THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(ETHYLENEDIAMINE) COPPER(II) SELENOCYANATE

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The crystal structure of $[Cu(en)_2](SeCN)_2$ was solved by the heavy atom method and refined by the least squares method using the full matrix and anisotropic thermal parameters to a value of $R = 0{\cdot}063$ for 660 observed reflections. The crystals are triclinic, with a space group of $P\bar{1}$ and lattice parameters of $a = 6{\cdot}660(2)$, $b = 9{\cdot}360(2)$, $c = 7{\cdot}754(2) \,.\, 10^{-10}$ m, $\alpha = 129{\cdot}22(2)$, $\beta = 109{\cdot}87(2)$ and $\gamma = 92{\cdot}38(2)°$, $Z = \bar{1}$. The structure consists of discrete molecules that are centrosymmetric. The Cu(II) atom occupies a special position at the centre of symmetry and is coordinated by 4 nitrogen atoms from two bidentate ethylenediamine molecules: C—N 1·999(8) and 2·033(8) . 10^{-10} m and angle N1—Cu—N2, 84·1(3)°. The selenium atom in the SeCN group completes this square planar arrangement to form a deformed octahedron along the longer Cu...Se distance of 3·263(2) . 10^{-10} m. The ethylenediamine molecule has a non-symmetrical gauche arrangement with the carbon atoms C1 and C2 + 0·542 and −0·095 . 10^{-10} m above and below the N1—Cu—N2 coordination plane, respectively.

Bivalent copper and nickel form a number of interesting coordination compounds. The close positions of these elements in the periodic system suggest certain analogies in the chemistry of coordination compounds of Cu(II) and Ni(II). A detailed study revealed that they formed identical structures with some ligands and considerably different structures with other ones.

Solution of the structures of two analogous compounds, $Cu(en)_2[(SCN)_2]$ (ref.[1]) and $Ni(en)_2[(SCN)_2]$ (ref.[2]) revealed interesting differences in their symmetries and ligand bonding properties: *1*) The ethylenediamine molecules have a *gauche* asymmetrical arrangement of carbon atoms above and below the N–M–N plane in the former compound, while this arrangement is symmetrical in the latter; *2*) the bond between the central atom and the thiocyanate group in the former compound is through the sulphur atom on the long coordinate and in the latter through the nitrogen atom; *3*) The valence angle in the thiocyanate group, 140°C (Ni–N–C), is sharper than in other octahedral thiocyanate complexes whose structures have been solved.

As the $SeCN^-$ anions have stronger reduction properties than the SCN^- anions, the presence of a nitrogen donor in the coordination sphere is a necessary condition for formation of selenocyanate copper(II) complexes. This σ-donor is a good stabilizer of the copper oxidation state by preventing electron transfer from the anionic ligand to Cu(II) by decreasing the effective positive charge on the divalent copper. In general, tetragonal coordination formed by four nitrogen atoms in the equatorial plane is a necessary condition for the redox stability of Cu(II) in its complexes. This square planar coordination is usually completed to form a deformed octahedron with various axial distortion.

A special case consists of complexes with tetravalent bulky ligands, *e.g.* $[Cu(tren).(CN)_2](BPh_4)_2$ (ref.[3]) and $[Cu_2(mdien)_2(CN)](ClO_4)_3$ (ref.[4]) (tern = 2,2′,2″-triaminotriethylamine and mdien = 5,7,7′,12,14,14′-hexamethyl-1,4,8,11-tetraza-cyclo tetradeca-4,11-diene), in which the steric conditions in the polyamine ligand are deformed by the square planar arrangement of the Cu(II). This is then changed to trigonal pyramidal, which then becomes trigonal bipyramidal as a result of bonding of a pseudo-halide ligand in the axial direction.

EXPERIMENTAL

$[Cu(en)_2](SeCN)_2$ was prepared by mixing an aqueous solution of $CuSO_4.5\,H_2O$ with a concentrated ethylenediamine solution and subsequent addition of an aqueous KSeCN solution. The blue-purple solution produced was left to crystallize at about 25°C. After about 20 h, flat crystals began to be formed in the solution, which had a component molar ratio of Cu^{2+} : : en : $SeCN^-$ of 1 : 2·5 : 1·5; these crystals were filtered off under vacuum and rinsed with tetrachloromethane. The crystals are readily soluble in water and other polar solvents.

