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Bis(1,10-phenanthroline)copper(II)-μ-cyano-cyano(1,10-phenanthroline)copper(I) Thiocyanate Dihydrate

IVAN POTOČŇÁK, MICHAL DUNAJ-JURČO AND MÁRIA KABEŠOVÁ

Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava, Slovakia

DUŠAN MIKLOŠ

Institute of Inorganic Chemistry, Slovak Academy of Sciences, 842 36 Bratislava, Slovakia

VIKTOR KETTMANN

Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, 832 32 Bratislava, Slovakia

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Abstract

By reaction of $Cu(NO_3)_2$, NH_4OH, phen (1,10-phenanthroline), KSCN and KCN in the molar ratio 1:40:2:1:1 in a water–ethanol solution a new mixed-valence complex, μ-cyano-1κN:2κC-cyano-2κN-

tris(1,10-phenanthroline)-1$\kappa^4 N,N'$;2$\kappa^2 N,N'$-dicopper-(I,II) thiocyanate dihydrate, $[Cu_2(phen)_3(CN)_2]$-(SCN).$2H_2O$, was prepared. The $[Cu^{II}(phen)_2]^{2+}$ and $[Cu^I(phen)CN]$ moieties are bridged by a CN ion giving rise to a binuclear cation with deformed trigonal-bipyramidal and deformed tetrahedral coordination for the divalent and univalent Cu atoms, respectively. SCN anions do not enter the inner coordination sphere of the Cu atoms. Uncoordinated H_2O molecules are held together by hydrogen bonds forming a four-membered ring. Two SCN anions are bonded, also by hydrogen bonds, to this ring forming a central $[SCN—4(H_2O)—NCS]^{2-}$ grouping. The latter is further attached by two other HOH⋯NC hydrogen bonds to the binuclear cations forming a centrosymmetric adduct of composition $\{[Cu_2(phen)_3(CN)_2](NCS)(H_2O)_2\}_2$. These adducts are packed by van der Waals forces in the crystal structure.

Comment

As a part of our studies of the synthesis, crystallo-chemistry and properties of mixed-valence Cu compounds with pseudohalogenide anions, the title compound (I) was prepared by mixing $Cu(NO_3)_2$, NH_4OH, phen (1,10-phenanthroline), KSCN and KCN in the molar ratio 1:40:2:1:1 in a water–ethanol solution. After slow crystallization (for several months) dark green crystals appeared. Details of preparation, identification and properties will be published elsewhere (Dunaj-Jurčo, 1993).
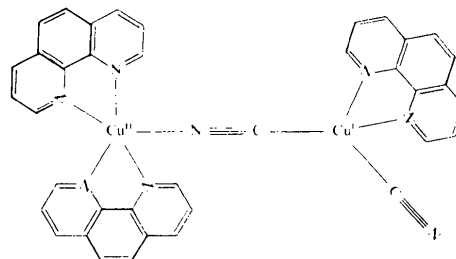
(I)

The crystal structure is formed by discrete binuclear $[Cu^{II}Cu^I(phen)_3(CN)_2]$ cations, SCN anions and uncoordinated H_2O molecules. These moieties, which associate *via* hydrogen bonds, give a centrosymmetric adduct of composition $\{[Cu_2(phen)_3(CN)_2](NCS).(H_2O)_2\}_2$. Fig. 1 shows one formula unit along with the atomic labelling scheme. The Cu^{II} atom is coordinated by two phen molecules, while the Cu^I atom binds one phen molecule and one terminal CN group through the C atom. Coordination geometries around the Cu^{II} and Cu^I atoms are completed to form approximately trigonal-bipyramidal and tetrahedral polyhedra, respectively,
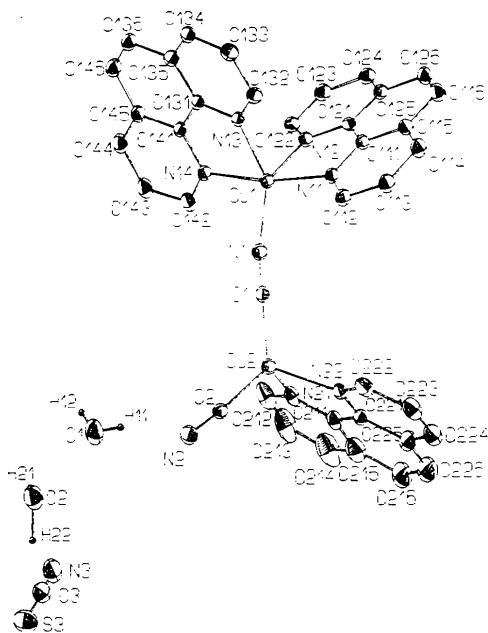
Fig. 1. *ORTEP* (Johnson, 1965) drawing of the formula unit with labelling of atoms.

by the linearly bridging CN^- anion (bonded through the N atom to the Cu^{II} atom).

