THE CRYSTAL AND MOLECULAR STRUCTURE OF AQUA-BIS(ETHYLENEDIAMINE)CUPRIC-TRIS(CYANO)-SELENOCYANATODICUPRATE

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The crystal structure of $[Cu(H_2O)(en)_2][Cu_2(CN)_3(SeCN)]$ was solved by single-crystal X-ray structural analysis in the triclinic system with a space group of P1 and in the monoclinic system with a space group of C2. In the triclinic system the unit cell has dimensions of $a = 0{\cdot}8445$ (3), $b = 0{\cdot}7903$ (3), $c = 0{\cdot}8444$ (3) nm, $\alpha = 119{\cdot}58$ (2), $\beta = 118{\cdot}59$ (2) and $\gamma = 93{\cdot}63$ (3)° and, in the monoclinic system, $a = 1{\cdot}3331$ (4), $b = 0{\cdot}8670$ (2), $c = 0{\cdot}8267$ (3), $\beta = 122{\cdot}60$ (2)°. The structure was refined by the least squares method to a final value of $R = 5{\cdot}5\%$ in the triclinic system and $R = 7{\cdot}8\%$ in the monoclinic system. The coordination sphere around the Cu(II) atom is square pyramidal, formed of two ethylenediamine molecules and one water molecule. The Cu(I) atoms are tetrahedrally coordinated by bridging SeCN and CN ligands to form infinite three-dimensional chains. The SeCN group is bonded to the Cu(I) atoms through the Se atom at distances of 0·2731 (3) and 0·2745 (3) nm.

In the presence of some ions, such as cyanate, thiocyanate, and selenocyanate, divalent copper is readily reduced to univalency. Under suitable conditions, where the redox process is not too rapid, crystalline cuprous-cupric compounds can be formed in the chemical reaction. Crystals in which some of the selenocyanate ions are replaced by cyanide were prepared from aqueous solutions of the Cu(II)–en–$SeCN^-$ system[1]. The CN^- ions were formed during the redox reaction by the decomposition of selenocyanate. It follows from solution of the cuprous-cupric structure[2-6] that a necessary condition for maintenance of equilibrium in the redox reaction

$$Cu^{2+} + e \rightleftharpoons Cu^+$$

in favour of cupric ions is the formation of a coordination sphere of four nitrogen atoms around the Cu(II) atom. The structure of the coordination sphere with the CuN_4 chromophore is always planar. Consequently, the polyhedra around Cu(II) in cuprous-cupric compounds will always have very different geometry from that around Cu(I). The type of Cu(I) polyhedron is dependent on the Cu(I) : X^- ratio, where X^- is a halogen or pseudo-halogen ion[7]. When this ratio equals 1/4, isolated tetrahedra can be formed; when it decreases, the bridging function of the anionic ligands becomes important, leading to one-, two or three-dimensional cuprous-cupric complex structures. This approach is a useful method which permits prediction of the type of structure of a substance provided that the stoichiometric formula of the cuprous-cupric complex is known.

Divalent copper contributes to an increase in the stability of the whole structure primarily by filling vacancies formed by the Cu(I) polyhedra and by compensating the electric charge of the polymeric skeleton.

It is known from the results of X-ray structural analysis that the SCN^- and OCN^- groups can be bonded to the central atom of the complex through a single bond to the sulphur, oxygen or nitrogen atom or by a bridge through the sulphur and nitrogen or oxygen and nitrogen atoms simultaneously[6,8-10]. Selenocyanate complexes of copper have been studied because of the possibility of formation of similar types of bonds in this group and also because of the formation of various types of complex compounds in which the copper atoms are in mixed oxidation states.