The percent contents of N, C and H were determined using a model 1102 CHNO analyzer, Carlo Erba. Copper was determined complexometrically using murexide indicator after decomposition of the sample with sulphuric acid and potassium peroxide. The solution was evaporated to dryness and the residue was dissolved in distilled water; the pH was adjusted and the solution titrated. Analysis for $C_2H_{16}CuN_6Se$ (939·7): calculated: N 21·35%, C 18·30%, H 4·10%, Cu 16·14% and found N 20·92%, C 18·29%, H 4·09%, Cu 16·28%. The crystal density D_0=2·05 Mg . . m^{-3} was found at room temperature by the flotation method (bromoform–tetrachloromethane)

TABLE I

Basic crystallographic data for $[Cu(en)_2](SeCN)_2$

Crystallographic system	Triclinic	Volume of a unit cell	$V = 329.7 \cdot 10^{-3}\ nm^3$
Space group	$P\bar{1}$	number of formula units	$Z = 1$
Dimensions of a unit Cell and standard deviations	$a = 6.660(2) \cdot 10^{-10}$ m	measured density	$D_m = 2.05\ Mg\ m^{-3}$
	$b = 9.360(2)$.	calculated density	$D_c = 2.09\ Mg\ m^{-3}$
	$c = 7.454(2)$.	number of electrons per unit cell	$F(000) = 191$
	$\alpha = 129.22(2)°$		
	$\beta = 100.87(2)$	Linear absorption coefficient	$\mu = 9.9\ mm^{-1}$
	$\gamma = 92.38(2)$		

The calculated density for a single formula unit per unit cell yielded $D_c = 2{\cdot}09$ Mg m^{-3}. The remaining basic crystallographic data are given in Table I.

The lattice parameter values obtained from rotation and Weissenberg films were refined on a Syntex P2_1 diffractometer by the least squares method on the basis of 10 precisely centred reflections.

A crystal with dimensions of $0{\cdot}1 \times 0{\cdot}2 \times 0{\cdot}2$ mm was selected to yield the basic crystallographic data for intensity measurements. The integral intensities were measured on a four-ring computer-controlled Syntex P2_1 diffractometer equipped with a scintillation counter and pulse-height analyzer. Monochromatic CuK$_\alpha$ radiation was employed for the measurements and the intensities were recorded in the range $0° \leq 2\theta \leq 110°$. Of the total of 687 recorded reflections, 660 were classified as observed with $I \geqq 1{\cdot}96\sigma(I)$. The crystal was recentred (repeated refinement of the orientation matrix describing the orientation of the reciprocal of the crystallographic coordinate system with respect to the Cartesian system precisely connected with the diffractometer), after each 90 intensity measurements. All the intensities were corrected for Lorentz and polarization factors and converted to an absolute scale by the Wilson method. No correction was made for absorption ($\mu = 9{\cdot}9$ mm^{-1}).

Structure Solution and Refinement

Two possible space groups P1 and P$\bar{1}$. followed from the measured reflection intensities (no systematic extinction was observed). The positions of the Cu and Se atoms were localized in three-dimensional Patterson synthesis calculated for 660 observed non-zero reflections. The central copper atom was assigned position (0,0,0) resulting in centrosymmetric space group P$\bar{1}$. Fourier synthesis phased from the contributions of these two heavy atoms indicated the positions of the other nonhydrogen atoms in the complex.

The structure was refined in 3 cycles by the least squares method using the full matrix, isotropic thermal parameters for the nonhydrogen atoms and the Cruickshank weighing scheme[5], $w = (a + |F_0| + b|F_0|^2)^{-1/2}$ where $a = 1{\cdot}4$ and $b = 0{\cdot}004$ to yield a value of $R = 0{\cdot}17$. In the next 6 refinement cycles, anisotropic thermal vibrations of all the atoms were assumed that were refined together with the positional parameters by the least squares method using the minimization function $\sum W(|F_0| - |F_c|)^2$ in 9×9 block-diagonal approximation leading to a decrease in the R-factor, defined as $\sum||F_0| - |F_c||/|F_0|$, to a value of 0·09.

Introduction of the hydrogen atoms of ethylenediamine into the structure, whose positions were calculated assuming sp^3 hybridization of the carbon and nitrogen atoms (Table II) decreased the R factor to a final value of 0·063. The positions of the hydrogen atoms were not refined. The shifts of all the positional parameters in the last refinement cycle were less than $0{\cdot}1\sigma$. Differential Fourier synthesis of the residual electron density did not exhibit significant fluctuations; the largest maximum, $1{\cdot}2 \, . \, 10^3$ e nm^{-3}, appeared at sites corresponding to the positions of the selenium atoms. The scattering curves for the neutral atoms were taken from the Table I (ref.[6]).