For the above trigonal-bipyramidal system, the out-of-plane Cu—N11 [1.968 (4) Å] and Cu—N14 [1.971 (4) Å] distances are not significantly different, with the bonds being almost linear [N11—Cu—N14 = 169.1 (4)°]. The two in-plane distances (Cu—N12 and Cu—N13) are also not significantly different (average 2.107 Å) and are on average longer than the out-of-plane Cu—N distances by 0.137 Å. The third in-plane Cu—N1 distance of 1.920 (5) Å is significantly shorter than the other two. The out-of-plane angles are within 80–100°. These values agree with those observed previously for $[Cu(phen)_2CN]^+$ systems with nearly trigonal-bipyramidal chromophore stereochemistry (Dunaj-Jurčo, Kabešová, Kettmann, Cisařová & Mikloš, 1993; Dunaj-Jurčo, Potočňák, Cíbik, Kabešová, Kettmann & Mikloš, 1993; Anderson, 1975). The bond angles in the equatorial plane are considerably distorted from the ideal trigonal angle of 120°, with two large angles of 134.4 (3) (α_1 = N1—Cu1—N12) and 127.7 (3)° (α_2 = N1—Cu1—N13) and one small angle of 97.9 (3)° (α_3 = N12—Cu1—N13). Thus, relative to a regular trigonal-bipyramidal CuN_5 chromophore, the Cu1—N1 bond shows a significant shortening. The angle α_3, which is opposite to the Cu1—N1 bond, shows a significant narrowing (by 22.1°) relative to 120° and there is a difference of 6.7° between α_1 and α_2. According to Harrison & Hathaway (1980), who have studied $[Cu(bipy)_2X]Y$ complexes (bipy =

2,2'-bipyridyl), the coordination polyhedron around Cu^{II} can be described most appropriately as trigonal-bipyramidal with near C_{2v} symmetry.

The sum of the bond angles in the equatorial plane amounts precisely to 360°, indicating coplanarity of the Cu^{II} atom with the three coordinated atoms. The Cu^I atom forms a substantially distorted tetrahedron with the donor atoms. The bond distances range from 1.897 (4) to 2.142 (6) Å and bond angles from 77.3 (3) to 122.7 (4)°. A similar binuclear cation with trigonal-bipyramidal and tetrahedral coordination of the Cu^{II} and Cu^I atoms, respectively, was also observed in the $[Cu_2(phen)_3(CN)_2][Se(S)-CN].0.5EtOH$ complex (Dunaj-Jurčo, Kabešová, Kettmann, Cisařova & Mikloš, 1993).

Similar structural features have been observed for $[Cu_2(phen)_3(CN)_3].5H_2O$ (Dunaj-Jurčo, Potočňák, Cíbik, Kabešová, Kettmann & Mikloš, 1993), which contains discrete $[Cu^{II}(phen)_2(CN)]^+$ cations and $[Cu^I(phen)(CN)_2]$ anions. The trigonal-bipyramidal coordination for the Cu^{II} atom has also been found in $[Cu(bipy)_2NCS]NO_3.H_2O$ (Manríquez, Brito, Andrade, Wittke, von Schnering & Peters, 1988), $[Cu(bipy)_2NCS]BF_4$ (Tyagi & Hathaway, 1981), $[Cu(bipy)_2(NH_3)]BF_4$ (Stephens, 1972), $[Cu(phen)_2(C_7H_9N)](ClO_4)_2$ (Jeter, Casteel, Condren, Hobson, Stiles & Cordes, 1988) and $[Cu(phen)_2CN]NO_3.H_2O$ (Anderson, 1975).

