

The Crystal Structure of Bis(ethylenediamine)copper(II) Thiocyanate

BY BRUCE W. BROWN AND E. C. LINGAFELTER

Department of Chemistry, University of Washington, Seattle, Washington, U.S.A.

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The crystal structure of bis(ethylenediamine)copper(II) thiocyanate, $[\text{Cu}(\text{en})_2](\text{SCN})_2$, has been determined by three-dimensional X-ray methods. The compound is triclinic with space group $P\bar{1}$ and cell dimensions

$$a = 7.352, b = 9.364, c = 6.585 \text{ \AA}; \alpha = 86^\circ 56', \beta = 113^\circ 23', \gamma = 125^\circ 8'.$$

The intensities were obtained from unidirectionally integrated equi-inclination Weissenberg photographs from $h0l$ to $h5l$, with 276 of the 912 reflections too weak to be recorded. The structure was refined to an R of 0.077, individual atom anisotropic temperature factor coefficients being used with the Busing & Levy full-matrix least-square program.

The arrangement of the ligands about the copper atom has the amino nitrogen atoms at the corners of a rectangle with a mean Cu-N distance of 2.00 Å and the sulfur atom of (SCN) completing a distorted octahedron at the longer distance of 3.27 Å. The ethylenediamine molecule has an unsymmetrical *gauche* form with the carbon atoms +0.16 and -0.53 Å from the N-Cu-N plane.

Introduction

Two transition metal ions whose coordination configurations have been of interest to inorganic chemists for many years are bivalent nickel and copper. These ions bear the interesting relationship that with some ligands identical structures are formed whereas with other ligands the structures are different.

The structure of *trans*-bis(ethylenediamine)bis(isothiocyanato)nickel(II) (Brown & Lingafelter, 1963) exhibits some interesting features: first, the ethylenediamine molecule has the *gauche* form with the carbon atoms symmetrically arranged above and below the N-Ni-N plane; second, the bond to the thiocyanate group is through the nitrogen atom as in other coordination compounds of metals of the first transition period (Shaffer, 1959); and, third, the valence angle of 140° (Ni-N-C) to the thiocyanate group is more acute than in any other octahedral thiocyanate complex whose structure has been determined.

In view of the structural features of $[\text{Ni}(\text{en})_2(\text{NCS})_2]$, it was felt that the copper compound would provide an interesting comparison.

The dihydrate of bis(ethylenediamine)copper(II) thiocyanate has been prepared (Grossman & Schuck, 1906) by the addition of a potassium thiocyanate solution to an alcoholic solution of bis(ethylenediamine)copper(II) bromide. No crystallographic data have been reported concerning this compound.

Experimental

Bis(ethylenediamine)copper(II) sulfate was prepared by the addition of a stoichiometric amount of ethylenediamine to an aqueous solution of copper sulfate at room temperature. Conversion to the thiocyanate

was accomplished by adding a barium thiocyanate solution with rapid stirring, and filtering off the precipitated barium sulfate. The aqueous solution was vacuum dried over anhydrous calcium chloride, and deep blue-violet prismatic crystals of the anhydrous compound were obtained from slow cooling of a hot methanol solution. The crystals are tablets on $\{101\}$, elongated in the b direction.

Cell dimension data were obtained from rotation and zero level Weissenberg films, taken about the three axes, on which the diffraction pattern of sodium chloride ($a_0 = 5.63874 \text{ \AA}$) was superimposed to calibrate the camera dimensions. The cell parameters are:

$$\begin{array}{ll} a = 7.352 \pm 0.008 \text{ \AA} & \alpha = 86^\circ 56' \\ b = 9.364 \pm 0.005 & \beta = 113^\circ 23' \\ c = 6.585 \pm 0.016 & \gamma = 125^\circ 8' \end{array}$$

There were no systematic extinctions, indicating, with the Laue symmetry $\bar{1}$, that the space group is probably $P\bar{1}$ (C_1^1) or $P1$ (C_1^1). The observed density of 1.569 g.cm^{-3} corresponds to a formula weight of 297.8, which agrees with the calculated formula weight of 299.9 for $[\text{Cu}(\text{en})_2](\text{SCN})_2$, indicating that there is one molecule per cell.

