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The Factors Stabilizing Square-planar Geometries in σ-Bonding Amine Adducts: Crystal and Molecular Structure of Bis(*N*-tosyl-β-alaninato)bis(piperidine)copper(II)

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Abstract

A violet, air-stable, crystalline compound of empirical formula [Cu(Ts-β-ala)$_2$(pipd)$_2$] (Ts = 4-toluene sulfonyl group, hereafter abbreviated as tosyl group, Ts-β-ala = *N*-tosyl-β-alaninate ion, pipd = piperidine) was synthesized and characterized by means of structural and spectroscopic measurements. The crystal structure of the compound was determined from three-dimensional diffractometric data. The crystals are triclinic, space group $P\bar{1}$, $a = 9.305(1)$, $b = 9.637(2)$, $c = 12.727(2)$ Å, $\alpha = 61.50(2)$, $\beta = 63.26(1)$, $\gamma = 71.68(1)°$, $Z = 1$. The structure was solved by the heavy atom method and refined through least-squares calculations to $R = 0.032$ for 2911 observed reflections. The copper atom lies on the symmetry center coordinating two piperidine and two carboxylic oxygens of *N*-tosyl-β-alanine in a square-planar arrangement. The second carboxylic oxygen is not involved in metal coordination. Electronic data are also discussed in comparison with those of other ternary Cu(II) carboxylate amine complexes.

Introduction

It is well documented that low-molecular-weight ternary complexes of copper(II), abundant in living systems, are involved in the transport of the metal ion through biological fluids and living tissues, and investigations performed have revealed that a mixed N,O-atom donor set is the preferred chromophore [1, 2].

Subsequent comparative studies on small synthetic systems duplicating this metal ion arrangement have indicated the relatively high stability as mainly responsible for the diffuse natural occurrence of mixed complexes; the major contribution on the stability derives from the presence in the metal coordination sphere of an imidazole moiety which allows a π-back-donation from metal to unsaturated ligand π-orbitals, lowering the electron concentration near the central ion [3].

In this area, our modelistic approach on ternary copper(II)–*N*-protected amino acidate complexes provided many closely related structural and spectroscopic results which rationalized the coordination behavior of aromatic monodentate amines as imidazoles and pyridines [4, 5].

Actually for imidazole the resultant effect of basic properties, expressed by pK_a (~7.0) and π-back-donation power, invariably leads to essentially square-planar geometries, while for pyridines the markedly lower pK_a (~5.0–6.3) prevails on π-back-donation power and tetragonal octahedral geometries are preferred. As a consequence, only in imidazole complexes may the fifth and sixth positions react further with an additional ligand, as suggested for substrate–metallo-enzyme reactions.

Another class of biologically important ligands is represented by monodentate cyclic aliphatic σ-bonding amines such as morpholine and piperidine [6, 7], to which the high basic character (pK_a > 9.0), not supported by π-back-donation effect, should assign a weakly coordinating ability. Very few structural data are available on these ternary copper(II) complexes [8] and, in order to compare their structural parameters with those of above mentioned imidazole and pyridine analogues, we report here the crystal and molecular structure of the bis(*N*-tosyl-β-alaninato)bis(piperidine)copper(II) complex.

Experimental

Materials

[Cu(Ts-β-ala)$_2$(pipd)$_2$] was prepared by adding to 50 ml of a methanolic solution of the green [Cu(Ts-β-ala)$_2$] [4b] (10^{-2} mol/dm^3) 15 mmol of piperidine. On adding diethyl ether and cooling at 4 °C for 48 h, violet crystals separated. *Anal.* Found: C, 49.98; H,

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6.73; N, 7.76; S, 8.86. $C_{30}H_{46}CuN_4O_8S_2$ requires: C, 50.13; H, 6.46; N, 7.80; S, 8.93%.

Physical Measurements

The electronic, infrared and EPR spectra in the solid state were recorded as in ref. 4a.

