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Structure of a Mixed-Valence Copper Complex with 1,10-Phenanthroline and Pseudohalogenide Ligands

MICHAL DUNAJ-JURČO AND MÁRIA KABEŠOVÁ

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

VIKTOR KETTMANN

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

IVANA CÍSAŘOVÁ

Institute of Physics, Czechoslovak Academy of Sciences,
180 40 Praha 8, Czechoslovakia

DUŠAN MIKLOŠ

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

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Abstract

The reaction of $Cu(NO_3)_2$, NH_4OH, 1,10-phenanthroline (phen), KSCN and KSeCN in the molar ratio 1:10:2:2:2 in a water–ethanol solution gives a new mixed-valence compound, μ-cyano-$1\kappa N$:$2\kappa C$-(seleno,thio)cyanato-$2\kappa N$-tris(1,10-phenanthroline)-$1\kappa^4 N,N'$;$2\kappa^2 N,N'$-dicopper(I,II) (seleno,thio)cyanate semiethanolate, for which the X-ray structure analysis reveals the composition $[Cu^{II}Cu^{I}(phen)_3(CN)(SeCN)_{0.65}(SCN)_{0.35}]^+(SeCN)^-_{0.45}(SCN)^-_{0.55}.0.5C_2H_5OH$. The $[Cu^{II}(phen)_2]^{2+}$ and $[Cu^{I}(phen)\{(Se,S)CN\}]$ moieties are bridged by CN^-, giving rise to a binuclear cation with deformed trigonal-bipyramidal and deformed tetrahedral coordination for the bivalent and monovalent Cu atoms, respectively.

Comment

This work is part of a project aimed at exploring the structural and chemical properties of mixed-valence copper complexes with organic and inorganic ligands. In this report we describe the crystal structure of a compound which was obtained by mixing $Cu(NO_3)_2$, NH_4OH, phen, KSCN and KSeCN in the molar ratio 1:10:2:2:2 in a water–ethanol solution. The $SeCN^-$ anion serves both as a ligand and as a reducing agent in the reaction. Thus, although the cyanide anion was not added to the reaction mixture, it appears in the system as a consequence of the following redox and protolytic reactions:

$$2Cu^{II}(solv.) + 2SeCN^- \rightleftarrows (CN)_2 + 2Cu^{I} + Se_2$$

$$(CN)_2 + H_2O \rightleftarrows HCN + HCNO$$

Several other bi- and polynuclear-ligand(s) bridged copper(I) and copper(II) compounds are known to be prepared by similar reactions (Dunaj-Jurčo, Ondrejovič, Melník & Garaj, 1988, and references therein).

The crystal structure was found to consist of discrete $[Cu^{II}Cu^{I}(phen)_3(CN)\{(Se,S)CN\}]^+$ cations, $[(Se,S)CN]^-$ anions and solvated ethanol molecules. One of the two crystallographically independent complex cations, which are nearly centrosymmetrically related, is shown in Fig. 1. The CN^- anion linearly bridges the Cu^{II} and Cu^{I} ions and the coordination environments around Cu^{II} and Cu^{I} are distorted trigonal bipyramidal and tetrahedral, respectively. The bridging cyanide ion is coordinated to Cu^{II} through its N atom and occupies an equatorial position. The axial Cu—N(11) and Cu—N(102) bonds are slightly but significantly longer than the corresponding in-plane bonds and almost linear, with an N(11)—Cu—N(102) angle of 177.3 (5)°. Similar stereochemical features for Cu^{II} have been observed previously in the compounds $[Cu^{II}(phen)_3CN]NO_3$ (Anderson, 1975) and $[Cu^{II}(bipy)_2CN]NO_3.2H_2O$ (Harrison & Hathaway, 1980). As suggested by Harrison & Hathaway (1980), the type and extent of distortion of the trigonal-bipyramidal geometry around Cu^{II} can best be

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described in terms of the mechanistic pathway of the Berry twist (Berry, 1960), based on the in-plane angles, α_1 = N(101)—Cu—N(2) = 136.5 (4), α_2 = N(12)—Cu—N(2) = 123.9 (4) and α_3 = N(101)—Cu—N(12) = 99.6 (4)°. The present complex belongs to the most frequently observed group among the five-coordinate Cu^{II} complexes and is characterized by trigonal-bipyramidal stereochemistry with near C_{2v} symmetry. Thus, the observed distortion from the regular trigonal-bipyramidal geometry is not electronic in nature and results entirely from the small 'bite' of the rigid phen ligands. The latter effect seems also to be responsible for the distortion of the tetrahedral geometry around Cu^{I}.

