BILLIG, E., WILLIAMS, R., BERNAL, I., WATERS, J. H. & GRAY, H. B. (1964). *Inorg. Chem.* **3**, 663–666.

BRAY, J. W., HART, H. R. JR, INTERRANTE, L. V., JACOBS, I. S., KASPER, J. S., WATKINS, G. D., WEE, S. H. & BONNER, J. C. (1975). *Phys. Rev. Lett.* **35**, 744–747.

EISENBERG, R. (1970). *Prog. Inorg. Chem.* **12**, 295–391.

ENDRES, H., KELLER, H. J., MORONI, W., NÖTHE, D. & VU DONG (1978a). *Acta Cryst.* **B34**, 1703–1705.

ENDRES, H., KELLER, H. J., MORONI, W., NÖTHE, D. & VU DONG (1978b). *Acta Cryst.* **B34**, 1823–1827.

EPSTEIN, A. J., CONWELL, E. M., SANDMAN, D. J. & MILLER, J. S. (1977). *Solid State Commun.* **23**, 355–358.

FORRESTER, J. D., ZALKIN, A. & TEMPLETON, D. H. (1964). *Inorg. Chem.* **3**, 1507–1515.

FRITCHIE, C. J. (1966). *Acta Cryst.* **20**, 892–898.

FUJII, G., SHIROTANI, I. & NAGANO, H. (1977). *Bull. Chem. Soc. Jpn*, **50**, 1726–1730.

GOLDBERG, I. & SHMUELI, U. (1973a). *Acta Cryst.* **B29**, 421–431.

GOLDBERG, I. & SHMUELI, U. (1973b). *Acta Cryst.* **B29**, 1440–1446.

HOVE, M. J., HOFFMAN, B. M. & IBERS, J. A. (1972). *J. Chem. Phys.* **56**, 3490–3502.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

INTERRANTE, L. V., BRAY, J. W., HART, H. R. JR, KASPER, J. S., PIACENTE, P. A. & WATKINS, G. D. (1977). *J. Am. Chem. Soc.* **99**, 3523–3524.

INTERRANTE, L. V., BROWALL, K. W., HART, H. R. JR, JACOBS, I. S., WATKINS, G. D. & WEE, S. H. (1975). *J. Am. Chem. Soc.* **97**, 889–890.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KASPER, I. S., INTERRANTE, L. V. & SECAUR, C. A. (1975). *J. Am. Chem. Soc.* **97**, 890–891.

KELLER, H. J. (1977). Editor. *Chemistry and Physics of One-Dimensional Metals.* NATO ASI Series 25. New York & London: Plenum.

KELLER, H. J., NÖTHE, D., MORONI, W. & SOOS, Z. G. (1978). *J. Chem. Soc. Chem. Commun.* pp. 331–332.

KOBAYASHI, A. & SASAKI, Y. (1977). *Bull. Chem. Soc. Jpn*, **50**, 2650–2656.

McCLEVERTY, J. A. (1968). *Prog. Inorg. Chem.* **10**, 49–221.

MILLER, J. S. (1978). Editor. *Synthesis and Properties of Low-Dimensional Materials.* Ann. NY Acad. Sci. **313**.

MILLER, J. S. & EPSTEIN, A. J. (1978). *J. Am. Chem. Soc.* **100**, 1639–1641.

MOROSIN, B. (1978). *Acta Cryst.* **B34**, 1905–1909.

MOROSIN, B., PLASTAS, H., COLEMAN, L. B. & STEWART, J. M. (1978). *Acta Cryst.* **B34**, 540–543.

PEREZ-ALBUERNE, N. A., ISETT, L. C. & HALLER, R. K. (1977). *J. Chem. Soc. Chem. Commun.* pp. 417–418.

SANDMAN, D. J. (1978). *J. Am. Chem. Soc.* **100**, 5230–5232.

SANZ, F. & DALY, J. J. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 1146–1150.

