

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

Viktor VRÁBEL and Ján GARAJ

Institute of Chemical Technology,

Slovak Institute of Technology,

Department of Analytical Chemistry, 880 37 Bratislava

Received October 30th, 1980

The crystal structure of $[\text{Cu}(\text{en})_2(\text{NO}_3)]\text{SeCN}$ was solved by the single-crystal X-ray structural analysis method. The compound crystallizes in the monoclinic system with space group Pc . The unit cell has dimensions: $a = 0.9254(3)$, $b = 1.4018(3)$, $c = 0.9722(5)$ nm, $\beta = 99.20(3)^\circ$. The structure was refined by the least squares method to a final value of $R = 6.8\%$ for 1965 observed reflections.

The crystal structure consists of polymeric cation chains $[\text{Cu}(\text{en})_2(\text{NO}_3)]^+$ and of free uncoordinated SeCN^- anions. The nitrate ion NO_3^- forms a bridging unit between two $[\text{Cu}(\text{en})_2]^{2+}$ cations. The coordination polyhedron around the Cu(II) atom is a deformed octahedron, formed of two ethylenediamine molecules and two oxygen atoms of the NO_3^- ions, bonded to divalent copper in the axial direction along the long coordinates. The crystal structure contains selenocyanate which is not bonded through a covalent bond to the central atom, but there are intermolecular contacts with its immediate surroundings.

Coordination compounds of divalent copper containing pseudohalide ligands CN^- , OCN^- , SNC^- and SeCN^- have a number of unusual stereochemical properties, which have led to rather intensive study of these substances. These unusual properties result from the fact that divalent copper as the central atom has a tendency to form more or less deformed polyhedra and from the fact that these pseudohalide ligands are characterized by considerable variability in the manner of coordination to the central Cu(II) atom. They can be bonded either monofunctionally or through bridges in compounds, whereas the manner and tendency to form bridges is very different for individual ligands.

The thiocyanate complexes of Cu(II) are among the most intensively studied pseudohalide complexes of copper. It follows from data on the known crystal structures of thiocyanate compounds of copper¹⁻⁹ that the thiocyanate ligand has at most 3 coordination bonds to the sulphur atom¹⁰ and a maximum of two coordination bonds to the nitrogen atom¹¹⁻¹². While the Cu(II)-S-CN bond angle in these compounds lies close to the tetrahedral value, the Cu(II)-N-CS bond angle approaches the linear values. Provided steric conditions are suitable, the SCN^- ion in coordination compounds prefers bonding through the sulphur atom, on which a larger portion of the negative charge is localized¹³.

Structural data on selenocyanate compounds of divalent copper are lacking in the literature. Only two crystal structures of copper(II) selenocyanate compounds are known, $[\text{Cu}(\text{N},\text{N}'\text{-dimethylethylenediamine})_2(\text{NCSe})_2]^{14}$ and $[\text{Cu}(1,3\text{-diamino-2-propanol})_2(\text{SeCN})_2]^{15}$, in which the SeCN group is bonded monofunctionally to divalent copper, through the nitrogen atom in the former compound and through the selenium atom in the latter. The coordination polyhedron around the Cu(II) atom in both compounds is an elongated bipyramid.

EXPERIMENTAL

The blue-purple crystals with the composition $[\text{Cu}(\text{en})_2(\text{NO}_3)]\text{SeCN}$ were prepared from an aqueous solution of the $\text{Cu}(\text{NO}_3)_2\text{-en-NH}_4\text{OH-KSeCN}$ system in the following manner: an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ was mixed with a concentrated ethylenediamine solution, with subsequent addition of concentrated ammonia and an aqueous solution of KSeCN ; a blue-purple solution was formed which could be crystallized in open crystallization dishes at a temperature of about 25°C . The resultant solution had a molar ratio of components of $\text{Cu}^{2+} : \text{en} : \text{NH}_4\text{OH} : \text{SeCN}^- = 1 : 2 : 1 : 1$; plate-shaped crystals started to form after about 30 h and were filtered under vacuum and washed with carbon tetrachloride. The crystals are easily soluble in water and other polar solvents.

