C25	0.3825 (6)	−0.0651 (5)	0.3934 (5)	0.062 (4)
C26	0.3304 (6)	0.0204 (5)	0.3745 (4)	0.043 (3)
C31	0.1624 (5)	0.1970 (4)	0.4543 (3)	0.029 (2)
C32	0.2179 (6)	0.1543 (5)	0.5274 (4)	0.039 (3)
C33	0.2440 (8)	0.2093 (6)	0.6103 (4)	0.053 (4)
C34	0.2133 (8)	0.3058 (5)	0.6207 (4)	0.054 (4)
C35	0.1578 (7)	0.3467 (5)	0.5495 (4)	0.050 (3)
C36	0.1311 (6)	0.2942 (5)	0.4652 (4)	0.043 (3)
C41	0.3655 (5)	0.4888 (4)	0.1634 (3)	0.027 (2)
C42	0.4055 (6)	0.5276 (4)	0.2516 (4)	0.034 (3)
C43	0.4351 (7)	0.6336 (5)	0.2772 (4)	0.044 (4)
C44	0.4250 (7)	0.7019 (5)	0.2137 (5)	0.049 (4)
C45	0.3879 (8)	0.6654 (5)	0.1275 (4)	0.053 (4)
C46	0.3586 (7)	0.5594 (5)	0.1007 (4)	0.045 (3)
C51	0.2238 (6)	0.3342 (4)	0.0226 (4)	0.036 (3)
C52	0.0982 (7)	0.3592 (5)	0.0187 (4)	0.048 (4)
C53	0.0061 (9)	0.3434 (7)	−0.0611 (5)	0.066 (5)
C54	0.039 (1)	0.3014 (7)	−0.1350 (5)	0.074 (7)
C55	0.163 (1)	0.2769 (7)	−0.1315 (5)	0.075 (7)
C56	0.2578 (8)	0.2943 (6)	−0.0529 (4)	0.053 (4)
C61	0.4985 (6)	0.3285 (4)	0.1156 (3)	0.034 (2)
C62	0.5075 (6)	0.2285 (5)	0.0891 (4)	0.049 (3)
C63	0.6359 (7)	0.2077 (5)	0.0882 (4)	0.060 (3)
C64	0.7508 (7)	0.2864 (7)	0.1111 (5)	0.073 (5)
C65	0.7424 (7)	0.3855 (7)	0.1347 (5)	0.060 (5)
C66	0.6150 (6)	0.4078 (5)	0.1367 (4)	0.042 (3)
C71	0.5033 (6)	0.3142 (5)	0.3657 (4)	0.037 (3)
C72	0.6174 (7)	0.2953 (5)	0.3324 (5)	0.050 (4)
C73	0.7459 (7)	0.3322 (6)	0.3821 (6)	0.056 (5)
C74	0.7649 (9)	0.3796 (6)	0.4644 (5)	0.061 (5)
C75	0.6493 (9)	0.4005 (6)	0.4971 (5)	0.053 (5)
C76	0.5254 (7)	0.3683 (6)	0.4515 (4)	0.049 (4)

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

Re—P1	2.506 (1)	N1—C1	1.166 (8)
Re—P2	2.507 (1)	N2—C2	1.149 (8)
Re—N1	2.051 (5)	O—C3	1.407 (7)
Re—N2	2.057 (5)	N3—C71	1.368 (7)
Re—N3	1.744 (4)	C1—S1	1.606 (6)
Re—O	1.922 (3)	C2—S2	1.612 (6)
P1—Re—P2	178.78 (4)	N2—Re—N3	93.0 (2)
P1—Re—N1	93.1 (1)	N1—Re—O	86.0 (2)
P1—Re—N2	86.9 (1)	N2—Re—O	83.7 (2)
P1—Re—N3	89.9 (1)	N3—Re—O	175.9 (2)
P1—Re—O	92.2 (1)	Re—O—C3	140.2 (4)
P2—Re—N1	86.9 (1)	Re—N1—C1	173.5 (5)
P2—Re—N2	93.3 (1)	Re—N2—C2	168.4 (4)
P2—Re—N3	88.8 (1)	Re—N3—C71	172.2 (4)
P2—Re—O	89.1 (1)	N1—C1—S1	178.2 (5)
N1—Re—N2	169.8 (2)	N2—C2—S2	177.8 (6)
N1—Re—N3	97.3 (2)		