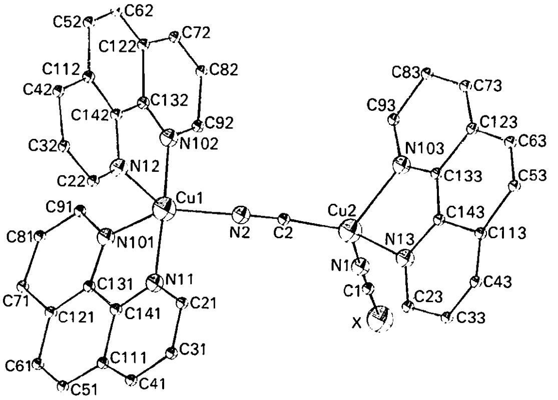
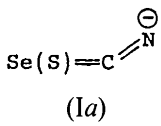


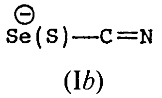
Fig. 1. Perspective drawing of one of the two independent complex cations of the title compound. Atoms of different kind are represented by spheres of different radius. X denotes a substitutionally disordered Se/S site.

To our knowledge, the overall structure observed for the present compound is unique among the complexes containing the cyanide ion(s) and either Cu^{I} or mixed-valence Cu^{II},Cu^{I} metal ions. In these systems, Cu^{I} (usually in a trigonal-planar environment) invariably prefers the formation of one-dimensional polymers or two-dimensional networks, and Cu^{II}, if present, forms isolated units situated between the chains or sheets (Vaira & Mani, 1985; Dyason, Healy, Engelhardt, Pakawatchai, Patrick & White, 1985; Morpurgo, Dessy & Fares, 1984). This clearly demonstrates the sensitivity of the resulting structure of the above systems to the particular reaction conditions applied.

The SeCN$^-$ and SCN$^-$ anions show substitutional disorder at both coordinated and uncoordinated sites. Based on the refined occupancy factors, the percentages of SeCN$^-$ are 65 and 45% in the coordinated and uncoordinated sites, respectively, thus yielding the above composition. The N atoms of both crystallographically independent uncoordinated (Se,S)CN$^-$ ions are positionally disordered between two positions with occupancy factors of 0.55/0.45 and 0.75/0.25 (based on heights of maxima in the difference Fourier map and not refined). The disorder originates from two different orientations of either (Se,S)CN$^-$ in the structure. In three of these four independent orientations the (Se,S)CN$^-$ anions exist in the bent (I*a*) form (central C atom predominantly sp^2-hybridized) and in one orientation in the linear (I*b*) form (C atom *sp*-hybridized) according to whether the negative charge of the anion is localized, due to the polarizing effects of the environmental positive charges, essentially on the N or on the (Se,S) atom.



(I*a*)



(I*b*)

Experimental

Crystal data

$[Cu_2(C_{12}H_8N_2)_3\{(Se,S)CN\}(CN)][(Se,S)CN].0.5C_2H_5OH$
M_r = 884.5
Monoclinic
Cc
a = 17.792 (18) Å
b = 16.491 (18) Å
c = 24.276 (35) Å
β = 94.01 (10)°
V = 7105 Å^3
Z = 8
D_x = 1.653 Mg m^{-3}

D_m = 1.66 (1) Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 15 reflections
θ = 6-15°
μ = 2.556 mm^{-1}
T = 293 K
Prism
0.5 × 0.25 × 0.2 mm
Dark green
Crystal source: crystallization from aqueous ethanol

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4138 measured reflections
3954 independent reflections
1948 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.028
$\theta_{\rm max}$ = 21°
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 16$
$l = -24 \rightarrow 24$
2 standard reflections frequency: 100 min intensity variation: 5%

Refinement

Refinement on F
Final R = 0.065
wR = 0.056
S = 2.16
1948 reflections
469 parameters
$w = 1/[\sigma^2(F_o) + (0.03F_o^2)^2]$