The percent contents of C, N and H were determined on a CHNO analyzer, model 1 102, from Carlo Erba. Copper was determined complexometrically using murexide indicator after prior decomposition of the sample with sulphuric acid and potassium peroxodisulphate. The solution was evaporated to dryness and the residue was dissolved in distilled water. The pH was adjusted and the resultant solution was titrated. Analysis: for $\text{C}_5\text{H}_{16}\text{N}_6\text{O}_3\text{SeCu}$ (350.7) was

TABLE I
Basic crystallographic data for $[\text{Cu}(\text{en})_2(\text{NO}_3)][(\text{SeCN})]$

Crystallographic system	monoclinic
Space group	Pc
Dimensions of the unit cell and their standard deviations	$a = 0.9254 (3) \text{ nm}$ $b = 1.4018 (3)$ $c = 0.9722 (5)$ $\beta = 99.20 (3)^\circ$
Volume of the unit cell	$V = 1.2450 \text{ nm}^3$
Number of formula units per unit cell	$Z = 4$
Number of electrons per unit cell	$F(000) = 700$
Measured crystal density	$D_0 = 1.86 \cdot 10^3 \text{ kg m}^{-3}$
Calculated crystal density	$D_c = 1.87 \cdot 10^3 \text{ kg m}^{-3}$
Linear absorption coefficient	$\mu = 4380 \text{ m}^{-1}$

calculated: 23.96% N, 17.12% C, 4.60% H, 18.12% Cu and found 16.90% C, 4.55% H, 23.90% N, 18.36% Cu. The crystal density, $D_0 = 1.86 \cdot 10^3 \text{ kg m}^{-3}$, was found at room temperature by the flotation method (bromoform-carbon tetrachloride). The calculated density for $Z = 4$ per unit cell is $D_c = 1.87 \cdot 10^3 \text{ kg m}^{-3}$.

The compound $[\text{Cuen}_2(\text{NO}_3)]\text{SeCN}$ crystallizes in the monoclinic system (Table I). It follows from the rules for systematic absences of reflections of the $[h0l]$ type that there are two possible

TABLE II

Calculated values of the fractional coordinates for the hydrogen atoms in the ethylenediamine molecules in $[\text{Cuen}_2(\text{NO}_3)]\text{SeCN}$

Atom	x/a	y/b	z/c
H1(N1)	0.0514	0.2740	0.6013
H2(N1)	0.0811	0.3758	0.6828
H1(N2)	0.0720	0.3817	0.2387
H2(N2)	0.0400	0.4781	0.3232
H1(N3)	0.3423	0.3902	0.2659
H2(N3)	0.3936	0.4784	0.3725
H1(N4)	0.3743	0.3640	0.7222
H2(N4)	0.3745	0.2597	0.6474
H1(C1)	-0.1767	0.3391	0.5523
H2(C1)	-0.1018	0.4554	0.5430
H1(C2)	-0.0950	0.2909	0.3286
H2(C2)	-0.1810	0.4040	0.2955
H1(C3)	0.5040	0.2803	0.3883
H2(C3)	0.6071	0.3878	0.3844
H1(C4)	0.5446	0.4308	0.6067
H2(C4)	0.6043	0.3100	0.6201
H1(N5)	0.0028	0.0028	0.1171
H2(N5)	0.0642	0.0641	0.2169
H1(N6)	0.0304	0.0305	-0.2274
H2(N6)	0.0206	0.0208	-0.1231
H1(N7)	0.3282	0.1362	-0.2027
H2(N7)	0.3580	0.2299	-0.1023
H1(N8)	0.3309	0.0990	0.2507
H2(N8)	0.3560	0.0035	0.1613
H1(C5)	-0.2025	0.1272	0.0981
H2(C5)	-0.0873	0.2270	0.0824
H1(C6)	-0.1487	0.0629	-0.1361
H2(C6)	-0.2171	0.1814	-0.1604
H1(C7)	0.4764	0.0379	-0.0545
H2(C7)	0.5744	0.1473	-0.0539
H1(C8)	0.4752	0.1975	0.1330
H2(C8)	0.5762	0.0894	0.1627

space groups with symmetry Pc or $P2/c$ for $l = 2n + 1$ (ref.¹⁶). The alternate space groups Pc and $P2/c$ of the studied crystal structure differ in that the $P2/c$ group is centrally symmetrical. Both groups exhibit the same extinction but have different intensity statistics which, however, did not unambiguously differentiate between group Pc and $P2/c$. The approximate values of the

