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## Structure of Bis(di-*O*-propyl 1-cyano-2-oxopropylphosphonato)copper(II)

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**Abstract.** [Cu(C<sub>10</sub>H<sub>17</sub>NO<sub>4</sub>P)<sub>2</sub>],  $M_r = 555.99$ , monoclinic,  $P2_1/c$ ,  $a = 10.588$  (2),  $b = 13.395$  (3),  $c = 9.540$  (5) Å,  $\beta = 90.32$  (3)°,  $V = 1353$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.365$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 9.7$  cm<sup>-1</sup>,  $F(000) = 582$ ,  $T = 292$  K,  $R = 0.075$  for 1738 observed reflections. The structure consists of centrosymmetric CuL<sub>2</sub> molecules,  $L = \text{CH}_3\text{COC}(\text{CN})\text{PO}(\text{OC}_3\text{H}_7)_2$ , associated in infinite layers parallel to (001). The coordination of the Cu atom is an elongated rhombic octahedron of four O atoms at 1.948 (7) and 1.958 (7) Å and two N atoms from two adjacent CuL<sub>2</sub> units at 2.516 (5) Å. The ligands  $L$  perform both chelating (O=C–C–P=O fragment) and intermolecular-linking (C≡N groups) functions. The propoxy groups in the crystal lattice are poorly located.

**Introduction.** IR spectroscopic studies of several metal complexes with dialkoxyphosphonyl acetones (dapac) suggested that their coordination properties resembled those of 1,3-diketones (Petrov, 1972). X-ray structure analysis of Mg<sub>3</sub>(acac)<sub>6</sub> (acac = acetylacetonate) along with Mg<sub>3</sub>(depac)<sub>6</sub> (depac = diethoxyphosphonyl acetone) (Weiss, Kopf, Gardein, Corbelin, Schuman, Kirilov & Petrov, 1985) corroborated this suggestion. The introduction of a cyano group into the  $\alpha$ -position relative to the P=O group in dapac creates a new coordinating site and the ligand becomes potentially tridentate. Earlier the chelation of copper by 1-cyano-2-oxopropylphosphonic acid dipropyl ester was unequivocally established by IR investigations (Petrov & Kirilov, 1968) but before the present work it was difficult to ascertain the structural role of the C≡N group.

**Experimental.** Crystals obtained by recrystallization from an ether solution of the complex synthesized as described by Petrov & Kirilov (1968). A light-green prismatic crystal with approximate dimensions 0.12 × 0.17 × 0.22 mm investigated.  $D_m$  not determined. Enraf–Nonius CAD-4 diffractometer (graphite monochromator, Mo  $K\alpha$  radiation);  $\omega/2\theta$  scan: speed 2 to 10° min<sup>-1</sup>, width = (0.9 + 0.350 tan  $\theta$ )°. Cell constants from least-squares refinement of 22 reflections with  $22 < \theta < 24$ °. 5888 reflections measured in range of  $(\sin \theta)/\lambda < 0.616$  Å<sup>-1</sup> ( $h$ : 0 to 11,  $k$ : 0 to 16,  $l$ : -13 to 13 and their Friedel equivalents). Three standard reflections (monitored every 2.0 h), intensity variation < 0.1%. No decay correction. Lorentz and polarization correction; empirical absorption correction, transmission factors varied from 0.935 to 0.999. 1806 unique reflections with  $R_{\text{int}} = 0.016$ ; 2126 reflections considered unobserved [ $I < 3\sigma(I)$ ]. Structure solved by heavy-atom method and refined by restrained least squares on  $F^2$ 's (program *LSRE*, restraints applied to propoxy groups with distances for O–C = 1.35, C–C = 1.54 Å and angles at C atoms of 109.5°). Attempts to determine any disorder scheme were unsuccessful. H atoms not included in refinements. Final  $R = 0.050$ ,  $wR = 0.065$  and  $S = 6.017$  for 1530 observed reflections with  $|F_o - |F_c|| < 9\sigma(F_o)$ ;  $R = 0.075$ ,  $wR = 0.128$  for all 1738 observed reflections; weights  $w$  defined as  $4F_o^2/[\sigma^2(F_o)]^2$ . Max.  $(\Delta/\sigma) = 0.19$ ; max. residual density  $\pm 1.0$  e Å<sup>-3</sup>. Empirical correction for secondary extinction,  $F_{\text{corr}} = F/(1+gI)$  with  $g = 0.774 \times 10^{-6}$ . Atomic scattering factors and anomalous-dispersion coefficients from *SDP/PDP V3.0* software package (Enraf–Nonius, 1985) used for