EXPERIMENTAL

Blue-purple shiny crystals with well-formed edges with the composition $[Cu_3(H_2O)(en)_2(CN)_3.(SeCN)]$ were formed after about 3 hours in the aqueous Cu^{2+}–en–$SeCN^-$ system using the procedure described in work[1]. The percent contents of C, N and H were determined using microanalytical analyzer CHNO model 1 102, Carlo Erba. Copper was determined electrolytically after prior decomposition of the sample using sulphuric acid and potassium peroxodisulphate. For $C_8H_{18}N_8OSeCu_3$ (m.w. 511·9) was calculated: 37·24% Cu, 18·77% C, 21·89% N, 3·54% H, and found: 37·36% Cu, 18·80% C, 21·95% N, 3·55% H. The crystal density at room temperature, $D_0 = 2{\cdot}11 \,.\, 10^3$ kg m^{-3}, was measured by the flotation method (methyl iodide–acetone). The calculated density for one formula unit per unit cell in the triclinic system is $D_c = 2{\cdot}15 \,.\, 10^3$ kg . . m^{-3}. The approximate values of the lattice constants found from rotation and Weissenberg films were refined by the least squares method using 8 centred reflections on a Syntex $P2_1$ diffractometer.

The intensity was measured using a rhombohedral prismatic crystal with dimensions of 0·1 × × 0·15 × 0·2 mm. The integral intensities were measured using a four-circle automatic Syntex $P2_1$ diffractometer. Graphite monochromatic $MoK\alpha_1$ radiation ($\lambda = 0{\cdot}070926$ nm) was used for the measurements under working conditions using a 50 kV, 20 mA generator and $\Theta : 2\Theta$ scanning technique (the crystal moves through the Bragg reflection position at an angular speed of $\omega = \Theta$ and detector speed of 2Θ). The crystal was recentred after each 400 measured intensities.

The integral intensities were measured in the range $0° < 2\Theta \leqq 55°$ and only those values for which $I \geqq 1{\cdot}96\sigma(I)$ were classified as observed and used for the final structure solution. All the intensities were corrected for the Lorentz and polarization factors. Absorption was neglected.

The crystal structure of $[Cu_3(H_2O)(en)_2(CN)_3(SeCN)]$ was solved in the two symmetry groups, C2 and P1. Systematic absences of reflections of the $[hkl]$ type for $h + k = 2n + 1$ corresponds to space group C2. A monoclinic centred cell was selected and refinement yielded the dimensions: $a = 1{\cdot}3331\,(4)$, $b = 0{\cdot}8670\,(2)$, $c = 0{\cdot}8267\,(3)$ nm and $\beta = 122{\cdot}60\,(2)°$. It follows from the calculated number of formula units per unit cell for group $C2$ ($Z = 2$) that the independent part of the molecule corresponds to 1/2 of a formula unit. This is valid assuming that part of the atoms lie in a special position on the two-fold axis.

It was found from solution of the crystal structure in the $C2$ group that all the atoms of the SeCN group lie on the two-fold axis, along with the divalent copper atom and the oxygen atom of the water molecule. In this arrangement, one cyanide group must have a statistical content of C and N atoms. For the given reasons of restricted positions of some atoms, the structure was also solved in the $P1$ group.

The selected unit cell with dimensions $a = 0{\cdot}8445\,(3)$, $b = 0{\cdot}7903\,(3)$, $c = 0{\cdot}8444\,(3)$, nm $\alpha = 119{\cdot}58\,(2)$, $\beta = 118{\cdot}59\,(2)$ and $\gamma = 93{\cdot}63\,(3)°$ can be transformed into a centred monoclinic cell using the vectors:

$$\mathbf{a}^{\mathrm{mon}} = -\mathbf{a} - 2\mathbf{b} - \mathbf{c}$$

$$\mathbf{b}^{\mathrm{mon}} = -\mathbf{a} - \mathbf{c}$$

$$\mathbf{c}^{\mathrm{mon}} = \mathbf{b} + \mathbf{c}$$

Structural refinement in both symmetry groups yielded a better reliability factor for the $P1$ group, $R = 5{\cdot}5\%$, with a value of $R = 7{\cdot}8\%$ for $C2$. In this group, statistical contents of the atoms of the CN group were excluded and in the SeCN group atomic deviations from linearity

TABLE I

Calculated values of the fractional coordinates of the hydrogen atoms of the ethylenediamine molecule in $[Cu(H_2O)(en)_2][Cu_2(CN)_2(SeCN)]$