TABLE III

Refined positional parameters for the nonhydrogen atoms in the two monomer units in the crystal structure of the compound $[Cuen_2(NO_2)] [(SeCN)] \cdot 10H_2O$ (standard deviations given in parentheses)

Atom	x/a	y/b	z/c
Se1	7851 (0)	1201 (2)	5110 (0)
Se2	6163 (3)	3803 (2)	9838 (4)
Cu1	2119 (3)	3750 (2)	4772 (3)
Cu2	1783 (3)	1778 (2)	-0001 (2)
N1	0566 (18)	3447 (12)	5894 (15)
N2	0499 (16)	4071 (10)	3291 (15)
N3	3736 (17)	4083 (15)	3658 (20)
N4	3790 (19)	3302 (13)	6325 (19)
N5	0280 (20)	0927 (17)	1188 (25)
N6	0173 (20)	1704 (11)	8689 (19)
N7	3467 (20)	1589 (11)	8960 (21)
N8	3459 (24)	0745 (15)	1574 (28)
N9	1788 (14)	1208 (10)	4694 (13)
N10	2350 (27)	3780 (15)	0067 (19)
N11	5045 (24)	1202 (16)	6185 (25)
N12	8969 (28)	3802 (19)	8762 (32)
C1	9114 (25)	3803 (15)	5190 (22)
C2	9112 (23)	3664 (17)	3557 (21)
C3	5109 (27)	3540 (18)	4246 (27)
C4	5171 (23)	3578 (14)	5739 (24)
C5	8938 (27)	1518 (19)	0569 (30)
C6	8713 (32)	1373 (18)	8935 (34)
C7	4765 (28)	1133 (21)	9729 (29)
C8	4764 (35)	1218 (18)	1076 (41)
C11	6115 (26)	1208 (18)	5752 (22)
C12	7898 (23)	3796 (15)	9196 (25)
O1	1986 (34)	1941 (13)	3929 (26)
O2	2008 (14)	0391 (8)	4050 (13)
O3	1765 (19)	1297 (11)	5886 (17)
O4	2442 (19)	4592 (10)	0724 (16)
O5	2075 (18)	3065 (10)	0842 (15)
O6	2436 (18)	3767 (11)	8901 (16)

lattice parameters, calculated from rotation and Weissenberg patterns, were refined on a Syntex $P2_1$ diffractometer by the least squares method on the basis of 8 precisely centred reflections using MoK_α radiation.

A crystal with dimensions $0.2 \times 0.2 \times 0.3$ mm was chosen to determine the basic crystallographic data and for measuring the intensities. The integral intensity was measured on a Syntex $P2_1$ four-circle computer-controlled diffractometer, equipped with a scintillation counter and a pulse height analyzer. Graphite monochromatic MoK_α radiation was used and the intensities were recorded in the range $0^\circ < 2\theta \leq 55^\circ$. Of the overall number of 2 888 recorded reflections, only 1 965 with $I \geq 1.96\sigma(I)$ were considered as observed. All the intensities were corrected for the Lorentz and polarization factors and were converted to an absolute scale. No correction was made for absorption.

On the basis of systematic absences of reflections, the structure of the $[\text{Cuen}_2(\text{NO}_3)]\text{SeCN}$ compound was solved by the heavy atom method in the two symmetry groups Pc and $P2/c$. In the first phase of the solution the positions of two heavy atoms were found from the three-dimensional Patterson function. The positions of a further two heavy atoms in $1/2$ of the unit cell were found from the three-dimensional Fourier maps calculated for the Pc and $P2/c$ symmetry groups phased for the contributions of the heavy atoms found from the Patterson functions. The distribution of the maxima for the Cu and Se atoms in the whole cell suggested group Pc , for which the structure was finally successfully solved. For this group, the independent part

TABLE IV

Bonding interatomic distances (nm) in the two crystallographically independent monomer units in the structure of $[\text{Cuen}_2(\text{NO}_3)][\text{SeCN}]$ and their standard deviations

