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The Crystal and Molecular Structure of μ-Dithiocyanatotetrakis(methyldiphenylphosphine)dicopper(I)

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The crystal and molecular structure of μ-Dithiocyanatotetrakis(methyldiphenylphosphine)dicopper(I) [$CuNCS(PCH_3(C_6H_5)_2)_2]_2$ has been determined from three-dimensional X-ray data collected from a single crystal. The material crystallizes in the space group $P\bar{1}$ of the triclinic system with two molecules in a cell of dimensions $a=10.32\pm0.02$, $b=11.24\pm0.02$, $c=12.00\pm0.02$ Å, $\alpha=90.4\pm0.1°$, $\beta=106.9\pm0.1°$, $\gamma=106.2\pm0.2°$. The observed density of 1.36 ± 0.02 g/cm³ agrees well with the calculated density of 1.36 g/cm³. Intensity data were collected on multiple films by the integrated equi-inclination Weissenberg technique. The structure was refined by full-matrix least-squares methods to a final R factor of 8.7% for 1195 non-zero independent reflections. The complex exists as a dimer in the solid state in which the thiocyanates bridge the two copper atoms. The two thiocyanate moieties and the copper atoms form an eight membered ring which is only approximately planar. The geometry around the copper atom can be described as a higly distorted tetrahedron.

Introduction

The tendency of Cu^I to form four-coordinate tetrahedral complexes with ligands containing donor atoms such as phosphorus and arsenic is well established.[2] With ammonia and halide ions, cuprous complexes are usually most stable as two-coordinate complexes with linear geometry.[3] Three-coordination on the other hand is very scarce, and it has been shown to occur in the solid state only in polymeric structures.[4,5]

Recently, it was reported that complexes such as $CuX(P(C_6H_5)_3)_2$ (X = N_3 and NCS) are monomeric in chloroform solution and presumably three-coordinate with trigonal planar geometry.[6,7] However, crystal structure analysis of $CuN_3(P(C_6H_5)_3)_2$ [8] has shown that in the crystal this complex exists as a dimer and hence four-coordination is imposed on the copper atom.

To better understand the factors which influence the coordination number and the stereochemistry around Cu^I we have determined the structure of the complex $CuNCS(PCH_3(C_6H_5)_2)_2$. This paper reports the results of this study.

Experimental Section

A solution of 0.3 g of KNCS in 50 ml of methanol was added slowly to 100 ml of chloroform solution containing 1.4 g of $CuCl(PCH_3(C_6H_5)_2)_3$. The resulting solution was stirred for one hour and then filtered. Addition of 100 ml of hexane and cooling caused the precipitation of the colorless complex. An analytically pure sample was obtained by recrystallization from a chloroform-hexane solution. *Anal.* Calcd. for $CuNCS(PCH_3(C_6H_5)_2)_2$: C, 62.1; H, 4.99. Found: C, 61.8; H, 5.08.

Crystals suitable for the crystallographic analysis were obtained by slow evaporation of a chloroform-hexane solution.

Collection and Reduction of the X-ray Data. The colorless crystals of $[CuNCS(PCH_3(C_6H_5)_2)_2]_2$ were examined by optical, precession, and Weissenberg techniques and were found to belong to the triclinic system. A Delaunay reduction showed no symmetry higher than triclinic. A convenient cell chosen for the indexing of the Weissenberg photographs has the dimensions $a=10.32\pm0.02$, $b=11.24\pm0.02$, $c=12.00\pm0.02$ Å, $\alpha=90.4\pm0.1°$, $\beta=106.9\pm0.1°$, $\gamma=106.2\pm0.2°$, and a cell volume 1272 Å³. An experimental density of $1.36\pm0.02°$ g/cm³ obtained by flotation in CCl_4-benzene solution agrees well with the density of 1.36 g/cm³ calculated for two molecules in the primitive cell. A negative piezoelectric test is in agreement with the centrosymmetric space group $P\bar{1}$. The satisfactory agreement ultimately obtained between observed and calculated structure factors confirms this choice.

