published atomic values [8].

X-Ray Analysis of Compounds **2** *and* **3**. The diffraction data for both compounds were collected on a *Philips PW1100* diffractometer using MoK_α radiation (λ = 0.71069 Å). In spite of efforts only very small crystals of **3** could be obtained and consequently a parallelepiped of dimensions 0.03 × 0.05 × 0.07 mm was used for the data collection. The needle-shaped crystal of **2** had dimensions 0.1 × 0.2 × 0.4 mm. In both cases the setting angles of 25 random reflections were used to determine by least-squares fit accurate cell constants and orientation matrices. The crystallographic data are listed in *Table 1*.

The intensities were corrected for *Lorentz* and polarization effects. Absorption corrections were applied for both **2** and **3** although the maximum and minimum transmission factors were not significantly different (5% at most) in any case.

All computations were performed using the SHELX 76 program package [9]. The structure of **3** was solved by conventional heavy-atom techniques (*Patterson* and *Fourier* maps). Since the crystal was diffracting rather weakly, the number of significant reflections with $I > 2.5\sigma(I)$ was limited to 955. Full matrix least-squares refinement with anisotropic temperature factors for all but carbon non-H-atoms gave a final R of 0.062 (R_w = 0.060).

The structure of **2** was solved by direct methods (MULTAN 80). 1429 reflections with $I > 3\sigma(I)$ were used for a full-matrix refinement with anisotropic temperature factors for all non-H-atoms which converged at an R of 0.041 (R_w = 0.042). In both structures, contribution from the H-atoms in their idealized positions (C–H = 1.0 Å) were included during the refinement. In compound **2**, some residual peak density was indeed found, which could be attributed to the presence of the H-atoms engaged in H-bonding with the coordinated O-atoms of TRIS. Unfortunately the peaks were quite low (less than 0.6 e/Å^3) and broad. Therefore the position of these important H-atoms were calculated by making the best fit with the atoms of a similar structure

Table 2. *Atomic Coordinates* (× 10^4) *for* [Cu(TRISH)$_{-1}$)Cl]$_4$ (**2**)

Atom	x	y	z	U or U_{eq} (Å^2)
Cu(1)	145(1)	3445(1)	2986(1)	20(1)
Cu(2)	– 95(1)	3255(1)	– 202(1)	20(1)
Cl(1)	– 1424(2)	2044(3)	– 1752(2)	28(1)
Cl(2)	1850(3)	3776(3)	4672(3)	35(1)
O(1)	– 1408(6)	3305(6)	1604(6)	23(2)
O(2)	1033(6)	4385(6)	1208(6)	22(2)
O(3)	– 3810(7)	3543(7)	5729(7)	43(3)
O(4)	– 1812(7)	– 557(7)	4067(8)	46(3)
O(5)	4787(8)	1845(8)	– 2066(9)	54(3)
O(6)	1520(7)	1283(7)	1356(7)	39(3)
N(1)	– 1048(7)	2272(8)	4397(7)	24(2)
N(2)	1798(7)	3005(8)	– 1408(8)	26(3)
C(1)	– 2148(10)	2045(10)	2012(9)	23(3)
C(2)	– 2474(8)	2052(9)	3724(9)	21(3)
C(3)	– 3633(10)	3294(10)	4136(10)	28(3)
C(4)	– 3013(10)	591(10)	4278(11)	33(3)
C(5)	2570(9)	4169(9)	841(10)	26(3)
C(6)	2934(8)	2866(10)	– 223(9)	23(3)
C(7)	4448(9)	2976(10)	– 997(10)	30(3)
C(8)	2924(9)	1396(10)	593(11)	34(3)

Equivalent temperature factors (× 10^3) are in the form: $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