Bond	Bond length	Bond	Bond length
Cu1-N1	0.1984 (16)	Cu2-N5	0.1977 (21)
Cu1-N2	0.1958 (15)	Cu2-N6	0.1945 (18)
Cu1-N3	0.2037 (17)	Cu2-N7	0.2071 (19)
Cu1-N4	0.2078 (18)	Cu2-N8	0.2088 (25)
Cu1-O1	0.2662 (20)	Cu2-O2	0.2407 (12)
Cu1-O4	0.2515 (15)	Cu2-O5	0.2770 (15)
Se1-C11	0.1815 (24)	Se2-C12	0.1814 (22)
C11-N11	0.1136 (33)	C12-N12	0.1138 (35)
N1-C1	0.1493 (28)	N5-C5	0.1533 (33)
N2-C2	0.1465 (26)	N6-C6	0.1484 (34)
N3-C3	0.1513 (31)	N7-C7	0.1457 (32)
N4-C4	0.1530 (27)	N8-C8	0.1523 (39)
C1-C2	0.1600 (29)	C5-C6	0.1583 (44)
C3-C4	0.1445 (35)	C7-C8	0.1315 (48)
N9-O1	0.1298 (26)	N10-O4	0.1289 (26)
N9-O2	0.1337 (18)	N10-O5	0.1303 (25)
N9-O3	0.1167 (21)	N10-O6	0.1139 (24)

of 1/2 of the unit cell contains two formula units. The positions of the other non-hydrogen atoms of the complex were found by further application of Fourier synthesis on the electron density phased from the contributions of two copper atoms and two selenium atoms.

The structure was refined to a value of $R = 0.13$ in 3 least squares cycles using the diagonal matrix, isotropic thermal parameters for the non-hydrogen atoms and the weighing scheme according to Cruickshank¹⁷, $w = (a + |F_0| + |F_0|^2)^{-1/2}$, where $a = 9.32$ and $b = 0.001$, to a value of $R = 0.13$. In a further 5 refinement cycles, anisotropic thermal vibrations were assumed for all the atoms, which, together with the positional parameters, were refined by the least squares method using the minimization function $\sum w(|F_0| - |F_c|)^2$ in a 9×9 block-dia-

TABLE V

Bonding angles ($^\circ$) in the two crystallographically independent monomer units in the structure of $[\text{Cuen}_2(\text{NO}_3)](\text{SeCN})$

Atom	Angle	Atom	Angle
Cu1-N1-C1	110.8 (1.2)	Cu2-N5-C5	106.0 (1.6)
Cu1-N2-C2	111.7 (1.1)	Cu2-N6-C6	113.4 (1.5)
Cu1-N3-C3	109.1 (1.4)	Cu2-N7-C7	104.5 (1.5)
Cu1-N4-C4	102.8 (1.2)	Cu2-N8-C8	100.0 (1.9)
Cu1-O1-N9	125.5 (1.6)	Cu2-O2-N9	125.0 (0.9)
Cu1-O4-N10	129.3 (1.3)	Cu2-O5-N10	125.6 (1.2)
Se1-C11-N11	178.2 (2.2)	Se2-C12-N12	178.3 (2.4)
N1-Cu1-N2	85.2 (0.6)	N5-Cu2-N6	85.0 (0.8)
N1-Cu1-N3	178.6 (0.7)	N5-Cu2-N7	171.8 (0.9)
N1-Cu1-N4	93.2 (0.7)	N5-Cu2-N8	91.7 (0.9)
N1-Cu1-O1	87.9 (0.8)	N5-Cu2-O2	100.0 (0.8)
N1-Cu1-O4	92.9 (0.6)	N5-Cu2-O5	92.4 (0.8)
N2-Cu1-N4	175.7 (0.6)	N6-Cu6-N8	172.9 (0.8)
N2-Cu1-O1	90.1 (0.7)	N6-Cu2-O2	101.5 (0.6)
N2-Cu1-O4	95.1 (0.5)	N6-Cu2-O5	81.9 (0.5)
N3-Cu1-N4	86.0 (0.7)	N7-Cu2-N8	84.8 (0.9)
N3-Cu1-O1	93.2 (0.9)	N7-Cu2-O2	85.2 (0.7)
N3-Cu1-O4	85.9 (0.7)	N7-Cu2-O5	92.0 (0.7)
N4-Cu1-O1	85.9 (0.8)	N8-Cu2-O2	87.1 (0.6)
N4-Cu1-O4	89.0 (0.6)	N8-Cu2-O5	80.4 (0.6)
O1-Cu1-O4	174.9 (0.7)	O2-Cu2-O5	167.4 (0.5)
N1-C1-C2	105.8 (1.6)	N5-C5-C6	107.0 (2.1)
N2-C2-C1	105.4 (1.6)	N6-C6-C5	98.3 (2.1)
N3-C3-C4	104.9 (1.9)	N7-C7-C8	109.8 (2.4)
N4-C4-C3	117.6 (1.8)	N8-C8-C7	113.8 (2.7)
O1-N9-O2	111.3 (1.5)	O4-N10-O5	112.8 (1.7)
O1-N9-O3	120.7 (1.7)	O4-N10-O6	119.6 (2.0)
O2-N9-O3	125.8 (1.5)	O5-N10-O6	127.5 (2.0)

