

O—H...N, 159 (3)°] as shown in Fig. 1. The monomeric molecule is approximately planar and the relevant least-squares planes are given in Table 3.

The structure of  $\alpha$ -*p*-nitrobenzaldoxime may be compared with that of  $\alpha$ -*p*-dimethylaminobenzaldoxime (Bachechi & Zambonelli, 1972). Neglecting the oxime groups we may regard the two molecules as symmetrical with a binary axis passing through C(1) and C(4). This assumption can be made since the values of the 'symmetry'-related bond distances and angles are not significantly different. In Fig. 2 the two molecules with averaged values for the 'symmetry'-related bond distances and angles are shown together with a schematic representation of the *para*-substituted benzaldoximes, in which the bonds and angles, to be used in the following discussion, are indicated by symbols.

In both molecules the aromatic carbon atom C(4) bearing the substituent X [—NO<sub>2</sub> or —N(CH<sub>3</sub>)<sub>2</sub>] does not show perfect trigonal symmetry, the deviations depending on the nature of the substituents.

It is well-known (Bent, 1961) that carbon  $\sigma$  orbitals directed towards a strong electron-withdrawing substituent (like —NO<sub>2</sub>) have more than average *p* character while those directed towards a strong electron-donating substituent [like —N(CH<sub>3</sub>)<sub>2</sub>] have less than average *p* character. In  $\alpha$ -*p*-nitrobenzaldoxime the valence angle  $\alpha$  at the carbon atom C(4) is larger than 120°, revealing a more than average *s* character of the  $\sigma$  orbitals in the directions of the *c* bonds, consistent with the enhanced *p* character of the  $\sigma$  orbital directed towards the —NO<sub>2</sub> group. Accordingly, *c* bonds are shorter than *a* bonds and than *c* bonds in  $\alpha$ -*p*-dimethylaminobenzaldoxime, and the *d* bond is considerably lengthened to approximately that of a C(*sp*<sup>3</sup>)—N(*sp*<sup>3</sup>) bond. Antithetical geometric features are observed in  $\alpha$ -*p*-dimethylaminobenzaldoxime, in conformity with a less than average *s* character of the C(4)  $\sigma$  orbitals directed along the *c* bonds. Therefore,  $\alpha$  is less than

120°, *c* bonds are longer than *a* bonds and than *c* bonds of the nitro derivative, and *d* is even shorter than a C(*sp*<sup>2</sup>)—N(*sp*<sup>2</sup>) single bond.

A possible contribution of a quinoid canonical form to the ground state of the two molecules, which would affect the  $\pi$ -components of the bonds, is masked in the nitro compound, while it appears to be enhanced in the other. From a comparison of the *b* bonds, a contribution of a quinoid form seems more pronounced in the dimethylamino derivative.

Apart from the N—O bond, significantly shorter in the nitro derivative, the oxime groups have geometry and dimensions which compare well in the two compounds. The exocyclic C(oxime)—C—C angles are significantly different in both molecules, C(7)—C(1)—C(6) being the largest, as expected from steric considerations. Valence angles and bonds of the —NO<sub>2</sub> group of the present compound compare well with the values given by Barve & Pant (1971) and Tavale & Pant (1971).

The technical part of this work was performed by P. Mura.

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## The Crystal Structure of Bis(propane-2-nitronato)copper(II)

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**Abstract.** Single crystals of bis(propane-2-nitronato)-copper(II), Cu[(CH<sub>3</sub>)<sub>2</sub>CNO<sub>2</sub>]<sub>2</sub>, are monoclinic, space group *P*2<sub>1</sub>/*a*, with unit-cell dimensions *a* = 6.792 (6), *b* = 10.343 (8), *c* = 13.366 (9) Å,  $\beta$  = 90.76 (5)°. The observed density is 1.70 g cm<sup>-3</sup> and, with four molecules per unit cell, the calculated density is 1.70 g cm<sup>-3</sup>. Each copper atom in these crystals is surrounded in a grossly

distorted octahedral manner by six oxygen atoms from four different propane-2-nitronate ions. The nitronate groups themselves are all planar.

**Experimental.** The substance was prepared by mixing, at 0°C, aqueous solutions of CuSO<sub>4</sub> · 5H<sub>2</sub>O (2 ml, 1.0M) and K[(CH<sub>3</sub>)<sub>2</sub>CNO<sub>2</sub>] (3 ml, 1.0M). Suitable single crys-

tals were formed when this mixture was slowly heated. Their unit-cell dimensions were determined by a least-squares refinement of data measured from a Guinier powder photograph taken with Cu  $K\alpha$  radiation and calibrated with quartz as an internal standard.