Table 3. *Atomic Coordinates* (× 10^4) *for* $[Cu(TRISH_{-1})(TRIS)]_2Br_2$

Atom	*x*	*y*	*z*	*U* or U_{eq} (Å^2)
Br	10051(2)	282(2)	– 2478(2)	32(1)
Cu	7107(2)	5550(2)	– 286(2)	20(1)
O(1)	5728(9)	6696(11)	– 373(9)	24(4)
O(2)	6381(9)	4007(11)	465(9)	22(4)
O(3)	5207(10)	7157(12)	– 3491(10)	33(5)
O(4)	7763(10)	8527(13)	– 3363(10)	35(5)
O(5)	6783(11)	3536(14)	– 1841(10)	47(5)
O(6)	10170(9)	2282(14)	– 301(10)	39(5)
N(1)	7743(12)	6864(12)	– 1303(12)	24(6)
N(2)	8530(11)	4382(15)	– 114(11)	27(6)
C(1)	6720(14)	7521(19)	– 1938(14)	29(5)
C(2)	5871(15)	7849(18)	– 1051(14)	28(4)
C(3)	6145(15)	6585(19)	– 2778(15)	32(5)
C(4)	7070(15)	8828(18)	– 2453(15)	28(5)
C(5)	7111(14)	2851(19)	553(14)	28(5)
C(6)	8123(14)	2987(16)	– 189(14)	23(4)
C(7)	7699(13)	2707(18)	– 1404(13)	24(4)
C(8)	9156(16)	2023(18)	177(16)	37(6)

Equivalent temperature factors (× 10^3) are in the form: $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

reported in the literature. The program used was BMFIT, written by *Nyburg* [10]. Final difference maps were essentially featureless showing some minor peaks of no chemical significance. The final positional parameters for the structures are reported in *Tables 2* and *3*. Listings of the atomic thermal parameters and structure factor amplitudes are available as supplementary material.

Extended HMO Calculations. The program used was ICON 8 [11]. The model used to simulate compound **3** was $[(NH_3)_4Cu_2(H_2O)_2(OH)_2]^{2+}$. The Cu–O and Cu–N distances were all fixed at 2.0 Å. The separations between the bridging O-atoms were 2.5 Å with the H-atom being collinear with them. The parameters for copper were taken from [12].

Results and Discussion. – The reaction of Cu(II) halides with TRIS produces different compounds depending on the initial stoichiometric ratio between the metal ion and the ligand. The compound **2** in which this ratio is 1:1 contains the monodeprotonated ligand $TRISH_{-1}$, whereas the degree of deprotonation in **1** or **3** is only 0.5. As a consequence, the bonding capabilities of the ligand are quite different as shown by the X-ray analyses of the compounds. When the degree of deprotonation is lower the stability of the complex is provided by a cooperative H-bonding that favours binuclearity of the system. In the other case a tetranuclear species is obtained where the deprotonated OH-groups serve as bridges between different copper ions.

The structure of **3** is presented in *Fig. 1*. Bond lengths and angles are listed in *Table 4*. Each copper ion is coordinated by two ligands TRIS, which use, as donors, the N-atom and one of the three terminal O-atoms. The coordination geometry at each metal is square planar with a *cis*-arrangement of the TRIS chelate ligands. Intermolecular and intramolecular contacts of Cu- with uncoordinated O-atoms of TRIS can be as short as 2.778 and 2.551 Å (with O(5) and O(4), respectively). The Cu–O and Cu–N distances are all in the range 1.94–2.02 Å and the bond angles around the central Cu(II) ion have values within the limit of 82.3–96.4°. As said, one of the interesting features of the structure is the formation of H-bonded associates between two

$[Cu(TRISH_{-1})(TRIS)]^+$ mononuclear units. The associates contain an inversion center (at 1/2, 1/2, 0). The dimers are held together by strong O–H···O H-bonds involving the metal-coordinated O-atoms O(1) and O(2) from two neighbouring units. Thus the two metals are members of a ring formed by eight atoms altogether. The O(1)···O(2) donor-acceptor distances are 2.50(2) Å. The occurrence of H-bonded polynuclear complexes of this sort has been documented relatively well for transition metal complexes with other amino alcohols [13]. A particular attention was focused on establishing relationships between unusual magnetic properties of the compounds and structural parameters like the metal-metal and donor-acceptor distances, and the separations between the coordination planes. Recently, the structures and magnetic properties of the