gonal approximation and the R factor, defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$, decreased to a value of 0.085.

Introduction of hydrogen atoms into the structure, whose positions were calculated on the assumption that sp^3 hybridization exists for the carbon and nitrogen atoms of the ethylenediamine molecules (Table II), reduced the R factor to a final value of 0.068. The positions of the hydrogen atoms were not refined. In the last refining cycle, the shifts in all the parameters were less than 0.2σ . Differential Fourier synthesis of the residual electron density, calculated without the hydrogen atoms, did not contain maxima higher than $1.2 \cdot 10^3 \text{ e nm}^{-3}$ at the positions corresponding to the hydrogen atoms.

The refined fractional coordinates of the non-hydrogen atoms are given in Table III. The interatomic bonding distances and valence angles with standard deviations and values of the coefficients of the equation of the plane are given in Tables IV, V and VI. In Fig. 1 is given the unit cell projection into the (100) plane with designation of the atoms. Fig. 2 gives a stereographic projection of the monomer unit of $[\text{Cu}(\text{en})_2(\text{NO}_3)]\text{SeCN}$. All the calculations were carried out on a Siemens 4004/150 computer using a system of programs¹⁸.

Description of the Structure and Discussion

The crystal structure of the studied complex consists of a polymeric $[\text{Cu}(\text{en})_2(\text{NO}_3)]^+$ cationic chain and of free uncoordinated SeCN^- ions (Fig. 1). The Cu(II) atom is surrounded by a tetragonally deformed octahedron formed of 4 nitrogen atoms

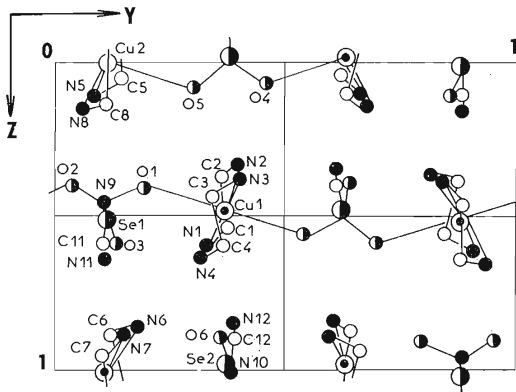


FIG. 1

The unit cell of the structure of the compound $[\text{Cu}(\text{en})_2(\text{NO}_3)] [\text{SeCN}]$ projected into the [100] plane

from two ethylenediamine molecules at a distance of 0.201 and 0.202 nm and two oxygen atoms from the NO_3^- ions, bonded in the axial direction along the long coordinates. Tetragonal conformation in common in copper compounds of the type $[\text{Cu}(\text{en})_2]\text{X}_2$ and this regular presence of long axial bonding distances is usually included in the concept of semi-coordination¹⁹.

