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The Crystal and Molecular Structure of Dimeric [3-(Salicylideneamino)-1-propanolato(2−)]copper(II)

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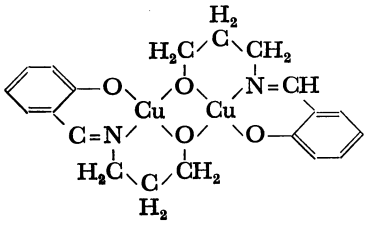
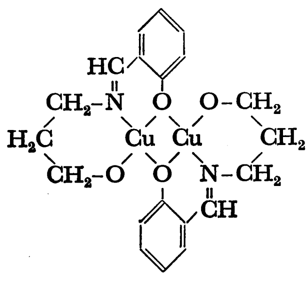
Synopsis. The crystal structure of dimeric[3-(salicylideneamino)-1-propanolato(2−)]copper(II) has been determined by X-ray diffraction. The two copper atoms are square planar with a separation of 3.021(4) Å and are bridged with aliphatic oxygens. The unusually low antiferromagnetism, explained by superexchange, has been correlated with the Cu–O–Cu angles of similar complexes.

Tridentate Schiff bases which contain an alcoholic side chain occasionally form 1 : 1 copper(II)-ligand complexes which have unusually low antiferromagnetic moments.[1,2] At room temperature the moments for these compounds lie between 0.3 and 0.7 BM, compared to the more usual values which are in the range 1.1 to 1.7 BM. The title compound, abbreviated [Cu(3-PrO·Sal)]$_2$, is of this type; molecular weight measurements indicate a dimer.[1]

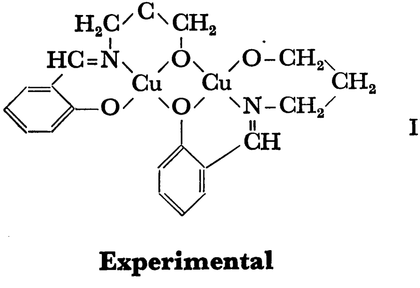
Three possible dimeric structures have been discussed in the literature.[3] These involve bridging with the aliphatic oxygens, I, bridging with the phenolic oxygens, II, or a combination of both, III. Infrared studies strongly favor structure I.[3] It is clear that a crystal structure determination is desirable, and this is the purpose of the present work.



I



II



III

Experimental

Bis[3-(Salicylideneamino)-1-propanolato(1-)]copper(II) was converted into [Cu(3-PrO·Sal)]$_2$ by refluxing in DMF for 5 hr (52% yield). Violet crystals were crystallized from DMF. Found: Cu, 26.51; C, 50.02; H, 4.70; N, 6.50%.[4] Calcd for Cu($C_{10}H_{11}NO_2$): Cu, 26.40; C, 49.89; H, 4.60; N, 5.81%.

The smaller crystals were plates having a predominant (100) face, and examination under polarized light showed that extensive twinning occurs. A crystal of dimensions 0.5×0.5×0.1 mm in which a small amount of twinning could be seen around the edges was mounted for X-ray investigation.

Crystal data: $Cu_2C_{20}H_{22}N_2O_4$; Monoclinic, space group $P2_1/c$, a=9.018(5),[5] b=10.810(4), c=10.233(5) Å, β=106.62 (9)°, D_m=1.667, D_x=1.673, Z=2, F(000)=984. Absorption for Ni-Kα radiation, 37.0 cm^{-1}.

Using Ni-Kα radiation, multiple-film equi-inclination Weissenberg photographs were taken for the layers *h0l* to *h5l*. Because of the twinning problem, the same crystal was then used to obtain the *hk*0 and *hll* zones. The intensities were visually estimated, and no corrections for absorption or extinction effects were made. Standard treatment of the data produced 860 observed independent structure factors.

Structure Determination

Space group considerations require the dimer to have a center of symmetry which coincides with one in tke unit cell. A Patterson synthesis produced the approximate location of the copper atom, and an electron density map was computed employing the signs determined from its coordinates. An outstanding feature of the map was a large peak in a position which would correspond to a bridging oxygen. Assuming that this was a bridging oxygen, and that the dimer for the most part was expected to be planar, the electron density map for the plane determined by the copper and oxygen positions and the center of symmetry of the dimer was calculated. The observed regions of high electron

TABLE 1. FINAL POSITIONAL AND THERMAL PARAMETERS FOR [Cu(3-PrO·Sal)]$_2$

Atom	X	Y	Z	B, Å
Cu	0.0675(2)	0.0935(3)	0.4233(2)	2.81(4)
O1	0.0875(12)	−0.0758(14)	0.4813(11)	3.06(24)
O2	0.1989(14)	0.0680(15)	0.3106(12)	3.68(27)
N	0.0411(13)	0.2657(17)	0.3898(12)	2.25(26)
C1	0.2687(16)	0.1574(20)	0.2599(15)	2.18(30)
C2	0.2414(16)	0.2853(20)	0.2691(15)	2.31(31)
C3	0.3162(20)	0.3702(22)	0.2055(17)	3.16(36)
C4	0.4167(20)	0.3349(23)	0.1364(18)	3.34(37)
C5	0.4443(18)	0.2159(20)	0.1255(16)	2.72(33)
C6	0.3719(20)	0.1172(23)	0.1818(18)	3.47(38)
C7	0.1210(20)	0.3313(24)	0.3244(18)	3.46(39)
C8	0.0759(22)	−0.3350(24)	0.5632(19)	3.94(43)
C9	0.2162(25)	−0.2551(30)	0.5766(22)	5.19(51)
C10	0.2007(17)	−0.1625(21)	0.4718(16)	2.40(31)