Table 1. Atomic coordinates, equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) and their e.s.d.'s
$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}$
Cu	0.000	0.500	0.500	4.51 (4)
P	0.1701 (3)	0.3867 (2)	0.2916 (3)	5.79 (6)
O(1)	-0.1039 (7)	0.3983 (5)	0.4098 (8)	5.8 (2)
O(2)	0.1371 (7)	0.4804 (5)	0.3658 (7)	5.4 (2)
O(3a)	0.228 (1)	0.3986 (7)	0.144 (1)	8.7 (2)
O(3b)	0.2850 (9)	0.3286 (7)	0.364 (1)	10.9 (3)
N	0.082 (1)	0.1422 (7)	0.147 (1)	7.1 (3)
C(1)	0.045 (1)	0.3043 (7)	0.280 (1)	4.9 (2)
C(2)	-0.0742 (9)	0.3223 (7)	0.338 (1)	5.2 (2)
C(3)	-0.178 (1)	0.249 (1)	0.321 (2)	8.9 (4)
C(4)	0.065 (1)	0.2147 (7)	0.208 (1)	5.2 (2)
C(5a)	0.163 (2)	0.445 (1)	0.041 (2)	12.7 (4)
C(5b)	0.359 (2)	0.370 (2)	0.458 (2)	16.0 (5)
C(6a)	0.225 (3)	0.492 (2)	-0.088 (2)	17.0 (5)
C(6b)	0.473 (2)	0.306 (2)	0.497 (3)	17.4 (5)
C(7a)	0.364 (3)	0.512 (3)	-0.054 (4)	25 (1)
C(7b)	0.554 (2)	0.356 (3)	0.604 (2)	17.3 (6)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

Cu—O(1)	1.948 (7)	O(3b)—C(5b)	1.31 (2)
Cu—O(2)	1.958 (7)	N—C(4)	1.15 (1)
Cu—N	2.52 (1)	C(1)—C(2)	1.40 (1)
P—O(2)	1.484 (8)	C(1)—C(4)	1.40 (1)
P—O(3a)	1.55 (2)	C(2)—C(3)	1.48 (2)
P—O(3b)	1.60 (2)	C(5a)—C(6a)	1.55 (3)
P—C(1)	1.73 (2)	C(5b)—C(6b)	1.52 (3)
O(1)—C(2)	1.27 (1)	C(6a)—C(7a)	1.53 (5)
O(3a)—C(5a)	1.36 (2)	C(6b)—C(7b)	1.49 (3)
O(1)—Cu—O(2)	87.9 (3)	P—O(3b)—C(5b)	123 (1)
O(1)—Cu—N	95.3 (4)	P—C(1)—C(2)	123.8 (7)
O(2)—Cu—N	89.7 (3)	P—C(1)—C(4)	117.7 (8)
O(2)—P—C(1)	112.9 (5)	C(2)—C(1)—C(4)	118.5 (9)
O(2)—P—O(3a)	116.2 (5)	O(1)—C(2)—C(1)	125.3 (9)
O(2)—P—O(3b)	112.7 (5)	O(1)—C(2)—C(3)	114.0 (9)
O(3a)—P—C(1)	108.4 (5)	C(1)—C(2)—C(3)	120.7 (9)
O(3a)—P—O(3b)	98.0 (6)	N—C(4)—C(1)	178 (2)
O(3b)—P—C(1)	107.4 (5)	O(3a)—C(5a)—C(6a)	124 (2)
Cu—O(1)—C(2)	131.2 (7)	O(3b)—C(5b)—C(6b)	114 (3)
Cu—O(2)—P	127.1 (5)	C(5a)—C(6a)—C(7a)	108 (2)
P—O(3a)—C(5a)	121 (1)	C(5b)—C(6b)—C(7b)	111 (2)

all crystallographic calculations on a PDP 11/44 computer at the Institute of Applied Mineralogy in Sofia.