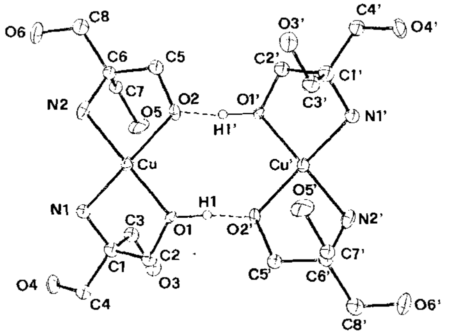


Fig. 1. *ORTEP drawing of the dimeric unit* $[Cu(TRISH_{-1})(TRIS)]_2^{2+}$

Table 4. *Selected Interatomic Distances and Angles for* $[Cu(TRISH_{-1})Cl]_4$

Interatomic Distances [Å]					
Cu(1)–Cu(2)	2.841(1)	Cu(2)–Cl(1)	2.253(2)	N(1)–C(2)	1.498(10)
Cu(2)–Cu(2)′	3.233(2)	Cu(2)–N(2)	1.984(7)	N(2)–C(6)	1.510(10)
Cu(1)–O(1)	1.939(5)	O(1)–C(1)	1.425(9)	C(1)–C(2)	1.523(11)
Cu(1)–O(2)	1.954(5)	O(2)–C(5)	1.426(9)	C(2)–C(3)	1.509(12)
Cu(1)–N(1)	1.985(7)	O(3)–C(3)	1.425(11)	C(2)–C(4)	1.532(11)
Cu(1)–Cl(2)	2.260(2)	O(4)–C(4)	1.447(11)	C(5)–C(6)	1.526(12)
Cu(2)–O(1)	1.945(5)	O(5)–C(7)	1.410(12)	C(6)–C(7)	1.529(11)
Cu(2)–O(2)	2.020(6)	O(6)–C(8)	1.436(10)	C(6)–C(8)	1.510(12)
Cu(2)–O(2)′	2.407(6)				
Bond Angles [deg]					
O(1)–Cu(1)–O(2)	81.6(2)	Cu(1)–O(2)–C(5)	121.8(5)	C(2)–C(3)–O(3)	113.2(7)
O(1)–Cu(1)–N(1)	84.8(2)	Cu(2)–O(2)–C(5)	111.3(5)	C(2)–C(4)–O(4)	108.1(6)
O(2)–Cu(1)–Cl(2)	98.9(2)	Cu(1)–N(1)–C(2)	110.3(4)	O(2)–C(5)–C(6)	110.6(7)
N(1)–Cu(1)–Cl(2)	95.1(2)	Cu(2)–N(2)–C(6)	103.9(5)	N(2)–C(6)–C(5)	106.8(6)
O(1)–Cu(2)–O(2)	79.8(2)	O(1)–C(1)–C(2)	108.3(6)	N(2)–C(6)–C(7)	109.2(6)
O(1)–Cu(2)–Cl(1)	98.8(2)	N(1)–C(2)–C(1)	105.2(6)	N(2)–C(6)–C(8)	110.0(7)
O(2)–Cu(2)–N(2)	83.8(3)	N(1)–C(2)–C(3)	111.1(7)	C(5)–C(6)–C(7)	108.8(7)
N(2)–Cu(2)–Cl(1)	97.9(2)	N(1)–C(2)–C(4)	110.6(7)	C(5)–C(6)–C(8)	112.7(7)
Cu(1)–O(1)–Cu(2)	94.0(2)	C(1)–C(2)–C(3)	109.8(7)	C(7)–C(6)–C(8)	109.2(7)
Cu(1)–O(1)–C(1)	108.9(4)	C(1)–C(2)–C(4)	111.0(7)	C(6)–C(7)–O(5)	110.6(7)
Cu(2)–O(1)–C(1)	119.5(5)	C(3)–C(2)–C(4)	109.0(6)	C(6)–C(8)–O(6)	110.1(7)
Cu(1)–O(2)–Cu(2)	91.3(2)				