$(\Delta/\sigma)_{\rm max}$ = 0.24
$\Delta\rho_{\rm max}$ = 1.33 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.19 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Refinement was carried out by block-diagonal approximation. All calculations were performed with the *NRC Crystallographic Programs for the IBM*360 *System* (1973).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu1	0.2704 (1)	0.0245 (1)	0.5795 (1)	3.93 (14)
Cu2	0.2166 (1)	0.1355 (1)	0.7588 (1)	4.46 (5)
N11	0.2106 (5)	−0.0786 (6)	0.5919 (3)	4.93 (2)
C21	0.1382 (5)	−0.0788 (6)	0.6045 (4)	3.91 (3)
C31	0.1050 (6)	−0.1542 (7)	0.6118 (4)	5.63 (3)
C41	0.1405 (6)	−0.2272 (6)	0.5975 (4)	4.47 (3)
C51	0.2632 (5)	−0.2929 (6)	0.5741 (4)	3.35 (2)
C61	0.3324 (6)	−0.2891 (6)	0.5600 (4)	4.58 (3)
C71	0.4441 (6)	−0.1943 (6)	0.5405 (4)	4.53 (3)
C81	0.4732 (6)	−0.1187 (6)	0.5396 (4)	4.47 (3)
C91	0.4220 (6)	−0.0494 (7)	0.5508 (5)	6.11 (3)
N101	0.3527 (4)	−0.0651 (5)	0.5635 (3)	3.29 (2)
C111	0.2136 (6)	−0.2254 (6)	0.5832 (4)	4.27 (3)
C121	0.3679 (5)	−0.2088 (6)	0.5556 (4)	3.85 (3)
C131	0.3246 (5)	−0.1372 (6)	0.5647 (4)	3.27 (2)
C141	0.2505 (6)	−0.1502 (6)	0.5798 (4)	4.27 (3)
N12	0.2304 (4)	0.0519 (4)	0.4982 (3)	2.58 (2)
C22	0.1849 (6)	0.0167 (7)	0.4599 (4)	4.94 (3)
C32	0.1652 (6)	0.0469 (7)	0.4063 (5)	5.59 (3)
C42	0.2061 (6)	0.1114 (7)	0.3881 (5)	6.24 (3)
C52	0.2980 (7)	0.2211 (7)	0.4085 (5)	6.60 (3)
C62	0.3532 (6)	0.2528 (7)	0.4479 (5)	5.62 (3)
C72	0.4125 (6)	0.2561 (7)	0.5479 (4)	4.88 (3)
C82	0.4247 (6)	0.2266 (6)	0.5953 (5)	5.56 (3)
C92	0.3844 (7)	0.1578 (8)	0.6098 (5)	7.32 (4)
N102	0.3329 (4)	0.1219 (4)	0.5669 (3)	2.35 (2)
C112	0.2555 (6)	0.1468 (6)	0.4255 (4)	4.19 (3)
C122	0.3694 (6)	0.2233 (7)	0.5016 (5)	5.23 (3)
C132	0.3219 (6)	0.1508 (6)	0.5179 (4)	4.55 (3)
C142	0.2679 (5)	0.1177 (6)	0.4768 (4)	3.78 (3)
N13	0.1166 (4)	0.1471 (5)	0.7930 (3)	3.71 (2)
C23	0.0632 (7)	0.0885 (7)	0.8064 (5)	6.61 (3)
C33	−0.0034 (7)	0.1180 (7)	0.8298 (5)	6.57 (3)
C43	−0.0263 (7)	0.1883 (8)	0.8359 (5)	7.54 (4)
C53	0.0069 (7)	0.3318 (7)	0.8258 (5)	7.06 (4)
C63	0.0557 (7)	0.3908 (7)	0.8150 (5)	7.69 (4)
C73	0.1750 (7)	0.4249 (7)	0.7777 (5)	6.73 (3)
C83	0.2434 (6)	0.4041 (7)	0.7593 (5)	5.31 (3)
C93	0.2582 (7)	0.3181 (7)	0.7557 (5)	6.53 (3)
N103	0.2092 (4)	0.2669 (5)	0.7694 (3)	4.08 (2)
C113	0.0269 (7)	0.2430 (7)	0.8237 (5)	6.67 (3)
C123	0.1256 (6)	0.3703 (7)	0.7929 (5)	5.80 (3)