Multiple film equi-inclination Weissenberg photographs were taken about the b axis with a Nonius integrating camera for all levels from the zero to the fifth. The singly integrated photographs were photometered in a direction normal to the integration direction, a Moll-type densitometer being used. The interfilm ratio was determined for each level from the measured values for common reflections. The intensities were corrected for Lorentz and polarization factors in the usual manner. Additional photographs were taken of the a^*b^* net with an integrating preces-

sion camera (Stewart & Lingafelter, 1960) in order to scale the several Weissenberg photographs together. More accurate scaling of the levels was done by comparing the observed structure factors with the calculated values in later stages of the structure determination.

A total of 912 reflections were observed, with 276 having relative intensities 'less-than' 1 in a range of 5000, except that on the fifth level the minimum observed intensity was 5.

The structure determination

The space group was assumed to be $P\bar{1}$, and this choice of space group was corroborated by the structure determination. The copper was assigned the position 0, 0, 0.

The Patterson projection $P(x, z)$ was calculated from the values of F_{rel}^2 for the 61 observed non-zero $h0l$ reflections, and the prominent copper-sulfur vector gave an approximate sulfur position, but no additional structural details were obtainable. The electron-density projection $\rho(x, z)$ was obtained with the phase angles determined from a structure factor calculation based on the copper and sulfur positions. This calculation, which has an R of 0.48, when compared with the final results, had 16 terms with erroneous phase angles accounting for 8% of the ΣF_o ; the discrepancy index, R , is defined as $\Sigma[|F_o| - |F_c|] / \Sigma|F_o|$ for observed non-zero reflections only.

It was not possible to obtain a trial structure from subsequent electron-density and difference synthesis maps on the $h0l$ data.

The atomic scattering factors used for these and all subsequent structure factor calculations were: for copper, those of Thomas & Umeda (1957); sulfur, values obtained by interpolation between those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and Hartree (1935); carbon and nitrogen, Berghuis *et al.* (1955); and hydrogen, McWeeny (1951).

The three-dimensional Patterson synthesis was then calculated from the values of F_{rel}^2 for the 636 observed non-zero $h0l$ through $h5l$ reflections. Five of the six light atoms and the sulfur atom were located in this Patterson synthesis, and the remaining light atom from a subsequent Fourier synthesis using phase angles determined from a structure factor calculation using those atomic positions obtained from the Patterson synthesis. Successive refinement cycles were used to refine the atomic parameters and individual atom isotropic temperature factor coefficients to give a structure which, when used in a structure factor calculation, gave an R of 0.14. The $\bar{1}01$, 010 , and $\bar{1}20$ reflections were not included in these or subsequent calculations because of partial obscuring of the diffracted X-ray beam by the camera beam-stop. The value of F_c was used in place of F_o for these reflections in electron-density calculations.

The atomic parameters and the individual atom isotropic temperature factors were refined by two cycles of full-matrix least-squares refining as programmed by Busing & Levy (1959) for the IBM Type 704 EDPM. The function $\Sigma w(F_o - |F_c|)^2$ was minimized with a modified version of the Hughes weighting

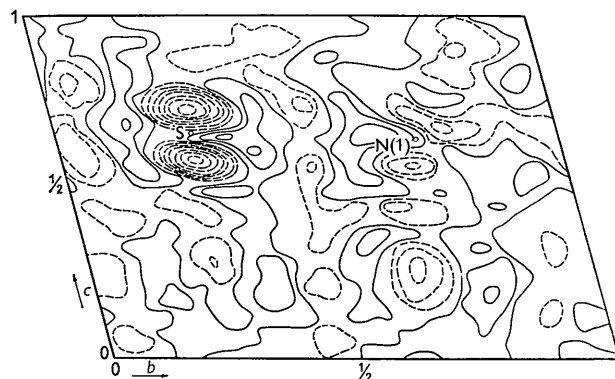


Fig. 1. Difference synthesis section at $x = 0.40$ with individual atom isotropic temperature factor coefficients. Contour interval $0.25 \text{ e.}\text{\AA}^{-2}$, negative contours broken.

