A Cu(II) POLYMERIC COMPLEX SURVEYING TRIETHANOLAMINE AND 1,2-DI(4-PYRIDYL)ETHYLENE AS BRIDGING LIGANDS

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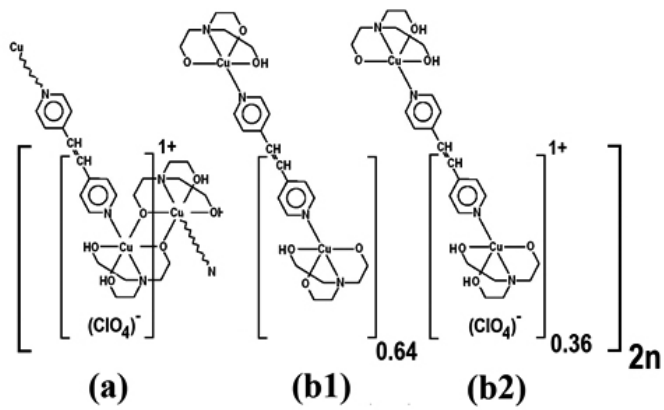
ABSTRACT

We report the synthesis and crystal structure of a copper (II) polymeric complex **(I)** prepared by reaction of $Cu(ClO_4)_2 \cdot 5H_2O$ with H_3tea (triethanolamine,) and dpe (1,2-di(4-pyridyl)ethylene). in ethanol. The compound is made up of two well differentiated substructures, the first one being a cationic 1D polymer balanced by ClO_4^- counteranions $\{[Cu_2(H_2tea)_2(dpe)]\cdot(ClO_4)_2\}_n$ and the second one made is up of two dimers of different occupancies and charge content, viz., $[Cu_2(Htea)_2(dpe)]$ (neutral, 64% occupancy) and $[Cu_2(H_2tea)_2(dpe)]^{2+}$ (cationic, 36% occupancy), this latter fraction balancing the charge introduced by ClO_4^- anions with 72% occupancy.

Both substructures differ in that the $H_m$tea anions in the dimers (m = 1,2) do not bridge cations as their homologue H_2tea does in the polymer, but chelate instead one single Cu each. As shown in scheme.

The structure of **(I)** is compared with its close relative $[Cu_2(H_2tea)_2(dpe)]\cdot(bpe)\cdot(ClO_4)_2\cdot H_2O$ **(II)**, where the same original constituents assemble in a slightly different way[1].



Scheme

1. INTRODUCTION

When looking for the generation of coordination networks (viz., coordination compounds extending in 1, 2 or 3 dimensions), the so-called "node and spacer" approach is often preferred. In its simplest description it consists on metal ions, or conglomerates (the nodes) linked by bridging ligands (the spacers) into 1, 2 or 3D arrays[2,3].

The final dimensionality of the crystal structure depends on a number of factors such as reaction conditions, solvent system, counterions, ligand to metal ratio. It is known that 1:1 Ratio often favours 1D structures, larger ratios generally giving rise to larger dimensionalities[4-9]. But not only covalence is relevant to these constructions: the bridging action of non-covalent interactions as hydrogen bonds or $\pi\cdots\pi$ stacking can alter the final results, even in structures with extremely similar constituents. This fact strongly depends in the interplay of H-bonding donor/acceptor eagerness of the species involved.

Two ligands which satisfy these conditions are 1,2-di(4-pyridyl) ethylene (dpe) and trietanolamine (H_3tea). The first one is a rigid ligand with good bridging capabilities; we have already described some lanthanide and cobalt (II) complexes displaying 1,2-di(4-pyridyl)ethylene bridges[10,11]. Triethanolamine, in turn, may be considered as a flexible ligand which can act with different degrees of protonation and participates in the formation of nodes or conglomerate[12].

We present herein an example of an unreported Copper (II) complex surveying both ligands,

$\{[Cu_2(H_2tea)_2(dpe)]\cdot(ClO_4)_2\}n \cdot 0.64n[Cu_2(Htea)_2(dpe)]\cdot 0.36n\{[Cu_2(H_2tea)_2(dpe)]\cdot(ClO_4)_2\}$.

The compound is strongly related to a close relative $[Cu_2(H_2tea)_2(dpe)]\cdot(bpe)\cdot(ClO_4)_2\cdot H_2O$ **(II)** where the same original constituents ensamble slightly differently, in such a way that H-bonding ends up being crucial in defining the final dimensionality of the supramolecular arrangement of both compounds[1].

