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Cyano[3,3'-(1,3-propanediamino)bis(3-methyl-2-butanone oximato)]copper(II)– ½ Acetonitrile

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Abstract. [Cu(C₁₃H₂₇N₄O₂)CN] · ½ C₂H₃N, [Cu(CN)(pnao-H)] · ½ CH₃CN, orthorhombic, *Fdd2*, *a* = 18.993 (2), *b* = 32.352 (2), *c* = 11.799 (1) Å, *V* = 7250.0 Å³, *M_r* = 381.48, *Z* = 16, *ρ*_{calc} = 1.40 (1), *ρ*_{obs} = 1.41 (1) Mg m⁻³. Three-dimensional counter X-ray data were used to solve and refine the structure to a final *R*(*F*²) of 0.054 for 2600 independent reflections. The structure consists of discrete monomeric square-pyramidal Cu complex molecules with a strong intramolecular hydrogen bond. The α-amine-oxime ligand is quadridentate with an average Cu–N(amine) distance = 2.043 (3) Å and Cu–N(oxime) = 1.978 (3) Å. The cyanide ion is carbon bonded at the apical position with a Cu–C bond distance of 2.154 (5) Å. The strong Cu–CN bond pulls the Cu²⁺ ion out of the plane of the four N atoms by 0.499 (6) Å. The short intramolecular hydrogen bond of 2.475 (4) Å is not appreciably modified by the presence of CN⁻. The acetonitrile molecule is not coordinated to the Cu^{II} atom, but packs between the Cu complexes as solvent of crystallization.

Introduction. The deep-purple crystals (Murmman & Monzyk, 1978) were consistently twinned when grown from aqueous media but gave satisfactory crystals from anhydrous acetonitrile. They crystallize with primarily {010}, {011}, and {110} facial development. The crystal selected was semi-spherical and had a volume of about 0.023 mm³. The space group and cell dimensions were first determined by precession film data, and the final cell dimensions were obtained with a Picker diffractometer from a least-squares refinement of the

setting angles of 18 manually centered reflections. Intensity data were collected for 4094 reflections by the *θ*–2*θ* scan method using Mo *K*α radiation (*λ* = 0.7107 Å) filtered with Nb. The data were corrected for background, *L_p* and absorption (*μ* = 1.27 mm⁻¹).* The transmission factor ranged from 0.89 to 0.73. Standards monitored about every 75 reflections showed no significant systematic variation with time.

The structure was solved by Patterson and Fourier methods. The acetonitrile was revealed by a difference Fourier map and its occupancy factor refined to 0.5. After a few cycles of least-squares refinement with all non-hydrogen atoms present, a difference Fourier map revealed most of the H atoms. When ambiguities occurred, idealized positions for these H atoms were calculated and were found to be consistent with difference Fourier peaks. Refinement was made using anisotropic temperature factors for all non-hydrogen atoms, with fixed H atoms. H atoms on the CH₃CN molecule were treated as disordered around the twofold axis. Full-matrix refinement minimizing $\sum w(F_o^2 - kF_c^2)^2$, using 2600 independent reflections, 213 variables, scattering factors of Cromer & Waber (1962), and anomalous scattering for Cu (Cromer, 1962), gave

* All calculations were performed on the University of Missouri IBM 370/168 computer system with the following programs: *ANGSET* (angle settings program); *SORTH* (sorting program; W. C. Hamilton); *HORSE* (general absorption-correction programs; W. C. Hamilton); *FORDAP* (Fourier synthesis program; A. Zalkin); *NUCLS* (least-squares program; R. Doedens and J. A. Ibers); a modification of *ORFLS* (Busing, Martin & Levy, 1962); *ORFFE* (Busing, Martin & Levy, 1964); *ORTEP* (Johnson, 1965).