The refined fractional coordinates of the non-hydrogen atoms and their anisotropic temperature parameters are given in Table. III and IV. The interatomic bond distances and valence angles with standard deviations are listed in Table V. The composition of the unit cell projected onto the (001) plane is depicted schematically in Fig. 1. The calculations were carried out on an XTL Syntex P2_1 module and using a Siemens 4004/150 computer.

Structure Description and Discussion

It followed from the results of the X-ray structural analysis that compound $[Cu(en)_2]$.$(SeCN)_2$ is isostructural with its thiocyanate analogue[1] and significant differences were found only in some bond angles and distances in the ethylenediamine molecules.

The crystals are formed of discrete $[Cu(en)_2](SeCN)_2$ molecules that are centrosymmetric with the Cu(II) atom at the centre of symmetry (0, 0, 0). The copper atom is coordinated by two pairs of nitrogen atoms of two bidentally coordinated ethylenediamine molecules. The geometry of the coordination sphere of CuN_4 is thus completely planar. The selenium atom of the SeCN group completes this square-planar arrangement to form a deformed octahedron, bonded along the long coordinate in the axial direction with a Cu–Se distance of $3{\cdot}263 \, . \, 10^{-10}$ m. The Cu–Se distance

TABLE II

Calculated positional parameters (x 10^4) of the hydrogen atoms

Atom	X	Y	Z
HA(N1)	3 127	2 342	811
H2(N1)	1 971	264	−2 144
H3(N2)	−1 820	2 548	2 120
H4(N2)	−3 487	930	− 932
H5(C1)	1 168	3 136	−1 325
H6(C1)	−1 178	904	−3 383
H7(C2)	448	4 470	2 150
H8(C2)	−2 198	3 504	− 477

TABLE III

Refined positional parameters (x 10^4) for the nonhydrogen atoms (standard deviation given in brackets)

Atom	X	Y	Z
Cu	0 000	0 000	0 000
Se	3 495(2)	3 577(2)	6 029(3)
N1	1 593(13)	1 288(11)	− 703(16)
N2	−1 845(13)	1 785(12)	485(17)
N3	6 609(16)	1 977(13)	4 021(18
C1	175(18)	2 008(15)	−1 539(19)
C2	− 838(18)	3 092(15)	214(24)
C3	5 428(15)	2 655(14)	4 870(19)

corresponds to the sum of the van der Waals radii[7] of selenium, 1·97 . 10^{-10} m, and Cu, 1·30 . 10^{-10} m, equal to 3·27 . 10^{-10} m, which is roughly the observed distance. Kivekas[8] came to a similar conclusion in investigation of the complex compound $[Cu(amp)_2](SeCN)_2$, where amp = 1,3-diamino-2-propanol, in which the selenium atoms lie in the axial direction at a distance of 3·113 . 10^{-10} m. In con-

TABLE IV

Anisotropic thermal parameters (x 10^4) of the nonhydrogen atoms

Atom	*B*11	*B*22	*B*33	*B*23	*B*13	*B*12
Cu	328	252	641	650	469	281
Se	449	275	602	520	725	315
N1	281	164	435	414	360	167
N2	279	201	496	450	375	74
N3	417	232	456	352	471	218
C1	409	278	382	572	513	485
C2	325	135	627	442	266	106
C3	181	201	426	384	426	269

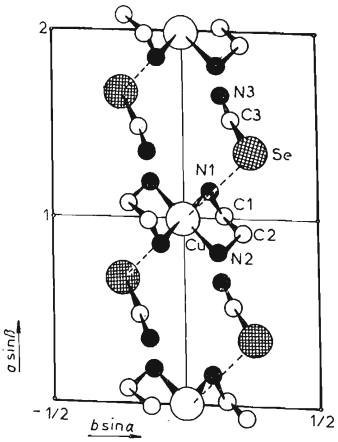


FIG. 1

Projection of the structure of $[Cu(en)_2]$. $(SeCN)_2$ onto the (001) plane trast, Pajunen and Korvenranta[9] found for the compound $[Cu(den)_2](NCSe)_2$ (den = N,N'-dimethylethylenediamine) that the selenocyanate group is bonded through the long coordinates by the nitrogen atoms at a distance of Cu...NCSe = = 2·553 . 10^{-10} m. The selenium atom is almost perpendicular to the $Cu(II)N_4(en)$ coordination plane (Table VI). the bond angle N—Cu(I)—N value of 84° in $[Cu(en)_2](SeCN)_2$ is in agreement with the values found for the compounds $[Cu(en)_2](SCN)_2$, 85° (ref.[1]), $[Cu(en)_2](NO_3)_2$, 86° (ref.[10]). and $[Cu(en)_2(NO_3)]$.(SeCN), 86° (ref.[11]).

