

The Crystal Structure of β, β', β'' -Triaminotriethylamineisothiocyanatocopper(II) Thiocyanate¹

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Abstract: A three-dimensional X-ray diffraction analysis of β, β', β'' -triaminotriethylamineisothiocyanatocopper(II) thiocyanate, $[\text{Cu}(\text{tren})(\text{NCS})](\text{SCN})$ (where $\text{tren} = \text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$), has been completed. The crystals have space group $\text{P}2_12_1$ and a cell with $a = 9.158$, $b = 14.000$, and $c = 11.285$ Å containing four molecules. The crystal structure consists of trigonal bipyramidal $[(\text{tren})(\text{SCN})\text{Cu}]^+$ cations and SCN^- anions, connected by a network of $\text{NH} \cdots \text{N}$ and $\text{NH} \cdots \text{S}$ hydrogen bonds.

In recent years a number of compounds of copper(II) having five-coordination have been synthesized and studied by X-ray diffraction techniques.²⁻²⁸ Most of these have been found to have a "square"-pyramidal configuration, while CuCl_3^{3-} in $[\text{Cr}(\text{NH}_3)_6]\text{CuCl}_3$,³ CuN_4I in $\text{Cu}(\text{dipy})_2\text{I}_2$,⁹ CuO_2Cl_3 in μ_4 -oxo-hexa- μ -chloro-tetrakis{(triphenylphosphine oxide)copper(II)},²⁸ CuO_5 in $\text{Cu}_2(\text{OH})(\text{PO}_4)$, $\text{Cu}_2(\text{OH})(\text{AsO}_4)$,² and $\text{Cu}_2\text{O}(\text{SO}_4)$,¹⁴ and CuN_3 in $\text{Cu}(\text{NH}_3)_2\text{Ag}(\text{SCN})_3$ ²⁷ have been found to have trigonal bipyramidal configurations.

Raymond and Basolo²⁹ have recently reported the preparation of β, β', β'' -triaminotriethylamineisothiocyanatocopper(II) thiocyanate, $[\text{Cu}(\text{tren})(\text{NCS})](\text{SCN})$. They suggested a *cis*-octahedral configuration with mixed Cu-NCS and Cu-SCN bonding on the basis of

the infrared spectrum and the similarity of the space group and lattice parameters with those of $[\text{Ni}(\text{tren})(\text{NCS})_2]$ ³⁰ which has a distorted *cis*-octahedral coordination. We have already reported in our earlier communication¹ that the copper ion in $[\text{Cu}(\text{tren})(\text{NCS})](\text{SCN})$ is five-coordinate through four nitrogen atoms from the quadridentate ligand and one nitrogen atom from one of the thiocyanate groups. The other thiocyanate ion is not bonded to copper. We have now completed the refinement of the crystal structure.

Experimental Section

Samples of $[\text{Cu}(\text{tren})(\text{NCS})](\text{SCN})$ were generously supplied to us by Professor F. Basolo.

The dark blue crystal utilized was a nearly equidimensional fragment cut from a cluster of crystals, with dimensions $0.34 \times 0.36 \times 0.23$ mm and mounted along the c axis. Oscillation and equi-inclination Weissenberg photographs showed the crystal to be orthorhombic with space group $\text{P}2_12_1$.

The lattice parameters were determined using Mo $K\alpha$ radiation (λ 0.71069 Å) from the least-squares fit to measurements of 26 θ values taken on a Picker single-crystal diffractometer fitted with a General Electric goniostat.³¹

Crystal Data. The crystals have lattice parameters $a = 9.158 \pm 0.001$, $b = 14.000 \pm 0.002$, and $c = 11.285 \pm 0.001$ Å; cell volume = 1446 Å³. The density measured by the flotation method, 1.467 g cm⁻³, compares favorably with the calculated density of 1.475 g cm⁻³ for four formula units per cell. The total number of electrons per cell, $F(000) = 676$. The linear absorption coefficient for Mo $K\alpha$ radiation is 12.3 cm⁻¹. The space group $\text{P}2_12_1$ is noncentrosymmetric and requires all atoms to be in fourfold sets of general positions.³²