The positions of the H atoms were calculated and included in the structure-factor calculations. Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *SDP* (Enraf–Nonius, 1985). Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Programs used to refine structure: *SDP*. Refinement by full-matrix least-squares methods. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SDP*; *UTABLE* (Kretschmar, 1989). All computation was performed on a DEC VAX Station 3100.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: JZ1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris[bis(ethylenediamine)copper(II)] Poly[hexakis(μ-cyano)hexakis(μ-selenocyanato)hexacopper(I)], [$Cu^{II}en_2$]$_3$-[$Cu^{I}_6(CN)_6(SeCN)_6$]

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Abstract

The structure of the title compound, [$Cu(C_2H_8N_2)_2$]$_3$-[$Cu_6(CN)_6(SeCN)_6$], consists of a three-dimensional skeleton formed by the polymeric chains of anions, [$Cu^{I}_6(CN)_6(SeCN)_6$]$^{6-}$. In the cavities are located

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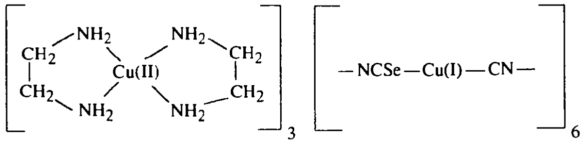
Cu^{II} atoms, coordinated by two molecules of ethylenediamine. One Cu^{II} atom occupies a special position. The ethylenediamine molecules have a *gauche* conformation. The Cu^{I} atoms are coordinated tetrahedrally by cyano and selenocyanato groups acting as bridging ligands. The average Cu^{I}—NC and Cu^{I}—CN bond lengths are 1.981 (6) and 1.913 (6) Å, respectively.

Comment

Under suitable conditions, where the redox process is not too rapid, crystalline cuprous–cupric compounds can be formed in the chemical reaction. The equilibrium shift of the redox reaction $Cu^{2+} + e \leftrightarrow Cu^{+}$ depends mainly on the concentration of the N-containing ligands and ligands with π-releasing properties which stabilize the oxidation state of Cu^{II}. Crystals in which some of the selenocyanate ions are replaced by cyanide were prepared from aqueous solution of the $CuSO_4$–en–KSeCN system (Vrábel, Garaj & Kutschabsky, 1979; Vrábel, Lokaj, Garaj & Pavelčík, 1982). The CN^- ions were formed during the redox reaction by the decomposition of selenocyanate.

Brown–violet crystals of the title compound, (I), were synthesized as reported previously (Vràbel, Kellö, Dunaj-Jurčo, Melník & Garaj, 1975). The structure and the atom numbering of the title compound are shown in Fig. 1.



(I)

The crystal structure consists of an infinite three-dimensional skeleton formed by polymeric $[Cu^{I}_6(CN)_6(SeCN)_6]^{6-}$. In the cavities and channels of the skeleton are located complex $[Cu^{II}(en)_2]^{2+}$ cations. Cu^{I} atoms are coordinated tetrahedrally by cyano and selenocyanato groups which are present as bridging groups. The Cu^{I}—NC distances are somewhat longer than those of Cu^{I}—CN. This difference is one of the factors which allows distinction between the N and C atoms in the cyano groups. There are considerable stereochemical differences between the bivalent $Cu^{II}1$ and $Cu^{II}2$ atoms. Cu1, which occupies a centre of symmetry, has a symmetrically elongated tetragonal bipyramidal coordination environment, with two molecules of ethylenediamine in the plane and two Se atoms of the SeCN group in the axial direction [Cu1···Se3 3.124 (2) Å]. Cu2 displays distorted square-pyramidal coordination, with two molecules of ethylenediamine approximately in the plane and N2 of the SeCN group at the apex. Cu2 lies 0.097 Å from this plane on the same side as N2. The vector N2—Cu2 is almost perpendicular to the coordination plane of CuN_4 [89.4 (2)°]. All the ethylenediamine molecules have a *gauche* asymmetrical arrangement of C atoms above and below the N—Cu—N plane.