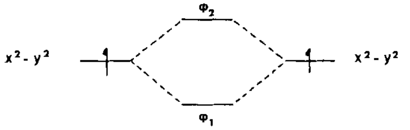
Cu(II) complexes of 2-aminoethanol (EtaH), [Cu(Eta)(EtaH)](NO_3) (**4**), 2-amino-2-methylpropanol (MepH), [Cu(Mep)(MepH)(H_2O)](NO_3) (**5**), and *N*,*N'*-bis(2-hydroxyethyl)-2,4-pentanediimine ($DiimH_3$), $[Cu(DiimH)]_2$ (**6**) have been investigated [6] [7]. The complex cations in the structures associate in dimeric units related by inversion symmetry and joined by two H-bonds, O–H···O with O–O distances of 2.44, 2.52, and 2.32 Å in **4**, **5**, and **6**, respectively. The magnetic moments of the complexes decrease as the temperature is lowered. Values of 1.78, and 1.75 B.M. at 298 K and 1.59 and 1.57 B.M. at 93 K were measured for **4** and **5**, whereas the magnetic moment of **6** dropped from 1.68 at 293 K to 1.14 B.M. at 77 K. These data are consistent with an antiferromagnetic coupling in these complexes. The structure of the Cu(II)-TRIS complex presented here exhibits many similarities with those of the complexes mentioned above. The O–O distance 2.50(2) Å of the O–H···O H-bonds is within the range observed previously. Furthermore, the Cu–Cu distance of 5.044 Å is only slightly longer than that for the compounds **4**, **5**, and **6**, 4.94, 4.93, and 4.99 Å, respectively. In no case the two squares formed by each Cu-center are coplanar as the separation between the planes varies in the range 1.66–0.22 Å in **5** and **6**, respectively. Indeed, we find an intermediate value of 0.93 Å in **3**. In spite of these structural analogies the magnetic moment (1.80 B.M., at room temperature) for **3** is practically unchanged at least down to the temperature of liquid N_2. Notice that the value in question is slightly above that due to spin only (1.73 B.M.). The fact is quite surprising as it renders at least questionable all of the previous attempts to correlate the structure and the magnetic properties in the series of the three binuclear Cu(II)-complexes, containing H-bonded bridges. On the other hand, magnetic measurements down to very low temperatures would be required to establish whether antiferromagnetic of ferromagnetic interactions, although weak, are operative or not.

Table 5. *Selected Interatomic Distances and Angles for* $[Cu(TRISH_{-1})(TRIS)]_2Br_2$