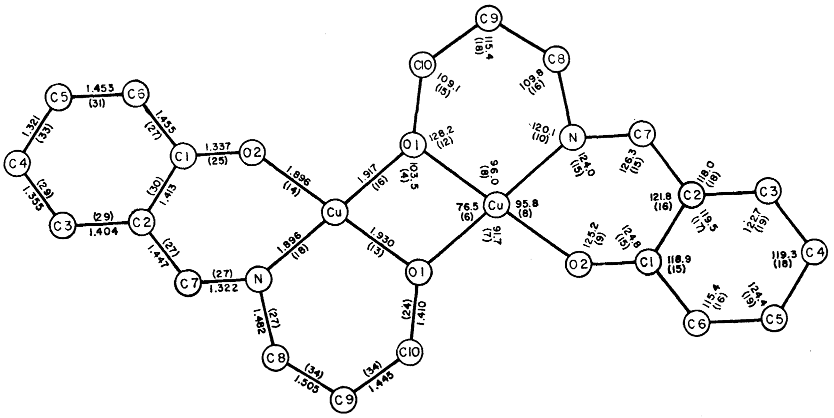


Fig. 1. Bond distances and bond angles of [Cu(3-PrO·Sal)]$_2$.

density in this plane were interpreted on the basis of isomer I, and a full trial structure developed.

The structure was then refined by the block-diagonal least-squares technique with isotropic thermal parameters. After several cycles, 25 strong reflections with low Bragg angles had calculated structure factors well exceeding the observed values. These reflections were suspected of suffering from absorption or extinction effects and were removed from the refinement process which was then continued until convergence to an R value of 0.132. The R value for all observed structure factors was 0.136. An anisotropic treatment of the copper atom reduced R slightly and produced no significant shifts in the atomic coordinates. Consequently, the refinement process was considered complete. Table 1 lists the final atomic coordinates and thermal parameters.

Discussion

The bond distances and angles of the final structure are shown in Fig. 1; there are no short intermolecular contacts. The structure is that which has been proposed by Miners and Sinn on the basis of infrared studies.[3] The dimer may be considered to be approximately planar with the exception of C9 which is 0.72 Å out of the least-squared plane of the other atoms. A better description, however, is provided by the use of two planes which have a dihedral angle of 11°. The first plane is determined by the Cu, N, O1, C7, and C8 atoms and is restricted to go through the center of symmetry of the dimer at 0 0 1/2. The maximum deviation of the atoms used in the determination is 0.05 Å. Atoms C9 and C10 are out of this plane by 0.84 and 0.25 Å, respectively. The second plane is determined by atoms C1 through C6 and the phenolic oxygen, O2. The maximum deviation of those atoms from the plane is 0.02 Å. The two benzene rings are stepped with an interplanar distance of 0.50 Å.

Our results are compared in Table 2 with two previously reported copper(II) alkoxy-bridged dimer complexes with ligands prepared by the addition of acetylacetone to 2-amino-1-ethanol (EIA) and 3-amino-1-propanol (PIA).[6] It is seen that the Cu–Cu separations are similar.

Table 2. Magnetic and structural properties of alkoxy-bridged copper(II) dimers

Compound	Cu–Cu distance, Å	Cu–O–Cu angle	$2J$, cm^{-1}
[Cu(EIA)]$_4$[a)]	3.006(8)	97.8(8)	0
[Cu(3-PrO·Sal)]$_2$[b)]	3.021(4)	103.5(4)	− 890[c)]
[Cu(PIA)]$_2$[a)]	3.026(6)	106.4(6)	−1100[d)]

a) Ref. 6. b) Present authors. c) Magnetic susceptibility measurement from Ref. 7. d) Magnetic susceptibility measurement from Ref. 6.

The magnetic susceptibility of the series can be correlated with the Cu–O–Cu angle.[8] Relatively large Cu–Cu separations rule out direct interactions. Consequently the principal path for magnetic interaction is the mechanism of superexchange through the Cu–O–Cu bridge.[9] The values of the singlet-triplet energy level splitting, $2J$, may be calculated by using the Bleaney-Bowers equation for exchanged-coupled copper(II) dimers. With $g=2.10$ and $N\alpha=6\times10^{-5}$, the resulting values are listed in Table 2. The value of $2J$ for [Cu(PIA)]$_2$ is based only on the room temperature magnetic susceptibility. [Cu(EIA)]$_4$ is a tetramer and is considered magnetically normal. The values of $2J$ show the same trend as previously reported,[8] *i.e.*, an increasing negative $2J$ with increasing Cu–O–Cu bond angle.

References

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