Bond distances and angles in phen molecules bonded to the Cu^{II} atom of the present compound are normal (Anderson, 1973). The situation is more complicated for the phen molecule bonded to the Cu^I atom. The thermal motions of the C atoms of one 'arm' of this phen molecule are unusually large. Also, the bond distances and angles deviate from the expected range of 1.38 ± 0.05 Å and $120 \pm 4°$, found in the other phen ligands.
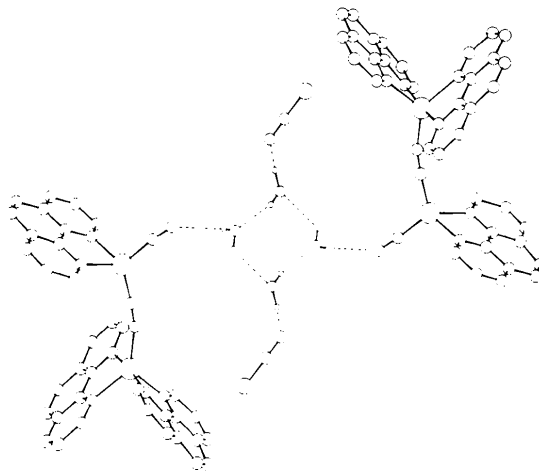

Fig. 2. A schematic drawing of the complete adduct with the hydrogen-bonding system.

The SCN⁻ anion is not coordinated to any Cu atom; it serves as a counterion to the binuclear cation. Bond distances and the S—C—N angle in the anion are within the expected range.

Uncoordinated H_2O molecules are joined by hydrogen bonds forming a four-membered ring. This ring forms the central part of a centrosymmetric adduct of composition {[Cu₂(phen)₃(CN)₂](NCS)-(H₂O)₂}₂, with the two SCN⁻ anions and the two binuclear complex cations bonded to this ring by additional hydrogen bonds (Fig. 2, Table 3). The adducts are held together by van der Waals forces.

Experimental

Crystal data

[Cu₂(CN)₂(C₁₂H₈N₂)₃]-
(SCN).2H₂O
$M_r = 813.86$
Triclinic
$P\bar{1}$
$a = 12.363\ (15)$ Å
$b = 13.134\ (14)$ Å
$c = 13.584\ (12)$ Å
$\alpha = 65.57\ (7)°$
$\beta = 64.92\ (8)°$
$\gamma = 65.18\ (8)°$
$V = 1737\ (4)$ Å³
$Z = 2$
$D_x = 1.556$ Mg m⁻³
$D_m = 1.50\ (1)$ Mg m⁻³
D_m measured by flotation in CHCl₃-CHBr₃

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 3.4$–$6.95°$
$\mu = 1.341$ mm⁻¹
$T = 293$ K
Plates
$0.6 \times 0.3 \times 0.15$ mm
Dark green
Crystal source: crystallization from aqueous ethanol solution

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.78$, $T_{max} = 1.00$
8032 measured reflections
7497 independent reflections
3733 observed reflections
$[F_o > 4\sigma(F_o)]$

$R_{int} = 0.024$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 16$
2 standard reflections monitored every 100 reflections intensity variation: <6%

Refinement

Refinement on F
$R = 0.046$
$wR = 0.052$
$S = 0.46$
3733 reflections
563 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F) + 0.01223F^2]$