The crystal was mounted with the c axis parallel to the φ axis of a General Electric single-crystal orienter on a Picker diffractometer equipped with a pulse-height analyzer. The data were collected using Mo $K\alpha$ (λ 0.709260 Å) radiation. Diffractometer settings for each possible reflection for the ω - 2θ scan method were calculated by using the formula of Alexander and Smith:³³ scan range = $A + B(\tan \theta)$, with A set equal to 1.60 and B equal to 1.00. Before scanning through the reflection, a background count (B_1) was taken for a time equal to one-half of the scan time. The scan (S) was then taken and another background count (B_2) was taken at the end of the scan for one-half of the scan time. The intensity of each reflection was calculated as $I = S - (B_1 + B_2)$, and the standard deviation of this intensity was calculated as $\sigma_I = (S + B_1 + B_2)^{1/2}$. All reflections in one octant of the reciprocal lattice out to $2\theta = 55^\circ$ were measured (*i.e.*, all unique reflections which would be obtainable with Cu $K\alpha$ radiation).

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Table II. Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^3$)^a

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	3412 (1)	1075 (0)	1709 (0)	307 (2)	332 (2)	323 (2)	37 (2)	25 (2)	-38 (2)
S(1)	7253 (2)	-0619 (1)	-0021 (2)	498 (7)	538 (7)	582 (7)	198 (6)	144 (6)	82 (6)
S(2)	7420 (2)	2902 (1)	2518 (2)	498 (7)	363 (5)	601 (7)	14 (5)	-83 (6)	45 (6)
N(1)	1965 (4)	1788 (2)	2749 (3)	352 (17)	276 (14)	347 (15)	61 (12)	6 (13)	-4 (13)
N(2)	1687 (5)	0165 (2)	1418 (3)	434 (18)	311 (14)	431 (19)	-54 (15)	-6 (17)	-37 (13)
N(3)	3359 (5)	2352 (3)	0662 (3)	495 (18)	403 (16)	358 (16)	-112 (19)	-54 (19)	72 (14)
N(4)	4770 (4)	1182 (3)	3153 (4)	339 (14)	421 (16)	422 (17)	10 (15)	-34 (15)	1 (23)
N(5)	4822 (5)	0356 (3)	0756 (5)	455 (21)	565 (23)	609 (25)	81 (21)	146 (21)	-121 (21)
N(6)	5754 (6)	4088 (3)	1058 (4)	656 (26)	474 (22)	476 (21)	84 (20)	-72 (21)	32 (18)
C(1)	0496 (5)	1365 (3)	2582 (5)	313 (18)	429 (22)	469 (26)	53 (17)	25 (21)	-25 (20)
C(2)	0604 (5)	0305 (4)	2362 (5)	360 (21)	427 (21)	581 (27)	-13 (18)	17 (22)	-7 (22)
C(3)	1957 (6)	2812 (3)	2401 (5)	528 (28)	283 (17)	520 (26)	10 (18)	-37 (22)	15 (19)
C(4)	2088 (7)	2897 (4)	1072 (6)	672 (33)	363 (21)	584 (30)	5 (24)	-147 (26)	144 (22)
C(5)	2453 (6)	1664 (4)	4002 (4)	481 (25)	500 (24)	317 (21)	71 (22)	58 (19)	4 (19)
C(6)	4098 (6)	1779 (4)	4068 (5)	506 (24)	479 (24)	347 (22)	-18 (21)	-74 (20)	34 (20)
C(7)	5828 (6)	-0062 (3)	0454 (4)	460 (23)	371 (19)	337 (20)	6 (18)	39 (19)	42 (17)
C(8)	6457 (5)	3602 (3)	1676 (5)	391 (19)	374 (17)	422 (18)	-63 (17)	35 (23)	-81 (19)
Positional Parameters ($\times 10^3$) and Isotropic Thermal Parameter ($\times 10^6$)									
H(11)	-021 (9)	152 (5)	287 (7)	6.7 (2)					
H(12)	002 (8)	163 (5)	164 (7)	5.8 (2)					
H(21)	117 (5)	-001 (3)	307 (4)	1.2 (1)					
H(22)	-026 (7)	008 (4)	190 (5)	3.9 (1)					
H(31)	083 (6)	309 (4)	260 (5)	3.6 (1)					
H(32)	274 (5)	314 (3)	261 (4)	1.8 (1)					
H(41)	125 (5)	270 (4)	058 (5)	2.2 (1)					
H(42)	222 (8)	356 (6)	085 (7)	7.9 (2)					
H(51)	190 (5)	220 (3)	449 (5)	2.6 (1)					
H(52)	224 (8)	078 (5)	443 (7)	6.4 (2)					
H(61)	439 (11)	230 (8)	394 (10)	10.2 (3)					
H(62)	446 (5)	148 (3)	480 (5)	2.8 (1)					
H(221)	112 (8)	019 (5)	070 (6)	5.6 (2)					
H(222)	198 (9)	-030 (6)	132 (8)	8.3 (2)					
H(331)	434 (6)	267 (4)	077 (6)	4.2 (1)					
H(332)	298 (11)	200 (7)	-001 (10)	12.4 (3)					
H(441)	508 (7)	070 (4)	350 (6)	4.6 (1)					
H(442)	553 (5)	141 (3)	278 (4)	1.9 (1)					