2. EXPERIMENTAL

2.1. Synthesis

To an aqueous solution (200 mL) of copper perchlorate pentahydrate (0.55mmol, 0.2037 g) was added a solution of triethanolamine (0.981mmol, 0.1462g) in 25 mL of ethanol with constant stirring. The resulting suspension was stirred and heated for 15 min. Then 2,2 mmol (0.4009g) of 1, 2-di(4-pyridyl)ethylene dissolved in the same solvent (25 mL) was added and the resulting mixture was refluxed for 4h and filtered while hot. The filtrate was left at room temperature. On standing, single crystals suitable for X-ray analysis were obtained, which were used without further processing.

2.2. X-Ray crystallography

The diffractometer data set was collected up to a 2θ max of ca. 58° using monochromatic Mo Ka radiation, α=0.7107Å, T=295K on a Bruker Smart diffractometer. The following software was used in different stages of the crystal structure analysis process: Data collection: CrysAlis PRO (Oxford Diffraction, 2009)[13] program(s) used to solve structure: SHELXS97; program(s) used to refine structure: SHELXL97; molecular graphics: SHELXTL[14]

2.3. Refinement

The structure showed disorder around both perchlorate anions (PCA), viz., PCA#1, split into two rotationally disordered halves around a unique C11—O41 bond (occupation factors: 0.637, 0.363 (4)) and PAC#2 with C12 sitting on an inversion centre and showing, in addition to the concomitant disorder, incomplete occupation. Steric hindrance between the major component of PCA#1 and the PCA#2 unit, forced the depleted occupation of the latter to be equal to that of the minor component of PCA#1 (0.363 (4)). Charge balance required that the negative charge introduced by this latter fraction ought to be balanced by an equivalent positive charge from the $H_m$tea groups in the dimeric

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moieties. Even if the trustable finding of the corresponding hydrogens proved illusory, due to the prevailing disorder, there is in the structure strong evidence of their whereabouts: when the set of short O···O contacts in the structure is analyzed, it is found that all of them could be satisfactory explained by H-bonds from the H_2tea groups in the polymeric subunit, except O13···O12 = 2.560 (6) and O33···O12^{ii} = 2.660 (6), (ii) = -x+1, -y+2, -z+1. This fact strongly suggests the presence of unnoticed, disordered H's attached to O13 and O33 in the remaining subunit, thus giving support to the proposed formulation.

2.4. Physical measurements.

The UV–Vis spectrum was recorded with 1.0 cm quartz cells on a UNICAM UV3 spectrophotometer in the DMSO solution at room temperature.

3. RESULTS AND DISCUSSION

Crystal data, data collection and structure refinement details are summarized in Table 1, while Table 2 presents coordination distances and Table 3 the most relevant H-bonding interactions. The compound consists of two well differentiated 2:2:1 Cu-$H_m$tea-dpe substructures, m =1, 2 (Fig.1, (a) and (b)) completed by perchlorate anions as solvates.

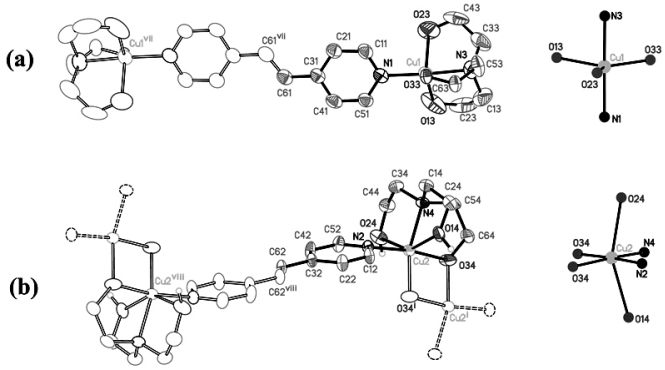

Figure 1: Ellipsoid plots (drawn at a 30% probability level) of the three components in the structure. In full ellipsoids, the independent part. H atoms attached to C not shown. (a) The centrosymmetric dimeric spacers built up around Cu1. (b) The centrosymmetric elemental brick for the Cu2 chains. Symmetry codes: (i) -*x*+1, -*y*+1, -*z*; (vii) -*x*+1, -*y*+1, -*z*+1; (viii) -*x*+2, -*y*+1, -*z*+1.