Three-dimensional equi-inclination multiple-film Weissenberg photographs were taken with Cu  $K\alpha$  radiation. The systematic absences were  $h0l$  for  $h$  odd and  $0k0$  for  $k$  odd. Two crystals, each with approximate dimensions  $0.05 \times 0.01 \times 0.3$  mm, were used since the compound decomposed slowly. The intensities of the diffraction spectra were measured with a Nonius microdensitometer. Some of the stronger reflexions were re-measured using a Nonius three-circle diffractometer, and these were later used to bring the photographic intensities on to a common scale. Lorentz and polarization factors were applied to all the observations, but no absorption corrections were made. Of the 1180 possible independent reflexions, 610 had non-zero amplitudes, and these were used in the structure solution and refinement, which were carried out using Patterson, heavy-atom and full-matrix least-squares methods respectively. In the latter, layer-scale factors, position coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the copper atom and individual atomic isotropic temperature factors for the other non-hydrogen atoms were varied. Unit weights were used. The final residual,  $R$ , is 0.094.\*

\* A list of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30160 (10 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ( $\times 10^3$ ) and thermal parameters

The anisotropic parameters for the copper atom ( $\times 10^4$ ) are appropriate to the temperature factor in the form

$$\exp \{ -[\beta(11)h^2 + \beta(22)k^2 + \beta(33)l^2 + 2\beta(12)hk + 2\beta(23)kl + 2\beta(13)hl] \}.$$

The estimated standard deviation of each parameter is given in units of the least significant digit quoted for the value itself.

	$x$	$y$	$z$	$B(\text{\AA}^2)$
Cu	322.9 (8)	231.0 (3)	257.8 (3)	
O(1)	544 (3)	203 (1)	158 (1)	2.8 (4)
O(2)	333 (4)	55 (2)	206 (1)	3.7 (4)
O(3)	627 (4)	302 (2)	364 (1)	3.7 (4)
O(4)	354 (4)	403 (2)	299 (1)	3.7 (4)
N(1)	505 (4)	78 (2)	157 (1)	2.6 (4)
N(2)	524 (4)	412 (2)	352 (1)	2.6 (4)
C(1)	802 (7)	19 (3)	64 (2)	4.9 (8)
C(2)	619 (6)	986 (3)	114 (2)	3.7 (6)
C(3)	528 (6)	848 (2)	123 (2)	3.5 (6)
C(4)	803 (6)	524 (3)	441 (2)	4.1 (7)
C(5)	596 (5)	523 (2)	388 (2)	3.0 (6)
C(6)	473 (6)	644 (3)	368 (2)	4.1 (7)

	$\beta(11)$	$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(23)$
Cu	283 (24)	65 (22)	42 (2)	-7 (7)	9 (4)	-10 (2)

**Discussion.** This structure determination forms part of an investigation of the geometry of the nitronate ion and of its function as a ligand in the formation of transition metal complex compounds.

The final structural parameters are given in Table 1. The copper atoms and the nitronate groups in the crystals are bound to each other in such a way that the structure consists of chains of bis(propene-2-nitronato)copper(II) units. Each copper atom is coordinated in a distorted octahedral ( $4+1+1$ ) manner to six oxygen atoms from four different propene-2-nitronate ions (Table 2). Similar copper-oxygen arrangements have been observed in other compounds. The atoms O(1), O(2), O(3') and O(4) (Figs. 1 and 2) form strong bonds ( $1.88-2.04 \text{ \AA}$ ) with the copper atom of each asymmetric unit, and are approximately coplanar with it (Table 3, plane A).

Table 2. Angles ( $^\circ$ ) made at the copper atom by the coordinating oxygen atoms

The estimated standard deviations of the angles are between 2 and 3 $^\circ$ .

	O(1)	O(1')	O(2)	O(3)	O(3')	O(4)
O(1)						
O(1')	105					
O(2)		96				
O(3)			115			
O(3')					101	
O(4)						91

There are two kinds of propene-2-nitronate ion. Both have two short Cu-O distances but in one they are to the same copper atom while in the other they are to different copper atoms. Consequently the O-N-O angles are quite different in the two types:  $110$  and  $117^\circ$  respectively.