Table 1. $[\text{Cu}(\text{en})_2](\text{SCN})_2$ — Final atomic parameters

Atom	x/a	y/b	z/c	B	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.0000	0.0000	0.0000		5.87	6.33	4.06	3.67	2.91	4.06
S	0.5945	0.2303	0.3451		6.94	9.76	6.70	5.19	5.11	6.70
N(1)	0.4142	0.2138	0.6521		5.92	9.38	5.52	5.33	3.28	5.52
N(2)	0.0765	0.1994	-0.1661		5.23	6.46	4.21	3.46	2.68	4.21
N(3)	-0.0403	0.1316	0.1859		4.46	4.92	3.86	3.15	2.12	3.86
C(1)	0.4959	0.2226	0.5294		2.95	5.69	4.23	2.03	1.64	4.23
C(2)	0.1582	0.3588	-0.0149		7.67	5.03	7.84	8.32	5.16	7.84
C(3)	-0.0260	0.2801	0.0922		7.24	6.11	6.28	5.67	4.68	6.28
H(1)	-0.077	0.159	-0.310	3.807						
H(2)	0.213	0.232	-0.205	3.807						
H(3)	0.146	0.452	-0.112	4.801						
H(4)	0.346	0.426	0.115	4.801						
H(5)	0.039	0.383	0.226	4.151						
H(6)	-0.207	0.233	-0.037	4.151						
H(7)	0.096	0.180	0.346	3.254						
H(8)	-0.207	0.047	0.186	3.254						

Note: The several U_{ij} are listed as $U \cdot UU \times 10^2 \text{ \AA}^2$.

Table 2. Observed and calculated structure factors
 Values shown are $10F_o$ and $10F_c$. Minus sign on F_o signifies 'less-than'.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	0	0	100	100	1	0	0	100	100	1	0	0	100	100	1	0	0	100	100	1	0	0	100	100
1	0	1	100	100	1	0	1	100	100	1	0	1	100	100	1	0	1	100	100	1	0	1	100	100
1	0	2	100	100	1	0	2	100	100	1	0	2	100	100	1	0	2	100	100	1	0	2	100	100
1	0	3	100	100	1	0	3	100	100	1	0	3	100	100	1	0	3	100	100	1	0	3	100	100
1	0	4	100	100	1	0	4	100	100	1	0	4	100	100	1	0	4	100	100	1	0	4	100	100
1	0	5	100	100	1	0	5	100	100	1	0	5	100	100	1	0	5	100	100	1	0	5	100	100
1	0	6	100	100	1	0	6	100	100	1	0	6	100	100	1	0	6	100	100	1	0	6	100	100
1	0	7	100	100	1	0	7	100	100	1	0	7	100	100	1	0	7	100	100	1	0	7	100	100
1	0	8	100	100	1	0	8	100	100	1	0	8	100	100	1	0	8	100	100	1	0	8	100	100
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1	0	19	100	100	1	0	19	100	100	1	0	19	100	100	1	0	19	100	100	1	0	19	100	100
1	0	20	100	100	1	0	20	100	100	1	0	20	100	100	1	0	20	100	100	1	0	20	100	100
1	0	21	100	100	1	0	21	100	100	1	0	21	100	100	1	0	21	100	100	1	0	21	100	100
1	0	22	100	100	1	0	22	100	100	1	0	22	100	100	1	0	22	100	100	1	0	22	100	100
1	0	23	100	100	1	0	23	100	100	1	0	23	100	100	1	0	23	100	100	1	0	23	100	100
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1	0	26	100	100	1	0	26	100	100	1	0	26	100	100	1	0	26	100	100	1	0	26	100	100
1	0	27	100	100	1	0	27	100	100	1	0	27	100	100	1	0	27	100	100	1	0	27	100	100
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1	0	37	100	100	1	0	37	100	100	1	0	37	100	100	1	0	37	100	100	1	0	37	100	100
1	0	38	100	100	1	0	38	100	100	1	0	38	100	100	1	0	38	100	100	1	0	38	100	100
1	0	39	100	100	1	0	39	100	100	1	0	39	100	100	1	0	39	100	100	1	0	39	100	100
1	0	40	100	100	1	0	40	100	100	1	0	40	100	100	1	0	40	100	100	1	0	40	100	100

scheme (Hughes, 1941). These and subsequent cycles were carried out on the IBM Type 709 at the University of Washington Research Computer Laboratory, utilizing the IBM Compatibility II program to simulate the Type 704 on the Type 709 machine.