Atom	x/a	y/b	z/c
H1(N5)	0·4804	0·2769	0·1787
H2(N5)	0·2822	0·2882	0·0130
H1(N6)	0·7277	0·2881	−0·1029
H2(N6)	0·5019	0·2207	−0·3022
H1(N7)	0·8987	0·7230	0·2126
H2(N7)	0·7246	0·7092	−0·0007
H1(N8)	0·4725	0·7684	0·2841
H2(N8)	0·6142	0·7051	0·4420
H1(C5)	0·3255	−0·0566	−0·1321
H2(C5)	0·2336	0·0292	−0·3057
H1(C6)	0·6457	0·0882	−0·0117
H2(C6)	0·4873	−0·0719	−0·3110
H1(C7)	0·9165	1·0526	0·3811
H2(C7)	0·6570	0·9627	0·1995
H1(C8)	0·7418	1·0678	0·5488
H2(C8)	0·8947	0·9231	0·5670

(~5°) were observed. Below, only solution for the structure of $[Cu_3(H_2O)(en)_2(CN)_3(SeCN)]$ with *P*1 symmetry are given. Structural data for solution of the structure in the *C*2 group are available on request from the authors.

Solution and Refinement of the Structure

The crystal structure was solved by the heavy atom method. The positions of all four heavy atoms were found from the three-dimensional Patterson function calculated from the contributions of 1415 observed reflections. Subsequent Fourier synthesis and utilization of the distribution of the electron density around the heavy atoms enabled distinguishing of the positions of the copper atoms from that of the selenium atom. The positions of all the nonhydrogen atoms in the complex were found by further stepwise application of Fourier synthesis of the electron density. After determination of the correct model, the structure was further refined in two cycles by the least squares method using the full matrix and isotropic thermal parameters. At this stage in the calculation, the *R* factor, defined as $\sum||F_0| - |F_c||/\sum|F_0|$, had a value of 0·16. In the next 5 refinement cycles, anisotropic thermal vibration of all the nonhydrogen atoms was assumed which,

TABLE II

Refined positional parameters (. 10^4) of the nonhydrogen atoms in the crystal structure of $[Cu(H_2O)(en)_2].[Cu_2(CN)_3(Se(CN)]$. (Standard deviations are given in brackets)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Se	0 000 (0)	0 000 (0)	0 000 (0)
Cu1	1 238 (3)	4 301 (4)	2 674 (4)
Cu2	5 738 (3)	5 000 (3)	0 741 (3)
Cu3	8 358 (3)	5 677 (4)	6 927 (4)
O	2 988 (25)	4 951 (40)	8 035 (32)
N1	9 824 (19)	5 008 (21)	9 039 (24)
N2	9 754 (18)	4 865 (25)	3 958 (23)
N3	4 010 (23)	4 992 (22)	4 913 (23)
N4	3 344 (55)	0 022 (41)	3 460 (60)
N5	4 061 (25)	2 687 (25)	0 390 (27)
N6	5 897 (18)	2 538 (24)	8 498 (25)
N7	7 666 (24)	7 291 (23)	1 422 (26)
N8	5 949 (27)	7 407 (21)	3 361 (25)
C1	0 495 (22)	4 723 (24)	0 392 (25)
C2	9 071 (20)	5 116 (24)	4 871 (26)
C3	5 645 (21)	5 235 (24)	5 733 (25)
C4	2 044 (43)	0 013 (33)	2 156 (43)
C5	3 595 (33)	0 652 (28)	8 494 (37)
C6	5 264 (28)	0 732 (31)	8 434 (37)
C7	7 769 (42)	9 300 (33)	2 934 (47)
C8	7 613 (39)	9 265 (34)	4 529 (36)

