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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond distances involving H atoms and torsion angles, have been deposited with the IUCr (Reference: MU1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(dicyanamide)bis(1,10-phenanthroline)-copper(II)

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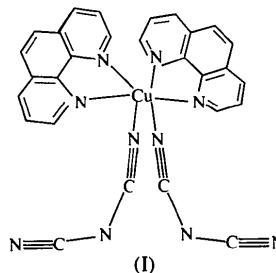
Abstract

The title compound, [Cu(C₂N₃)₂(C₁₂H₈N₂)₂], was prepared and its crystal structure was solved as a part of our study on synthesis, crystallochemistry and properties of copper compounds with pseudohalogenide anions. The structure, which is formed by discrete molecules, is presented. The dicyanamide and phen ligands are bonded to the Cu atom with elongated tetragonal bipyramidal

(4+2) coordination geometry, with the dicyanamide ligands in a *cis* arrangement.

Comment

The crystal structure of the title compound, (I), is formed by discrete molecules held together by van der Waals forces. Fig. 1 shows a molecule of (I) with the atomic labelling scheme.



From a chemical point of view the structure studied is rather uncommon. Coordination polyhedra in copper compounds containing two phen (1,10-phenanthroline) molecules and two monoanions are mostly in the form of distorted trigonal bipyramids (or tetragonal pyramids) with an uncoordinated second monoanion. The Cu atom in (I) is coordinated by two phen molecules and by the dicyanamide anions in a *cis* arrangement, forming an elongated tetragonal bipyramid (4+2). One N atom (N1) of the dicyanamide anion occupies an axial position while the second (N10) is equatorial. The same coordination polyhedron was observed for [Cu(NCS)₂(phen)₂] and [Cu(NCSe)₂(phen)₂], but in these complexes the cyanate ligands (thio- or seleno-) occupy two equatorial positions (Kabešová & Kožíšková, 1992; Sedov, Kabešová, Dunaj-Jurčo, Gažo & Garaj, 1982). Cyano

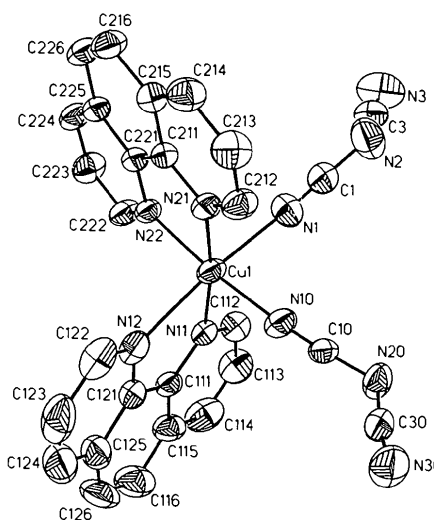


Fig. 1. ORTEP (Johnson, 1965) drawing of the formula unit and labelling of atoms. Displacement ellipsoids are drawn at the 40% probability level.

groups that are in axial as well as equatorial positions have been observed in the *cis*-[μ -CN-Cu(bipy)₂- μ -NC-Ag]⁺ cation (bipy = 2,2'-bipyridine), but the Cu atom has very deformed tetragonal bipyramidal (4+1+1) coordination geometry (Černák, Gérard & Chomič, 1993).

Three N atoms of the two phen molecules lie in the equatorial plane at distances of 2.008 (2)–2.045 (3) Å. The distance of the fourth N atom (in the axial position) is 2.312 (3) Å. The bond distances and angles in the phen molecules are normal (Anderson, 1973) and range from 1.302 (5) to 1.420 (4) Å, and 115.9 (5) to 125.5 (5)°, respectively. Both phen molecules are nearly planar; the largest deviation of atoms from their mean planes is less than 0.058 Å. The mean planes of the two phen molecules are inclined at 102.6 (1)°. There are three canonical formulae describing the mode of bonding in the dicyanamide ligand. Inspection of the bond lengths (Table 2) shows that no canonical formula properly describes the bonding mode in the two dicyanamide ligands in (I). All N_{cyno}≡C distances [1.091 (5)–1.130 (4) Å] are usual for N≡C triple bonds and the N_{amide}=C distances [1.270 (4)–1.324 (5) Å] are usual for N=C double bonds. These values, and also the values of the C—N_{amide}—C [120.6 (4) and 121.2 (3)°] and N_{amide}—C—N_{cyno} angles [169.0 (5)–173.1 (4)°], are comparable with values found in other dicyanamide structures (Chow, 1971; Jensen, Klewe & Tjelta, 1977; Britton, 1990). Both dicyanamide ligands are perfectly planar, with the largest deviation of atoms from the mean planes being less than 0.01 Å.