The value of R remained at 0.14 after these two refinement cycles with isotropic temperature factors. A difference synthesis showed the presence of anisotropic thermal motion in the molecule. A section at

$x = 0.40$ is shown in Fig. 1, where the anisotropy about the sulfur and nitrogen atoms in the thiocyanate group is clearly seen. The Busing & Levy program was coded to convert the isotropic temperature factor coefficients to the form of equation (1) and two further cycles were carried out, refining the positional and anisotropic thermal motion parameters.

$$\exp [-(h^2b_{11} + hkb_{12} + k^2b_{22} + hlb_{13} + klb_{23} + l^2b_{33})] \quad (1)$$

where:

$$b_{11} = 2\pi^2 a^*{}^2 U_{11}$$

$$b_{12} = 4\pi^2 a^* b^* U_{12}, \text{ etc.}$$

The value of R reduced further to 0.077 by the corrections for the anisotropic thermal motion of the atoms.

For these final computations, the hydrogen atom positions were calculated assuming a tetrahedral configuration about the carbon and nitrogen atoms in the ethylenediamine group, and C-H and N-H distances of 1.075 and 1.005 Å, respectively, and an isotropic temperature factor approximately equal to the isotropic temperature factor of the carbon or nitrogen atom to which the hydrogen atom is attached.

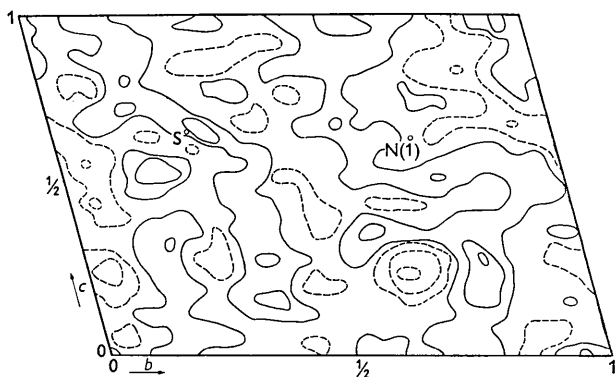


Fig. 2. Difference synthesis section at $x=0.40$ with individual atom anisotropic temperature factor coefficients. Contour interval $0.25 \text{ e.}\text{\AA}^{-2}$, negative contours broken.

A difference synthesis section at $x=0.40$ calculated from the results of the final refinement cycle shows the degree of correction for the anisotropic thermal motion of the sulfur and nitrogen atoms in the thiocyanate group (Fig. 2). The positional and thermal motion parameters for this final calculation are listed in Table 1. A list of the 912 observed and calculated structure factors from this final calculation is given in Table 2. Table 3 lists the agreement for selected groups of reflections, where R^* includes $|F_{\min}/2|$ and $|F_{\min}/2| - |F_c|$ for those reflections with F_c greater than F_{\min} .

Table 3. Agreement for selected groups of reflections

Group	R	R^*
$hk0$	0.083	0.101
$0kl$	0.082	0.090
$h0l$	0.061	0.070
$h1l$	0.064	0.081
$h2l$	0.089	0.108
$h3l$	0.078	0.098
$h4l$	0.075	0.097
$h5l$	0.097	0.120
Overall	0.077	0.096

A structure factor calculation based on the final parameters for the (010) projection had an R value of 0.061. An electron-density projection on (010), using the phase angles determined from this structure factor calculation, is shown in Fig. 3. A representation of the structure projected on (100) is shown in Fig. 4.

