Bis(tropolonato)copper(II)

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Abstract. $Cu(C_7H_5O_2)_2$, monoclinic, $P2_1/a$, $a = 11.551$ (8), $b = 13.707$ (4), $c = 3.783$ (2) Å, $\beta = 92.77$ (4)°, $Z = 2$, $V = 598.3$ Å^3, $D_x = 1.69$ g cm^{-3}, μ(Cu $K\alpha$) = 27.0 cm^{-1}. The final R value is 0.035 for 939 reflexions. No significant bond-length alternation has been found in the significantly non-planar seven-membered ring.

Introduction. The crystal structure of cupric tropolone, CuT_2, was determined from two-dimensional data by Robertson (1951) and refined from three-dimensional data by Macintyre, Robertson & Zahrobsky (1965). In these investigations bond alternation in the seven-membered ring was observed as well as unequal bond lengths for the C—O bonds. However, the rather high R value in these two investigations prompted us to reinvestigate the CuT_2 structure.

The title compound was obtained from a mixture of 0.20 g of tropolone and 0.16 g of cupric acetate in 7 ml of MeOH and 3 ml of H$_2$O, after refluxing for 40 min and slow recrystallization from dioxane–10% acetic acid (1 : 1) at room temperature.

A green crystal of dimensions 0.51 × 0.07 × 0.07 mm was selected for the X-ray investigation. Three-dimensional data were collected on a Philips PW 1100 diffractometer, using graphite-monochromated Cu $K\alpha$ radiation and a θ–2θ scan procedure. 1256 reflexions were accessible ($2\theta \leq 140°$); 939 independent reflexions of these had intensities above the threshold value determined by the criterion $\sigma(I)/I \leq 0.33$. These were used in the refinements. Lorentz, polarization and absorption, but no extinction, corrections were applied. Lattice constants were obtained from powder data (Guinier–Hägg camera; Cu $K\alpha_1$ radiation, $\lambda = 1.54018$ Å; internal standard: KCl, $a = 6.2930$ Å). The structure, which was redetermined by means of the *SHELX* program system (Sheldrick, 1976), was refined by standard full-matrix least-squares methods, using unitary weights, to a final R value of 0.035.

Discussion. The final coordinates are listed in Table 1.* For the H atoms only the positional parameters were refined. The isotropic temperature factors ($U = 0.064$ Å^2), equal to the overall temperature factor obtained from the Wilson plot, were held fixed. The molecular geometry in CuT_2 is shown in Fig. 1, which also shows the numbering scheme for the atoms. Bond lengths and angles involving the non-hydrogen atoms are listed in Tables 2 and 3, respectively.

The Cu atom is positioned at the center of symmetry $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, coordinated to two tropolonate ions. The Cu

Table 1. *Positional parameters with e.s.d.'s in parentheses*

Values are ×10^4 for the non-hydrogen atoms and ×10^3 for the hydrogens.

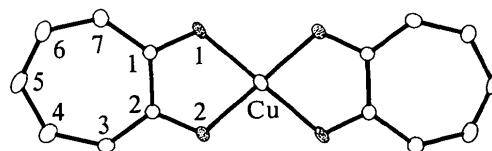|	x	y	z
Cu	5000	5000	5000
O(1)	3630 (3)	5263 (2)	2112 (9)
O(2)	4399 (2)	3699 (2)	5064 (8)
C(1)	2948 (4)	4510 (3)	1759 (11)
C(2)	3404 (4)	3615 (3)	3414 (11)
C(3)	2865 (4)	2697 (3)	3297 (13)
C(4)	1792 (4)	2422 (4)	1890 (14)
C(5)	951 (4)	2983 (4)	87 (13)
C(6)	996 (4)	3955 (4)	−737 (13)
C(7)	1872 (4)	4624 (4)	−20 (13)
H(C3)	330 (5)	216 (4)	428 (15)
H(C4)	163 (5)	174 (4)	211 (15)
H(C5)	41 (5)	270 (5)	−44 (16)
H(C6)	38 (5)	418 (4)	−202 (15)
H(C7)	175 (5)	524 (4)	−120 (15)

Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the molecule. Oxygens are shaded.

atom has planar four-coordination. The Cu—O bonds are equivalent, 1·913 and 1·915 Å, respectively, and the angle O(1)—Cu—O(2) is 83·8°. The Cu—O bond lengths conform with observations on other Cu complexes (Robertson & Truter, 1967).