^a The thermal parameters are of the form $\exp(-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^*)$.

No corrections were made for absorption or for anomalous dispersion.

Calculations. All calculations were done on an IBM 7094 using the programs written or adapted by Stewart.³⁴ The atomic-scattering factors used were those from the "International Tables for X-ray Crystallography" for copper,³² those of Berghuis, *et al.*, for nitrogen and carbon,³⁵ those of Viervoll and Ögrim for sulfur,³⁶ and those from Table II of Stewart, Davidson, and Simpson³⁷ for hydrogen.

All full-matrix least-squares refinements were carried out with the modified version of the ORFLS program of Busing, Martin, and Levy.³⁸ This program minimizes $\sum w(|F_o| - |F_c|)^2$. The reliability index is defined throughout as $R = \sum |F_o| - |F_c| / \sum |F_o|$, where the summation is over the observed unique reflections only.

Determination of the Structure. Positions of the copper atoms were found from a three-dimensional sharpened, origin-removed Patterson synthesis. Starting with these positions, the remaining nonhydrogen atoms were located by a series of three-dimensional Fourier syntheses.

Refinement was carried out by full-matrix least-squares, giving equal weight to all reflections (except that in each cycle unobserved reflections with $F_o < F_c$ were given zero weight). Three cycles

of least-squares refinement with individual isotropic temperature factors reduced R to 0.080.

A three-dimensional ΔF synthesis calculated at this stage revealed clearly the positions of some of the hydrogen atoms, but in other cases smearing in the electron density was observed. Therefore the hydrogen atoms were placed in calculated positions (assuming a C-H distance of 1.05 and a N-H distance of 0.95 Å), reducing R to a value of 0.073. A total of 226 parameters including anisotropic temperature factors of nonhydrogen atoms, isotropic temperature factors of hydrogen atoms, and the scale factor were to be adjusted. Because of the limited core storage available in the computer, further refinements were carried out in two stages. After three cycles of refinement of the nonhydrogen atoms with individual anisotropic temperature factors followed by three cycles of refinement of hydrogen atoms with individual isotropic temperature factors, the value of R had dropped to 0.042.

At this stage it was thought worthwhile to reexamine the positions of the hydrogen atoms. A three-dimensional Fourier difference map based on the final nonhydrogen atoms with their anisotropic thermal parameters showed all 18 hydrogen peaks and showed no residual electron density greater than 1.3 e/Å³ except for some density anisotropically distributed around the copper and sulfur positions. All of these hydrogen positions compared well with the calculated positions and the maximum difference in any of the positions was less than two standard deviations.