C133	0.1485 (5)	0.2859 (6)	0.7893 (4)	3.69 (3)
C143	0.0976 (5)	0.2265 (6)	0.8001 (4)	2.92 (2)
Se1	0.3960 (1)	0.0242 (1)	0.8979 (1)	8.27 (7)
C1	0.3261 (6)	0.0612 (7)	0.8478 (5)	6.06 (3)
N1	0.2907 (5)	0.0864 (6)	0.8161 (4)	5.49 (2)
C2	0.2276 (5)	0.1008 (6)	0.6868 (4)	3.54 (3)
N2	0.2338 (4)	0.0767 (4)	0.6447 (3)	2.49 (2)
Se2	0.0050 (1)	0.0612 (1)	0.5326 (1)	5.55 (6)
C3	0.0033 (6)	−0.0314 (5)	0.4943 (4)	3.24 (3)
N31	−0.0022 (8)	−0.0539 (8)	0.4500 (6)	2.23 (3)
N32	0.0032 (6)	−0.0868 (7)	0.4750 (5)	1.41 (3)
Cu3	0.7280 (1)	−0.0246 (1)	0.4203 (1)	3.83 (4)
Cu4	0.7818 (1)	−0.1357 (1)	0.2405 (1)	4.70 (5)
N14	0.7846 (4)	0.0785 (5)	0.4102 (3)	4.29 (2)
C24	0.8594 (7)	0.0798 (8)	0.3966 (5)	6.74 (3)
C34	0.8941 (6)	0.1575 (7)	0.3950 (5)	6.17 (3)
C44	0.8540 (5)	0.2299 (6)	0.4005 (4)	3.69 (3)
C54	0.7370 (6)	0.2969 (7)	0.4242 (5)	5.28 (3)
C64	0.6667 (6)	0.2838 (6)	0.4404 (4)	4.15 (3)
C74	0.5594 (5)	0.1969 (6)	0.4609 (4)	3.86 (3)
C84	0.5325 (6)	0.1175 (6)	0.4652 (4)	4.41 (3)
C94	0.5754 (5)	0.0508 (5)	0.4524 (4)	2.80 (2)
N104	0.6473 (4)	0.0578 (4)	0.4371 (3)	2.97 (2)
C114	0.7805 (5)	0.2237 (5)	0.4129 (4)	2.91 (2)
C124	0.6344 (5)	0.2053 (5)	0.4482 (4)	2.38 (2)
C134	0.6724 (5)	0.1424 (6)	0.4345 (4)	3.67 (2)
C144	0.7526 (5)	0.1463 (6)	0.4212 (4)	3.28 (2)
N15	0.7640 (4)	−0.0500 (5)	0.4996 (3)	3.95 (2)
C25	0.8215 (5)	−0.0158 (6)	0.5375 (4)	2.90 (2)
C35	0.8342 (6)	−0.0466 (6)	0.5889 (4)	4.55 (3)
C45	0.7978 (6)	−0.1120 (7)	0.6125 (5)	5.67 (3)
C55	0.7074 (5)	−0.2214 (6)	0.5907 (4)	3.64 (3)
C65	0.6596 (5)	−0.2542 (6)	0.5561 (4)	2.96 (2)
C75	0.5914 (5)	−0.2590 (6)	0.4572 (4)	2.83 (2)
C85	0.5742 (7)	−0.2275 (7)	0.4049 (5)	7.02 (3)
C95	0.6115 (5)	−0.1515 (6)	0.3957 (4)	3.74 (3)
N105	0.6611 (4)	−0.1225 (5)	0.4342 (3)	4.08 (2)
C115	0.7422 (6)	−0.1492 (6)	0.5736 (4)	5.05 (3)
C125	0.6397 (5)	−0.2280 (5)	0.4994 (3)	3.61 (2)
C135	0.6739 (5)	−0.1550 (5)	0.4843 (4)	4.10 (2)
C145	0.7261 (6)	−0.1187 (6)	0.5211 (4)	4.40 (3)
N16	0.8909 (5)	−0.1478 (5)	0.2058 (4)	5.45 (2)
C26	0.9349 (7)	−0.0835 (8)	0.1969 (5)	8.11 (4)
C36	1.0034 (7)	−0.0972 (8)	0.1759 (5)	8.33 (4)
C46	1.0238 (6)	−0.1795 (7)	0.1721 (5)	6.30 (3)
C56	0.9870 (8)	−0.3293 (8)	0.1777 (5)	8.72 (4)
C66	0.9503 (6)	−0.3893 (6)	0.1898 (4)	4.50 (3)
C76	0.8171 (6)	−0.4276 (8)	0.2226 (5)	6.55 (3)
C86	0.7565 (7)	−0.4041 (7)	0.2391 (5)	6.47 (3)
C96	0.7340 (6)	−0.3235 (7)	0.2439 (5)	6.28 (3)