SCHMITT, R. D., WING, R. M. & MAKI, A. H. (1969). *J. Am. Chem. Soc.* **91**, 4394–4401.

SOOS, Z. G. & KELLER, H. J. (1977). In *Chemistry and Physics of One-Dimensional Metals*, edited by H. J. KELLER, pp. 391–412. NATO ASI Series 25. New York & London: Plenum.

VU DONG, ENDRES, H., KELLER, H. J., MORONI, W. & NÖTHE, D. (1977). *Acta Cryst.* **B33**, 2428–2431.

WEIHER, J. F., MELBY, L. R. & BENSON, R. E. (1964). *J. Am. Chem. Soc.* **86**, 4329–4333.

WHELAND, R. C. & GILSON, J. L. (1976). *J. Am. Chem. Soc.* **98**, 3916–3925.

WUDL, F. (1975). *J. Am. Chem. Soc.* **97**, 1962–1963.

WUDL, F., HO, C. H. & NAGEL, A. (1973). *J. Chem. Soc. Chem. Commun.* p. 923.

The Crystal and Molecular Structure of the Cuprous–Cupric Complex Aquabis(ethylenediamine)copper(II) Dicyanodi(selenocyanato)cuprate(I)

BY V. VRABEL AND J. GARAJ

Department of Analytical Chemistry, Slovak Technical University, Janska 1, 880 37 Bratislava, Czechoslovakia

AND L. KUTSCHABSKY

Zentralinstitut für physikalische Chemie, DAW, 1199 Berlin, Adlershof, Rudower Chaussee 5, German Democratic Republic

Abstract

$[Cu(C_2H_8N_2)_2(H_2O)][Cu_2(CN)_2(SeCN)_2]$, $C_8H_{18}Cu_3N_8OSe_2$ is monoclinic, space group Cc, with $a = 8·879$ (2), $b = 15·824$ (1), $c = 13·493$ (2) Å, $\beta = 106·80$ (1)°, $Z = 4$. The structure was refined to $R = 0·069$ for 1381 counter reflections. The crystal structure is formed of cations $[Cuen_2.H_2O]^{2+}$ and polymeric anions $[Cu_2(CN)_2(SeCN)_2]^{2-}$. The coordination about the Cu^{II} atom is square-pyramidal with two molecules of ethylenediamine and one molecule of water at the apex. The Cu^I atoms are tetrahedrally bonded by SeCN and CN, these being present as bridges.

Introduction

From the system Cu^{II}–en–SeCN–H_2O the formation of cuprous–cupric complexes containing cyano groups in addition to selenocyano groups may occur. These are formed after redox changes in the system. Depending on the conditions, solid crystalline substances $Cu_3en_2(SeCN)_x(CN)_{4-x}.H_2O$ where $x = 1$ and 2 (Vrabel, Kellö, Dunaj-Jurčo, Melnik & Garaj, 1975) precipitate. From the cyanide systems the complex where $x = 0$ is formed (Williams, Larson & Cromer, 1972). The equilibrium shift of the reaction $Cu^{2+} + e \rightleftharpoons Cu^+$ depends mainly on the concentration of N-containing ligands, e.g. ethylenediamine, ammonia and ligands with π-releasing properties which stabilize the oxidation state of Cu^{2+}.

Only a few crystal structures where Cu has mixed valency (Cooper & Plane, 1966; Dunaj-Jurčo & Poraj-Košic, 1967; Garaj, 1969) have been described. It appears that all ammonia or ethylenediamine molecules are bonded to divalent Cu. If their number is not sufficient to form planar coordination, they will be replaced by N atoms from the anionic ligands (e.g. NC, NCS) which form bridges. The cyanide group forms bonds between Cu atoms of different oxidation states Cu^{II}–CN–Cu^I, and the complex consists of neutral polymeric chains, as in $Cu_3(NH_3)_3(CN)_4$ (Williams, Cromer & Larson, 1971).