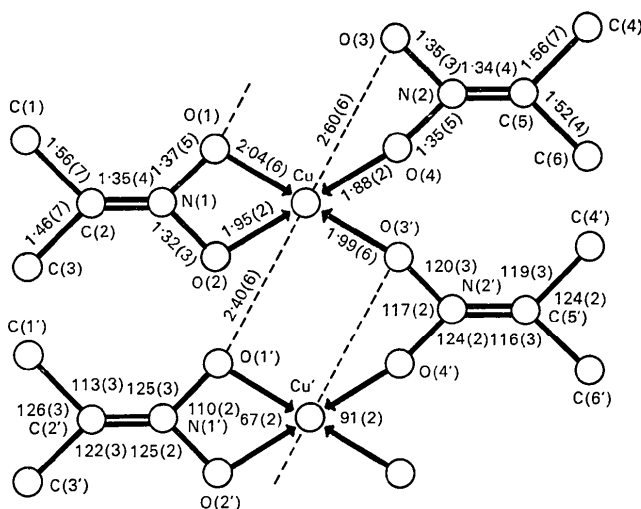


Fig. 1. Schematic diagram of the crystal structure coordination system showing interatomic distances (in  $\text{\AA}$ ) and angles ( $^\circ$ ). The estimated standard deviations of the distances and angles are given in units of the least significant digit of the quoted values themselves.

Table 3. Distances of atoms (in Å) from least-squares planes

The planes are in the form  $q_1x + q_2y + q_3z = q_4$ . The coordinates  $x$ ,  $y$  and  $z$  are expressed parallel to the orthogonal axial directions  $a$ ,  $b$  and  $c^*$ .

Plane	$q_1$	$q_2$	$q_3$	$q_4$
A	4.57576	-2.66624	9.13646	3.30525
B	3.33097	1.28538	11.44128	3.37712
C	-3.23805	-1.58250	11.65506	1.73297

Plane A		Plane B		Plane C	
Cu	-0.089	Cu*	0.350	Cu'*	-1.818
O(1)	0.086	O(1)	-0.018	Cu*	-0.139
O(2)	-0.049	O(2)	0.014	O(3)	0.007
O(3')	0.078	N(1)	0.002	O(4)	-0.026
O(4)	-0.026	C(1)	0.008	N(2)	0.015
		C(2)	0.012	C(4)	-0.026
		C(3)	-0.018	C(5)	0.029
				C(6)	0.001

\* These atoms were not included in the calculation of the least-squares plane. The fractional coordinates ( $\times 10^3$ ) for the Cu' atom are:  $x=822.9$ ,  $y=268.9$ ,  $z=257.8$ .

The propane-2-nitronate ions are planar (Table 3, planes B and C). The observed C-N distances (1.34, 1.35 Å) lie between those for oximes (1.26–1.31 Å: Calleri, Ferraris & Viterbo, 1966; Bednowitz, Fankuchen, Okaya & Soffer, 1966; Oijen & Romers, 1966; Mootz & Berking, 1969; Andreetti, Cavalca, Manfredotti & Muscatti, 1969) and for nitro compounds (1.46–1.52 Å: Duffin & Wallwork, 1966; Cox & Waring, 1972; Sutor, Calvert & Llewellyn, 1954). It seems likely that these bonds have appreciable double-bond character. A similar comparison of the N-O distances (1.32–1.37 Å) with those of oximes (1.36–1.42 Å) and of nitro compounds (1.22–1.25 Å) leads to the conclusion that they represent basically single bonds. These results are in agreement with those obtained from a spectroscopic investigation of  $\text{Na}[\text{CH}_2\text{NO}_2]$  and  $\text{Na}[(\text{CH}_3)_2\text{CNO}_2]$  (Jonathan, 1961).

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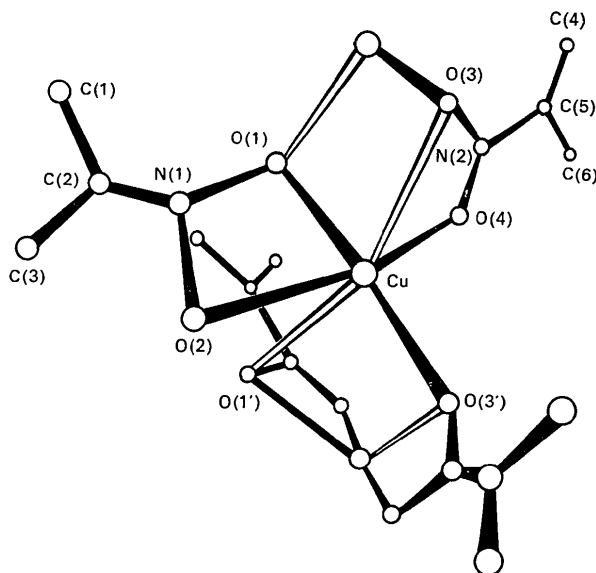


Fig. 2. A perspective view of the crystal structure illustrating the geometry of the coordination of propane-2-nitronate ions to copper.

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