N106	0.7835 (4)	−0.2619 (5)	0.2283 (3)	3.91 (2)
C116	0.9850 (7)	−0.2534 (7)	0.1802 (5)	6.26 (3)
C126	0.8720 (7)	−0.3728 (8)	0.2087 (5)	8.20 (4)
C136	0.8540 (6)	−0.2907 (7)	0.2123 (4)	4.90 (3)
C146	0.9118 (6)	−0.2262 (7)	0.1990 (5)	6.19 (3)
Se3	0.6036 (1)	−0.0259 (1)	0.1027 (1)	8.20 (8)
C4	0.6661 (5)	−0.0634 (6)	0.1498 (4)	3.29 (2)
N4	0.7116 (4)	−0.0916 (5)	0.1845 (3)	3.90 (2)
C5	0.7793 (5)	−0.0990 (6)	0.3112 (4)	3.10 (2)
N5	0.7712 (4)	−0.0784 (5)	0.3571 (3)	4.51 (2)
Se4	0.0465 (1)	0.1207 (1)	0.2911 (1)	8.37 (9)
C6	0.0010 (7)	0.1240 (6)	0.2302 (4)	5.29 (3)
N61	−0.0532 (8)	0.1497 (9)	0.2067 (6)	8.80 (4)
N62	−0.0168 (12)	0.0986 (13)	0.1920 (9)	2.25 (5)
O1	0.4660 (7)	0.1438 (7)	0.7631 (6)	17.16 (5)
C7	0.5177 (17)	0.1310 (13)	0.7260 (11)	25.37 (11)
C8	0.5867 (9)	0.1193 (9)	0.7680 (6)	11.47 (5)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Cu1—N11	2.040 (9)	Cu3—N14	2.000 (8)
Cu1—N101	2.137 (8)	Cu3—N104	2.037 (8)
Cu1—N12	2.100 (8)	Cu3—N15	2.028 (8)
Cu1—N102	1.989 (7)	Cu3—N105	2.048 (8)
Cu1—N2	1.952 (8)	Cu3—N5	1.975 (9)
Cu2—N13	2.025 (8)	Cu4—N16	2.179 (9)
Cu2—N103	2.187 (9)	Cu4—N106	2.102 (8)
Cu2—N1	2.017 (9)	Cu4—N4	1.924 (8)
Cu2—C2	1.861 (10)	Cu4—C5	1.823 (10)
Se1—C1	1.786 (11)	Se3—C4	1.657 (10)
C1—N1	1.045 (14)	C4—N4	1.219 (12)
C2—N2	1.110 (12)	C5—N5	1.184 (13)
Se2—C3	1.787 (10)	Se4—C6	1.636 (11)
C3—N31	1.135 (17)	C6—N61	1.165 (18)
C3—N32	1.025 (15)	C6—N62	1.048 (24)
N102—Cu1—N2	89.5 (4)	N105—Cu3—N5	92.0 (4)
N12—Cu1—N2	123.9 (4)	N15—Cu3—N5	122.0 (5)
N12—Cu1—N102	80.7 (4)	N15—Cu3—N105	80.2 (4)
N101—Cu1—N2	136.5 (4)	N104—Cu3—N5	140.6 (5)
N101—Cu1—N102	97.6 (4)	N104—Cu3—N105	93.9 (4)
N101—Cu1—N12	99.6 (4)	N104—Cu3—N15	97.4 (4)
N11—Cu1—N2	92.4 (4)	N14—Cu3—N5	93.5 (4)
N11—Cu1—N102	177.3 (5)	N14—Cu3—N105	173.7 (5)
N11—Cu1—N12	99.9 (4)	N14—Cu3—N15	99.4 (4)
N11—Cu1—N101	79.7 (4)	N14—Cu3—N104	79.9 (4)
N1—Cu2—C2	114.7 (5)	N4—Cu4—C5	118.8 (5)
N103—Cu2—C2	115.2 (5)	N106—Cu4—C5	117.6 (5)
N103—Cu2—N1	111.0 (5)	N106—Cu4—N4	106.8 (4)
N13—Cu2—C2	124.5 (6)	N16—Cu4—C5	118.4 (6)
N13—Cu2—N1	107.8 (5)	N16—Cu4—N4	108.3 (5)
N13—Cu2—N103	78.2 (4)	N16—Cu4—N106	80.4 (4)
Se1—C1—N1	172.8 (13)	Se3—C4—N4	179.4 (10)
Cu2—N1—C1	175.9 (12)	Cu4—N4—C4	178.7 (10)
Cu2—C2—N2	176.9 (9)	Cu4—C5—N5	173.8 (11)
Cu1—N2—C2	164.8 (10)	Cu3—N5—C5	160.2 (10)
Se2—C3—N32	175.8 (12)	Se4—C6—N62	152.5 (15)
Se2—C3—N31	140.3 (10)	Se4—C6—N61	142.6 (12)