Although at this stage the reliability index was low and the average shift/error was small, it was noted that there were eight observed reflections which had rather large discrepancies between $|F_o|$ and $|F_c|$ values. In order to ascertain that they did not suffer from secondary extinction, a Housty and Clastre³⁹ plot was made. This plot did not show any evidence of secondary extinction. A series of least-squares refinement was carried out using a set of

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Table III. Additional Bond Angles (in degrees) Not Shown in Figure 1

N(1)	Cu	N(2)	84.0 (0.2)	N(2)	C(2)	H(21)	100 (2)
N(1)	Cu	N(3)	83.9 (0.2)	N(2)	C(2)	H(22)	97 (4)
N(1)	Cu	N(4)	84.3 (0.2)	C(1)	C(2)	H(21)	109 (2)
N(1)	Cu	N(5)	177.9 (0.2)	C(1)	C(2)	H(22)	110 (3)
				H(21)	C(2)	H(22)	131 (4)
C(1)	N(1)	C(3)	110.3 (0.4)	N(1)	C(3)	H(31)	107 (3)
C(1)	N(1)	C(5)	110.2 (0.4)	N(1)	C(3)	H(32)	115 (3)
C(3)	N(1)	C(5)	111.4 (0.4)	C(4)	C(3)	H(31)	104 (3)
				C(4)	C(3)	H(32)	99 (3)
Cu	N(2)	H(221)	122 (4)	H(31)	C(3)	H(32)	121 (4)
Cu	N(2)	H(222)	108 (7)				
C(2)	N(2)	H(221)	104 (4)				
C(2)	N(2)	H(222)	119 (7)	N(3)	C(4)	H(41)	107 (3)
H(221)	N(2)	H(222)	96 (8)	N(3)	C(4)	H(42)	109 (5)
				C(3)	C(4)	H(41)	119 (3)
Cu	N(3)	H(331)	106 (4)	C(3)	C(4)	H(42)	110 (5)
Cu	N(3)	H(332)	91 (6)	H(41)	C(4)	H(42)	103 (6)
C(4)	N(3)	H(331)	116 (3)				
C(4)	N(3)	H(332)	103 (6)	N(1)	C(5)	H(51)	105 (3)
H(331)	N(3)	H(332)	130 (7)	N(1)	C(5)	H(52)	114 (3)
				C(6)	C(5)	H(51)	112 (3)
Cu	N(4)	H(441)	122 (4)	C(6)	C(5)	H(52)	103 (3)
Cu	N(4)	H(442)	97 (3)	H(51)	C(5)	H(52)	114 (4)
C(6)	N(4)	H(441)	105 (4)				
C(6)	N(4)	H(442)	118 (3)	N(4)	C(6)	H(61)	105 (8)
H(441)	N(4)	H(442)	105 (5)	N(4)	C(6)	H(62)	102 (3)
				C(5)	C(6)	H(61)	115 (7)
N(1)	C(1)	H(11)	128 (6)	C(5)	C(6)	H(62)	109 (3)
N(1)	C(1)	H(12)	108 (4)	H(61)	C(6)	H(62)	116 (8)
C(2)	C(1)	H(11)	114 (6)				
C(2)	C(1)	H(12)	100 (3)				
H(11)	C(1)	H(12)	89 (7)				

weights calculated by the method suggested by Wiesner and Lingafelter.⁴⁰ From a plot of ΔF vs. F_o , expressions were obtained giving ΔF as a linear function of F_o for several ranges of F_o . Weights were assigned on the following basis: for unobserved reflections for which $|F_o| \leq F_{\min}$, $\sqrt{w} = 0.0$; for unobserved reflections with $|F_o| \geq F_{\min}$ and for observed reflections with $|F_o| \leq 18$, $\sqrt{w} = 1/(2,100 - 0.0689F_o)$; and for observed reflections with $|F_o| \geq 18$, $\sqrt{w} = 1/(0.50 + 0.0204F_o)$. Two cycles of least-squares refinement of nonhydrogen atoms with individual anisotropic temperature factors and two cycles of refinement of hydrogen atoms with isotropic temperature factors reduced R to 0.040. Even now the earlier mentioned eight reflections had large discrepancies. These reflections were therefore remeasured and the new values of F_o were found to be in good agreement with their F_o values. Including these new values and doing another cycle of refinement resulted in a final value of R of 0.037, with the average shift/error ratio of 0.04 σ and the maximum ratio of 0.15 σ in the final cycle. It is interesting to report that the comparison of parameters of this set with that at $R = 0.040$ showed changes in many of the positions and in temperature factors up to the extent of two standard deviations. The maximum changes were in the z coordinates due to the high l indices of the corrected reflections. The final values of observed and calculated structure factors are given in Table I. The final atomic parameters and their standard deviations, calculated in the usual way from the least-squares matrix, are given in Table II.