The nitrate ion NO_3^- forms a bridging unit between two $[\text{Cu}(\text{en})_2]^{2+}$ cations and thus forms an infinite chain structure. The four donor nitrogen atoms of the ethylene-

TABLE VI

Values of the coefficients of the equation of the plane $AX + BY + CZ = D$ constructed by the least squares method through selected atoms

Plane	Atoms	A	B	C	D
(1)	N1, N2, N3, N4	0.0174	-0.9322	-0.3615	-6.5099
(2)	N2, N4, O1, O4	0.7691	0.1805	-0.6130	-0.9429
(3)	N1, N3, O1, O4	-0.5781	0.2947	-0.7609	-2.6914
(4)	N1, N2, Cu1	0.0300	-0.9446	-0.3267	-6.4251
(5)	N3, N4, Cu1	0.0061	-0.9198	-0.3924	-6.6242
(6)	N5, N6, N7, N8	-0.0188	-0.9061	-0.4226	-1.6505
(7)	N6, N8, O2, O5	0.7642	0.2438	-0.5971	1.7750
(8)	N5, N7, O2, O5	-0.5761	0.2504	-0.7781	-0.5946
(9)	N5, N6, Cu2	-0.1045	-0.9008	-0.4215	-1.6597
(10)	N7, N8, Cu2	0.0618	-0.9065	-0.4175	-1.3948

TABLE VII

Angles ($^\circ$) between planes (1) to (10)

Plane	Angle	Plane	Angle
(1)-(2)	86.2	(6)-(7)	89.0
(1)-(3)	90.6	(6)-(8)	83.5
(2)-(3)	85.7	(7)-(8)	85.1
(2)-(4)	87.0	(7)-(9)	92.7
(2)-(5)	85.5	(7)-(10)	85.7
(3)-(4)	92.7	(8)-(9)	80.6
(3)-(5)	88.6	(8)-(10)	86.4
(4)-(5)	4.2	(9)-(10)	9.5

diamine molecules form roughly a square planar base of the bipyramid. The Cu(II) atoms are not located in the plane constructed by the least squares method through the 4 nitrogen atoms of the ethylenediamine molecule, but lie slightly outside of this plane at distances of 0.002 and 0.01 nm (Fig. 2).

The N–Cu–N intrachelate angles are 85.2 and 86.0° or 85.0 and 84.8° in the second crystallographically independent $\text{Cuen}_2(\text{NO}_3)$ SeCN monomer unit (Table VI) and the angles between the Cu–O bonds and the CuN_4 coordination plane are 86.2 and 90.6° or 89.0 and 83.5° (Table VII) and are comparable with the corresponding values found for the similar compound $\text{Cuen}_2(\text{NO}_3)_2$ (ref.²⁰)

In contrast to the symmetrical “gauche” conformation of the ethylenediamine molecule which has frequently been observed for complex compounds of Ni(II) and Co(III) (refs^{21–24}), the gauche conformation is unsymmetrical in this compound with the C1 and C2 atoms 0.0287 nm above and 0.0417 nm below the N1–Cu1–N2 coordination plane and with the C3 and C4 atoms 0.0486 nm above and 0.0127 nm below the N2–Cu1–N4 coordination plane. The conditions are similar in the second

TABLE VIII
Deviations (nm · 10⁴) of some atoms from planes (1) to (10)

Atom	(1)	(4)	(5)	Atom	(6)	(9)	(10)
Cu1	– 24	–	–	Cu2	123	–	–
N1	– 48	–	– 43	N5	– 11	–	–255
N2	46	–	135	N6	10	–	–223
N3	– 44	– 41	–	N7	– 10	– 279	–
N4	44	144	–	N8	10	– 228	–
C1	–289	–287	–244	C5	–489	–376	–829
C2	464	417	552	C6	358	464	13
C3	482	528	486	C7	237	–127	338
C4	– 89	4	–127	C8	–413	–757	–322

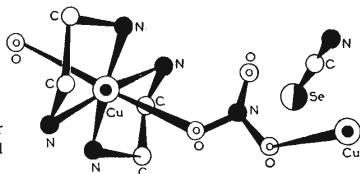


FIG. 2
Stereographic projection of the monomer unit of the crystal structure of the compound $[\text{Cu}(\text{en})_2(\text{NO}_3)](\text{SeCN})$

monomeric unit (Table VIII). The asymmetry of the ethylenediamine molecule with respect to the CuN_4 coordination plane is similar to that found for copper(II) compounds: $[\text{Cu(en)}_2](\text{SCN})_2$ (ref.³), $[\text{Cu(en)}_2]\text{Hg}(\text{SCN})_4$ (ref.²⁵), $[\text{Cu(en)}_2](\text{NO}_3)_2$ (ref.²⁰) and $[\text{Cu}(\text{H}_2\text{O})\text{Cl}(\text{en})_2]\text{Cl}$ (ref.²⁶).