Table 1. Atomic positional parameters for non-hydrogen atoms

Estimated standard deviations from the least-squares refinement are given in parentheses here and elsewhere in this paper.

	x	y	z	B _{eq} (Å ²)*
Cu(1)	0.2583 (1)	0.5216 (1)	0.0	2.48
C(1)	0.3923 (1)	0.5259 (1)	-0.1248 (3)	3.57
C(2)	0.3210 (1)	0.5899 (1)	-0.1304 (3)	3.47
N(1)	0.3451 (2)	0.5004 (1)	-0.0719 (3)	3.15
N(2)	0.2388 (1)	0.4597 (1)	0.0040 (4)	2.70
N(3)	0.1531 (1)	0.5355 (1)	-0.0069 (4)	2.75
N(4)	0.2612 (2)	0.5755 (1)	-0.0792 (3)	3.08
N(5)	0.3104 (2)	0.5389 (1)	0.2592 (4)	5.38
N(6)†	0.2500	0.7500	0.0966 (9)	7.92
C(1)	0.3604 (2)	0.4623 (1)	-0.0619 (4)	2.67
C(2)	0.3072 (2)	0.4357 (1)	0.0014 (4)	2.88
C(3)	0.4275 (2)	0.4436 (2)	-0.1077 (4)	3.79
C(4)	0.2960 (3)	0.3937 (1)	-0.0537 (5)	4.07
C(5)	0.3330 (3)	0.4300 (2)	0.1241 (4)	4.03
C(6)	0.1855 (2)	0.4472 (1)	0.0864 (4)	3.43
C(7)	0.1143 (2)	0.4661 (1)	0.0625 (5)	3.71
C(8)	0.1107 (2)	0.5135 (1)	0.0809 (4)	3.23
C(9)	0.2069 (2)	0.5990 (1)	-0.0754 (4)	2.51
C(10)	0.1428 (2)	0.5817 (1)	-0.0128 (4)	2.76
C(11)	0.2056 (2)	0.6417 (1)	-0.1210 (5)	4.05
C(12)	0.1413 (3)	0.6003 (1)	0.1058 (4)	4.10
C(13)	0.0754 (2)	0.5923 (1)	-0.0775 (5)	4.30
C(14)	0.2908 (2)	0.5343 (1)	0.1713 (4)	3.12
C(15)†	0.2500	0.7500	0.0015 (11)	4.34
C(16)†	0.2500	0.7500	-0.1211 (9)	5.68

* $B_{eq} = \frac{1}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha)$.

† These atoms lie on the twofold axis and have occupancy factors of 0.5.

Table 2. Atomic positional parameters for hydrogen atoms

	x	y	z
H(1)	0.0786	0.4530	0.1065
H(2)	0.1026	0.4610	-0.0169
H(3)	0.1823	0.4172	0.0871
H(4)	0.2011	0.4552	0.1609
H(5)	0.1255	0.5190	0.1578
H(6)	0.0632	0.5228	0.0741
H(7)	0.2180	0.4571	-0.0700
H(8)	0.1398	0.5245	-0.0796
H(9)	0.3401	0.3791	-0.0607
H(10)	0.2757	0.3959	-0.1265
H(11)	0.2660	0.3810	0.0
H(12)	0.1000	0.5940	0.1441
H(13)	0.1450	0.6302	0.0980
H(14)	0.1813	0.5917	0.1484
H(15)	0.3710	0.4478	0.1401
H(16)	0.3470	0.4020	0.1320
H(17)	0.2930	0.4350	0.1720
H(18)	0.0400	0.5790	-0.0440
H(19)	0.0800	0.5840	-0.1550
H(20)	0.0680	0.6220	-0.0750
H(21)	0.4433	0.4190	-0.0550
H(22)	0.4205	0.4342	-0.1833
H(23)	0.4639	0.4644	-0.1097
H(24)	0.2059	0.6407	-0.2014
H(25)	0.2450	0.6580	-0.0986
H(26)	0.1640	0.6565	-0.0981
H(27)*	0.2336	0.7739	-0.1480
H(28)*	0.2210	0.7290	-0.1525
H(29)*	0.2960	0.7480	-0.1525
H(30)	0.3630	0.5580	-0.1280

* These are the disordered H atoms of the CH₃CN and have occupancy factors of 0.5.