together with the positional parameters, refined by the least squares method using the minimization function $\sum w(|F_0| - |F_c|)^2$ and the weighting scheme described by Cruickshank[11], $w = (a + |F_0| + b|F_0|^2)^{-1/2}$, where $a = 17{\cdot}02$, and $b = 0{\cdot}014$, reduced the R factor to a value of 0·071. The positions of the hydrogen atoms were calculated assuming tetragonal coordination of the carbon and nitrogen atoms of ethylenediamine (Table I). Their coordinates were not refined further and were fixed together with the isotropic thermal parameters at a distiance of 0·095 nm from the N and C atoms. After introducing these values into the structure, the R factor was reduced in 3 refinement cycles to a final value of 0·055. In the final refinement cycle, the shift in this parameter was not greater than $0{\cdot}15\sigma$. Differential Fourier synthesis of the residual electron density calculated without the hydrogen atoms did not contain maxima greater than $1{\cdot}1 \cdot 10^3$ e nm^{-3}. The refined atomic coordinates are given in Table II. The interatomic bonding distances and valence angles are given in Table III. The atomic distribution in the unit cell projected into the (010) plane is shown in Fig. 1. The scattering curves for the neutral atoms were taken from the tables[12].

All the calculations were carried out on the SIEMENS 4004/150 computer using programs from the authors A. Zelkin, O. Lingren and F. Wengelin. The atomic positions were refined by the least squares method using the NRC crystallographic program for the IBM/360 system[13].

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal structure of the $[Cu_3(H_2O)(en)_2(CN)_3(SeCN)]$ complex consists of an infinite three-dimensional skeleton, formed of polymeric $[Cu_2(CN)_3(SeCN)]^{2-}$ anions. The skeletal part contains channels containing eccentrically localized discrete $[Cu(H_2O)(en)_2]^{2+}$ cations.

From a stereochemical point of view, there are marked differences between the Cu(I) and Cu(II) atoms. Univalent copper is coordinated tetrahedrally by one seleno-

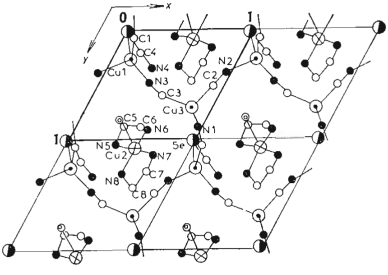
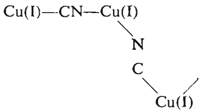


FIG. 1
Projection of the structure of $[Cu(H_2O)(en)_2][Cu_2(CN)_3(SeCN)]$ into the (010) plane

cyanate and three cyanide groups. The valence deficit necessary for formation of tetrahedral coordination of the Cu(I) atom is compensated by increased functionality of the SeCN and CN ligands with bridge formation. The cyanide groups form bridges between the Cu(I) atoms, which are connected in bent polymeric chains:



In the selenocyanate group, the selenium atoms act as bridges connecting two Cu(I) atoms shifted in the direction of the *y*-axis (dashed line in Fig. 1), forming an infinite three-dimensional cross-linked structure. The Cu(I)–Se–CN bonding angle varies around the tetrahedral value and the Cu–C–N bonding angle approaches the linear value (Table IV). It follows that there is greater steric requirement for the SeCN group. There are no significant differences in the lengths of the Cu1–Se–Cu3 bonds, which differ by only 0·001 nm. A similar disfunctionality of the atoms of a pseudohalide ligand was observed in the compound[6] $[Cu_2(NH_3)_3(SCN)_3]$, where the sulphur of the SCN group forms a bridge between the Cu(I) and Cu(II) atoms.

TABLE III

Intramolecular bonding distances and their standard deviations (nm) in the crystal structure of $[Cu(H_2O)(en)_2][Cu_2(CN)_3(SeCN)]$

Atoms	Bonding distance	Atoms	Bonding distances
Cu1—Se	0·2731 (3)	Cu2—O	0·2331 (19)
Cu1—N2	0·1960 (13)	Se—C4	0·1807 (28)
Cu1—N3	0·1964 (15)	N1—C1	0·1152 (21)
Cu1—C1	0·1929 (15)	N2—C2	0·1120 (20)
Cu3—Se	0·2745 (3)	N3—C3	0·1157 (21)
Cu3—N1	0·1973 (14)	N4—C4	0·1119 (47)
Cu3—C2	0·1962 (15)	N5—C5	0·1442 (25)
Cu3—C3	0·1931 (15)	N6—C6	0·1458 (25)
Cu2—N5	0·2041 (16)	N7—C7	0·1426 (27)
Cu2—N6	0·2008 (15)	N8—C8	0·1147 (29)
Cu2—N7	0·1993 (15)	C5—C6	0·1433 (30)
Cu2—N8	0·1998 (14)	C7—C8	0·1428 (36)