In contrast to the symmetrical gauche conformation of the ethylenediamine molecule, often observed in complexes of Ni(II) and Co(III) (ref.[12-16]), the gauche conformation of this compound is unsymmetrical with carbon atom C1 and C2 0·542 . 10^{-10} m above and 0·095 . 10^{-10} m below the N1—Cu(II)—N2 coordination plane, respectively (Table VI).

The selenocyanate ion in $[Cu(en)_2](SeCN)_2$ is practically linear, with a Se—C—N bond angle differing only slightly from 180°. The Se—C and C—N bond distances of 1·763 . 10^{-10} m and 1·149 . 10^{-10} m, respectively, are in good agreement with the values found for the three given selenocyanate compounds of divalent copper. Because of its ionic character, $[Cu(en)_2](SeCN)_2$ is readily soluble in water and other polar solvents.

Bonding Properties and Coordination Ability of the SeCN *Ligands in Compounds of Mono- and Divalent Copper*

It follows from our calculations and the studies of Wagner[17] and Norbury[18] that the behaviour of the selenocyanate ion lies between those of the thiocyanate and cyanate ions. The charge distribution is such as to favour coordination through

TABLE V

Bonding distances (m . 10^{-10}) and angles (°) in $[Cu(en)_2](SeCN)_2$ (standard deviations in brackets)

Cu—Se	3·263(2)	Se—Cu—N1	89·3(2)
Cu—N1	1·999(8)	Se—Cu—N2	86·3(3)
Cu—N2	2·033(8)	N1—Cu—N2	84·1(3)
Se—C3	1·763(9)	Cu—Se—C3	79·3(3)
N1—C1	1·398(13)	Cu—N1—C1	110·2(6)
N2—C2	1·531(14)	Cu—N2—C2	107·1(6)
N3—C3	1·149(13)	N1—C1—C2	107·2(9)
C1—C2	1·507(16)	N2—C2—C1	109·4(8)
		Se—C3—N3	177·0(9)

selenium but the charge on the nitrogen is also sufficient to permit coordination in this manner.

It follows from the crystallochemical analysis of the bonding properties of the selenocyanate ligand, obtained from two cuprous-cupric compounds, $Cu_3(en)_2.(SeCN)_2(CN)_2.H_2O$ (ref.[19,20]) and $Cu_3(en)_2(SeCN)(CN)_3.H_2O$ (ref.[20]) and one cupric compound, $[Cu(en)_2(NO_3)]SeCN$ (ref.[11]), as well as on the basis of the results of two solved cupric structures, $[Cu(amp)_2](SeCN)_2$ (ref.[8]) and $[Cu(den)_2](NCSe)_2$ (ref.[9]), that, compared with the SCN and OCN groups, the selenocyanate group has coordination properties very similar to those of the thiocyanate ligand. The SeCN group can act in compounds as a ligand (coordinated) and as an ion (not bonded

TABLE VI

The values of the coefficients of the equation of the planes (x 10^4) $AX + BY + CZ = D$ and designation of atoms through which the plane is constructed by the least squares method

Plane	Atoms defining the plane	*A*	*B*	*C*	*D*
1	N1, N2, Cu	−2 323	− 457	−9 816	0 000
2	N1, N$\bar{1}$, Cu, Se	7 539	−6 516	− 842	0 000
3	N2, N$\bar{2}$, Cu, Se	7 041	6 818	−1 982	0 000

Distances of some atoms from the plane (m . 10^{-10})

Plane	N1	N2	C1	C2	Se
1	—	—	0·5425	−0·0951	−3·2559
2	—	−2·0182	−1·2266	−2·0182	—
3	1·9880	—	2·3443	1·4601	—

Angles between planes (°)

Plane	angle
1—2	93·6
1—3	90·1
2—3	84·1

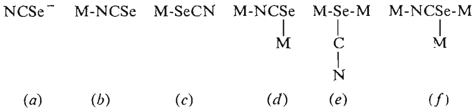
to the central atom). Coordination of the selenocyanate ligand to the central Cu(I) or Cu(II) atom may occur through the selenium or nitrogen monofuctionally, as a bridge through the selenium and nitrogen atoms simultaneously, or through the selenium atom to two central copper atoms as in the compound $Cu_3(en)_2(SeCN).(CN)_3.H_2O$.