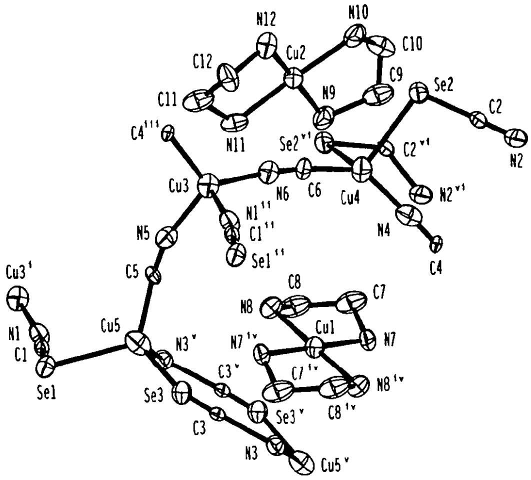


Fig. 1. Structure of the title compound with atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Symmetry codes: (i) $x, y, 1+z$; (ii) $x, y, z-1$; (iii) $1-x, y, z$; (iv) $1-x, -y, 1-z$; (v) $1-x, -y, 2-z$; (vi) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

The Se1—C1—N1 group forms a bidentate bridge through the Se and N atoms, linking two $Cu^{I}3$ and $Cu^{I}5$ atoms. A further two SeCN groups form a tridentate bridge between two Cu^{I} atoms and one Cu^{II} atom. The Se2—C2—N2 and Se3—C3—N3 groups are bonded to Cu^{II} atoms in the axial direction by N2 and Se3, respectively. In all structures of cuprous–cupric complex compounds solved so far (Cooper & Plane, 1966; Williams, Larson & Cromer, 1972; Vrábel, Garaj & Kutschabsky, 1979; Vrábel, Lokaj, Garaj & Pavelčík, 1982), two ethylenediamine or four ammonia molecules are coordinated to the bivalent copper. If their number is not sufficient to form the planar coordination system around the Cu^{II} atom, this function is fulfilled by N, Se or S atoms of pseudohalogenide ligands (Dunaj-Jurčo & Poraj-Koshits, 1967; Garaj, 1969; Williams, Cromer & Larson, 1971).

The preliminary results of the crystal structure determination have been partly given by Vrábel, Lokaj & Garaj (1983).

Experimental

The title compound was prepared as reported by Vràbel, Kellö, Dunaj-Jurčo, Melník & Garaj (1975). Crystals were obtained by crystallization from the original solution. The crystal density D_m was measured by flotation in bromoform–CCl_4.

Crystal data

$[Cu(C_2H_8N_2)_2]_3$- $[Cu_6(CN)_6(SeCN)_6]$	Cu $K\alpha$ radiation $\lambda = 1.54178$ Å

$M_r = 1718.5$
Monoclinic
$P2_1/c$
$a = 9.083\ (6)$ Å
$b = 31.918\ (2)$ Å
$c = 8.594\ (3)$ Å
$\beta = 93.1\ (2)^\circ$
$V = 2488\ (1)$ Å^3
$Z = 2$
$D_x = 2.29$ Mg m^{-3}
$D_m = 2.32\ (4)$ Mg m^{-3}

Cell parameters from 15 reflections
$\theta = 4$–13°
$\mu = 9.66$ mm^{-1}
$T = 293$ K
Prismatic
0.2 × 0.15 × 0.1 mm
Brown–violet

Data collection

$XP2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.684$, $T_{\max} = 0.979$
2684 measured reflections
2562 independent reflections
2195 observed reflections [$I > 1.96\sigma(I)$]

$R_{\rm int} = 0.028$
$\theta_{\max} = 55^\circ$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 31$
$l = -8 \rightarrow 8$
2 (004, 204) standard reflections monitored every 98 reflections intensity decay: <5%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.034$
$S = 0.94$
2195 reflections
286 parameters
H-atom parameters not refined

$w = 1/(6 + |F_o| + 0.005|F_o|^2)^{1/2}$
$(\Delta/\sigma)_{\max} = 0.1$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ 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* (Å^2)