X-ray Data Collection and Structure Determination

Crystal data: $C_{30}H_{46}CuN_4O_8S_2$, $M = 718.42$; triclinic, $a = 9.305(1)$, $b = 9.637(2)$, $c = 12.727(2)$ Å, $\alpha = 61.50(2)$, $\beta = 63.26(1)$, $\gamma = 71.68(1)°$, $V = 888.48$ Å^3, space group $P\bar{1}$ (C_i^1, No. 2), $D_m = 1.35$ g cm^{-3} (by flotation), $Z = 1$, $D_c = 1.343$ g cm^{-3}, $F(000)$ 390.99, μ(Mo Kα) = 7.31 cm^{-1}, 293 K.

A violet, air-stable crystal of approximate dimensions 0.35 × 0.20 × 0.25 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 (Mo Kα radiation). Intensity data were collected at room temperature, by using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) with the ω–2θ scan technique up to $\theta \leqslant 25°$, scan width $0.90 + 0.35 \tan\theta$, and scan speed 0.82–4.16 deg 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 [9] was applied ($1.00 \leqslant T$ factor $\leqslant 0.980$). A total of 3134 independent nonzero reflections ($\pm h, \pm k, +l$) were measured, of which 2911 having $I \geqslant 3\sigma(I)$ were used in the structure determination.

The structure was solved by conventional Patterson and Fourier techniques, and refined through full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located in a ΔF map and refined isotropically. Four hydrogen atoms, belonging to C(8) and C(10), were added as fixed contributors at their observed positions. Final R and R_w value was 0.032*. Unit weights were used at all stages, and no trend of $\Sigma w(|F_o|) - (|F_c|)^2$ vs. $|F_o|$, $\sin\theta$, or Miller indices was observed. A final difference map was featureless, with no peaks higher than 0.25 Å^{-3}. There was no evidence of secondary extinction.

Complex neutral atom scattering factors [10] were used throughout; major calculations were carried out on a Vax-11/750 computer using the SHELX-76 system of programs [11] and ORTEP plotting program [12].

TABLE I. Final Positional Parameters[a]

Atom	x/a	y/b	z/c
Cu	0.0000(0)	0.0000(0)	0.0000(0)
O(1)	0.1169(2)	0.1772(2)	−0.0583(2)
O(2)	0.2322(2)	−0.0168(2)	0.0737(2)
C(1)	0.2180(3)	0.1238(3)	−0.0021(2)
C(2)	0.3246(4)	0.2395(4)	−0.0340(3)
C(3)	0.4394(3)	0.2889(3)	−0.1727(3)
N(1)	0.5401(3)	0.1482(3)	−0.1946(2)
S	0.6020(1)	0.1363(1)	−0.3302(1)
O(3)	0.6725(3)	−0.0245(2)	−0.3103(2)
O(4)	0.4681(2)	0.2016(3)	−0.3741(2)
C(4)	0.7593(3)	0.2552(3)	−0.4417(2)
C(5)	0.9175(3)	0.1863(4)	−0.4662(3)
C(6)	1.0403(4)	0.2803(4)	−0.5561(3)
C(7)	1.0068(4)	0.4415(4)	−0.6208(3)
C(8)	0.8469(4)	0.5107(4)	−0.5937(3)
C(9)	0.7238(4)	0.4173(4)	−0.5046(3)
C(10)	1.1399(5)	0.5454(5)	−0.7203(3)
N(2)	0.1856(3)	−0.0734(3)	−0.1337(2)
C(11)	0.1476(4)	−0.0473(4)	−0.2436(3)
C(12)	0.2919(5)	−0.0975(4)	−0.3434(3)
C(13)	0.3602(5)	−0.2691(4)	−0.2852(4)
C(14)	0.4013(4)	−0.2944(4)	−0.1744(3)
C(15)	0.2568(4)	−0.2397(3)	−0.0771(3)

[a] The origin of the unit cell was arbitrarily defined by assigning the values of 0.0/0.0/0.0 to the coordinates of the Cu atom.

Final positional parameters for non-hydrogen atoms are given in Table I. Lists of anisotropic temperature factors, hydrogen atom parameters, and observed and calculated structure factors are available (see Supplementary Material).