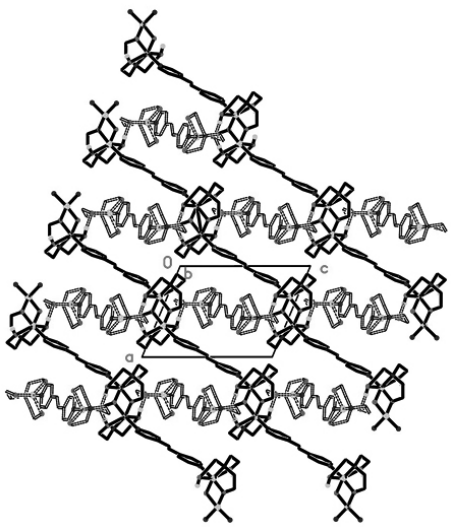

Figure 2: A projection of the structure along [010], showing in full lining the chains parallel to (Fig1 (b)), and in double broken lines, the spacers linking them (Fig 1 (a)) into the (010) undulating planes.

The substructure (b) associated to Cu1 consists of two types of dimers appearing in a disordered fashion, almost identical in structure but with a different charge content, viz., (b1), formulated as $[Cu_2(Htea)_2(dpe)]$ and (b2), as $[Cu_2(H_2tea)_2(dpe)]^{2+}$, in a 0.64:0.36 ratio.

Table 1: Experimental details.

Crystal data	
Chemical formula	$2(C_{12}H_{19}CuN_2O_3\cdot ClO_4]\cdot 1.28[C_{12}H_{18}CuN_2O_3].$ $0.72[C_{12}H_{19}CuN_2O_3\cdot ClO_4)]$
M_r	1479.09
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	294
a, *b*, *c* (Å)	10.504 (3), 12.935 (3), 13.685 (3)
α, β, γ (°)	106.951 (5), 104.640 (4), 109.350 (5)
V (Å^3)	1547.4 (6)
Z	1
Radiation type	Mo *K*α
μ (mm^{-1})	1.555
Crystal size (mm)	0.41 × 0.31 × 0.15
Data collection	
Diffractometer	Bruker *SMART* CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS* in *SAINT-NT* (Bruker, 2002)
T_{min}, T_{max}	0.58, 0.82
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12834, 6592, 5181
R_{int}	0.014
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.659
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.057, 0.162, 1.02
No. of reflections	6592
No. of parameters	451
No. of restraints	147
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta>_{max}$, $\Delta>_{min}$ (e Å^{-3})	0.62, -0.94

The dimers are centrosymmetric and are made up of a dpe molecule halved by an inversion centre at the central C═C bond, bound to two symmetry related Cu(II) cations through the outermost N's in a bridging mode. The Cu(II) cations, in turn, are further chelated by partially deprotonated $H_m$tea anions (either Htea in (b1) or H_2tea in (b2); see discussion about charge balance at the end of the discussion), binding in k^4-N,O,O',O'' mode. Cu1 is thus five coordinated, inmersed in a distorted Trigonal Bipyramidal environment (Fig. 1(a), inset), as disclosed by the τ parameter (τ = 0.70. Expected values: 0.00 for and ideal Square pyramid; 1.00 for an ideal Trigonal Bipyramid[15] .The triangular base is defined by the three alkoxo oxygens (O13,O23,O33) with Cu1 being 0.169 (2) Å away from the plane, and the amino nitrogen N1 and

the dpe nitrogen N3 in apical positions, subtending to the plane normal N—Cu angles of 1.5 (1)° (N1—Cu1) and 3.2(1)° (N3—Cu1).

The subunit (a) associated to Cu2, is instead a 1D polymeric structure bearing only minor differences to the previous one. Here the H_2tea anion acts in a μ_2k^4-N,O,O',O'' mode due to the unprotonated alkoxo oxygen (O34) binding a second copper cation of a neighbouring unit and thus bridging dimers around a second inversion centre and defining a catemer as a result. The effect of the O34 bridging is the appearance of a rombic O—Cu—O—Cu loop with a rather short Cu2···Cu2 [1-x,-y,-z] distance of 2.9229 (12) Å. As a consequence of the different coordination of the anion the Cu2 ion presents a strongly distorted square bipyramidal geometry (Fig. 1(b), inset), with the base defined by N2, N4, O34 and O34 [1-x,-y,-z] (maximum departure from the L.S. plane: 0.053 (1) Å for O34, with Cu2 being 0.055 (1) Å away from the plane). The apical sites are occupied by the weakly coordinated O14 and O24 from OH groups, subtending O—Cu angles of 13.6 (1) ° (O14—Cu2) and 14.9 (1)° (O24—Cu2).

Table 2: Selected bond lengths (Å) for (I).

Cu1—O23	1.926 (3)	Cu2—O34^{i}	1.910 (3)
Cu1—N1	1.981 (4)	Cu2—O34	1.924 (3)
Cu1—O13	2.006 (5)	Cu2—N2	2.035 (3)
Cu1—N3	2.012 (5)	Cu2—N4	2.062 (3)
Cu1—O33	2.155 (5)	Cu2—Cu2^{i}	2.9222 (11)

Symmetry code: (i) -*x*+1, -*y*+1, -*z*.