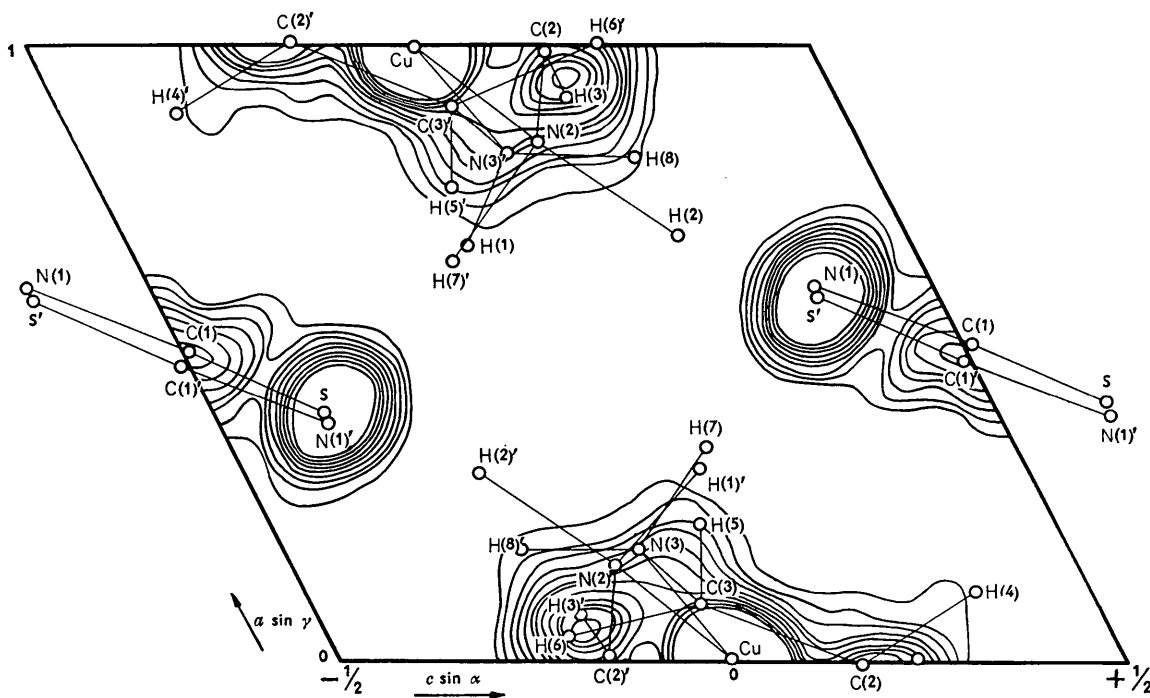


Fig. 3. Final electron-density projection on (010). Contour interval $2 \text{ e.}\text{\AA}^{-2}$ (except at Cu and S centers), lowest contour $4 \text{ e.}\text{\AA}^{-2}$.

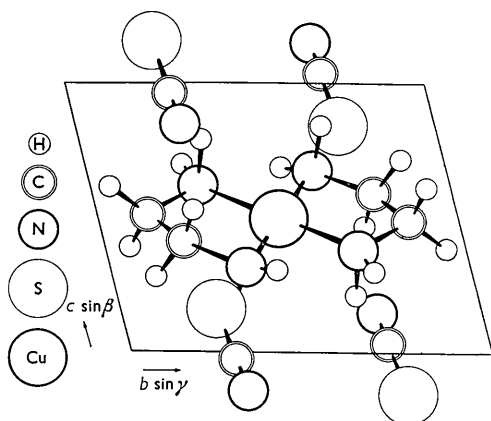


Fig. 4. Representation of structure projected on (100) plane.

Discussion

The arrangement of the ligands about the copper atom in $[\text{Cu}(\text{en})_2](\text{SCN})_2$ has the four short bonds and two long bonds frequently encountered with Cu^{2+} ions. The four amino nitrogen atoms are located at the corners of a rectangle with a mean Cu–N distance of 2.00 Å. The sulfur atom of the thiocyanate group completes a distorted octahedron at a distance of 3.27 Å. The nearest thiocyanate nitrogen atom to the copper atom in $[\text{Cu}(\text{en})_2](\text{SCN})_2$ is much too far at 4.07 Å to be considered in the coordination sphere. The interatomic distances and angles are shown in Fig. 5 and 6, where the standard deviations were ob-

tained from the estimated atomic positional errors calculated by the Busing & Levy least-squares program.

The observed Cu–N bond lengths in the ethylenediamine ring of 2.02 and 1.99 Å agree with the Cu–N(en) bond lengths in $[\text{Cu}(\text{en})_3](\text{NO}_3)_2$ of 2.02 and 2.01 Å (Komiyama & Lingafelter, 1964), 1.98 and 1.99 Å in $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}$ and 1.97 and 1.98 Å in $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Br}]\text{Br}$ (Mazzi, 1953).