Analysis

Nitrogen, carbon, hydrogen and sulfur were analysed with a Carlo Erba Model 1106 Elemental Analyser Instrument by Mr. G. Pistoni.

Results and Discussion

Bond distances and angles are given in Table II with atoms labelled as in Fig. 1.

The structure consists of discrete [Cu(Ts-β-ala)$_2$(pipd)$_2$] units in which the copper atom, lying on the symmetry center, coordinates two centrosymmetrically *trans*-disposed piperidine and amino acid molecules, in a square-planar arrangement. The tosyl-β-alaninate moiety acts as a simple carboxylate ligand through a carboxylic oxygen, while the second carboxylic oxygen is 2.652(1) Å from the copper in an 'out-of-plane' position. As a consequence of the angle between the Cu–O(2) vector and the normal to the equatorial plane being 36.15(2)°, the Cu···O(2) distance must be considered essentially non-bonding

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

TABLE II. Bond Distances (Å) and Bond Angles (deg)[a]

Cu–O(1)	1.970(2)	C(5)–C(6)	1.385(4)
Cu–N(2)	2.028(2)	C(6)–C(7)	1.376(4)
C(1)–O(1)	1.269(3)	C(7)–C(8)	1.383(4)
C(1)–O(2)	1.241(3)	C(7)–C(10)	1.516(4)
C(1)–C(2)	1.514(3)	C(8)–C(9)	1.383(4)
C(2)–C(3)	1.518(4)	C(9)–C(4)	1.382(4)
C(3)–N(1)	1.456(3)	N(2)–C(11)	1.483(3)
N(1)–S	1.603(2)	C(11)–C(12)	1.515(4)
S–O(3)	1.425(2)	C(12)–C(13)	1.511(5)
S–O(4)	1.436(2)	C(13)–C(14)	1.515(5)
S–C(4)	1.762(2)	C(14)–C(15)	1.516(4)
C(4)–C(5)	1.370(4)	C(15)–N(2)	1.478(3)
O(1)–Cu–N(2)	89.0(1)	O(3)–S–C(4)	106.6(1)
O(1)–Cu–O(1′)	180.0(1)	S–C(4)–C(5)	119.7(2)
O(1)–Cu–N(2′)	91.0(1)	S–C(4)–C(9)	120.4(2)
N(2)–Cu–N(2′)	180.0(2)	C(4)–C(5)–C(6)	119.3(3)
Cu–O(1)–C(1)	107.3(2)	C(5)–C(6)–C(7)	121.5(3)
Cu–N(2)–C(11)	114.7(2)	C(6)–C(7)–C(8)	118.9(3)
Cu–N(2)–C(15)	112.5(2)	C(6)–C(7)–C(10)	122.0(3)
O(1)–C(1)–O(2)	122.3(2)	C(10)–C(7)–C(8)	119.1(3)
O(1)–C(1)–C(2)	116.8(2)	C(7)–C(8)–C(9)	119.8(3)
O(2)–C(1)–C(2)	120.9(3)	C(8)–C(9)–C(4)	120.6(3)
C(1)–C(2)–C(3)	110.8(2)	C(9)–C(4)–C(5)	119.9(3)
C(2)–C(3)–N(1)	109.4(2)	C(11)–N(2)–C(15)	111.1(2)
C(3)–N(1)–S	121.7(2)	N(2)–C(11)–C(12)	112.8(3)
N(1)–S–O(3)	106.2(1)	C(11)–C(12)–C(13)	111.4(3)
N(1)–S–O(4)	106.9(1)	C(12)–C(13)–C(14)	109.8(3)
N(1)–S–C(4)	109.6(1)	C(13)–C(14)–C(15)	111.5(3)
O(4)–S–O(3)	119.7(1)	C(14)–C(15)–N(2)	113.4(2)
O(4)–S–C(4)	107.7(1)		

[a] Primed atoms are related to unprimed atoms by the symmetry transformation $-x$, $-y$, $-z$ of the reference coordinates.

because of the low degree of overlap between copper and O(2) orbitals.