The small 'bite' (separation between donor atoms) of tropolonate ions probably contributes to the effectiveness of these ions in forming complexes with metals. The O—O distance in CuT_2 is 2·557 Å, in good agreement with observations on other tropolonates (Avdeef, Costamagna & Fackler, 1974; Davis & Einstein, 1974).

The observed successive decrease in bond lengths proceeding from C(1) and C(2) respectively to the central ring atom C(5) found in e.g. tris(tropolonato)-aluminum(III) (Muetterties & Guggenberger, 1972) is not significant in CuT_2. The C(1)—C(2) bond is significantly longer than the others indicating that it is not involved to the same extent in the π-electron

delocalization of the tropolonate system. The value of 1·463 Å measured for the C(1)—C(2) bond is close to that expected for a $C(sp^2)$—$C(sp^2)$ single bond (1·47–1·48 Å) (Sutton, 1965). This is a common feature of the tropolonates and tropolones (Karlsson, Pilotti & Wiehager, 1976) and is also observed in systems such as azulene (Hanson, 1965; Ammon & Sundaralingam, 1966) and an amino-imino-cycloheptatriene (Goldstein & Trueblood, 1967) containing ten π-electrons.

The observed C—O bond lengths agree with those found in other metal tropolonates (1·27–1·29 Å). The C(1)—O(1) bond is slightly longer (3σ) than the C(2)—O(2) bond.

The tropolonate ligands show significant deviations from planarity as can be seen from Table 4.

The ligand folding is described by the angle 5·6° between the normal of plane II and a plane through O(1), Cu and O(2). This is in agreement with the value of 5° calculated by Macintyre et al. for the angle between the whole seven-membered ring and that defined by O(1), Cu and O(2). The ligand-folding effect is also found in other tropolonate complexes (Irving, Post & Povey, 1973).

Table 2. *Bond distances (Å) between non-hydrogen atoms with e.s.d.'s in parentheses*

Cu—O(1)	1·913 (3)	C(2)—C(3)	1·404 (6)
Cu—O(2)	1·915 (3)	C(3)—C(4)	1·378 (7)
C(1)—O(1)	1·302 (5)	C(4)—C(5)	1·391 (8)
C(1)—C(2)	1·463 (6)	C(5)—C(6)	1·370 (8)
C(1)—C(7)	1·394 (6)	C(6)—C(7)	1·382 (7)
C(2)—O(2)	1·286 (5)		

Table 3. *Interatomic angles (°) with e.s.d.'s in parentheses*

O(1)—Cu—O(2)	83·8 (1)	C(1)—C(2)—O(2)	115·3 (4)
C(1)—O(1)—Cu	112·9 (3)	C(3)—C(2)—O(2)	118·7 (4)
C(2)—O(2)—Cu	113·1 (3)	C(2)—C(3)—C(4)	130·3 (5)
C(2)—C(1)—C(7)	126·5 (4)	C(3)—C(4)—C(5)	129·2 (5)
C(2)—C(1)—O(1)	114·7 (4)	C(4)—C(5)—C(6)	128·0 (5)
C(7)—C(1)—O(1)	118·8 (4)	C(5)—C(6)—C(7)	129·5 (5)
C(1)—C(2)—C(3)	126·0 (4)	C(6)—C(7)—C(1)	130·4 (5)

Table 4. *Least-squares planes and deviations (Å)*

The planes are described in terms of normalized equations in the orthogonal coordinate system (m,n,p) having $p \parallel c$, n in the bc plane, and m in the a, b, c octant.

Plane I $-0\cdot4121m + 0\cdot2250n + 0\cdot8829p = 0\cdot4437$
Plane II $-0\cdot4047m + 0\cdot2254n + 0\cdot8862p = 0\cdot4586$

	Plane I				Plane II		
Cu*	0·145	C(3)	−0·014	Cu*	0·180	C(3)	0·000
O(1)*	−0·020	C(4)	−0·005	O(1)*	0·001	C(4)	−0·002
O(2)*	0·080	C(5)	0·006	O(2)*	0·110	C(5)	0·001
C(1)	−0·013	C(6)	0·007	C(1)	0·002	C(6)	0·002
C(2)	0·025	C(7)	−0·006	C(2)*	0·045	C(7)	−0·003

* Atom not included in the least-squares plane.

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