$(\Delta/\sigma)_{max} < 0.1$
$\Delta\rho_{max} = 0.58$ e Å⁻³
$\Delta\rho_{min} = -0.67$ e Å⁻³
Extinction correction: none
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu1	−0.12148 (5)	0.98211 (4)	0.78401 (5)	0.0465 (3)
Cu2	−0.17194 (6)	0.59351 (5)	0.90385 (5)	0.0546 (3)
N11	0.0589 (3)	0.9247 (3)	0.7096 (3)	0.0435 (8)
N12	−0.1092 (3)	1.0989 (3)	0.6201 (3)	0.0469 (9)
N13	−0.0946 (3)	1.0829 (3)	0.8542 (3)	0.0466 (9)
N14	−0.2975 (3)	1.0693 (3)	0.8439 (3)	0.0495 (9)
N21	−0.2436 (3)	0.5929 (4)	0.7856 (3)	0.0594 (10)
N22	−0.0175 (3)	0.4914 (3)	0.8084 (3)	0.0467 (9)
N1	−0.1449 (4)	0.8294 (3)	0.8568 (4)	0.0615 (10)
C1	−0.1545 (4)	0.7400 (4)	0.8781 (4)	0.0572 (10)
N2	−0.2932 (4)	0.4554 (4)	1.1383 (4)	0.0747 (10)
C2	−0.2455 (4)	0.5023 (4)	1.0513 (4)	0.0538 (9)
N3	−0.5741 (5)	0.1306 (5)	0.6253 (5)	0.1236 (11)
C3	−0.5987 (5)	0.0561 (5)	0.7041 (5)	0.0776 (10)
S3	−0.6303 (2)	−0.0454 (2)	0.8144 (2)	0.1092 (8)
O1	−0.4158 (4)	0.4705 (4)	0.3628 (4)	0.1052 (9)
O2	−0.4875 (4)	0.3228 (4)	0.5722 (4)	0.1062 (10)
C111	0.1016 (4)	0.9959 (4)	0.6083 (4)	0.0444 (9)
C112	0.1406 (4)	0.8322 (4)	0.7559 (4)	0.0548 (10)
C113	0.2667 (5)	0.8129 (4)	0.7031 (5)	0.0622 (10)
C114	0.3112 (4)	0.8851 (5)	0.6031 (5)	0.0632 (10)
C115	0.2271 (4)	0.9810 (4)	0.5522 (4)	0.0503 (10)
C116	0.2633 (5)	1.0596 (5)	0.4443 (5)	0.0651 (10)
C121	0.0108 (4)	1.0894 (3)	0.5587 (4)	0.0418 (10)
C122	−0.1957 (4)	1.1828 (4)	0.5754 (4)	0.0527 (10)
C123	−0.1661 (5)	1.2584 (4)	0.4685 (4)	0.0571 (10)
C124	−0.0449 (5)	1.2490 (4)	0.4066 (4)	0.0599 (11)
C125	0.0484 (4)	1.1618 (4)	0.4535 (4)	0.0491 (10)
C126	0.1773 (5)	1.1455 (4)	0.3970 (4)	0.0625 (11)
C131	−0.2015 (4)	1.1620 (4)	0.8874 (4)	0.0448 (10)
C132	0.0066 (5)	1.0824 (4)	0.8654 (4)	0.0548 (10)
C133	0.0024 (5)	1.1613 (5)	0.9105 (4)	0.0635 (10)
C134	−0.1049 (5)	1.2418 (4)	0.9424 (4)	0.0602 (11)
C135	−0.2132 (5)	1.2457 (4)	0.9319 (4)	0.0515 (9)
C136	−0.3301 (5)	1.3285 (4)	0.9601 (5)	0.0680 (11)
C141	−0.3109 (4)	1.1558 (4)	0.8809 (4)	0.0456 (9)
C142	−0.3968 (4)	1.0586 (4)	0.8429 (4)	0.0597 (10)
C143	−0.5140 (5)	1.1334 (5)	0.8748 (5)	0.0684 (10)
C144	−0.5278 (5)	1.2208 (5)	0.9100 (5)	0.0659 (10)
C145	−0.4248 (5)	1.2361 (4)	0.9125 (4)	0.0577 (10)
C146	−0.4309 (5)	1.3246 (5)	0.9492 (5)	0.0701 (11)
C211	−0.1639 (4)	0.5185 (4)	0.7265 (4)	0.0570 (9)
C212	−0.3549 (5)	0.6451 (6)	0.7722 (6)	0.1036 (11)
C213	−0.3860 (6)	0.6129 (7)	0.6962 (6)	0.1183 (11)
C214	−0.3035 (7)	0.5369 (8)	0.6431 (7)	0.1376 (10)
C215	−0.1904 (6)	0.4848 (6)	0.6529 (5)	0.0919 (10)
C216	−0.0941 (7)	0.4017 (6)	0.5992 (5)	0.1042 (11)
C221	−0.0438 (4)	0.4657 (4)	0.7376 (4)	0.0501 (9)
C222	0.0966 (5)	0.4442 (5)	0.8160 (5)	0.0758 (10)
C223	0.1885 (5)	0.3695 (6)	0.7552 (6)	0.1052 (11)
C224	0.1675 (6)	0.3417 (5)	0.6879 (6)	0.1038 (11)
C225	0.0486 (6)	0.3873 (5)	0.6740 (5)	0.0777 (10)
C226	0.0169 (7)	0.3592 (6)	0.6040 (6)	0.1079 (11)

Table 2. *Selected geometric parameters* (Å, °)

