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Solid state behaviour of *N*-tosyl-DL-asparagine–Cu(II)–2,2′-bipyridine system

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Abstract

The structural and spectroscopic properties of $[Cu(bipy)(tsasnO)_2] \cdot 2H_2O$ are investigated. The complex crystallizes in the space group $P2_1/n$, with $a = 12.502(2)$, $b = 15.298(2)$, $c = 18.901(8)$ Å, $\beta = 96.80(2)°$ and $Z = 4$. The complex consists of discrete $[Cu(bipy)(tsasnO)_2]$ units and lattice water molecules. The Cu(II) ion is coordinated to two bipy nitrogens and two carboxylate oxygens from two aminoacidate anions in a square-planar geometry.

Introduction

The ternary 2,2′-bipyridine–Cu(II)–*N*-tosyl-DL-asparagine system was previously studied both in the solid and solution state by means of structural [1a] and electrochemical [1b] techniques in order to define the number and type of complexes formed and the coordination behaviour of the ligand as function of pH and metal-to-ligand molar ratio.

At pH values lower than 5, where the amino acid acts as a carboxylate ligand, the $[Cu(bipy)(tsasnO)_2]$ species prevails in solution and the corresponding solid $[Cu(bipy)(tsasnO)_2(H_2O)] \cdot 2H_2O$ (**I**) complex was separated. This complex shows a square-pyramidal geometry with two nitrogen donor atoms deriving from the bipy molecule, two aminoacidate carboxyl oxygens in the equatorial plane and one water oxygen in the axial position [1a].

From the same procedure used for **I**, operating in 1:1 methanol–water ratio, a solid blue–violet complex of empirical formula $Cu(bipy)(tsasnO)_2 \cdot 2H_2O$ is obtained. Its electronic spectrum is suggestive of a square planar coordination geometry which is uncommun for this type of ligand [2]. In order to obtain some information about the influence of such a coordination geometry on structural parameters we report here its X-ray and spectroscopic characterizations and the results are compared to those of **I**.

Experimental

Preparation of the complex

The $[Cu(bipy)(tsasnO)_2] \cdot 2H_2O$ complex was obtained by the same procedure followed for the corresponding aquo complex [1a] with a methanol:water ratio of 1:1. *Anal.* Calc. for $C_{32}H_{38}CuN_6O_{12}S_2$: C, 46.49; H, 4.64; N, 10.17. Found: C, 46.63; H, 4.42; N, 10.20%.

X-ray data collection and structure determination

Crystal data: $C_{32}H_{38}CuN_6O_{12}S_2$, $M = 826.35$, monoclinic, $a = 12.502(2)$, $b = 15.298(2)$, $c = 18.901(8)$ Å, $\beta = 96.80(2)°$, $V = 3589.54$ Å^3, space group $P2_1/n$, $D_m = 1.48$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.53$ g cm^{-3}, $F(000) = 1698$, $\mu(\text{Mo K}\alpha) = 7.88$ cm^{-1}.

A crystal of approximate dimensions $0.20 \times 0.30 \times 0.35$ mm was mounted on an Enraf-Nonius CAD4 single crystal diffractometer. Cell dimensions were determined from least-squares refinement on diffractometer angles for 25 automatically centered reflections from different regions of reciprocal space. Intensity data were collected at room temperature using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) with ω–2θ scan technique, 2θ limits 2.5–25.0°, scan width $1.0 + 0.35 \tan\theta$ and scan speed $2.35 - 8.24°$ min^{-1}. Three standard reflections monitored at 3 h intervals, showed no significant changes. The data were corrected for Lorentz and polarization effects and an empirical absorption correction, based on ψ scan [3] was applied ($0.85 < T < 1.0$). A total of 6799 independent non-

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zero reflections ($\pm h$, $+k$, $+l$) was measured, of which 4013 with $I > 2\sigma(I)$ were used in the structural determination. The structure was solved by conventional Patterson and Fourier techniques, and refined through full-matrix least-squares calculations. One water oxygen atom was identified, distributed in two positions with occupancy 0.6 and 0.4. All non-hydrogen atoms, except water oxygens, were refined anisotropically. Hydrogen atoms, excluding water hydrogens, were located in a ΔF map and then treated as fixed contributors ($B_H = B_C + 1.0$ Å^2). Final R and R_w values were 0.055 and 0.058 using weighting scheme $w = 2.2073/[\sigma^2(F_0) + 0.0005F_0{}^2]$*. Fifteen reflections, affected by extinction or counting error, were excluded from the final refinement. Complex neutral scattering factors [4] were used throughout; major calculations were carried out on a Vax-6310 computer using SHELX-76 [5], ORTEP [6] and PARST [7] programs. Final fractional coordinates for non-hydrogen atoms are given in Table 1.