If insufficient groups are present to form planar coordination about Cu^{II} then such complexes consist of a cationic part in the cavities formed by the polymeric anion (Williams, Larson & Cromer, 1972; Cooper & Plane, 1966).

Experimental

Blue-violet crystals of the title compound were prepared from the system Cu^{II}–H_2O–en–KSeCN (Vrabel et al., 1975). The crystals are monoclinic with systematic absences hkl with $h + k$ odd and $h0l$ with h, l odd, indicating space groups Cc or $C2/c$. The lattice constants determined from rotation and Weissenberg photographs were refined by a least-squares procedure from 12 reflections. Intensities were measured at room temperature on a Hilger automatic diffractometer with Mo $K\alpha$ radiation and a graphite monochromator (to $2\theta = 50°$). To obtain the reflections ($0kl$–$10kl$) a crystal $0.3 \times 0.2 \times 0.2$ mm was chosen. 1381 non-zero independent reflections were obtained. These were corrected for Lorentz and polarization factors. Absorption was neglected ($\mu R = 0.6$).

The density was determined by flotation in a mixture of methyl iodide and acetone. Crystal data are given in Table 1.

Table 1. Crystal data

$C_8H_{18}Cu_3N_8OSe_2$	Space group Cc
Monoclinic	$V = 1814.9$ Å^3
$a = 8.879$ (2) Å	FW $= 590.8$
$b = 15.824$ (1)	$Z = 4$
$c = 13.493$ (2)	$F(000) = 1140$
$\beta = 106.80$ (1)°	$D_m = 2.18$ Mg m^{-3}
λ(Mo $K\alpha$) $= 0.7107$ Å	$D_x = 2.16$
μ(Mo $K\alpha$) $= 7.92$ mm^{-1}	

Structure determination and refinement

The structure was solved by the heavy-atom method. A Patterson synthesis enabled the location of all the Cu and Se atoms. A Fourier synthesis differentiated between them. It was concluded that all five heavy atoms are in the general positions of Cc. Positions of the light atoms (N,O,C) were found from a Fourier synthesis. The structure was refined by a diagonal least-squares method; the function minimized was $\sum w(|F_o| - |F_c|)^2$, and the weighting scheme used was that of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961), $w = (a + |F_o| + b|F_o|^2)^{-1/2}$, where $a = 1.78$ and $b = 0.004$. After refinement with isotropic temperature parameters $R = \sum ||F_o| - |F_c||/\sum |F_o|$ was 0.179. After anisotropic refinement R fell to 0.076. Finally, the H atom positions of the ethylenediamines were calculated assuming sp^3 hybridization of the C and N atoms. The positions of the H atoms were not refined, but their introduction gave a final $R = 0.069$. In the last cycle the shifts of all parameters were $<2\%$ of their e.s.d. A final difference synthesis showed no peak >1.7 e Å^{-3}. Scattering factors for neutral atoms were taken from International Tables for X-ray Crystallography (1962).

The final atomic parameters are given in Table 2, bond distances and angles in Table 3.* The calculations were performed on a Siemens 4004/150 computer with the programs of Ahmed, Hall, Pippy & Huber (1966).

Discussion

The crystal structure consists of a three-dimensional skeleton formed by polymeric $[Cu_2(CN)_2(SeCN)_2]^{2-}$ anions. In the cavities are located Cu^{II} atoms, coordinated by two molecules of ethylenediamine and one of water (Fig. 1). This (in principle) planar coordination of Cu^{II} with CuN_4 chromophores has been found in all Cu^I–Cu^{II} complexes containing four NH_3 or two NH_2–$(CH_2)_2$–NH_2 molecules. If a water molecule occurs in the formula unit, it coordinates the Cu^{II} atom in an axial direction. In the present complex the Cu–O

Table 2. *Atomic parameters* (×10⁴) *with e.s.d.'s in parentheses*

Hydrogen atom positions are calculated values.