Interatomic Distances [Å]					
Cu–O(1)	1.943(11)	O(3)–C(3)	1.426(19)	C(1)–C(2)	1.555(22)
Cu–O(2)	2.018(11)	O(4)–C(4)	1.454(19)	C(1)–C(3)	1.489(24)
Cu–N(1)	1.993(13)	O(5)–C(7)	1.398(19)	C(1)–C(4)	1.525(25)
Cu–N(2)	1.995(13)	O(6)–C(8)	1.370(20)	C(5)–C(6)	1.541(21)
O(1)–C(2)	1.440(20)	N(1)–C(1)	1.486(20)	C(6)–C(7)	1.531(22)
O(2)–C(5)	1.426(19)	N(2)–C(6)	1.476(21)	C(6)–C(8)	1.554(22)
Bond Angles [deg]					
O(1)–Cu–O(2)	96.5(4)	N(1)–C(1)–C(4)	111.9(13)	N(2)–C(6)–C(5)	107.2(14)
O(1)–Cu–N(1)	85.2(5)	C(2)–C(1)–C(3)	110.3(14)	N(2)–C(6)–C(7)	107.5(14)
O(2)–Cu–N(2)	82.3(5)	C(2)–C(1)–C(4)	108.0(15)	N(2)–C(6)–C(8)	110.5(13)
N(1)–Cu–N(2)	96.4(6)	C(3)–C(1)–C(4)	112.2(15)	C(5)–C(6)–C(7)	111.5(14)
Cu–O(1)–C(2)	111.7(9)	O(1)–C(2)–C(1)	109.9(14)	C(5)–C(6)–C(8)	111.6(14)
Cu–N(1)–C(1)	107.5(10)	C(1)–C(3)–O(3)	114.3(15)	C(7)–C(6)–C(8)	108.5(14)
Cu–N(2)–C(6)	107.8(9)	C(1)–C(4)–O(4)	108.5(14)	C(6)–C(7)–O(5)	114.0(14)
N(1)–C(1)–C(2)	104.1(13)	O(2)–C(5)–C(6)	110.5(14)	C(6)–C(8)–O(6)	114.0(15)
N(1)–C(1)–C(3)	110.0(15)				

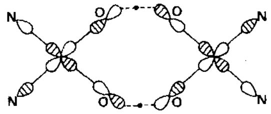
However, the coupling can be considered generally weak for this class of compounds if one assumes that the pathway of exchange involves the contribution of the hydrogen 1s orbitals.

In d^9 square planar metal centers the unpaired electron occupies a metal-ligand antibonding orbital, the metal orbital being x^2–y^2 in character. The singlet state is possible if the splitting between in-phase and out-of-phase combination of these orbitals is sufficiently large [14], as shown below:

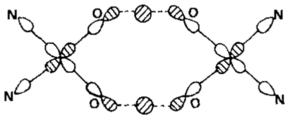


(1)

If the eight-membered bridging ring is considered planar, with D_{2h}-symmetry[1]), the φ_2 combination excludes the contribution of hydrogen on account of symmetry arguments as shown in (*2*). Thus, φ_2 does not undergo the destabilization that would be promoted, if the H-atoms had p orbitals of suitable energy. In turn, the symmetry



(2)



(3)

allows the hydrogen 1s orbitals to be used to stabilize φ_1 (see (**3**)). However, an extended *Hückel* calculation shows that their participation in φ_1 is very small because of poor energy match between interacting orbitals. Also consider that in the reality the two squares, centered at the copper atoms are parallel, but not coplanar, hence this stabilizing interaction is even diminished, and φ_1 and φ_2 are practically degenerate.

In conclusion, on the basis of the orbital interactions alone the triplet state seems favoured. More subtle arguments must be therefore sought to rationalize those cases where an antiferromagnetic behavior is observed.

In the case of compound **2**, the X-ray crystallography revealed a structure significantly different from that previously postulated [4]. The compound consists of two

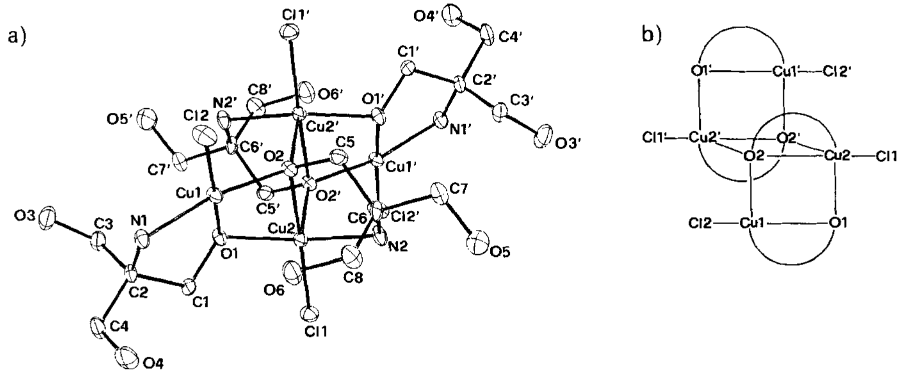


Fig. 2. a) *ORTEP drawing of the tetramer [Cu(TRISH$_{-1}$)Cl]$_4$.* b) *Schematic representation of the bonding system in the tetramer*