Lists of structure factors, anisotropic thermal parameters and complete bond distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71075 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1017]

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Mixed-Valence Cu^I–Cu^{II} Complexes. Structure of Cyanobis(1,10-phenanthroline)-copper(II) Bis(cyano)(1,10-phenanthroline)-cuprate(I) Pentahydrate

MICHAL DUNAJ-JURČO, IVAN POTOČŇÁK, JÁN CÍBIK AND MÁRIA KABEŠOVÁ

Department of Inorganic Chemistry,
Slovak Technical University, 812 47 Bratislava,
Czechoslovakia

VIKTOR KETTMANN

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

DUŠAN MIKLOŠ

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

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Abstract

Reaction of $Cu(NO_3)_2$, NH_4OH, phen (1,10-phenanthroline) and KCN in the molar ratio 1:40:2:2 in water–ethanol solution gives a new mixed-valence complex of composition $Cu_2(phen)_3(CN)_3.5H_2O$. X-ray structure analysis reveals the composition $[Cu^{II}(phen)_2(CN)]^+[Cu^I(phen)(CN)_2]^-.5H_2O$ with trigonal-bipyramidal and tetrahedral coordination for the divalent and univalent Cu atoms, respectively. The structure is built up of hydrated clusters comprising two formula units; the principal interactions within the cluster are hydrogen bonds between the water molecules and complex cations and anions.

Comment

This work is part of a project exploring the structural and chemical properties of mixed-valence copper complexes with organic and inorganic ligands. We have shown (Dunaj-Jurčo, Ondrejovič, Melník & Garaj, 1988) that all known Cu^I–Cu^{II} complexes can be subdivided into four groups according to the environment of the Cu^I and Cu^{II} atoms and their crystallostructural function. The title compound belongs to the first group containing Cu^I anion and Cu^{II} cation species; there are several routes for the preparation of this type of compound. In this work we have chosen that which utilizes CN$^-$ ions both as a reducing agent (to reduce Cu^{II} to Cu^I) and as a ligand coordinated to Cu^{II} and Cu^I. Previously, Wicholas & Wolford (1974) reported that Cu^{II} compounds in which the CN$^-$ ligand is directly bonded to Cu^{II} are relatively rare; these authors have also described the preparation of $Cu_2(phen)_3(CN)_3.6H_2O$. The title compound, $Cu_2(phen)_3(CN)_3.5H_2O$, was prepared in a similar way: 1 *M* aqueous solution of $Cu(NO_3)_2$ (10 ml), 26% NH_3 (30 ml), 1,10-phenanthroline monohydrate (3.6 g, 20 mmol) and ethanol (140 ml) were mixed; on dropwise addition of 1 *M* aqueous solution of KCN (20 ml) a violet non-crystalline precipitate formed; the mixture was allowed to stand for 7 d at room temperature, which yielded well shaped dark-green crystals. Since the crystals were unstable and cracked in air, they were sealed in epoxide for data collection.

The crystal structure was found to consist of discrete $[Cu^{II}(phen)_2CN]^+$ cations and $[Cu^I(phen)(CN)_2]^-$ anions held together by hydrogen-bonded water molecules. An *ORTEP* (Johnson, 1965) view of the cation and anion is shown in Fig. 1.

The complex cation exhibits approximately trigonal-bipyramidal coordination geometry about the Cu^{II} ion, with the cyanide ion occupying an equatorial position. The bond angles in the equatorial plane are considerably distorted from the ideal trigonal angle of 120°, with two large angles of 132.8 (6) (α_1 = C1—Cu—N13) and 123.3 (5)° (α_2 = C1—Cu—N12), and one small angle of 103.9 (5)° (α_3 = N12—Cu—N13). The distance of the Cu^{II} atom from the plane (C1, N12, N13) is 0.016 (8) Å,