According to Golub, Köhler & Skopenko (1986), the bonding mode to the Cu atom of one dicyanamide ligand can be considered as angular [C1—N1—Cu1 = 166.3 (4)°] and the second [C10—N10—Cu1 = 175.4 (3)°] as linear.

Experimental

Crystals were prepared by mixing 2.5 ml of a 1 M solution of Cu(NO₃)₂ with 7 ml of NH₄OH, 10 ml of a methanol solution of 0.9 g phen, and 4 ml of a water solution of 0.526 g KN(CN)₂. After several days, pseudo-cubic blue crystals of (I) appeared. The density D_m was measured by flotation in CCl₄/CHBr₃.

Crystal data

[Cu(C₂N₃)₂(C₁₂H₈N₂)₂]

$M_r = 556.05$

Monoclinic

$P2_1/c$

$a = 8.756 (4) \text{ \AA}$

$b = 14.611 (6) \text{ \AA}$

$c = 18.979 (8) \text{ \AA}$

$\beta = 101.21 (4)^\circ$

$V = 2381.7 (18) \text{ \AA}^3$

$Z = 4$

$D_x = 1.551 \text{ Mg m}^{-3}$

$D_m = 1.50 (1) \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 3.69\text{--}7.11^\circ$

$\mu = 0.959 \text{ mm}^{-1}$

$T = 295 (2) \text{ K}$

Pseudocube

$0.50 \times 0.50 \times 0.50 \text{ mm}$

Blue

Data collection

Syntex P2₁ diffractometer

θ - 2θ scans

Absorption correction:

empirical

$T_{\min} = 0.771$, $T_{\max} =$

0.971

5848 measured reflections

5509 independent reflections

2799 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0335$

$\theta_{\text{max}} = 27.57^\circ$

$h = 0 \rightarrow 11$

$k = 0 \rightarrow 19$

$l = -24 \rightarrow 24$

2 standard reflections

monitored every 100

reflections

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0405$

$wR(F^2) = 0.0933$

$S = 0.790$

5509 reflections

400 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0730P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.028$

$\Delta\rho_{\text{max}} = 0.393 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.327 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cu1	0.49882 (5)	0.21700 (3)	0.12925 (2)	0.04610 (14)
N11	0.6563 (3)	0.2457 (2)	0.06563 (13)	0.0461 (7)
N12	0.3836 (3)	0.3310 (2)	0.0524 (2)	0.0572 (7)
N21	0.3371 (3)	0.2057 (2)	0.19227 (12)	0.0443 (6)
N22	0.5947 (3)	0.3015 (2)	0.20913 (12)	0.0424 (6)
N1	0.6549 (4)	0.1016 (2)	0.1947 (2)	0.0754 (10)
N2	0.7369 (5)	-0.0296 (2)	0.2700 (2)	0.0945 (12)
N3	0.9836 (5)	-0.0620 (3)	0.3419 (2)	0.1042 (14)
C1	0.7014 (5)	0.0439 (3)	0.2294 (2)	0.0623 (10)
C3	0.8754 (5)	-0.0407 (3)	0.3069 (2)	0.0611 (9)
N10	0.3954 (3)	0.1258 (2)	0.06118 (14)	0.0557 (7)
N20	0.2771 (4)	0.0023 (2)	-0.0126 (2)	0.0616 (8)
N30	0.0313 (4)	0.0021 (2)	-0.0967 (2)	0.0838 (11)
C10	0.3327 (4)	0.0703 (2)	0.0256 (2)	0.0435 (7)
C30	0.1446 (5)	0.0076 (2)	-0.0566 (2)	0.0550 (9)
C11	0.6141 (4)	0.3048 (2)	0.0107 (2)	0.0477 (8)
C12	0.7894 (5)	0.2038 (3)	0.0714 (2)	0.0616 (10)
C13	0.8884 (5)	0.2147 (3)	0.0254 (2)	0.0753 (11)
C14	0.8503 (6)	0.2716 (3)	-0.0290 (2)	0.0803 (14)
C15	0.7098 (5)	0.3193 (3)	-0.0391 (2)	0.0641 (10)
C16	0.6605 (7)	0.3781 (3)	-0.0971 (2)	0.0878 (14)
C121	0.4696 (4)	0.3488 (2)	0.0032 (2)	0.0528 (8)
C122	0.2454 (6)	0.3707 (3)	0.0429 (3)	0.0846 (14)
C123	0.1928 (6)	0.4295 (3)	-0.0151 (3)	0.094 (2)
C124	0.2815 (8)	0.4452 (3)	-0.0618 (3)	0.095 (2)
C125	0.4238 (5)	0.4073 (3)	-0.0557 (2)	0.0714 (11)
C126	0.5254 (8)	0.4200 (3)	-0.1039 (2)	0.091 (2)
C211	0.3744 (4)	0.2549 (2)	0.25291 (15)	0.0416 (7)
C212	0.2101 (4)	0.1559 (3)	0.1833 (2)	0.0577 (9)
C213	0.1142 (4)	0.1549 (3)	0.2315 (2)	0.0648 (10)
C214	0.1493 (4)	0.2047 (3)	0.2923 (2)	0.0610 (10)
C215	0.2848 (4)	0.2565 (2)	0.3055 (2)	0.0489 (8)
C216	0.3377 (5)	0.3086 (2)	0.3683 (2)	0.0572 (9)
C221	0.5144 (4)	0.3054 (2)	0.26226 (14)	0.0406 (7)
C222	0.7265 (4)	0.3456 (2)	0.2177 (2)	0.0548 (9)
C223	0.7859 (5)	0.3950 (3)	0.2788 (2)	0.0618 (10)
C224	0.7058 (5)	0.3993 (3)	0.3320 (2)	0.0592 (10)
C225	0.5645 (4)	0.3543 (2)	0.32482 (15)	0.0456 (8)
C226	0.4699 (5)	0.3545 (3)	0.3777 (2)	0.0582 (10)