Physical measurements

The solid electronic spectrum was obtained with a Varian Cary 2300 spectrophotometer as a mull transmission spectrum and the IR spectrum as KBr pellets (4000–500 cm^{-1} spectral range) with a Perkin-Elmer 180 spectrophotometer.

Thermogravimetric measurements were made using a Mettler TA 3000 instrument at speed rate of 10 °C min^{-1}.

Carbon, nitrogen and hydrogen analyses were carried out using a C. ERBA model 1106 elemental analyser.

Results and discussion

The structure showing the labelling scheme is given in Fig. 1, and selected bond distances and angles are given in Table 2.

The complex consists of discrete [Cu(bipy)(tsasnO)$_2$] units and lattice water molecules. The Cu(II) ion is coordinated to two bipy nitrogens and two carboxylate oxygens from two aminoacidate anions in a square-planar geometry. The Cu–O distances are very close to those of complex **I** and the lack of axially coordinated water oxygen does not alter the in-plane ligand field strength [1a].

A non-bonding contact involves the uncoordinated O(2) carboxylate oxygen: Cu$\cdots$O(2) = 2.760(1) Å and the angle formed by this vector with the normal to the coordination plane is 40.2(1)°.

TABLE 1. Final positional parameters

Atom	*x/a*	*y/b*	*z/c*
Cu	0.08723(5)	0.06832(5)	0.15988(4)
S(1)	0.1223(1)	−0.1971(1)	0.42087(9)
S(2)	0.5013(1)	0.1206(1)	0.29461(9)
O(1)	0.0634(4)	0.0517(4)	0.2597(3)
O(2)	0.0613(4)	−0.0881(4)	0.2292(3)
O(3)	−0.1573(3)	−0.0555(3)	0.3072(3)
O(4)	0.0883(3)	−0.2861(3)	0.4135(3)
O(5)	0.1170(4)	−0.1536(3)	0.4875(2)
O(6)	0.2402(3)	0.0681(3)	0.1864(2)
O(7)	0.2522(3)	−0.0678(3)	0.1458(2)
O(8)	0.4459(4)	0.0233(3)	0.0756(2)
O(9)	0.5715(4)	0.0559(4)	0.3307(3)
O(10)	0.5410(4)	0.2051(3)	0.2781(3)
Ow(1)	−0.2399(5)	−0.2036(4)	0.2276(3)
Ow(2)^a	0.5489(9)	−0.2763(7)	0.1695(6)
Ow(3)^b	0.6037(10)	−0.2581(8)	0.1397(7)
N(1)	0.0479(4)	−0.1440(3)	0.3610(3)
N(2)	0.4548(4)	0.0802(3)	0.2191(3)
N(3)	−0.0698(4)	0.0815(3)	0.1286(3)
N(4)	0.0943(4)	0.0980(3)	0.0579(2)
N(5)	−0.2014(4)	0.0393(4)	0.3878(3)
N(6)	0.5266(4)	−0.1063(4)	0.0602(3)
C(1)	0.0622(5)	−0.0292(5)	0.2727(4)
C(2)	0.0647(4)	−0.0486(4)	0.3533(3)
C(3)	−0.0159(5)	0.0029(4)	0.3897(3)
C(4)	−0.1322(5)	−0.0081(4)	0.3571(4)
C(5)	0.2574(5)	−0.1903(4)	0.4033(3)
C(6)	0.3366(5)	−0.1664(4)	0.4568(3)
C(7)	0.4442(5)	−0.1646(5)	0.4426(4)
C(8)	0.4718(5)	−0.1876(4)	0.3770(4)
C(9)	0.5872(6)	−0.1829(5)	0.3623(5)
C(10)	0.3903(6)	−0.2141(5)	0.3245(4)
C(11)	0.2839(5)	−0.2148(5)	0.3380(3)
C(12)	0.2890(5)	−0.0037(4)	0.1773(3)
C(13)	0.4062(4)	−0.0064(4)	0.2142(3)
C(14)	0.4742(4)	−0.0704(4)	0.1775(3)
C(15)	0.4807(5)	−0.0471(4)	0.0995(3)
C(16)	0.3966(5)	0.1357(4)	0.3484(3)
C(17)	0.3753(5)	0.0705(4)	0.3957(4)
C(18)	0.2956(6)	0.0844(4)	0.4397(4)
C(19)	0.2366(5)	0.1615(4)	0.4371(4)
C(20)	0.1533(6)	0.1775(5)	0.4869(4)
C(21)	0.2591(5)	0.2246(4)	0.3876(4)
C(22)	0.3391(5)	0.2128(4)	0.3448(3)
C(23)	−0.1492(5)	0.0743(5)	0.1695(3)
C(24)	−0.2562(5)	0.0799(5)	0.1432(4)
C(25)	−0.2825(5)	0.0935(5)	0.0722(4)
C(26)	−0.2024(5)	0.1011(4)	0.0287(3)
C(27)	−0.0957(4)	0.0964(4)	0.0581(3)
C(28)	−0.0016(4)	0.1064(3)	0.0169(3)
C(29)	−0.0092(5)	0.1231(4)	−0.0539(3)
C(30)	0.0838(5)	0.1344(4)	−0.0856(3)
C(31)	0.1823(5)	0.1272(4)	−0.0448(4)
C(32)	0.1847(5)	0.1081(4)	0.0272(3)