$R(F^2) = \frac{\sum |F_o^2 - kF_c^2|}{\sum F_o^2} = 0.081$, $R_w(F^2) = \frac{[\sum w(F_o^2 - kF_c^2)^2 / \sum wF_c^4]^{1/2}}{\sum wF_c^4} = 0.127$ and the standard deviation of an observation of unit weight was 2.51. Refinement with N-bonded CN gave a significantly poorer agreement factor $R(F^2) = 0.083$ and improbable temperature factors (N greater than C). A least-squares evaluation of the extinction parameter showed it to be very small and negative; so it was set to zero. Since *Fdd2* is a noncentrosymmetric space group the signs of *h*, *k* and *l* were reversed to distinguish the direction of the polar axis. Refinement of the same parameters using the alternate data set led to a significantly lower $R(F_o^2)$ of 0.057 vs 0.083 using the same number of variables (213), so the second model was chosen for final refinement. Several least-squares cycles with all non-hydrogen atoms anisotropic, but H atoms held at chemically reasonable positions ($B = 5$ to 6 \AA^2), gave $R(F_o^2) = 0.054$, $R_w(F_o^2) = 0.081$ and the e.s.d. of an observation of unit weight = 1.60. $R(F)$ conventional = 0.033. The weighting in the least squares was based on $\sigma^2(F_o^2) = \sigma^2(\text{counting}) + (0.035F_o^2)^2$. The shifts in the last cycle were all less than 5% of the corresponding standard deviations. A difference Fourier map

Table 3. The best plane through N(1), N(2), N(3), and N(4)

$$\text{Equation: } 0.2652x + 0.2157y + 0.9398z = 4.4418$$

Perpendicular distances to the plane (Å)

N(1)	-0.0105 (10)	Cu	0.449 (6)
N(2)	0.0105 (10)	O(1)	-0.183 (3)
N(3)	-0.0103 (10)	O(2)	-0.153 (3)
N(4)	0.0104 (10)	C(14)	2.654 (8)

showed no electron density greater than 0.44 e \AA^{-3} . The positional parameters for the heavy atoms are given in Table 1, and for the unrefined H atoms in Table 2; the deviations from the least-squares plane through the four equatorial N atoms are in Table 3.*

Discussion. The primary interest in the structure of this molecule was a comparison of the bond distances and

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35600 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

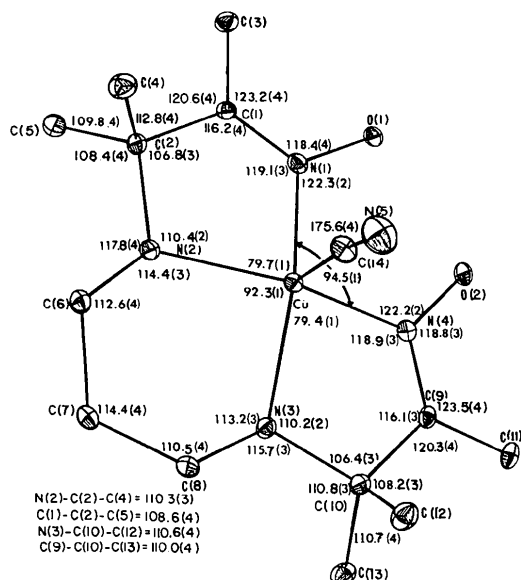


Fig. 1. Perspective view of [Cu(CN)(pnao-H)] showing the labeling of the atoms and selected bond angles ($^{\circ}$).