Intensity data were collected at room temperature by the multiple film integrating equi-inclination Weissenberg technique, using a Nonius Integrating Weissenberg camera. Zirconium-filtered MoKα radiation was employed. The layers hk0 to hk6 were photographed and the intensities of the independent reflections accessible within the angular range $\theta_{Mo}\leqslant22.0°$ were estimated visually with the aid of a calibrated intensity strip. The angular range of $\theta_{Mo}\leqslant22.0°$ was chosen because above this angle very few reflections

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[1] Temple University Fellow 1969-1970.
[2] G. Booth in «Advances in Inorganic and Radiochemistry», 6, 1 (1964).
[3] F. A. Cotton and G. Wilkinson, «Advanced Inorganic Chemistry», John Wiley and Sons, 1967, p. 750.
[4] Cromer, *J. Phys. Chem.*, *61*, 1388 (1957).
[5] W. A. Spofford and E. L. Amma, *Chem. Comm.*, 405 (1968).
[6] R. F. Ziolo and Z. Dori, *J. Am. Chem. Soc.*, *90*, 6560 (1968).
[7] W. Beck, W. Fehlhammer, P. Pollmann, and H. Schochl, *Chem. Ber.*, *102*, 1976 (1969)
[8] R. F. Ziolo, A. P. Gaughan, Z. Dori, C. Pirpoint, and R. Eisenberg, *J. Am. Chem. Soc.*, *92*, 738 (1970).

were observed for reasonable exposure times. Intensity photographs were taken for 27 hours (2 cycles of integration). A 54 hour exposure time for the level hk2 showed an additional 17 non-zero reflections. At the same time, 14 strong reflections became too intense for reliable visual estimation. Thus, in order to get a good intensity estimate for the strong reflections, 27 hour exposure times were chosen. The intensities of 1207 non-zero reflections were corrected for Lorentz, polarization and spot elongation effects to yield F_o^2 (where $|F_o|$ is the observed structure amplitude). Because of the smallness of the linear absorption coefficient ($\mu = 11.02$ cm^{-1}) and the uniformity of the crystal dimensions ($0.27 \times 0.25 \times 0.30$ mm corresponding approximately to the a, b and c directions), no absorption correction was applied. Consideration of the maximum and minimum path lengths for the crystal shows the transmission factors to range from about .82 to .86. The $|F_o|$ values were subsequently brought to an approximate scale through a modification of Wilson's procedure.

Solution and Refinement of the Structure. The positions of the heavy atoms were readily determined from a three dimensional map of a sharpened Patterson function.[9] The relatively short Cu–Cu Patterson vector (5.4 Å) and the spatial arrangement of the heavy atoms indicated to us immediately that the complex exists as a dimer in the solid state. We were, therefore, able to differentiate at this stage between the phosphorus and sulfur atoms.

The positional parameters of the heavy atoms along with isotropic temperature factors were refined through several cycles of least squares. All the light atoms were then located on subsequent difference Fourier maps.

Table I. Observed and Calculated Structure Factor Amplitudes (in Electrons) for $[CuNCS(PCH_3(C_6H_5)_2)_2]_2$[a]

[a] The calculated value of F(000) is 528.

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(9) The main programs for the CDC 6400 computer used in this work were local modifications of the Busing-Levy ORFLS Least-Squares Program, the Zalkin FORDAP Fourier Program, and the ORFFE Function and Error Program.

The complete trial structure was refined by a least-squares procedure. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where the weights were assigned in the following way:[10] $I \leqslant 7$, $w = 1/7$; $7 < I < 175$, $w = 1$; $I \geqslant 175$, $w = 175/I$. I is the average raw intensity for the particular reflection. The atomic scattering factors for the neutral atoms tabulated by Ibers were used.[11] The real and imaginary parts of anomalous dispersion for the Cu, P, and S atoms were included in the calculated structure factors and these were obtained from Templeton's tabulation.[12]

Five cycles of full-matrix least-squares refinement, with isotropic thermal parameters for all atoms in the complete trial structure, and variable scale factors for each of the Weissenberg levels, resulted in convergence with a conventional R factor of .126 and a weighted R factor, R′, of .139. R and R′ are defined as follows: $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R' = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2)^{1/2}$. The positions of the 20 phenyl hydrogen atoms were then calculated (C–H = 1.084 Å)[13] and their contributions to $|F_c|$ were included in subsequent calculations. A further refinement through three least-squares cycles, in which 12 badly indexed reflections were removed, converged to an R = .106 and R′ = .119. A difference Fourier map calculated at this stage showed anisotropic motion for the heavy atoms. A final full-matrix least-squares refinement with 1195 observed reflections and 134 variables which included the anisotropic thermal parameters for the heavy atoms converged to final R values of R = .087 and R′ = .098.

