Dedicated to Prof. P.T. Frangopol on the occasion of his 75th anniversary

The structure of $[Cu(bipy)_3][Cu(bipy)(ala)(ClO_4)_2]ClO_4$ – a Compound with Two Different Coordination Modes in the same Complex**

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The paper describes the solid state structure of a compound of composition $[Cu(bipy)_3][Cu(bipy)(ala)(ClO_4)_2]ClO_4$*, in which both the cation and anion are octahedral complex species with copper(II) as coordination center. The cation contains three chelate rings formed by bipy; the anion contains in the quatorial plane a* $CuONC_2$ *chelate ring formed by the alaninato ligand and a* CuN_2C_2 *chelate ring formed by bipy, with two monodentate perchorato ligands in axial positions completing the six-coordination. In the crystal π–π stackings lead to a supramolecular self-assembled structure.*

Keywords: copper(II) complexes, alaninato, perchlorato, ligands, coordination

In biological media most of the copper metalloproteins are involved in redox processes having electron transport functions [1,2]; the copper ion can also have a free radical trapping role [3]. The copper metalloproteins can act as oxygen transporters, oxidases or hydrolases, some others playing a role of Cu(I) and Cu(II) ion transport and storage.

As an essential microelement in living organisms, copper is a component of numerous enzymes and participates in at least the following processes [4]: a) production of energy as catalyst in the reduction of molecular O_2 to water through the action of *Cytochrome C oxidase;* b) tissue formation through the *lisyl oxidase*, with a role in the producion of *elastine* and *colagene*; c) in the iron metabolism (*ceruloplasmine*) though the intermediacy of two enzymes, *feroxidase I* and *ferroxidase II*, able to oxidise Fe^{2+} to Fe^{3+}. Copper also plays an essential role in the biological functions of several metaloproteins, namely: a) antioxidizing functions (*Ceruloplasmine, Superoxid dismutase SOD);* b) role in specific gene transcription; c) interactions with various nutrients (iron and zinc ion metabolisms, interaction with fructose, etc. The majority of copper proteins contain this metal ion in oxidation state II, those with monovalent copper being much less numerous; there are more common the metalloproteins containing copper in both oxidation states.

As an active center in biological compounds, the copper ion may occur as four- coordinate with a tetrahedral coordination geometry (in blue copper proteins) and five-coordinate with square pyramidal geometry (in non-blue copper proteins) [5].

For modelling the active centers of copper metaloproteins various ligands can be used, which can satisfy the coordination needs of the metal center. One of these is 2,2'-bipyridyl (abbreviated bipy). The high affinity of bipy towards copper favours the formation of the six-coordinate, octahedral cation $[Cu(bipy)_3]^{2+}$. Several such complexes are known, containing perchlorate [6-8], hexaiododimercurate [9] or 2-thioxo-1,3-dithiole-4,5-dithiolate [10] anions as counterions; their structures have been determined by single crystal X-ray diffraction.

Mixed complexes having two different types of ligands, *i.e.* 2,2'-bipyridyl and aminoacids, simultaneously coordinated to copper, form a series of compounds, some of which are of interest due to their intermolecular associations (self-assembly) through π-π stacking [11], hydrogen bonds [12-13] or succesive coordinations [14-17], leading to formation of supramolecular structures in the solid state. In general, they contain five- or six-coordinate metal ions, depending on the aminoacid coordinated to the copper(II) ion.

In the present paper we report the structure of a compound which contains a complex cation of the type *tris*-(2,2'-bipyridyl)copper(II) and an anion of the type $[Cu(2,2'\text{-bipyridyl})(alaninato)(ClO_4)_2]^-$. This complex is apparently the first one in which two octahedral Cu(II) centers, both chiral, are present, their association leading to a supramolecular structure.

Experimental part

Synthesis of $[Cu(bipy)_3][Cu(bipy)(ala)(ClO_4)_2]ClO_4$

To 10 mL of ethanolic solution of 2,2'-bipyridyl (2 mmoles) was added 1 mmole of $Cu(ClO_4)_2$/10 mL EtOH. The reaction mixture had *p*H = 5,5. The suspension containing an abundant blue precipitate was treated with 11 mL 0,1M NaOH solution (1.1 mmole), then under continuous stirring a mixture of 1 mmole L-alanine and 0.5 mmole NaOH/10 mL H_2O was added dropwise, until the reaction mixture became almost completely clear. The solution was filtered and the filtarte was left to slowly evaporate in open air. After a few weeks needle-like blue crystals separated.