Within the limits of the standard deviations, the lengths of the Cu(I)–CN and Cu(I)–NC bonds exhibited differences which allow distinction of the carbon atom from the nitrogen atom in the CN group. The average value of the length of the Cu(I)–C bond is 0·193 nm and of Cu(I)–N, 0·196 nm (Table III). A second factor which allows distinction between the C and N atoms in the cyanide groups is the difference in the electron densities ($\sim 0{\cdot}3 \,.\, 10^3$ e nm^{-3}) on the differential Fourier map at these locations of the CN groups, calculated without the contributions from these atoms.

The coordination of the polyhedron around the Cu(II) atom corresponds to an elongated tetragonal pyramid (Fig. 2). The base of the pyramid is formed by two molecules of ethylenediamine bonded to the Cu(II) atom through covalent chelate bonds to the nitrogen atom. A water molecule is located at the apex of the pyramid and is bonded to the divalent copper through its oxygen atom at a distance of 0·233 nm. The Cu–O vector is almost perpendicular to the plane of the base (90·4°) (Table V).

TABLE IV

Bonding angles (°) and their standard deviations in the crystal structure of $[Cu(H_2O)(en)_2]$.$[Cu_2(CN)_3(SeCN)]$

Atoms	Angle	Atoms	Angle
Cu1—Se—Cu3	172·9 (0·1)	N1—Cu3—C2	114·6 (0·6)
Cu1—Se—C4	93·0 (0·7)	N1—Cu3—C3	119·9 (0·6)
Cu1—C1—N1	170·1 (1·4)	N2—Cu1—N3	114·2 (0·6)
Cu1—N2—C2	170·5 (1·3)	N2—Cu1—C1	116·6 (0·6)
Cu1—N3—C3	167·6 (1·3)	N3—Cu1—C1	119·6 (0·6)
Cu2—N5—C5	109·1 (1·2)	N5—Cu2—N6	82·8 (0·6)
Cu2—N6—C6	107·6 (1·2)	N5—Cu2—N7	172·5 (0·7)
Cu2—N7—C7	109·8 (1·4)	N5—Cu2—N8	95·4 (0·6)
Cu2—N8—C8	108·6 (1·3)	N5—Cu2—O	92·2 (0·7)
Cu3—N1—C1	168·8 (1·3)	N5—C5—C6	108·3 (1·7)
Cu3—C2—N2	169·3 (1·3)	N6—Cu2—N7	97·4 (0·6)
Cu3—C3—N3	171·1 (1·4)	N6—Cu2—N8	169·8 (0·6)
Cu3—Se—C4	93·9 (0·7)	N6—Cu2—O	94·7 (0·7)
Se—Cu1—C1	98·1 (0·5)	N6—C6—C5	110·2 (1·6)
Se—Cu1—N2	105·0 (0·5)	N7—Cu2—N8	83·0 (0·6)
Se—Cu1—N3	98·2 (0·4)	N7—Cu2—O	95·2 (0·7)
Se—Cu3—N1	97·8 (0·4)	N7—C7—C8	109·1 (1·8)
Se—Cu3—C2	104·8 (0·4)	N8—Cu2—O	95·4 (0·7)
Se—Cu3—C3	98·6 (0·5)	N8—C8—C7	109·9 (1·8)
Se—C4—N4	175·5 (2·9)	C2—Du3—C3	115·9 (0·6)

TABLE V

Angles (°) between planes (1) to (5)

Planes	Angle	Planes	Angle
(1)—(2)	90·4	(2)—(5)	95·2
(1)—(3)	91·0	(3)—(4)	87·9
(2)—(3)	96·8	(3)—(5)	94·1
(2)—(4)	85·8	(4)—(5)	11·9