In this set of calculations the intensities of reflections $\bar{h}\bar{k}l$ and $\bar{h}kl$ which were read on the bottom part of the intensity photographs were corrected for spot elongation[14] by the method of Phillips.[15] Another set of calculations without the spot elongation correction produced final R values of R = .089 and R′ = .10 with no significant changes in the parameters. Thus, it is clear that with integrated Weissenberg data, errors due to spot elongation are very small.

The shifts of the variable parameters in the final cycle were all less than 1/5 of their estimated standard deviations. The highest peak on the final difference Fourier map was 0.37 E/Å^3 compared to the height of a carbon atom of 1.81 E/Å^3 in this structure.

The final values of $|F_o|$ and $|F_c|$ in electrons are given in Table I. The final positional and thermal parameters are given in Table II.

Discussion

The crystal structure consists of dimeric units of $[CuNCS(PCH_3(C_6H_5)_2)_2]$ with a Cu–Cu distance of 5.30±.02 Å and a center of symmetry midway between the two copper atoms. A perspective view of the molecular structure is shown in Figure 1 and a stereoscopic view of the coordination sphere is shown in Figure 2. The intramolecular bond lengths and

Table II. Positional and Thermal Parameters for $[CuNCS(PCH_3(C_6H_5)_2)_2]_2$

Atom	X	Y	Z	B, Å^2
Cu_1	.1820(3) [a]	.1880(2)	.1513(3)	—
P_1	.0521(5)	.2315(4)	.2609(6)	—
P_2	.4092(5)	.2942(4)	.1793(6)	—
S_1	—.1699(5)	.0246(4)	—.2062(5)	—
N_1	.0518(15)	.1563(13)	—.0147(17)	3.7(3)
C_1(NCS)	—.0363(18)	.1028(15)	—.0950(20)	2.9(3)
Me_1 [b]	—.1307(23)	.1317(19)	.2121(24)	5.4(5)
Me_2	.4476(24)	.4673(20)	.1744(26)	6.3(5)
$P_1R_1C_1$ [c]	—.0463(20)	.4209(16)	.3319(21)	4.0(4)
$P_1R_1C_2$	—.0796(20)	.5319(17)	.3148(22)	4.2(4)
$P_1R_1C_3$	—.0416(22)	.6090(19)	.2319(25)	5.0(5)
$P_1R_1C_4$	.0217(24)	.5697(20)	.1627(26)	5.9(6)
$P_1R_1C_5$	.0558(20)	.4600(18)	.1704(23)	4.4(5)
$P_1R_1C_6$	.0209(17)	.3838(15)	.2560(20)	2.8(3)
$P_1R_2C_1$	.2321(27)	.1978(22)	.6527(27)	6.7(6)
$P_1R_2C_2$	.2548(22)	.2571(17)	.5699(23)	4.7(5)
$P_1R_2C_3$	.1139(19)	.2174(15)	.4138(21)	3.5(4)
$P_1R_2C_4$	.3183(32)	.2486(25)	.5990(33)	8.2(7)
$P_1R_2C_5$	.0245(22)	.1637(17)	.4859(24)	5.0(5)
$P_1R_2C_6$	.0874(22)	.1573(17)	.6042(24)	5.0(5)
$P_2R_1C_1$	.4875(19)	.2555(16)	.0787(21)	3.7(4)
$P_2R_1C_2$	.4155(24)	.1560(19)	—.0062(25)	5.9(6)
$P_2R_1C_3$	.4745(25)	.1267(20)	—.0921(26)	6.1(6)
$P_2R_1C_4$	.6238(25)	.3262(20)	.0690(26)	5.9(6)
$P_2R_1C_5$	.6037(26)	.1915(21)	—.0944(25)	6.1(6)
$P_2R_1C_6$	.6798(29)	.2893(24)	—.0065(31)	8.0(7)
$P_2R_2C_1$	.5412(22)	.1528(19)	.3329(24)	5.4(5)
$P_2R_2C_2$	.5268(18)	.2682(16)	.3207(20)	3.6(4)
$P_2R_2C_3$	.6805(26)	.3357(24)	.5133(29)	7.1(6)
$P_2R_2C_4$	.6264(28)	.1321(23)	.4488(29)	7.9(7)
$P_2R_2C_5$	.6002(22)	.3673(18)	.4094(24)	4.8(5)
$P_2R_2C_6$	.6931(25)	.2259(22)	.5361(27)	6.5(6)

Atom	β_{11} [d]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu_1	.0113(3)	.0076(2)	.0059(4)	.0027(2)	.0026(2)	.0004(2)
P_1	.0107(8)	.0059(5)	.0082(10)	.0030(5)	.0025(6)	.0003(4)
P_2	.0108(7)	.0071(5)	.0086(10)	.0009(5)	.0025(6)	.0006(5)
S_1	.0149(8)	.0070(5)	.0076(10)	.0038(5)	.0012(6)	.0014(4)