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

	x	y	z	$B_{\rm eq}$
Cu1	1/2	0	1/2	2.8 (1)
Cu2	0.0532 (1)	0.1677 (1)	0.0503 (1)	2.9 (1)
Cu3	0.1345 (1)	0.1314 (1)	0.5984 (1)	3.5 (1)
Cu4	0.6383 (1)	0.1952 (1)	0.5275 (1)	4.5 (1)
Cu5	0.2142 (1)	0.0334 (1)	1.0392 (1)	3.8 (1)
Se1	0.0270 (1)	0.0120 (1)	1.2509 (1)	2.8 (1)
Se2	0.6635 (1)	0.2465 (1)	0.2859 (1)	3.0 (1)
Se3	0.4287 (1)	0.0599 (1)	1.2184 (1)	2.4 (1)
N1	0.1299 (6)	0.0793 (2)	1.4571 (7)	3.0 (2)
N2	0.9744 (7)	0.2279 (2)	0.2101 (8)	3.5 (2)
N3	0.6755 (6)	0.0157 (2)	1.0543 (6)	2.6 (2)
N4	0.8323 (7)	0.1728 (2)	0.5446 (7)	3.4 (2)
N5	0.1391 (6)	0.1041 (2)	0.8116 (7)	3.0 (2)
N6	0.3244 (6)	0.1615 (2)	0.5614 (7)	3.2 (2)
N7	0.6946 (6)	0.0299 (2)	0.5095 (7)	2.6 (2)
N8	0.4219 (6)	0.0467 (2)	0.6373 (6)	2.7 (2)
N9	−0.1304 (6)	0.1666 (2)	−0.0697 (7)	3.3 (2)
N10	−0.0547 (7)	0.1269 (2)	0.1903 (6)	2.8 (2)
N11	0.1654 (7)	0.2057 (2)	−0.1000 (8)	3.9 (2)
N12	0.2450 (7)	0.1614 (2)	0.1587 (9)	4.7 (2)
C1	0.0899 (7)	0.0528 (2)	1.3774 (7)	1.8 (2)
C2	0.8567 (7)	0.2359 (2)	0.2399 (8)	2.1 (2)
C3	0.5806 (7)	0.0338 (2)	1.1151 (7)	1.8 (2)
C4	0.9505 (6)	0.1591 (2)	0.5625 (7)	1.5 (2)
C5	0.1600 (7)	0.0795 (2)	0.9024 (8)	2.4 (2)
C6	0.4408 (7)	0.1762 (2)	0.5466 (8)	2.6 (2)
C7	0.6686 (9)	0.0721 (2)	0.5759 (10)	4.2 (2)
C8	0.5479 (10)	0.0688 (2)	0.7001 (9)	4.1 (2)
C9	−0.2241 (8)	0.1304 (3)	−0.0126 (10)	3.9 (2)
C10	−0.2131 (9)	0.1274 (3)	0.1559 (10)	4.3 (2)
C11	0.3035 (12)	0.2174 (4)	−0.0360 (15)	7.4 (4)
C12	0.3614 (10)	0.1843 (4)	0.0458 (23)	10.5 (6)

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

Cu1—N7	2.006 (6)	Cu4—N4	1.900 (6)
Cu1—N8	2.051 (6)	Cu4—C6	1.909 (6)
Cu2—N9	1.913 (6)	Cu4—Se2	2.664 (3)
Cu2—N10	2.057 (6)	Cu5—Se3	2.561 (2)
Cu2—N11	2.079 (7)	Cu5—C5	1.930 (7)
Cu2—N12	1.941 (7)	Cu5—Se1	2.646 (2)
Cu3—N5	2.027 (6)	Se1—C1	1.771 (7)
Cu3—N6	2.015 (6)	C1—N1	1.136 (9)
Cu3—C4$^{\rm i}$	1.901 (6)		
N7—Cu1—N8	87.8 (2)	Cu5—Se1—C1	92.0 (2)
Cu3—N5—C5	158.2 (6)	Cu5—Se3—C3	97.1 (2)
Cu3—N6—C6	174.2 (5)	Se1—C1—N1	179.2 (6)
Cu4—N4—C4	176.8 (6)	Se2—C2—N2	177.9 (6)
Cu5—C5—N5	172.0 (6)	Se3—C3—N3	176.8 (6)

Symmetry code: (i) $x - 1, y, z$.

The structure was solved by direct methods and refinement was on F by block-diagonal least squares. H atoms of the ethylenediamine groups were located at calculated positions; their coordinates and displacement paramaters were fixed. Calculations were performed using a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973) and *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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