Discussion

The crystal structure consists of discrete trigonal bipyramidal [(tren)(SCN)Cu]⁺ cations and SCN⁻ anions, connected by a network of NH...N and NH...S hydrogen bonds. The trigonal bipyramidal coordination polyhedron of the Cu(II) ion has the three primary amine nitrogen atoms, N(2), N(3), and N(4), in the equatorial positions and the tertiary amine nitrogen atom, N(1), and the thiocyanate nitrogen atom, N(5), in the apical positions. Bond lengths and angles are shown in Figure 1 and Table III. The constraints of the tetradentate ligand force some distortion of the coordi-

nation polyhedron from exact D_{3h} symmetry, but there are also slight additional distortions. Thus the intrachelate N-Cu-N bond angles, all three of which are equal to the mean value of 84.1° within one standard deviation, and which agree well with those reported for other, related structures (85° in Cu(en)₂(SCN)₂,⁴¹ 86° in Cu(en)₂(NO₃)₂,⁴²), require the copper atom to lie 0.22 Å below the equatorial plane, toward the thiocyanate nitrogen atom. The factors which cause the other slight distortions, *i.e.*, the nonequality of the equatorial bond angles and bond distances, are not obvious, although the presence of the long (2.144 Å) bond in the position opposite the large (129.6°) angle is the same distortion as that reported in Pt(QAS)X₂ and suggested by Dyer and Venanzi⁴³ as due to a tendency toward square-pyramidal five-coordination or planar four-coordination. The Cu-N(1) (tertiary amine) and the two shorter Cu-N (primary amine) distances do not differ significantly. However, the Cu-N(5) (thiocyanate) distance is significantly shorter, in agreement with the relative positions of thiocyanate ion and amines in the nephelauxetic series.

All three ethylenediamine chelate rings have the *gauche* configuration and all have the *k* conformation,⁴⁴ as is also the case in [Co(Me₆tren)Br].⁴⁵ In [Ni(tren)(NCS)₂],³⁰ which has the two thiocyanate ions in *cis* positions in a distorted octahedral coordination polyhedron, two of the rings have the *k'* conformation and one has the *k* conformation. The asymmetry of the ethylenediamine moiety with respect to the coordina-

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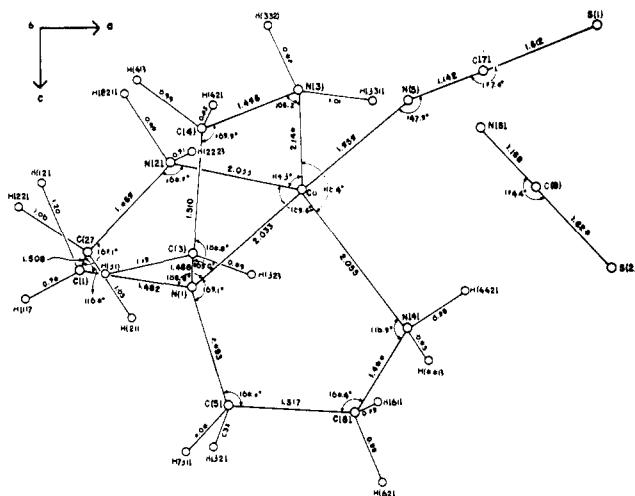