Crystalographic analysis

A crystal of the cited complex was selected for X–ray diffraction analysis. The crystallograhic data are listed in table 1.

Results and discussion

The compound described here contains the $[Cu(bipy)_3]^{2+}$ cation neutralised by a [Cu(bipy)(ala)

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**bipy = 2,2'-bipiridyl; ala = L-alaninato

Table 1
CRYSTALLOGRAPHIC DATA FOR
$[Cu(bipy)_3][Cu(bipy)(ala)(ClO_4)_2]ClO_4$

Composition	$Cu_2C_{43}H_{38}N_9O_{14}Cl_3$
Formula weight	1138,27
Crystal system	triclinic
Space group	*P* -1 (no. 2)
Unit cell dimensions	*a* = 12.9090(13) Å
	b = 13.4421(13) Å
	c = 13.5486(13) Å
	α = 96.67(0)°
	β= 94.29(0)°
	γ = 92.37(0)°
Unit cell volume	2325.6(4) $Å^3$
Z	4
Calculated density	1.283 g/cm^3
R_{all}	0.105
R	8.02%

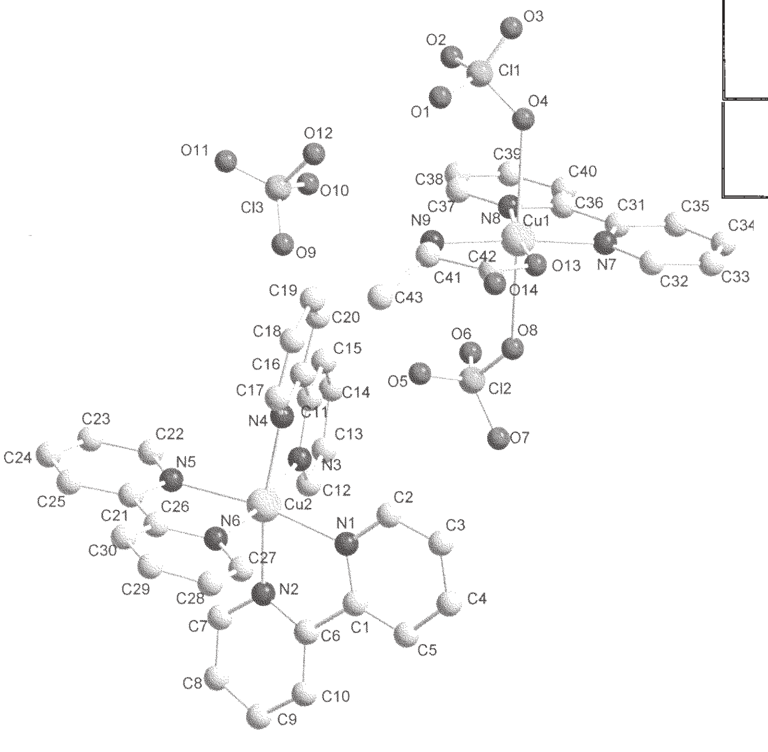

Fig. 1. The structure of $[Cu(bipy)_3][Cu(bipy)(ala)(ClO_4)_2]ClO_4$ complex

$(ClO_4)_2]^-$ complex anion and a perchlorate anion. The uniqueness of the compound is determined by the fact that both the cation and the anion are copper(II) complexes, with the metal exhibiting different coordination modes. The structure is shown in figure 1. Interatomic distances and bond angles are listed in table 2.

In the $[Cu(bipy)_3]^{2+}$ cation the metal is six-coordinate and displays a distorted octahedral geometry, reflected in bond angles less than 90°[interval 76.72(19)° – 77.97(21)°] in the CuN_2C_2 chelate rings imposed by the bidentate ligand.