Cu1—N11	1.968 (4)	Cu2—C1	1.897 (6)
Cu1—N12	2.102 (4)	Cu2—C2	1.913 (5)
Cu1—N13	2.111 (6)	N1—C1	1.133 (7)
Cu1—N14	1.971 (4)	N2—C2	1.112 (6)
Cu1—N1	1.920 (5)	N3—C3	1.142 (7)
Cu2—N21	2.142 (6)	C3—S3	1.570 (6)
Cu2—N22	2.077 (4)		
N14—Cu1—N1	95.9 (3)	C1—Cu2—C2	122.7 (4)
N13—Cu1—N1	127.7 (3)	N22—Cu2—C2	112.5 (4)
N13—Cu1—N14	81.0 (3)	N22—Cu2—C1	112.9 (3)
N12—Cu1—N1	134.4 (3)	N21—Cu2—C2	108.4 (4)
N12—Cu1—N14	92.0 (3)	N21—Cu2—C1	114.0 (3)
N12—Cu1—N13	97.9 (3)	N21—Cu2—N22	77.3 (3)
N11—Cu1—N1	95.0 (4)	Cu1—N1—C1	166.2 (5)

N11—Cu1—N14	169.1 (4)	Cu2—C1—N1	176.1 (6)
N11—Cu1—N13	92.4 (4)	Cu2—C2—N2	175.8 (8)
N11—Cu1—N12	80.2 (3)	N3—C3—S3	178.1 (9)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	A	D—H	H···A	D···A	D—H···A
O2	H21	O1	0.80 (1)	2.33 (1)	2.717 (7)	111 (1)
O2	H22	N3	1.12 (2)	1.74 (2)	2.854 (10)	173 (1)
O1	H11	N2^i	0.73 (1)	2.23 (2)	2.822 (8)	139 (2)
O1	H12	O2^{ii}	0.89 (1)	2.29 (2)	2.818 (9)	118 (1)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x - 1, -y + 1, -z + 1$.

Intensities were corrected for Lorentz and polarization factors using *XP*21 (Pavelčik, 1986). The structure was solved by direct methods with *XFPS* (Pavelčik, Rizzoli & Andreetti, 1990) and subsequent Fourier syntheses using *SHELX*76 (Sheldrick, 1976). Anisotropic displacement parameters were refined for all non-H atoms. All H atoms of water and phenanthroline molecules except H123 were located from difference Fourier maps and refined with isotropic displacement parameters fixed to U_{eq} of the respective bonded O or C atoms plus 0.01 Å^2. The position of H123 was calculated and then refined as for the other H atoms. At the final stage of the refinement, $(\Delta/\sigma)_{max}$ was smaller than 0.1 for non-H atoms (0.446 for H atoms). Geometric analysis was performed using *PARST* (Nardelli, 1983). *ORTEP* (Johnson, 1965) and *MOLDRAW* (Ugliengo, Borzani & Viterbo, 1988) were used to draw the structure.

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A Binuclear Silver Complex of a Tetrapyrazolyl Ligand

William Clegg,* Paul J. Cooper, Joyce C. Lockhart and David J. Rushton

Department of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, England

Abstract

Silver(I) nitrate forms a binuclear complex with the potentially multidentate ligand N,N',N'',N'''-tetrakis(1-pyrazolylmethyl)-1,2-ethanediamine, $[\mu\text{-}N,N',N'',N'''\text{-}$tetrakis(1-pyrazolyl-$\kappa N^2$-methyl)-1,2-ethanediamine]-disilver(I) dinitrate, $[Ag_2(C_{18}H_{24}N_{10})]2NO_3$. Each Ag ion is linearly coordinated by two pyrazole N^2 atoms. The aliphatic amine N atoms of the ligand play no primary coordination role. The two Ag ions are separated by 3.1599 (9) Å. There are additional weak interactions with the nitrate anions.

Comment

Polynuclear Ag complexes are currently of interest in redox chemistry (Che, Yip, Li, Peng, Lee, Wang & Liu, 1991; Gubelmann, Harriman, Lehn & Sessler, 1988) and provide experimental data with which to test bonding theories (Cotton, Feng, Matusz & Poli, 1988; Perreault, Drouin, Michel & Harvey, 1993). Our own investigations into force fields for molecular modelling of Ag chelates (Lockhart & Rushton, 1991) found crystallographic data on linear complexes of Ag ions with aromatic N ligands (related to imidazole, benzimidazole, pyrazole, *etc.*) to be scarce.

The tetrakis(1-pyrazolylmethyl)-1,2-ethanediamine ligand was first synthesized by Driessen (1982). It has been shown to form 1:1 complexes with most first-row transition-metal divalent ions (Hulsbergen, Driessen, Reedijk & Verschoor, 1984). In these complexes, the ligand is hexadentate, coordinating through both aliphatic amine N atoms and one N atom of each pyrazole ring. The crystal structure of the complex with $Mn(ClO_4)_2$