The different conformations of the ethylenediamine molecules do not have any effect on the minimum energy of the system, as was demonstrated by Gollogly and Hawkins²⁷. Using conformational analysis of cobalt(III) ethylenediamine complexes, these authors found that the minimum torsion and bonding energies of the ethylenediamine ring can be attained by both the symmetrical and asymmetrical forms.

The C-C and C-N bonding distances in the ethylenediamine molecules (Table IV) are comparable with the values found in compounds: average values of C-C 0.156 nm and C-N 0.146 and 0.149 nm in $[\text{Cu}(\text{en})_2](\text{SCN})_2$ (ref.³), C-C 0.154 nm and C-N 0.148 nm in $[\text{Cu}(\text{en})_2](\text{NO}_3)_2$ (ref.²⁰), C-C 0.150 nm and C-N 0.146 and 0.150 nm in $[\text{Ni}(\text{en})_2](\text{SCN})_2$ (ref.²²), C-C 0.150 nm and C-N 0.150 nm in $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ (ref.²³) and C-C 0.151 nm and C-N 0.150 nm in $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]$ (ref.²⁶).

The deformed octahedral surroundings of the central atom, Cu(II), are completed by the NO_3 groups located at the apexes of the bipyramid at distances of 0.266 and 0.251 nm or 0.241 and 0.277 nm.

The limiting value of the Cu- ONO_2 chemical interaction lies in the region 0.28 nm, which Addison and coworkers²⁸ took as a criterion for differentiation between monodentate asymmetrical and chelate symmetrical bonding of the NO_3^- ions in the complexes. Symmetrical bonding of NO_3^- ions to transition metals occurs rarely. The nitrate group is bonded in this manner in some complexes of trivalent cobalt and iron^{29,30}.

The deviation of the NO_3^- ions from planarity is small (the N atoms lie 0.0023 and 0.0027 nm out of the oxygen atoms plane) but significant. The bonding distances in the NO_3^- ions also differ significantly. The significant differences in the N-O

TABLE IX
Intermolecular distances <0.35 nm observed in the crystal structure of $[\text{Cu(en)}_2(\text{NO}_3)][(\text{SeCN})]$

N7-H...O3	0.3175	N7-H...O6	0.3196
N1-H...O3	0.3213	N3-H...O6	0.3268
N8-H...O3	0.3280	N7-H...N11	0.3150
H6-H...O3	0.3348	N4-H...N11	0.3174
H4-H...O3	0.3367	N8-H...N11	0.3311
N5-H...O3	0.3439	N6-H...N12	0.3149
N4-H...O6	0.3044	N2-H...N12	0.3363
N1-H...O6	0.3182	N1-H...N12	0.3395

bonding distances in the nitrate group are correlated with the participation of the O atoms in the formation of Cu–O coordination bonds (significantly longer N–O bonds) and with participation of the O atoms in formation of hydrogen bonds (significantly shorter N–O bonds). The average values of the N–O distances of 0.127 or 0.125 nm can be compared with the values found in compounds: 0.126 nm in $[\text{Cu}(\text{en})_2](\text{NO}_3)_2$ (ref.²⁰), 0.124 nm in N_2O_5 (ref.³¹) and 0.124 nm in $(\text{C}_2\text{H}_8\text{N}_3)\text{NO}_3$ (ref.³²). The O–N–O valence angles are close to 120° .

The arrangement of the atoms in 1/2 of the unit cell of two independent $[\text{Cu}(\text{en})_2 \cdot (\text{NO}_3)]\text{SeCN}$ monomer units is pseudocentrosymmetric. The "symmetry" centre is roughly located at the place where $x = 0.2$, $y = 0.25$ and $z = 0.25$, which can be multiplied to give 8 equivalent positions in the whole cell, by translation in the direction of the x , y and z axes by 1/2 of the basic vectors.

The selenocyanate groups act as discrete noncoordinating anions in the crystal structure. The shortest intermolecular distances between selenocyanate anions, NO_3 ligands and ethylenediamine molecules indicate the presence of weak hydrogen bonds of the $\text{O}_2\text{NO} \dots \text{N}-\text{H}(\text{en})$ and $\text{SeCN} \dots \text{H}-\text{N}(\text{en})$ types (Table IX). The selenocyanate ions in the crystal structure are practically linear and the values of the Se–C–N bond angles differ very little from 180° . Because of its ionic character, the compound $[\text{Cu}(\text{en})_2(\text{NO}_3)]\text{SeCN}$ is easily soluble in water and other polar solvents.