Table 2
INTERATOMIC DISTANCES AND BOND ANGLES IN
$[Cu(bipy)_3][Cu(bipy)(ala)(ClO_4)_2]ClO_4$

$[Cu(bipy)(ala)(ClO_4)_2]^-$			
Cu1-N7	1.979(4) Å	N8-Cu1-N7	81.16(17) °
Cu1-N8	2.001(4) Å	N9-Cu1-N7	175.22(20) °
Cu1-N9	1.970(6) Å	O8-Cu1-O4	171.09(23) °
Cu1-O4	2.691(7) Å	O13-Cu1-N8	173.11(17) °
Cu1-O8	2.601(8) Å	O13-Cu1-N9	84.95(20)°
Cu1-O13	1.907(4)Å	O8-Cu1-O13	95.77(25) °
		O8-Cu1-N9	91.63(27) °
		O8-Cu1-N7	84.33(24) °
		O8-Cu1-N8	87.17(27) °
		O4-Cu1-N8	83.94(22) °
		O4-Cu1-N7	93.75(20) °
		O4-Cu1-N9	90.63(23) °
		O4-Cu1-O13	93.01(21) °
$[Cu(bipy)_3]^{2+}$			
Cu2-N1	2.107(5) Å	N1-Cu2-N5	168.20(19)°
Cu2-N2	2.140(5) Å	N2-Cu2-N1	77.30(19) °
Cu2-N3	2.071(6) Å	N2-Cu2-N4	169.38(20)°
Cu2-N4	2.137(5) Å	N3-Cu2-N4	77.97(21) °
Cu2-N5	2.141(6) Å	N6-Cu2-N3	169.57(21)°
Cu2-N6	2.123(6) Å	N6-Cu2-N5	76.72(20) °
		N6-Cu2-N2	91.46(18) °
		N6-Cu2-N1	92.53(19) °
		N4-Cu2-N5	91.34(20) °
		N4-Cu2-N6	95.84(20) °
		N1-Cu2-N3	96.30(19) °
		N1-Cu2-N4	94.64(20) °
		N5-Cu2-N3	94.89(21) °
		N2-Cu2-N5	97.85(20) °
		N3-Cu2-N2	95.87(18) °

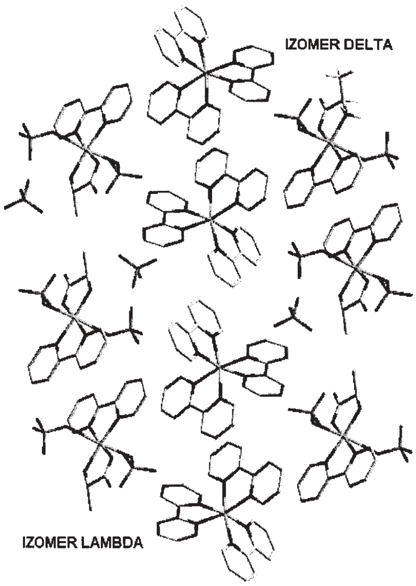

Fig. 2. Packing of the complex ions in the crystal

The structure of $[Cu(bipy)(ala)(ClO_4)_2]^-$ anion is more interesting. The octahedral geometry is less distorted than in the cation. In the equatorial plane the complex contains a molecule of 2,2'-bipyridyl forming a CuN_2C_2 chelate ring, through two nitrogen atoms [Cu1-N7 1.929(4) Å; Cu1-N8 2.001(4) Å] and an L-alaninato ligand, coordinated through nitrogen [Cu1-N9 1.970(6) Å] and oxygen [Cu1-O13

1.907(4) Å], to form another five-membered chelate $CuONC_2$ ring. It is observed that in the anion the Cu-N distances are shorter than in the cation [Cu2-N in 2.071(6)-2.141(6) Å interval]. The octahedral geometry is achieved by further coordination of two monodentate perchlorato anions, in *trans* axial positions, with slightly different Cu-O distances: Cu1-O4 2.691(7) Å and Cu1-O8 2.601(8) Å.

The packing of the complex ions in the crystal involves a linear arrangement of cations formed by alternation of Δ and Λ optical isomers of $[Cu(bipy)_3]^{2+}$ complex. The analysis of the packing shows the presence of π-π stacking interactions between the aromatic groups of the bipy ligands, suggesting that the structure can be described as supramolecular (fig.2).

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