**Discussion.** Final atomic parameters for all non-hydrogen atoms are listed in Table 1.\* The bond lengths and angles are given in Table 2. The  $\text{CuL}_2$  molecule and atom-numbering scheme are shown in Fig. 1. The structure consists of centrosymmetric  $\text{CuL}_2$  units associated in two-dimensional infinite networks parallel to (001) (Fig. 2). The central Cu atom has an elongated rhombic octahedral  $\text{CuO}_4\text{N}_2$  coordination. The equatorial part of the octahedron is formed by four O

atoms from two chelating  $\text{O}=\text{C}-\text{C}-\text{P}=\text{O}$  fragments, while the axial positions are occupied by cyano-group N atoms from neighbouring  $\text{CuL}_2$  molecules. The Cu—O(2) distance [1.958 (7)  $\text{\AA}$ ] is slightly longer than Cu—O(1) [1.948 (7)  $\text{\AA}$ ]. These values, as well as the O(1)—Cu—O(2) angle [92.1 (3) $^\circ$ ], are typical for metal acetylacetonate chelates (Lingafelter & Braun, 1966). The O(1)...O(2) chelate 'bite' distance is 2.81 (1)  $\text{\AA}$ . The apical N atoms at 2.516 (5)  $\text{\AA}$  form long coordination bonds with the central atom (Procter, Hathaway & Nichols, 1968; Tomlinson, Hathaway, Billing & Nichols, 1969).

The chelate ring adopts a half-chair conformation with a 0.5  $\text{\AA}$  displacement of the Cu atom from the chelate plane [the  $\text{OC}(\text{C})\text{C}(\text{CN})\text{PO}$  moiety is planar

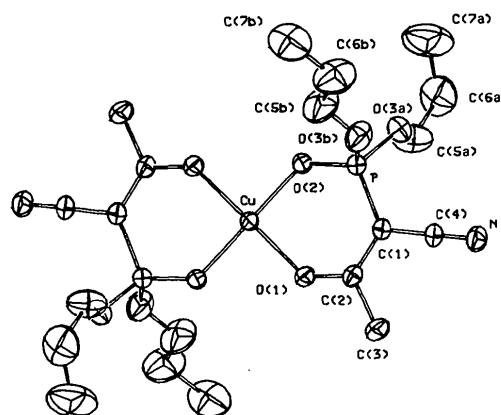
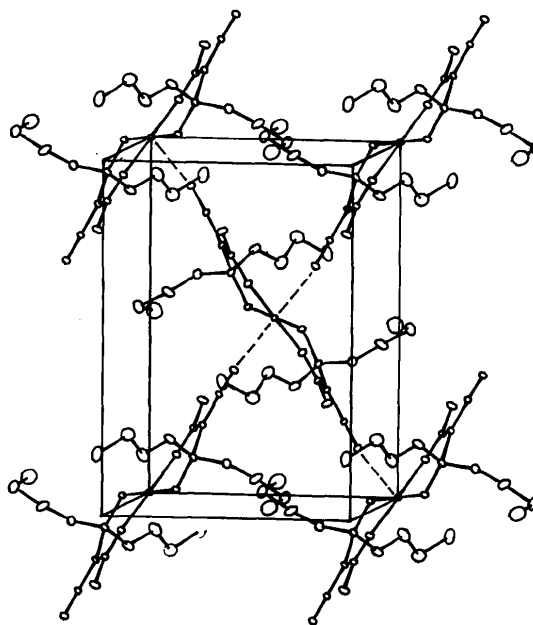


Fig. 1. Thermal-ellipsoid (20%) drawing with the atom-numbering scheme employed. H atoms not shown.