^{a}Population 0.6; ^{b}population 0.4.

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*The quantity minimized during refinement was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weighting factor. The unweighted and weighted residuals were defined as follows: $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

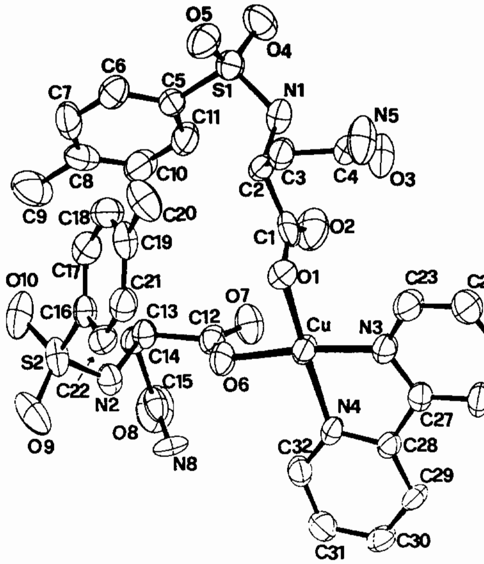

Fig. 1. ORTEP view of the $[Cu(bipy)(tsasnO)_2]$ moiety showing the atom numbering and thermal ellipsoids (40%) for the non-hydrogen atoms. The H atoms are omitted for sake of clarity.

TABLE 2. Selected bond distances (Å) and angles (°)