The crystal structure can be envisaged as a planar (010) layout of Cu2 chains running along [101] with interspersed Cu1 dimeric units acting as connectors (Fig. 2). Two strong H-bonding interactions (Table 3, #1,#2) serve to this end, linking the 1D structures through the dimeric spacers to define ondulating 2D structures parallel to (010) (Fig. 3).

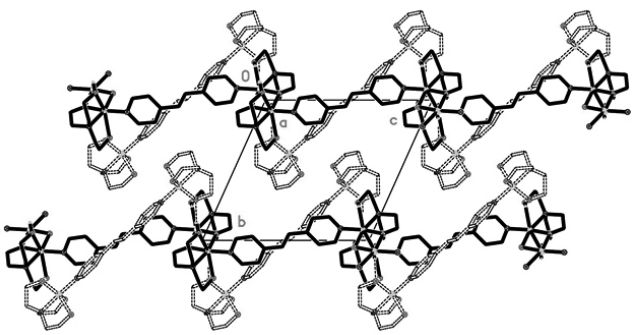

Figure 3: A projection of the structure along [100], showing sideways the planes presented in Fig. 2.

There are in addition two weaker, rather unusual π interactions complementing this linkage: a C—H—π one involving the C62═C62' double bond (Table 3, #3) and a T-shaped π—π one (Table 4).

Fig.4a shows a projection down [001] where columnar voids along c can be clearly seen. This is precisely the locus of the perchlorate anions (Fig.4b) which dispose in these unoccupied regions, with weak interactions between themselves (Table 3, #4) and to the main frame (Table 3, #5 to #16) It is interesting to compare **(I)** with its related structure $[Cu_2(H_2tea)_2(dpe)]\cdot 2\cdot(ClO_4)_n H_2O$ **(II)**, which is built up of exactly the same cationic 1D chains, but where the dimeric units in **(I)** are replaced by simple dpe spacers[1]. Charge balance is therein achieved by the presence of ordered perchlorate anions instead of the disordered ones in **(I)**. These compositional differences introduce in turn differences in the H-bonding scheme, which end up reflecting in the packing dimensionality. Both structures share the same elemental "brick" in the chain, with four H's, viz., those from the two "terminal" H_2tea anions, centrosymmetrically related in **I** (but independent in **II**) available for strong linkage. However, while in **I** all four are used in interchain connections with the result of the 2D structure already discussed, in **II** two of these H-bonds are lost for this latter purpose, one of them being intramolecular (to one vicinal oxo O) and a second ends up being received by a strong pendant chlorate acceptor. Under these conditions only two chains can be linked into a 1D strip, as shown in Fig. 4. Thus, the final dimensionality is defined by the different strength and capabilities of the H-bonding acceptors in both structures, viz., stronger deprotonated oxo O's in **I** vs weaker pyridyl N's in **II**.

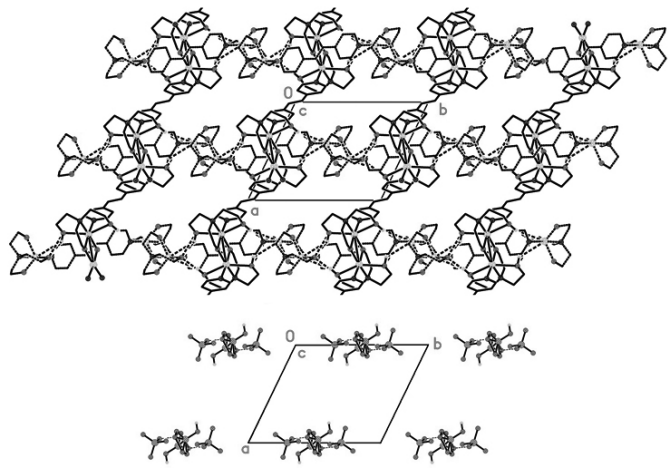

Figure 4: (a) Another sideways view of the 1D substructures, now projected down [001] and showing the columnar voids left between the 1D arrays. (b) The columnar disposition of the perchlorate anions, filling the voids shown above.