The selenocyanate group is bonded differently in each of the five known crystal structures. This fact indicates the great variability of bonding abilities in the selenocyanate ligand which is generally less willing to enter into bridging bonds and which is preferably coordinated to the central copper atom through the nitrogen atom.

Coordination of the SeCN group through the selenium or nitrogen atom involves different bond angles. The N–Se–C bond angle varies around the tetrahedral value (*e.g.* in $Cu_3(en)_2(SeCN)_2(CN)_2.H_2O$ it equals 99·9°, 96·6° and 93·0° in $Cu_3(en).(Se(CN)(CN)_3.H_2O)$ and the M–N–C bond angle approaches the linear value (*e.g.* in $Cu_3(en)_2(SeCN)_2(CN)_2.H_2O$ it equals 161·8° and 159·0°). Differences in the M—N—C bond angle were observed in both terminal and bridging coordination of the selenocyanate ligand.

The SeCN group in the crystal structures is not completely linear and the values of the N—C—Se bond angle differ significantly from 180°. A marked decrease in this angle was observed in both cuprous-cupric compounds. The values of the N—C—Se bond angle varied around 175°.

The internuclear distances of the C—N atoms in the SeCN group varied around a value of $1{\cdot}13 \,.\, 10^{-10}$ m. The minimal value of this distance, $1{\cdot}12 \,.\, 10^{-10}$ m, was observed in the compound $Cu_3(en)_2(SeCN)(CN)_3.H_2O$ and maximal values, $1{\cdot}15 \,.\, 10^{-10}$ m in the compound $Cu_3(en)_2(SeCN)_2(CN)_2.H_2O$. The internuclear distance Se—C differed little from a value of $1{\cdot}80 \,.\, 10^{-10}$ m. It follows from data[8,9,11,19,20] for known crystal structures of selenocyanate compounds that the SeCN ligand is bonded by a maximum of two coordination bonds through the nitrogen atom. Combination of these alternatives leads to 6 theoretically possible ways of bonding the selenocyanate group:



$$\begin{array}{cccccc} NCSe^- & M\text{-}NCSe & M\text{-}SeCN & M\text{-}NCSe & M\text{-}Se\text{-}M & M\text{-}NCSe\text{-}M \\ & & & | & | & | \\ & & & M & C & M \\ & & & & | & \\ & & & & N & \\ (a) & (b) & (c) & (d) & (e) & (f) \end{array}$$

Of these possibilities, so far only (*f*) has not been observed in the coordination of the SeCN ligand in compounds of mono- and divalent copper. The free nitrogen atom in variation (*a*) or (*c*) can also participate in weak hydrogen bonds, as, *e.g.*, in $Cu_3(en)_2(SeCN)(CN)_3.H_2O$ and $[Cu(en)_2(NO_3)](SeCN)$, where there is intermolecular contact between the SeCN group and the ethylenediamine molecules (SeCN...H—N).

Bridging coordination of the selenocyanate ligand, types (*d*) and (*e*), was found in two cuprous-cupric compounds. A tendency towards coordination through the selenium atom predominates in these different types of bridging coordination of SeCN ligands. A change in the bridging method of coordination of the selenocyanate group in the compound $Cu_3(en)_2(SeCN)(CN)_3.H_2O$ results from a change in the number of cyanate ligands present in the coordination sphere of the Cu(I) atom. Because of the grater length of the selenocyanate group compared to the CN group, the bridging type of bonding of —SeCN— in $Cu_3(en)_2(SeCN)(CN)_3.H_2O$ is unsuitable in the most closely packed arrangement of atoms in the unit cell of the crystal. The shorter bridging bond through the selenium atom, —Se—, becomes more favourable, where the sum of the bonding distances ($\sim 5 \cdot 10^{-10}$ m) is approximately equal to the sum of the covalant distances —C—N— N.

So far, the bonding distances and coordination ability of the selenocyanate ligand have been treated to a relatively small degree because of the small amount of experimental data so far obtained on the SeCN complexes of mono- and bivalent copper. More experimental information on the structure of selenocyanate compounds of mono- and divalent copper will be required before more general conclusions can be drawn on the properties of these compounds.

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