Cu–O(1)	1.960(5)	Cu–N(3)	1.992(5)
Cu–O(6)	1.919(4)	Cu–N(4)	1.993(4)
C(1)–O(1)	1.263(9)	C(12)–O(6)	1.277(8)
C(1)–O(2)	1.217(9)	C(12)–O(7)	1.210(8)
C(2)–N(1)	1.485(8)	C(13)–N(2)	1.456(7)
C(4)–O(3)	1.202(8)	C(15)–O(8)	1.228(8)
C(4)–N(5)	1.316(9)	C(15)–N(6)	1.342(8)
N(1)–S(1)	1.598(5)	N(2)–S(2)	1.600(5)
S(1)–O(4)	1.427(4)	S(2)–O(9)	1.440(5)
S(1)–O(5)	1.432(5)	S(2)–O(10)	1.432(5)
S(1)–C(5)	1.763(6)	S(2)–C(16)	1.765(6)
O(1)–Cu–N(4)	171.7(2)	N(3)–Cu–O(6)	173.9(2)
O(1)–Cu–O(6)	90.5(2)	N(3)–Cu–N(4)	81.1(2)
O(1)–Cu–N(3)	92.4(2)	N(4)–Cu–O(6)	95.5(2)
Cu–N(4)–C(28)	115.9(4)	Cu–N(3)–C(23)	126.6(4)
Cu–N(4)–C(32)	125.5(4)	Cu–N(3)–C(27)	118.5(4)
O(1)–C(1)–O(2)	126.4(7)	O(6)–C(12)–O(7)	127.1(6)
O(3)–C(4)–N(5)	123.7(6)	O(8)–C(15)–N(6)	123.0(6)
O(3)–C(4)–C(3)	122.3(6)	N(6)–C(15)–C(14)	116.8(5)
N(5)–C(4)–C(3)	114.0(6)	C(14)–C(15)–O(8)	120.1(5)

The lack of coordinated apical water removes the tetrahedral distortion of the equatorial plane, observed in complex **I**, the deviations from planarity being within experimental error; the Cu atom lies only 0.0921 Å out of this plane.

The opportunity to reach a regular geometry and the high hydrophobic character of both ligands seem to be the factors allowing the present complex to attain an exactly planar geometry without any additional out-of-plane interaction.

The carboxylate and side chain amide groups are planar and in each amino acid moiety the carboxyl and the amide groups are quite orthogonal.

Bond distances and angles in the amino acid skeleton are very close to those of complex **I**; the two bipyridine rings are nearly planar and twisted by 3.28(2)° about the 2–2′ bond.

The crystal packing is mainly determined by intermolecular ring-stacking interactions between bipyridine rings, with distances in the range 3.32–3.70 Å, and hydrogen bonds involving amidic and sulfonamidic nitrogens with sulfonic and amidic oxygen; short contacts (range 2.56–2.87 Å) involve the water molecule.

The role of water molecules in stabilizing this structure is evidentiated by its thermal behaviour; in fact a weight loss is observed in a very large temperature range (35–155 °C) corresponding to one water molecule; the second one is then lost with decomposition of the complex.

The electronic spectrum shows two bands (17 850, 15 150 (shoulder) cm^{-1}) which fall in the range observed for square planar bipy–Cu(II)–N-protected aminoacidate complexes [7, 8].

In the IR spectrum the bands assigned to stretching frequencies of NH_2 ($\nu(NH_2)_{as} = 3340m\ cm^{-1}$, $\nu(NH_2)_s = 3300m\ cm^{-1}$) and NH groups ($\nu(NH) = 3210\ cm^{-1}$) are slightly shifted with respect to the free amino acid ($\nu(NH_2)_{as} = 3390s$, $\nu(NH_2)_s = 3280w, 3240m$, $\nu(NH) = 3140m\ cm^{-1}$), suggesting a different involvement of hydrogen bonds. In the 1700–1500 cm^{-1} range an unambiguous assignment of bands present is prevented by the great number of vibrations falling in this range; the very strong $\nu(SO_2)_{as}$ (1320 cm^{-1}) and $\nu(SO_2)_s$ (1155 cm^{-1}) are unchanged with respect to the free amino acid.

As previously observed for the $[Cu(bipy)(tsasnO)_2(H_2O)]\cdot 2H_2O$ complex, also in the present case the side chain amide group is uncoordinated and only forms intermolecular contacts. As a consequence, its involvement in metal coordination may be excluded also in solution and its thermal motion may lower the stability of the $[Cu(bipy)(tsasnO)_2]$ solution species. This may provide a reasonable explanation for the lowest log β values observed for the Cu(II)–N-tosyl-DL-asparaginates in the series $[Cu(bipy)(LO)_2]$ and $[Cu(LO)_2]$ with LO = tosyl-, benzenesulfonyl-, dansyl-glycine, tosyl-DL-asparagine [9].

Supplementary material

Lists of anisotropic thermal parameters, hydrogen atoms parameters, bond distances and angles of the ligand molecules, least-squares planes, hydrogen bonds, observed and calculated structure factors (18 pp): ordering information is available from the authors on request.

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