Figure 1. [010] projection of the molecule of $[\text{Cu}(\text{tren})(\text{NCS})](\text{SCN})$ showing various bond lengths and angles between nonhydrogen atoms. The estimated standard deviations in bond lengths are; Cu-N(1), Cu-N(2), Cu-N(3), Cu-N(4), 0.004; Cu-N(5), S(1)-C(7), S(2)-C(8), 0.005; N(1)-C(1), N(1)-C(3), N(1)-C(5), 0.006; N(2)-C(2), N(4)-C(6), N(5)-C(7), N(6)-C(8), C(1)-C(2), 0.007; N(3)-C(4), C(5)-C(6), 0.008; C(3)-C(4), 0.009. The average esd in bond lengths involving hydrogen atoms is 0.07 (varying in the range of 0.04 to 0.11). The estimated standard deviations in bond angles are; N(2)-Cu-N(3), N(2)-Cu-N(4), N(3)-Cu-N(4), N(1)-Cu-N(5), 0.2; Cu-N(1)-C(1), Cu-N(1)-C(3), Cu-N(1)-C(5), Cu-N(2)-C(2), Cu-N(3)-C(4), Cu-N(4)-C(6), 0.3; N(1)-C(1)-C(2), N(2)-C(2)-C(1), N(1)-C(3)-C(4), N(1)-C(5)-C(6), N(4)-C(6)-C(5), 0.4; and N(3)-C(4)-C(3), S(1)-C(7)-N(5), S(2)-C(8)-N(6), 0.5.

tion plane can most conveniently be expressed by the angle between the coordination plane, defined by the metal atom and the two nitrogen atoms, and the plane defined by the two nitrogen atoms and the midpoint of the carbon-carbon bond. This angle is $+5.6$, -0.6 , and -7.3° for the N(2), N(3), and N(4) chelate rings, respectively, in $[\text{Cu}(\text{tren})(\text{NCS})]^+$, 15.6 , 25.5 , and 19.3° for the corresponding rings in $[\text{Ni}(\text{tren})(\text{NCS})_2]^{30}$ and 8.3° for all three rings in $[\text{Co}(\text{Me}_6\text{tren})\text{Br}]^+$.

Within the ethylenediamine groups, the three C-C bond lengths are equal, with an average value of 1.512 Å. The three C-N(primary) bond lengths are equal, with an average value of 1.487 Å, and the three C-N(tertiary) bond lengths are equal, with an average value of 1.466 Å, but these two lengths are significantly different. The bond angles on both the carbon atoms and the nitrogen atoms vary slightly but significantly. No attempt has been made to explain these small variations.

The Cu-N-C (thiocyanate) angle, 163.3° , agrees with the values observed in most isothiocyanate complexes; 163.4 and 156.3° in $\text{Ni}(\text{tren})(\text{NCS})_2$,³⁰ 160° in $\text{Cu}(\text{py})_2(\text{NCS})_2$,⁴⁶ 165° in $\text{Ni}(\text{py})_2(\text{NCS})_2$,⁴⁷ 156° in $(\text{C}_5\text{H}_{13}\text{N}(\text{OH}))[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]$,⁴⁸ 162.1° in $\text{Ni}(\text{etu})_2(\text{NCS})_2$,⁴⁹ 162.2° in $\text{Ni}(\text{tu})_2(\text{NCS})_2$,⁵⁰ 161.2° in $\text{Zn}(\text{N}_2\text{H}_4)_2(\text{NCS})_2$,⁵¹ and 154° in $(\text{CH}_3)_3\text{SiNCS}$.⁵² Smaller