Fig. 2. Layers of  $\text{CuL}_2$  molecules parallel to the  $ab$  plane. Dashed lines indicate the proposed intermolecular  $\text{Cu}\cdots\text{N}$  linkage.

\* Lists of structure factors, anisotropic thermal parameters, least-squares planes and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44609 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

within 0.04 Å]. The dihedral angle between the equatorial CuO<sub>4</sub> plane and the chelate plane is 158.3°. Bond lengths and bond angles in the ligand adopt values typical for acetylacetonates [C—C(C)=O fragment] (Lingafelter & Braun, 1966) and phosphonic acid derivatives [O=P(O)<sub>2</sub>—C fragment] (Naumov & Vilkov, 1986). The angles in the P(C)O<sub>3</sub> tetrahedron vary from 98.0 (6) [O(3a)—P—O(3b)] to 116.2 (5)° [O(2)—P—O(3a)]. The conformation of both propoxy groups is different and follows the requirements of molecular packing. Torsion angles P—O—C—C [O—C—C—C] are 158 (2), -172 (1) [-20 (3), -180 (2)°] for branches *a* and *b* respectively.

The cyano group with a C(4)—N bond length of 1.15 (1) Å has triple-bond character. Consideration of the relatively short Cu...N distance, and the geometry of the cyano groups within the copper coordination sphere [angle Cu...N≡C (-*x*,  $\frac{1}{2}+y$ ,  $\frac{1}{2}-z$ ) = 149.8 (9)°], indicates that π-electron delocalization of C≡N is effectively compensated by σ-electron transfer

from Cu to N. In this structure the ligand is tridentate and performs a chelate-bridging role (Shkolnikova & Poray-Koshits, 1982).

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## Structures of Chloro(glycinato)(1,10-phenanthroline)copper(II) Monohydrate (I) and Aqua(1,10-phenanthroline)(L-phenylalaninato)copper(II) Nitrate Monohydrate (II)

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**Abstract.** (I) [CuCl(C<sub>2</sub>H<sub>4</sub>NO<sub>2</sub>)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)]·H<sub>2</sub>O, *M<sub>r</sub>* = 371.28, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 6.795 (3), *b* = 12.496 (4), *c* = 17.273 (5) Å, *V* = 1467 (1) Å<sup>3</sup>, *D<sub>x</sub>* = 1.680 Mg m<sup>-3</sup>, *Z* = 4, *F*(000) = 756, λ(Mo *K*α) = 0.71069 Å, μ(Mo *K*α) = 1.742 mm<sup>-1</sup>. Room temperature. Final *R* = 0.046 for 1302 unique observed reflections. (II) [Cu(C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub>)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)]NO<sub>3</sub>·H<sub>2</sub>O, *M<sub>r</sub>* = 505.98, monoclinic, *P*2<sub>1</sub>, *a* = 5.782 (2), *b* = 20.700 (6), *c* = 9.355 (3) Å, β = 97.58 (2)°, *V* = 1110 (1) Å<sup>3</sup>, *D<sub>x</sub>* = 1.514 Mg m<sup>-3</sup>, *Z* = 2, *F*(000) = 522, λ(Mo *K*α) = 0.71069 Å, μ(Mo *K*α) = 1.076 mm<sup>-1</sup>. Room temperature. Final *R* = 0.069 for 1929 unique observed reflections. The Cu ion displays

distorted square-pyramidal coordination in both (I) and (II), with the chlorine atom (I) or the water molecule (II) in the apical position. The Cu—N bond lengths alter according to the electronegative character of the *trans* atom. The conformations of the five-membered chelate rings appear to depend on H bonding and van der Waals interactions.

**Introduction.** Interest in mixed-ligand chelate complexes has been clearly established in the last few years (Griesser & Sigel, 1970). A series of compounds with formula *M*(N—N)(O—N) (*M* = Cu, N—N = 1,10-phenanthroline, bipyridine, substituted 1,10-phenan-