	x	y	z
Se(1)	1544 (2)	2539 (1)	3924 (2)
Se(2)	6 (2)	2532 (1)	7924 (2)
Cu(1)	52 (3)	1434 (1)	2551 (2)
Cu(2)	1569 (3)	1396 (1)	9276 (2)
Cu(3)	769 (4)	4348 (1)	914 (3)
O	4340 (13)	621 (6)	4037 (10)
N(1)	3827 (17)	1750 (9)	9433 (12)
N(2)	2777 (22)	3292 (11)	7432 (16)
N(3)	1003 (20)	1642 (8)	559 (14)
N(4)	568 (22)	320 (11)	3265 (12)
N(5)	4209 (17)	1526 (9)	6223 (14)
N(6)	4331 (23)	185 (9)	1315 (15)
N(7)	2309 (19)	3504 (7)	610 (13)
N(8)	2205 (20)	4781 (8)	5537 (16)
C(1)	4919 (19)	1990 (12)	9251 (14)
C(2)	1717 (21)	2968 (9)	7599 (13)
C(3)	646 (19)	1565 (9)	1306 (10)
C(4)	1040 (19)	327 (10)	8622 (16)
C(5)	2888 (36)	1072 (16)	6301 (39)
C(6)	3233 (47)	247 (16)	6791 (40)
C(7)	3314 (27)	3941 (10)	70 (23)
C(8)	3644 (35)	4800 (13)	516 (29)
H(N5)	−1111	3053	648
H'(N5)	−286	3174	1889
H(N6)	−1289	5494	682
H'(N6)	−18	5597	1824
H(N7)	1667	5463	−159
H'(N7)	2441	5680	1066
H(N8)	2982	3260	1275
H'(N8)	1713	3041	162
H(C5)	−2895	4020	522
H'(C5)	−2706	3551	1751
H(C6)	−2848	5118	1658
H'(C6)	−1222	4678	2620
H(C7)	4413	3596	183
H'(C7)	2704	3984	−755
H(C8)	4214	5171	46
H'(C8)	4423	4753	1303

Table 3. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu(1)–Se(1)	2·613 (3)	Cu(3)–N(5)	2·083 (15)
Cu(1)–N(2)	2·026 (21)	Cu(3)–N(6)	2·019 (18)
Cu(1)–N(4)	1·997 (18)	Cu(3)–N(7)	2·036 (19)
Cu(1)–C(3)	1·912 (15)	Cu(3)–N(8)	2·035 (17)
Cu(2)–Se(2)	2·649 (3)	Cu(3)–O	2·483 (14)
Cu(2)–N(1)	2·033 (15)	N(5)–C(5)	1·403 (34)
Cu(2)–N(3)	1·977 (17)	N(6)–C(6)	1·481 (44)
Cu(2)–C(4)	1·904 (17)	N(7)–C(7)	1·477 (29)
N(1)–C(1)	1·132 (22)	N(8)–C(8)	1·452 (33)
N(2)–C(2)	1·151 (28)	C(5)–C(6)	1·454 (42)
N(3)–C(3)	1·147 (24)	C(7)–C(8)	1·481 (31)
N(4)–C(4)	1·157 (25)	Se(1)–C(1)	1·789 (17)
		Se(2)–C(2)	1·833 (18)
Cu(1)–Se(1)–C(1)	99·9 (0·6)	Cu(3)–N(5)–C(5)	107·0 (1·5)
Cu(1)–N(2)–C(2)	159·0 (1·8)	Cu(3)–N(6)–C(6)	109·0 (1·5)
Cu(1)–C(3)–N(3)	179·9 (2·3)	Cu(3)–N(7)–C(7)	109·2 (0·9)
Cu(1)–N(4)–C(4)	170·6 (1·7)	Cu(3)–N(8)–C(8)	108·4 (1·2)
Cu(2)–Se(2)–C(2)	96·6 (0·5)	N(5)–Cu(3)–N(6)	82·7 (0·6)
Cu(2)–N(1)–C(1)	161·8 (1·5)	N(5)–Cu(3)–N(7)	97·4 (0·6)
Cu(2)–N(3)–C(3)	162·5 (1·2)	N(5)–Cu(3)–N(8)	176·8 (0·7)
Cu(2)–C(4)–N(4)	172·2 (1·6)	N(6)–Cu(3)–N(7)	176·1 (0·7)
Se(1)–Cu(1)–N(2)	101·7 (0·6)	N(6)–Cu(3)–N(8)	96·4 (0·6)
Se(1)–Cu(1)–N(4)	104·5 (0·5)	N(7)–Cu(3)–N(8)	83·7 (0·6)
Se(1)–Cu(1)–C(3)	109·7 (0·4)	N(5)–Cu(3)–O	92·5 (0·5)
N(2)–Cu(1)–N(4)	108·2 (0·8)	N(6)–Cu(3)–O	94·8 (0·6)
N(2)–Cu(1)–C(3)	115·4 (0·8)	N(7)–Cu(3)–O	89·0 (0·5)
N(4)–Cu(1)–C(3)	115·8 (0·7)	N(8)–Cu(3)–O	84·5 (0·6)
Se(2)–Cu(2)–N(1)	101·0 (0·4)	N(5)–C(5)–C(6)	114·9 (1·3)
Se(2)–Cu(2)–N(3)	104·7 (0·4)	N(6)–C(6)–C(5)	107·3 (1·5)
Se(2)–Cu(2)–C(4)	105·9 (0·6)	N(7)–C(7)–C(8)	107·8 (2·2)
N(1)–Cu(2)–N(3)	110·3 (0·7)	N(8)–C(8)–C(7)	110·7 (2·1)
N(1)–Cu(2)–C(4)	113·4 (0·6)	Se(1)–C(1)–N(1)	174·5 (1·7)
N(3)–Cu(2)–C(4)	119·3 (0·7)	Se(2)–C(2)–N(2)	175·2 (1·6)