REFERENCES

1. Cannas M., Carta G., Marongiu G.: *J. Chem. Soc., Dalton Trans.* 550 (1974).
2. Cannas M., Carta G., Marongiu G.: *J. Chem. Soc., Dalton Trans.* 553 (1974).
3. Brown B. W., Lingafelter E. C.: *Acta Crystallogr.* 17, 254 (1964).
4. Garaj J., Dunaj-Jurčo M., Lindgren O.: *This Journal* 36, 3863 (1971).
5. Gaughan A. P., Ziolo R. F., Dori Z.: *Inorg. Chim. Acta* 4, 640 (1970).
6. Cannas M., Carta G., Marongiu G.: *J. Chem. Soc., Dalton Trans.* 556 (1974).
7. Porai-Koshits M. A., Tishchenko G. N.: *Kristallografiya* 4, 239 (1959).
8. Jain P. C., Lingafelter E. C.: *J. Amer. Chem. Soc.* 89, 6131 (1967).
9. Clark R. J. H., Williams C. S.: *Spectrochim. Acta* 22, 1081 (1966).
10. Kabešová M., Dunaj-Jurčo M., Serátor M., Gažo J., Garaj J.: *Inorg. Chim. Acta* 17, 161 (1976).
11. Andreotti G. D., Coghi L., Nardelli M., Scarabotto P.: *J. Cryst. Mol. Struct.* 1, 147 (1971).
12. Cannas M., Carta G., Marongiu G.: *J. Chem. Soc.* 251 (1973).
13. Wagner E. L.: *J. Chem. Phys.* 43, 2728 (1965).
14. Pajunen A., Korvenranta J.: *Suom. Kemistilehti B46*, 139 (1974).
15. Kivekas R.: *Finn. Lett.* 71 (1978).
16. *International Tables for X-Ray Crystallography*, Vol. I. Kynoch Press, Birmingham (1969).
17. Cruickshank D. W. J., Pilling D. E., Bujosa A., Lovell F. M., Truter M. R.: *Computing Methods and Phase Problems in X-Ray Analysis*, Symposium Publications Division, p. 32. Pergamon Press, New York 1961.
18. Ahmed F. R., Hall S. R., Pippy M. E., Huber C. P.: Biochemistry Laboratory, National Research Council of Canada, Ottawa 7, Canada.

19. Procter I. M., Hathaway B. J., Nicholls P.: *J. Chem. Soc. (A)* 1678 (1968).
20. Komiyama Y., Lingafelter E. C.: *Acta Crystallogr.* 17, 1145 (1964).
21. Brown B. W., Lingafelter E. C.: *Acta Crystallogr.* 16, 753 (1963).
22. Swink L. N., Ataji M.: *Acta Crystallogr.* 13, 539 (1960).
23. Mazus M. D., Ablov A. V., Biyushkin V. N., Popa E. V., Malinovskii T. I.: *Dokl. Akad. Nauk USSR* 215, 1376 (1974).
24. Iwata M., Nakutzu K., Saito Y.: *Acta Crystallogr.* B25, 2562 (1969).
25. Scouloudi H.: *Acta Crystallogr.* 6, 651 (1953).
26. Mazzi F.: *R. C. Soc. Mineral. Ital.* 9, 148 (1953).
27. Gollogly J. R., Hawkins C. J.: *Inorg. Chem.* 8, 1168 (1969).
28. Addison C. C., Logan N., Wallwork S. C., Garner C. D.: *Quart. Rev.* 25, 289 (1971).
29. Hilton J., Wallwork S. C.: *Chem. Commun.* 871 (1968).
30. King T. J., Logan N., Morris A., Wallwork S. C.: *Chem. Commun.* 554 (1971).
31. Grison E., Eriks K., de Vries J. L.: *Acta Crystallogr.* 3, 290 (1950).
32. Curtis R. M., Pasternak R. A.: *Acta Crystallogr.* 8, 675 (1955).

Translated by M. Štulíková.