The metal–ligand bond distances and angles are close to those found in the structurally analogous bis(acetato)bis(morpholine)copper(II)dihydrate [8] and bis(acetato)bis(amine)copper(II) [13]. A square-planar arrangement is always observed in N-protected aminoacidate–copper(II)–imidazole systems. The difference between saturated and aromatic amine adducts is the lengthening of the Cu–N bond, due to the lack of π-back-donation power of the saturated amine [4a].

The crystal packing is mainly determined by hydrogen bonding involving the uncoordinated carboxylate oxygen and amide nitrogen atoms (N(1)–O(2)^i = 2.802 Å, H···O(2)^i = 1.982 Å, N(1)–H···O(2)^i = 177.1°, $i = 1 - x, -y, -z$). This strong nearly linear interaction, also found in the bis(acetato)bis(morpholine) adduct, preventing O(2) from an effective metal bonding, can be considered as being responsible for the observed coordination geometry. The requirement of a further contribution for stabilizing square-planar geometries for saturated amine adducts is confirmed by the fact that, unlike the imidazoles, they frequently form complexes having other type of geometries [7, 14].

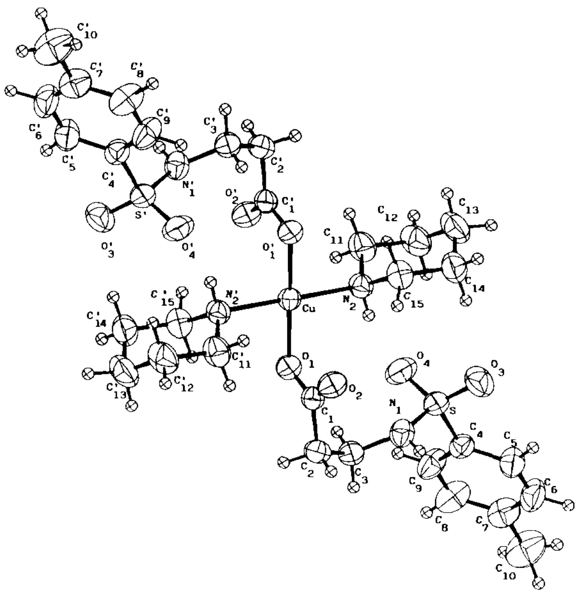

Fig. 1. ORTEP view of [Cu(Ts-β-ala)$_2$(pipd)$_2$] showing the atom numbering and the thermal motion ellipsoids (40%) for non-hydrogen atoms. The hydrogen atoms are represented as a sphere of arbitrary radius.

The dimensions of the tosyl-β-alaninate anion are normal and agree well with those reported for metal complexes of similar N-tosyl substituted aminoacidate ions [4b], while piperidine shows the usual chair conformation [4b].

The electronic and EPR data (d–d$_{max}$ = 18400, 15600(sh) cm^{-1}, $g_\parallel = 2.154$, $g_\perp = 2.054$) are consistent with the essentially square-planar geometry.

By comparing our spectral data with those of structurally analogous previously cited bis(morpholine) (19200, 15900(sh) cm^{-1}) [15] and bis(amine)–acetate adducts (18000, 15000(sh) cm^{-1}) [13], we can confirm, also for this class of ligands, the dependence of the d–d$_{max}$ position both on the distance of axial interaction and on the angle between the Cu–O$_{ax}$ vector and the normal to the equatorial plane. The significant lowering from the value of 20000 cm^{-1} found in truly square-planar CuN$_2$O$_2$ chromophores [16], substantiates the weak coordination ability of σ-bonding amines in which the lack of a π-back-donation effect, present in the imidazole adduct [3], overcomes the effect of their higher pK_a values.

The positions of more relevant IR bands (ν(OCO)$_{as}$ = 1580 vs, ν(OCO)$_s$ = 1410 vs, ν(SO$_2$)$_{as}$ = 1340, 1320 vs, ν(SO$_2$)$_s$ = 1160 vs, cm^{-1}) are typical of N-tosylamino acids coordinated only through the unidentate carboxylic group [4b].

Supplementary Material

Lists of observed and calculated structure factors, anisotropic temperature factors, hydrogen atom parameters and selected least-squares planes (22 pages) are available from the authors on request.

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