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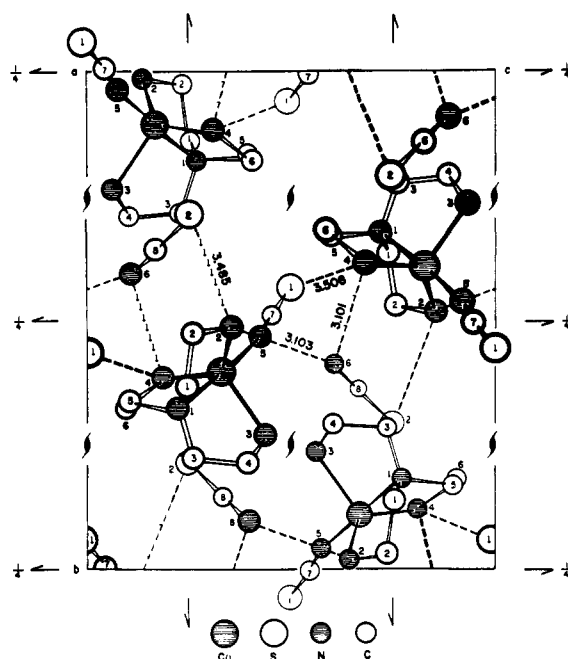


Figure 2. The structure of $[\text{Cu}(\text{tren})(\text{NCS})](\text{SCN})$ viewed down the a axis. Heavy solid lines indicate the coordination mechanism around copper. Dashed lines with interatomic distances represent the proposed hydrogen bonds. The numbers represent the numbering scheme used.

values have been reported in $\text{Ni}(\text{en})_2(\text{NCS})_2$,⁵³ 140° , and in $\text{Cd}(\text{etu})_2(\text{NCS})_2$,⁵⁴ 143° , while an angle of 179° has been reported in $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$.⁵⁵

The bond distances within the two thiocyanate ions are not significantly different, even though one is bonded to copper and the other is unbonded and their infrared spectra are clearly different. An examination of all reported C-N and C-S bond distances in thiocyanates shows a wide range of values, C-N from 1.13 to 1.34 Å and C-S from 1.55 to 1.76 Å. If we restrict our consideration to those reports, listed in Table IV, in which

Table IV. Bond Lengths (in Angstroms) in Thiocyanates

C-N	C-S	Compound	Ref
N-Bonded Covalent Compounds			
1.18 (1)	1.56 (1)	$(\text{CH}_3)_3\text{SiNCS}$	52
1.22	1.56	CH_2NCS	<i>a</i>
1.216 (2)	1.561 (2)	HNCS	<i>b</i>
1.172 (10)	1.560 (8)	$((\text{CH}_3)_3\text{CNBNCS})_4$	<i>c</i>
S-Bonded Covalent Compounds			
1.21	1.61	CH_3SCN	<i>a</i>
Metal Compounds			
1.149 (14)	1.689 (13)	KSCN	<i>d</i>
1.169 (14)	1.635 (13)	$\text{Ni}(\text{tu})_2(\text{NCS})_2$	50
1.128 (14)	1.655 (12)	$\text{Zn}(\text{N}_2\text{H}_4)_2(\text{NCS})_2$	51
(i) 1.142 (7)	1.612 (5)	$[\text{Cu}(\text{tren})(\text{NCS})](\text{SCN})$	Present work
(ii) 1.168 (7)	1.624 (5)		

^a C. I. Beard and B. P. Dailey, *J. Am. Chem. Soc.*, **71**, 929 (1949).

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^c P. T. Clarke and H. M. Powell, *J. Chem. Soc.*, 1172 (1966).

^d C. Akers, S. W. Peterson, and R. D. Willett, personal communication.

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the estimated standard deviations are less than 0.02 Å, there appear to be just three cases: (1) N-bonded covalent compounds, in which C–N is 1.17–1.22 Å and C–S is 1.56 Å; (2) one S-bonded covalent compound in which C–N is 1.21 Å and C–S is 1.61 Å; and (3) the metal complexes and salts, which include both N-bonded and nonbonded thiocyanate groups, in which C–N is 1.13–1.17 Å and C–S is 1.61–1.69 Å. It seems best to defer any attempt to explain these bond distances until more accurate values are available.

The general arrangement of the ions and the hydrogen-bond network are shown in Figure 2. The nitrogen atom, N(6), of the uncoordinated thiocyanate ion accepts two hydrogen bonds, with N···N distances of 3.10 Å, from N(2) and N(4) of two different

cations. The sulfur atom, S(2), of the uncoordinated thiocyanate ion accepts a hydrogen bond, with a N···S distance of 3.49 Å, from N(2), while the sulfur atom, S(1), of the coordinated thiocyanate ion accepts a hydrogen bond from N(4) with a N···S distance of 3.51 Å.