Table 4. *Deviations* (Å × 10⁴) *of atoms from the plane* $-0.294X + 0.004Y - 0.956Z = -1.200$ *through* N(5), N(6), N(7) *and* N(8)

N(5)	607	C(5)	3213
N(6)	−622	C(6)	−3114
N(7)	−606	C(7)	2859
N(8)	621	C(8)	−2936
Cu(3)	67	O	24818

distance is 2·48, while in $Cu_3en_2(CN)_4.H_2O$ it is 2·38 Å. The skeleton shape of the present complex is similar to that in $Cu_3en_2(CN)_4.H_2O$.

There are considerable stereochemical differences between the Cu^{II} and Cu^{I} atoms. Cu^{II} has a distorted square-pyramidal coordination, with two molecules of ethylenediamine approximately in the plane and a water molecule at the apex. The Cu^{II}–N distances are approximately equal (2·02–2·08 Å) and agree well with other results (Williams, Larson & Cromer, 1972; Brown, Lee & Melsom, 1968). The ethylenediamine molecules have a *gauche* configuration; the maximum deviation of a C atom from the plane defined by N(5), N(6), N(7), N(8) is 0·32 Å (Table 4). The Cu^{II} atom lies 0·007 Å from this plane on the same side as the water molecule.
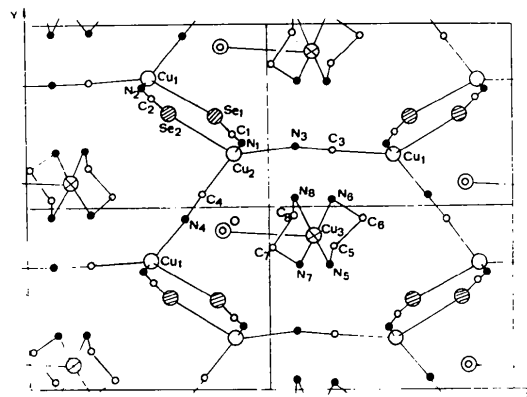

Fig. 1. The crystal structure of $[Cu(C_2H_8N_2)_2(H_2O)]|Cu_2(CN)_2(SeCN)_2]$.