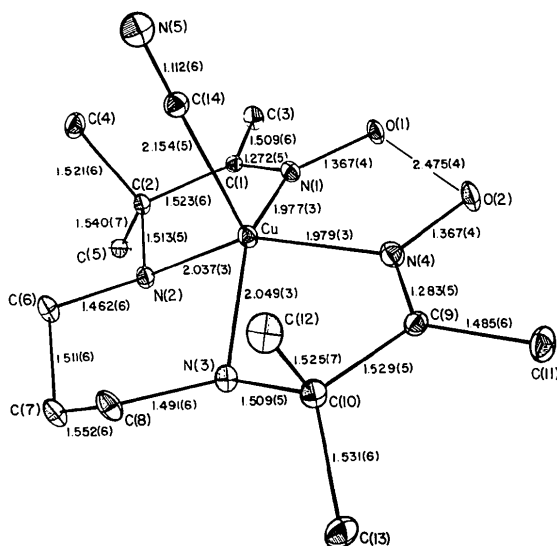


Fig. 2. Perspective view of [Cu(CN)(pnao-H)] showing bond distances (\AA).

angles with those of the analogous [Cu(pnao-H)(OReO₃)] (Liss & Schlemper, 1975). This comparison contrasts the strongest unidentate ligand (CN⁻) which has π -bonding capability with a very weak ligand (ReO₄⁻) which has only σ -bond characteristics. The major features of interest are the extent of metal displacement from the N₄ plane, and the intramolecular hydrogen-bond modification caused by the bonding change at the apical position.

A previous study (Murmman & Monzyk, 1978) investigated the thermodynamic quantities involved in

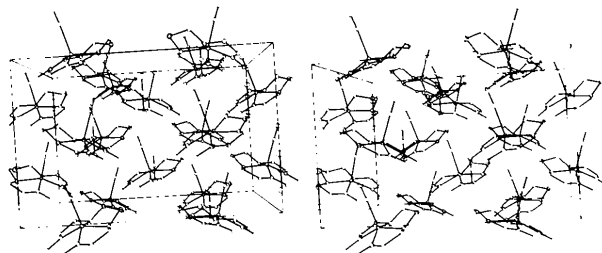


Fig. 3. Stereoscopic view of one quarter of the unit cell (without H atoms and ligand methyl groups).

the reaction of CN⁻ with [Cu(pnao-H)]⁺ in aqueous media. In contrast to an upper-limit formation-constant estimate (based on the lack of spectral changes in solution) of 20 mol⁻¹ for ReO₄⁻ the CN formation constant (298 K) was found to be remarkably large, 1.25 × 10³ mol⁻¹. As is well established in copper(II)-CN chemistry, the association is often so strong that oxidation-reduction rapidly proceeds giving Cu^I and (CN)₂. However, with the stoichiometric ratio 1/1 (CN⁻/complex) both the solid and aqueous solutions of the title complex are highly stable. Slight excesses of CN⁻ produce Cu(CN)₃²⁻ and oxidized products from pnao at a relatively rapid rate.

The structure consists of discrete mononuclear neutral Cu complex molecules with the Cu atom in a square-pyramidal configuration (Figs. 1, 2). The Cu coordination consists of four N atoms from the quadridentate amine-oxime ligand and the cyano group (C-bonded) occupying the fifth position. The C-N distance of 1.112 (6) \AA is about normal for a coordinated CN group. The acetonitrile is in a vacant position in the lattice and is not coordinated to the metal, nor is it hydrogen bonded to the neutral complex (for a stereoview of the unit cell, see Fig. 3).