TABLE VI

Deviations (nm . 10^4) of some atoms from planes (1) to (5)

Atom	(1)	(2)	(3)	(4)	(5)
Cu2	154	—	—	—	—
N5	23	—	2 011	—	−261
N6	− 23	1 996	—	—	−356
N7	23	—	−1 985	−260	—
N8	− 23	−1 966	—	−350	—
C5	154	1 343	2 338	270	−274
C6	−507	2 229	1 334	−375	−944
C7	202	−1 336	−2 312	−220	319
C8	−431	−2 244	−1 302	−866	−294
O	2 484	—	—	2 322	2 313

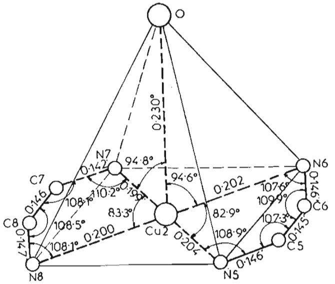


FIG. 2

Interatomic distances (nm) and angles in the coordination polyhedron around the Cu(II) atom

The geometry of the coordination sphere of $Cu(II)N_4$ is almost planar. The deviation of the Cu(II) atom from the plane constructed by the least squares method through the system of atoms N5, N6, N7, and N8 is 0·015 nm (Table VI), in the direction of the oxygen coordinated to water. This basically planar arrangement of the atoms in the CuN_4 chromophore was found in all cuprous-cupric compounds containing $4\,NH_3$ or 2 ethylenedimaine molecules: $[Cu_3(NH_3)_4(CN)_4]$ (ref.[2]), $[Cu_3(H_2O)(en)_2(CN)_2(SeCN)_2]$ (ref.[5]), and $[Cu_3(NH_3)_4X_4]$, where X = Cl, Br, I (ref.[14,15]), as well as $Na_4[Cu_3(NH_3)_4(S_2O_3)_2]$ (ref.[16]).

The chelate ring formed by two ethylenedimaine molecules around the Cu(II) atom has "gauche" asymmetric conformation. This asymmetry is exhibited by the carbon atoms which are located at unequal distances from the plane constructed through the N–Cu(II)–N atoms. Deviations of the C5, C6 and C7, C8 carbon atoms are 0·027 nm above and 0·037 nm below the N7–Cu2–N8 coordination plane (Table VI).

They asymmetric arrangement of the ethylenediamine molecule with respect to the N-Cu(II)-N coordination plane may be connected with interactions of the closest molecular environment of the type N...H–N(en), O...N–N(en) or Cu(II)...NC. These types of interactions were not observed[5] in the similar compound $[Cu_3.(H_2O)(en)_3(CN)_2(SeCN)]$, in which symmetrical – gauche – arrangement of the ethylenediamine molecule was found, because of formation of quite large channels in the structure matrix, containing complex cations of the type $[CuH_2O(en)_2]^{2+}$. The distance between the atoms of the complex cation and the closest environment is greater than 0·4 nm. In contrast, the molecular surroundings are closer to Cu(I) (~0·3 nm) in the compounds[4] $[Cu_3(H_2O)(en)_2(CN)_4]$ and $[Cu_3(H_2O)(en)_2(CN)_3.(SeCN)]$, as a result of decreasing in the channel dimensions in the polymeric crystal skeleton. Consequently, the given types of interaction begin to become important to a greater or lesser degree which can lead to deformation of the ethylenediamine ring.

Within the standard deviations the selenocyanate group exhibits significant deviations from linearity (175·5°). The high standard deviations of the C4 and N4 atoms is connected with the high thermal vibration of the terminal SeCN group. This type of bridge bonding of the selenocyanate group leads to formation of hydrogen bonds between the free nitrogen N4 of the SeCN group and the hydrogens of the NH_2 group of the opposite ethylenediamine molecules. This is confirmed by the intermolecular distances N4...H–N6 (0·29 nm) and N4...H–N8 (0·31 nm).

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