These Cu–N(en) distances may be compared with the Cu–N(*proline*) distance of 1.99 Å in $[\text{Cu}(\text{C}_5\text{H}_8\text{O}_2\text{N})_2] \cdot 2\text{H}_2\text{O}$ (Mathieson & Welsh, 1952), Cu–N(*NH*₃) distances of 2.06 and 2.04 Å in $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ (Mazzi, 1955), 2.05 Å in $\text{NH}_4[\text{Cu}(\text{NH}_3)_4](\text{ClO}_4)_3 \cdot \text{NH}_3$ (Bukovska & Porai-Koshits, 1960*b*), and Cu–N(*NCS*) of 2.10 Å and Cu–N(*py*) of 2.12 Å in $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ (Porai-Koshits & Tishchenko, 1959), 1.96 and 2.02 Å for the Cu–N(*succinonitrile*) distance in $[\text{Cu}(\text{sucnit})_2](\text{NO}_3)_2$ (Kinoshita, Matsuhara & Saito, 1959), and 2.04 Å for Cu–N(*NH*₃) in $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ (Bukovska & Porai-Koshits, 1960*a*).

In $[\text{Cu}(\text{en})_2](\text{SCN})_2$, the sulfur atom of the thiocyanate group completes the coordination sphere of the copper atom. The sulfur atom is almost perpendicular (89°) to the (en)N–Cu–N plane. The observed Cu–S(*SCN*) distance of 3.27 Å in $[\text{Cu}(\text{en})_2](\text{SCN})_2$ is significantly longer than the Cu–S(*SCN*) distance of 3.0 Å in the binuclear $[\text{Cu}(\text{py})_2(\text{NCS})_2]$. The sum of the square *dsp*² radius for copper(II) of ~ 1.30 Å and the van der Waals radius for sulfur of 1.85 Å (Pauling, 1960) equals 3.15 Å, which is approximately the observed distance.

The longer distances in the four-and-two complexes of copper have been observed in $\text{Cu}_2\text{Cl}(\text{OH})_3$ (Cu–Cl = 2.76 Å) (Wells, 1949), $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ (Cu–O = 3.37 Å) (Mazzi, 1955), $\text{NH}_4[\text{Cu}(\text{NH}_3)_4](\text{ClO}_4)_3 \cdot \text{NH}_3$ (Cu–NH₃ = 3.75 Å) (Bukovska & Porai-Koshits, 1960*b*), $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}$ (Cu–O = 2.68 Å and Cu–Cl = 2.89 Å) and $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Br}]\text{Br}$ (Cu–O = 2.78 Å and Cu–Br = 3.00 Å) (Mazzi, 1953), and other compounds.

The 85° N–Cu–N bond angle in $[\text{Cu}(\text{en})_2](\text{SCN})_2$ agrees with the angle of 86° in $[\text{Cu}(\text{en})_3](\text{NO}_3)_2$, 89° in $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}$, and 90° in $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Br}]\text{Br}$. The single-bond C–C distance in the ethylenediamine molecule of $[\text{Cu}(\text{en})_2](\text{SCN})_2$ of 1.56 Å is within one standard deviation of the 1.55 Å distance in $[\text{Cu}(\text{en})_3](\text{NO}_3)_2$, 1.51 Å in $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}$, and 1.53 Å in $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Br}]\text{Br}$.

Unlike the symmetrical *gauche* form observed in nickel and cobalt ethylenediamine complexes (Brown & Lingafelter, 1963), the spatial configuration of the ethylenediamine ring in the copper compounds has an unsymmetrical *gauche* form. This asymmetry in $[\text{Cu}(\text{en})_2](\text{SCN})_2$ has one carbon atom +0.16 Å from the N–Cu–N plane and the other carbon atom at a greater distance of -0.53 Å. The asymmetry in other bis(ethylenediamine)copper(II) complexes has observed distances of +0.16 and -0.35 Å in $[\text{Cu}(\text{en})_2](\text{NO}_3)_2$

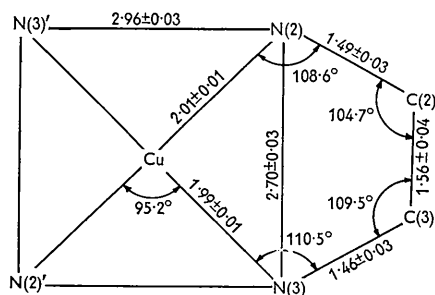


Fig. 5. Interatomic bond lengths and angles in the ethylenediamine ring.