The structure of the complex is basically the same as that of [Cu(pnao-H)(OReO₃)] (Liss & Schlemper, 1975). The Cu-C(CN) distance is 2.154 (5) \AA , appreciably shorter than the Cu-O(ReO₄) distance of 2.40 (1) \AA , and the Cu-C-N bond angle is slightly bent [175.6 (4) $^{\circ}$]. The square pyramid about the Cu atom is significantly distorted. The Cu atom is displaced by 0.50 (1) \AA out of the plane (Table 3) through the four N atoms toward CN⁻. With the OReO₃⁻ complex, the displacement was only 0.24 \AA and for [Cu(NH₃)₄(OH₂)]SO₄ (Morosin, 1969) a 0.19 \AA movement was noted. A similar effect has been observed (Anderson & Packard, 1979) for a related complex, [Cu(cyclops)(OH₂)]ClO₄, where the Cu^{II} ion is found to be displaced only 0.10 \AA above the N₄ plane. Because of the 0.5 \AA displacement of the Cu atom from the plane of the four N atoms, the N(X)-Cu-C(14) angles are all much larger than 90 $^{\circ}$ [X = 1, 103.2 (2) $^{\circ}$; X = 2, 102.6 (2) $^{\circ}$; X = 3, 106.0 (2) $^{\circ}$; and X = 4, 105.5 (2) $^{\circ}$].

As observed in [Co(pnao-H)(NO₂)₂] (Murmman & Schlemper, 1973) and [Co(pnao-H)(OREO₃)] (Liss & Schlemper, 1975), the Cu–N(amine) distances [2.049, 2.037 (3) Å] are longer than the Cu–N(oxime) distances [1.977, 1.979 (3) Å], suggesting a stronger Cu–N(oxime) bond. At least part of this difference can be attributed to the usual shortening of 0.03–0.04 Å on change of hybridization from *sp*³ to *sp*² for the N atom. The reason for the rest of the shortening is not clear.

The intramolecular hydrogen bond has an O···O distance of 2.475 (4) Å which compares well with the value of 2.46 (2) Å in the ReO₄⁻ complex. Thus, shifting the Cu atom away from the N₄ plane does not facilitate a shortening of the O···O distance. Both of these are significantly longer than the 2.432 (3) Å in [Co(pnao-H)(NO₂)₂]. All of the other bond distances and angles are in reasonable agreement with those of the perrhenate structure. Thus the strong CN⁻ coordination to the Cu^{II} atom has little effect on the ligand geometry: its main effect is displacing the metal from the plane of the organic ligand.

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The Structure of *poly-Bis(thiocyanato-N)bis-μ-(1,2,4-triazole-N²,N⁴)-iron(II)**

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Abstract. [Fe(C₂H₃N₃)₂(NCS)₂], C₆H₆FeN₈S₂, *M_r* = 310.0, orthorhombic, *a* = 7.882 (1), *b* = 16.312 (4), *c* = 9.890 (2) Å, *Z* = 4, *D_c* = 1.620 Mg m⁻³; *R* = 0.037 (*R_w* = 0.048) for 963 independent reflexions. The compound is isomorphous with [Co^{II}(C₂H₃N₃)₂(NCS)₂].

Introduction. Very recently, we reported the crystal structures of [*M*^{II}(trz)₂(NCS)₂] with *M* = Co, Zn, Cu and trz = 1,2,4-triazole (Engelfriet, den Brinker, Verschoor & Gorter, 1979). Although crystallizing in different space groups, the three compounds exhibit the

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same basic features: two-dimensional *M*^{II} networks with 2,4-bridging trz molecules and NCS⁻ groups, acting as N donors, on either side of the planes. From X-ray powder diffraction the Mn, Fe, Co and β-Ni members of the series were found to be isomorphous (Haasnoot & Groeneveld, 1977). Nevertheless, there were several reasons for examining a single crystal of the Fe compound as well: the Mössbauer spectrum of this compound showed a quadrupole doublet with strongly broadened lines, while for a proper refinement of the neutron powder diffraction pattern precise values of the positional parameters are needed (Engelfriet, Groeneveld & Nap, 1980). Single crystals were prepared in the following way. A solution of FeCl₂·4H₂O, slightly acidified with HCl, was added to a solution containing equimolar quantities of trz and

* 1,2,4-Triazole Complexes. XI. Part X: Donker, Haasnoot & Groeneveld (1980).

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