Table 3: Hydrogen-bond geometry (Å, º) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*A*···O42*A*^{ii}	0.93	2.37	3.188 (10)	146
C12—H12*A*···O14	0.93	2.35	3.016 (5)	128
C22—H22*A*···O31*A*^{iii}	0.93	2.50	3.375 (9)	157
C22—H22*A*···O11*B*^{iii}	0.93	2.34	3.092 (12)	137
C42—H42*A*···O32*A*^{iv}	0.93	2.50	3.284 (15)	142
C52—H52*A*···O24	0.93	2.43	3.098 (5)	129
C52—H52*A*···O22*A*^{iv}	0.93	2.54	3.391 (16)	152
C52—H52*A*···O42*A*^{ii}	0.93	2.27	2.996 (14)	135
C23—H23*B*···O32*A*	0.97	2.57	3.179 (14)	121
C63—H63*A*···O31*B*^{ii}	0.97	2.43	3.197 (13)	136
C14—H14*B*···O11*B*^{v}	0.97	2.44	3.225 (12)	138
C44—H44*A*···O22*A*^{iv}	0.97	2.48	3.133 (10)	124
C54—H54*B*···O11*A*^{v}	0.97	2.57	3.515 (8)	166
O14—H14···O23^{i}	0.85 (1)	1.87 (2)	2.688 (4)	163 (4)
O24—H24···O23	0.85 (1)	1.91 (3)	2.693 (5)	154 (5)

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*; (ii) *x*+1, *y*, *z*; (iii) *x*+1, *y*-1, *z*; (iv) -*x*+1, -*y*+2, -*z*+1; (v) -*x*+1, -*y*+2, -*z*.

Since some of the H atoms could not be trustable found, a discussion regarding the way in which charge balance has been justified is in force.

To begin with, if the depleted perchlorate anion were not present the formula of **(I)** could be written, for the sake of clarity, as a two member sum of two substructures, viz., a polymeric one (a) $\{[Cu_2(H_2tea)_2(dpe)]\cdot 2ClO_4)\}_n$ and a dimeric one (b) $[Cu_2(Htea)_2(dpe)]$, both neutral from a charge density point of view, where H_2tea and Htea stand for tea groups with one or two alkoxo groups lacking their respective H atoms.

The existence of the extra perchlorate charge (-0.72e) means there must be some extra positive charge balancing it, coming from $H_m$tea anions presenting an average negative charge smaller than so far described.

On one side the triethanolamine group bound to Cu2, (atoms defined by their training label 4) presents its two H's quite ordered and making clear, strong H-bonds, for what they could be ruled out for this purpose. The logical

candidate in the triethanolamine group 3, bound to Cu1 in the dimeric units, which ought to present a disordered protonation state in the form of Htea (m=1) and H_2tea (m=2) in a 0.64:0.36 ratio. With this formulation, the dimeric group (b2) would be a cation providing a formal charge of +0.72, thus balancing the 0.72 (ClO_4^-) depleted counterion.

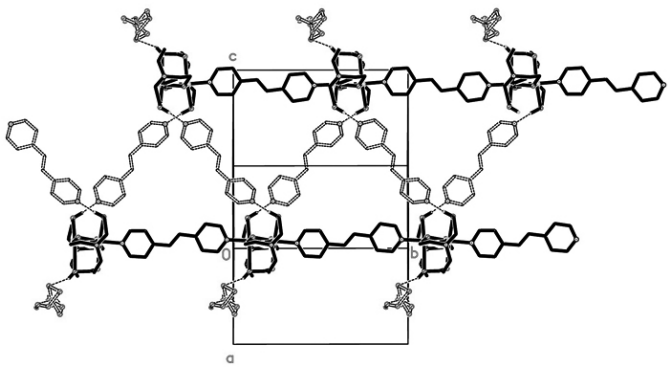

Figure 5: A view of the 1D strips built up in structure **II**, to be compared with the 2D structure in **I**, shown in Fig 2. Note the H-bonds ending up in perchlorate anions, interrupting the 2D H-bonding sequence.

The UV-vis spectrum of **(I)** has been measured. It shows a band at 302 nm and a shoulder at 318 nm which can be ascribed to the $\pi\cdots\pi$ interaction between ligands and to a charge transfer transition, respectively. The broad band centered at 748 nm in the visible region is assignable to a d-d transition of the copper ion[16].

CONCLUSION

In summary, a new copper (II) complex with (1,2-di(4-pyridyl)ethylene) and triethanolamine as bridging ligands was synthesized and characterized by X-ray diffraction. The structure shows an interesting behavior of the intervening ligands: while the former one fulfills its usual, well documented spacer role, the triethanolamine counterpart exhibits instead different degrees of deprotonation and coordination modes, a fact which in turn gives raise to well differentiated substructures. The fact that most of them are cationic introduces the need for charge balance, in turn achieved by a large, non-integer number of free perchlorate counterions. This fact introduces an extremely large number of H-bonding donors and acceptors in the structure, which leads to a very complex intermolecular interaction scheme, partially responsible of the final crystal cohesion.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nº 1054040.

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