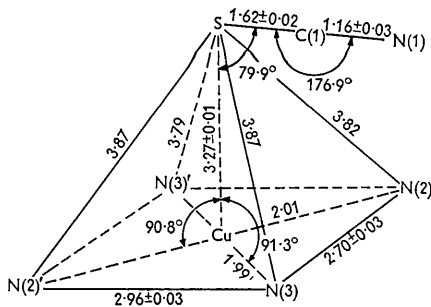
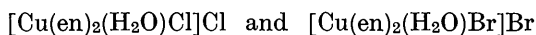


Fig. 6. Interatomic bond lengths and angles in the thiocyanate group and the coordination octahedron.

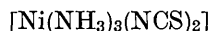
(Komiyama & Lingafelter, 1964), and +0.37 and -0.68 Å in [Cu(en)₂][Hg(SCN)₄] (Scouloudi, 1953). In



(Mazzi, 1953), the asymmetrical *gauche* ethylenediamine molecules have one carbon displaced +0.06 Å toward the water molecule and the other carbon atom displaced -0.53 Å toward the chloride ion and -0.49 Å toward the bromide ion.

The orientation of the thiocyanate group in the structure of [Cu(en)₂](SCN)₂ is unique in the reported coordination compounds of the thiocyanates. The coordination octahedron or tetrahedron is completed by the nitrogen atom of the thiocyanate group in complexes of the first transition row of metals and by the sulfur atom in complexes of the metals of the second and third transition rows (Shaffer, 1959). In compounds as Co(py)₂(SCN)₂ and Cu(py)₂(SCN)₂ (Porai-Koshits & Tishchenko, 1959), D-[Pt₂(SCN)₂Cl₂(PPr₃)₂] (Owston & Rowe, 1960), and the di-(2-thioimidazolidine) complexes of lead and cadmium thiocyanates (Cavalca, Nardelli & Fava, 1959) we have examples of the coordination to both ends of the thiocyanate group by alternate metal atoms.

The N-C and C-S distances in the linear thiocyanate group of 1.16 and 1.62 Å, respectively, in [Cu(en)₂](SCN)₂ agree with the values of 1.20 and 1.64 Å in [Ni(en)₂(NCS)₂] (Brown & Lingafelter, 1963), 1.20 and 1.60 Å in [Ni(NH₃)₄(NCS)₂] (Iukhno & Porai-Koshits, 1957), 1.13 and 1.67 Å in



(Porai-Koshits, Iukhno, Antsyshkina & Dikareva, 1957), and 1.23 and 1.59 Å in K₂[Co(NCS)₄] (Zhdanov & Zvonkova, 1950). These distances agree with the covalent distances of 1.22 and 1.56 Å in H₃C-NCS and 1.21 and 1.61 Å in H₃C-SCN (Beard & Daily, 1949), 1.22 and 1.56 Å in HNCS (Beard & Daily, 1950), and 1.13 and 1.69 Å in Se(SCN)₂ (Ohlberg & Vaughan, 1954).

The nearest intermolecular distances from the [Cu(en)₂](SCN)₂ molecule centered about (0, 0, 0) are listed in Table 4. Atoms labeled N(1), C(1), etc. are

Table 4. [Cu(en)₂](SCN)₂ — Nearest neighbors

Atom in molecule at (0,0,0)	Nearest neighbor	Distance	Translation vector of neighbor atom
Cu	N(1)'	4.07 Å	0,0,1
S	C(3)	3.59	1,0,0
N(1)	N(2)	3.09	0,0,1
N(2)	C(2)'	4.31	1,1,1
N(3)	N(1)'	3.30	0,0,1
C(1)	C(3)	3.75	1,0,1
C(2)	N(1)'	3.49	1,1,1
C(3)	C(1)'	3.97	1,1,1

located at the coordinates given in Table 1; atoms labeled N(1)', C(1)' etc. are related to this set by the symmetry center at (0, 0, 0). The translation vector

relating the nearest neighbor to the corresponding atom in the molecule centered on (0, 0, 0) is also listed.

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