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[1] The short O–O distance (< 2.60 Å) is suggestive that the H-atom is symmetrically located between the O-atoms [15].

dinuclear units related by the inversion symmetry and held together by weak Cu–O interactions *(Fig. 2)*. Thus, the complex should be considered as a tetramer with a step-like geometry of the central core. Each asymmetric unit of the tetramer contains two square planar Cu(II) atoms. The two distorted squares share the side defined by two bridging O-atoms O(1) and O(2). The coordination spheres of both Cu(II)-atoms are completed by the NH_2- and OH-groups of the TRIS ligands and the Cl-atoms. It should be noticed that, in contrast to the previous suggestions [4], TRIS is chelated to the central ions only within the same dinuclear unit and does not form bridges between those units. The Cu_2O_2-system is not planar as indicated by a dihedral angle of 42° between the CuO(1)O(2) planes.

One of the bridging atoms O(2), has μ_3 character as it is also weakly coordinated to the Cu(II)-atom of another dinuclear unit with the Cu–O separation of 2.407(6) Å. The direction of the Cu(2)–O(2′) vector almost coincides with the main axis of a square pyramid, whose basis is defined by the O(1), O(2),N(2) and Cl(1) atoms. By taking into account the additional apical coordination, the complex may be described as a tetramer of stepped geometry containing both four- and five-coordinate copper: a structure found earlier for Cu(II)-compound with acetylacetone-mono-(*o*-hydroxyanil) (**7**) [16]. However, again there is a significant difference in the magnetic properties of the two compounds, although the geometry of the bridging framework is similar in many respects. Thus, whereas **2** has a magnetic moment of 1.95 B.M. at room temperature, which remains practically unchanged down to the liquid N_2 temperature, **7** has an initial lower value of 1.37 B.M. and temperature-dependent behavior. *Hatfield & Inman* [17] warned that the magnetic properties must be described in terms of electron spin-spin interactions among all four Cu(II)-ions rather than considering the compound as formed by two weakly interacting dimers. On the other hand, the centrosymmetrically related geometrical arrangement in **2** that allows a square planar Cu(II)-ion to share in the apical position a basal ligand of another equivalent metal is unfavourable to promote significant exchange interactions [18]. Such a situation was also found in the molecule $Cu(pyNO)_2(NO_3)_2$ [19], where, even though the nature of the Cu–Cu interactions (ferromagnetic or antiferromagnetic) is still uncertain, even after measurements at very low temperatures, it is sure that they are extremely weak. In **2** and in **7**, the Cu–O–Cu angles are close to 90° (93.4 and 89.3°, respectively), thus further reducing the possibility of magnetic interactions. The different magnetic behaviour between **2** and **7** is thus probably originating within the terminal dimeric units of the tetramer. Interestingly, these roof-shaped units have different amount of puckering at the bridging O–O vector (dihedral angles of 42 and 24° in **2** and **7**, respectively). It has been recently shown [20] that the singlet-triplet separation is dependent on the value of this angle: the more planar the Cu_2O_2-arrangement, the higher the coupling between the metals.

As a final warning, on the basis of this work, a special awareness should be switched on while studying TRIS-buffered systems containing metals. Various forms of TRIS-metal complexes occur under relatively similar conditions (here with variation only of the ligand-metal molar ratio) thus changing the composition of the solution and ultimately the pathway of biochemical reactions.

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