Cu^I is coordinated tetrahedrally by cyano and selenocyanato groups which are present as bridging groups. The skeleton cavities are formed by six Cu^I atoms bonded together by CN and SeCN groups (Fig. 1). The Cu^I–NC distances are somewhat longer than the Cu^I–CN (Table 3). This difference is one of the factors which allows distinction between the N and C atoms in the cyano groups.

As a consequence of their bridging function, the selenocyanato groups lose their linearity. Deviations from linearity average 5°. This can be explained from steric factors. Cu^I–Se–C angles are near 100°, unlike the Cu^I–C–N and Cu^I–N–C angles which are near 180° (Table 3). This means that the latter bonds lie along the line connecting the Cu^I atoms.

Our results show that the crystallochemical generalizations of Garaj (1975) are valid also for this complex.

In cuprous–cupric compounds the (Cu^I):(X) ratio (where X represents an anionic ligand) may be classified into five groups. For each group the type of coordination of Cu^I, the function of the anionic ligands and the structure type of the skeleton are characteristic. In this classification Cu$_3$en$_2$(SeCN)$_2$(CN)$_2$.H$_2$O belongs to group II, with the ratio (Cu^I):(X) = 2:4.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. National Research Council, Ottawa, Canada.

BROWN, D. S., LEE, J. D. & MELSOM, B. G. A. (1968). *Acta Cryst.* B24, 730–736.

COOPER, D. & PLANE, R. A. (1966). *Inorg. Chem.* 5, 1677–1682.

CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 32. New York: Pergamon Press.

DUNAJ-JURČO, M. & PORAJ-KOŠIC, M. A. (1967). *Chem. Zvesti*, 21, 241–247.

GARAJ, J. (1969). *Inorg. Chem.* 8, 304–308.

GARAJ, J. (1975). *The Structure Aspects of the Coordination Compounds of Copper.* DSc Thesis, Vol. 1.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

VRABEL, V., KELLÖ, E., DUNAJ-JURČO, M., MELNIK, M. & GARAJ, J. (1975). *Z. Anorg. Allg. Chem.* 417, 154–160.

WILLIAMS, R. J., CROMER, D. T. & LARSON, A. C. (1971). *Acta Cryst.* B27, 1701–1706.

WILLIAMS, R. J., LARSON, A. C. & CROMER, D. T. (1972). *Acta Cryst.* B28, 858–864.

Conformational Polymorphism.
III. The Crystal and Molecular Structures of Form II and Form III of Iminodiacetic Acid

BY J. BERNSTEIN*

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801, USA

Abstract

The crystal structures of the second and third polymorphic forms of iminodiacetic acid [form I: Boman, Herbertsson & Oskarsson (1974), *Acta Cryst.* B30, 378–382] have been determined by X-ray single-crystal structure analysis. Form II crystallizes in space group $Pbc2_1$ with eight molecules in the unit cell $a = 5.267$ (2), $b = 14.140$ (4), $c = 14.933$ (5) Å; form III crystallizes in space group $P2_1/n$ with four molecules in the unit cell $a = 5.258$ (1), $b = 12.206$ (2), $c = 8.709$ (1) Å, $\beta = 100.14$ (1)°. Both structures were solved by direct methods and refined anisotropically to R factors of 0.052 and 0.042 respectively. Bond lengths and angles agree well among the four independent molecules in the three structures. However, molecular conformations, as measured by comparison of torsion angles, differ significantly among the three forms, and these differences are related to the packing scheme as determined predominantly by the hydrogen-bonding network.

Introduction

In two recent papers (Bernstein & Hagler, 1978; Hagler & Bernstein, 1978) we demonstrated the utility of studying conformational polymorphs to gain insight into the influence of crystal forces on molecular conformation. A pair of structures was analyzed in which the packing was dominated by van der Waals

* Permanent address: Chemistry Department, Ben-Gurion University of the Negev, Beersheva, Israel.