Table 2. Selected geometric parameters (Å, °)

Cu1—N10	1.951 (3)	N2—C3	1.287 (5)
Cu1—N22	2.008 (2)	N2—C1	1.324 (5)
Cu1—N21	2.030 (3)	N3—C3	1.091 (5)
Cu1—N11	2.045 (3)	N10—C10	1.128 (4)
Cu1—N12	2.312 (3)	N20—C10	1.270 (4)
Cu1—N1	2.365 (3)	N20—C30	1.293 (4)
N1—C1	1.098 (4)	N30—C30	1.130 (4)
N10—Cu1—N22	172.53 (11)	N21—Cu1—N1	91.76 (11)
N10—Cu1—N21	92.74 (11)	N11—Cu1—N1	93.96 (12)
N22—Cu1—N21	80.92 (10)	N12—Cu1—N1	168.97 (11)
N10—Cu1—N11	91.61 (11)	C1—N1—Cu1	166.3 (4)
N22—Cu1—N11	95.10 (10)	C3—N2—C1	120.6 (4)
N21—Cu1—N11	172.78 (10)	N1—C1—N2	172.0 (5)
N10—Cu1—N12	89.13 (11)	N3—C3—N2	169.0 (5)
N22—Cu1—N12	95.76 (10)	C10—N10—Cu1	175.4 (3)
N21—Cu1—N12	99.27 (11)	C10—N20—C30	121.2 (3)
N11—Cu1—N12	75.04 (11)	N10—C10—N20	173.1 (4)
N10—Cu1—N1	90.45 (12)	N30—C30—N20	172.3 (4)
N22—Cu1—N1	85.83 (11)		

Intensities were corrected for Lorentz and polarization factors using *XP21* (Pavelčík, 1993). The structure was solved by direct methods with *XFPS* (Pavelčík, Rizzoli & Andreetti, 1990) and subsequent Fourier syntheses using *SHELXL93* (Sheldrick, 1993). Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from difference Fourier maps and refined with isotropic temperature factors fixed to 0.06 Å². Geometrical analysis was performed using *PARST* (Nardelli, 1983) and molecular graphics were obtained using *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: KA1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[Bis(*o*-dimethylaminomethylphenyl)methylsilanol-*N,O*]dibromocobalt(II)

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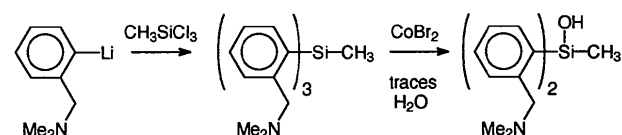
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Abstract

The Co^{II} atom in the title complex, [CoBr₂(C₁₉H₂₈N₂O-Si)], has a tetrahedral environment and is coordinated to bis(*o*-dimethylaminomethylphenyl)methylsilanol in a bidentate fashion and to two Br anions.

Comment

Tri(2-picoly)lmethylsilane has been shown to act as a tripod ligand, binding a metal centre to the three heterocyclic N atoms (Manzur & Musker, 1973). Preparation of similar complexes was attempted with tris(*o*-dimethylaminomethylphenyl)methylsilane. The isolated complex was found to contain the bis(*o*-dimethylaminomethylphenyl)methylsilanol ligand, which results from the hydrolysis reaction of the originally prepared tripod ligand:



The structure of the product, (I), corresponds to a cobalt(II) complex where the first coordination sphere is a tetrahedron formed by two Br ions and an O and N atom provided by the organic lig-