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Stereochemically Nonrigid Organometallic Molecules. VIII. Further Studies of σ -Cyclopentadienylmetal Compounds¹

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Abstract: The temperature dependence of the proton nmr spectrum of $(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\sigma\text{-C}_5\text{H}_5)$ has been studied down to -110° . The pattern of change is very similar to that previously observed in the isoelectronic $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$. It is concluded that the same mechanism (presumably a series of 1,2 shifts) is predominant for the intramolecular rearrangement ("ring whizzing") in both compounds, though the rate is greater in the chromium case. $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(1\text{-indenyl})$ has been prepared and found to be a rigid (nonfluxional) molecule up to 70° . It is shown that this would be expected if rapid 1,2 shifts, but not 1,3 shifts, are operative in the $\sigma\text{-C}_5\text{H}_5$ cases. By decoupling and deuteration experiments, it is shown that in the ABX spectrum of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(1\text{-indenyl})$, which closely resembles the low-temperature A_2B_2X spectrum of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$, $J_{BX} \ll J_{AX} \approx 2.2$ cps, and the A proton has a lower τ value than the B proton. These results support the arguments previously used to deduce the 1,2 shift mechanism for $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$.

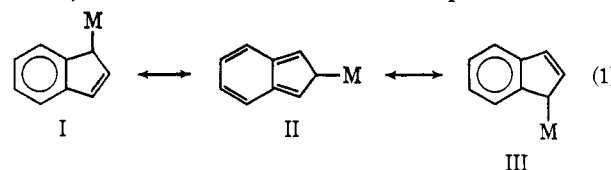
In an earlier paper in this series,² an investigation of the molecule $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$ was reported. A combination of X-ray work and study of the variation of the proton nmr spectrum as a function of temperature lead to the following main conclusions: (1) the molecule does have the kind of instantaneous structure implied by the formula $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$; (2) the intramolecular rearrangement process which causes the time-average equivalence of the five protons of the $\sigma\text{-C}_5\text{H}_5$ group at room temperature is a sequence of 1,2 shifts, probably having a polar metal-olefin complex as a transition state.

With these results in view, a number of further studies readily suggest themselves. Among these are (a) studies of homologous and/or isoelectronic molecules, such as $(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\sigma\text{-C}_5\text{H}_5)$, and (b) studies of some σ -indenylmetal compounds. The study of σ -indenyl compounds was expected to afford useful information regarding the validity of the previously proposed 1,2-shift mechanism (as opposed to a 1,3-shift mechanism) for $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$ in two ways.

(1) (a) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) Previous paper in this series, part VII: W. K. Bratton, F. A. Cotton, A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S. A.*, **58**, 1324 (1967).

(2) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

First, if the only low-energy path for rearrangement of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$ is indeed the one involving 1,2 shifts, then $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\sigma\text{-indenyl})$ should not exhibit fluxional behavior. This prediction is based on the fact that rearrangement by a sequence of 1,2 shifts would have to follow the course shown in eq 1. That is, in order to interconvert the equivalent struc-



tures I and III, and thus give the molecule a time-average plane of symmetry perpendicular to the molecular plane, it would be necessary to pass through structure II. However, on the basis of Hückel LCAO–MO calculations,^{3,4} the type of π -electron distribution in II is about

(3) The delocalization energies of I and II were taken to be equal to those of styrene and *o*-xyllylene, respectively, and the calculated values for the latter molecules were obtained from a published tabulation.⁴ Even if the absolute values for the individual systems may be somewhat uncertain, the difference should be rather reliable because of the cancellation of systematic errors in the two Hückel calculations.

(4) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π -Electron Calculations," W. H. Freeman & Co., San Francisco, Calif., 1965. Calculations with neglect of overlap ($S = 0$) yield a difference of 9.4 kcal/mole, while calculations with $S = 0.25$ yield a difference of 8.6 kcal/mole.