[a] Estimated standard deviations in the least significant figure(s) in this and other tables are given in parentheses. [b] In this and all subsequent tables, Me_1 and Me_2 refer to the methyl carbon atoms attached to P_1 and P_2 respectively (see Figure 1). [c] In this and all subsequent tables, $P_1R_1C_1$, for example, refers to a carbon atom forming part of a phenyl ring designated as P_1R_1; P_1 being the phosphorus atom to which R_1 is attached (see Figure 1). [d] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

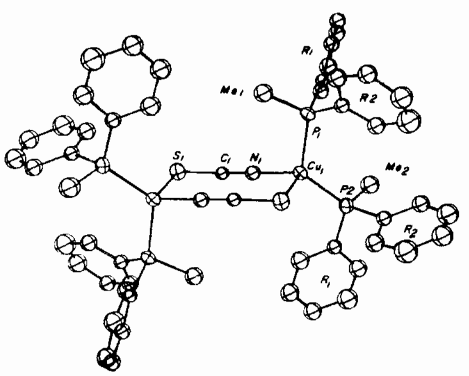

Figure 1. Perspective view of the Molecular Structure of $[CuNCS(PCH_3(C_6H_5)_2)_2]_2$.

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(10) D. W. Meek and J. A. Ibers, *Inorg. Chem.*, *8*, 1915 (1969).

(11) J. A. Ibers, «International Tables for X-ray Crystallography», Kynock Press, Birmingham, England, 1962, Vol. 3, Table III, IIII, I.

(12) D. H. Templeton, *ibid.*, Table III, III, II.

(13) «Tables of Interatomic Distances and Configuration in Molecules and Ions», Special Publication No. 18, The Chemical Society, London 1965, p. S18s.

(14) We wish to thank Dr. R. J. Fredricks from Allied Chemical Corporation for supplying us with a copy of his program

(15) D. C. Phillips, *Acta Cryst.*, *9*, 819 (1956).

bond angles are listed in Table III.

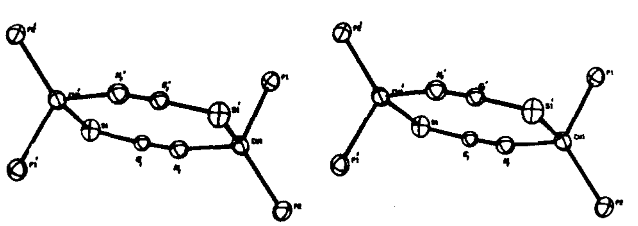


Figure 2. Stereoscopic view of the Coordination geometry of of $[CuNCS(PCH_3(C_6H_5)_2)_2]_2$ [a]

[a] The phenyl rings and methyl groups are omitted for clarity.

Table III. Selected Interatomic Distances (Å) and Angles for $[CuNCS(PCH_3(C_6H_5)_2)_2]_2$

Distances		Angle	
Cu_1—P_1	2.27(1)	P_1—Cu_1—P_2	123.0(1)
Cu_1—P_2	2.24(1)	P_1—Cu_1—N_1	105.1(6)
Cu_1—N_1	2.02(2)	P_2—Cu_1—N_1	117.1(5)
Cu_1—S_1'	2.46(1)	P_1—Cu_1—S_1'	97.1(3)
N_1—C_1(NCS)	1.14(2)	P_2—Cu_1—S_1'	108.6(3)
C_1(NCS)—S_1	1.64(2)	N_1—Cu_1—S_1'	102.2(4)
Cu_1—Cu_1'	5.30(2)	Cu_1—N_1—C(NCS)	158. (2)
P_1—Me	1.82(2)	S_1—C_1(NCS)—N_1	177. (2)
P_2—Me	1.89(2)	Cu_1—S_1'—C_1'(NCS)	99.1(6)
P_1—P_1R_1 [a]	1.83(2)		
P_1—P_1R_2 [a]	1.78(3)		
P_2—P_2R_1 [a]	1.75(3)		
P_2—P_2R_2 [a]	1.86(2)		
C_1(NCS)—N_1'	3.19(2)		

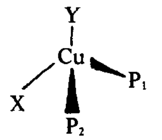
[a] These are the distances between the phosporus atoms and the phenyl carbon atom attached to the phosphorus atoms.

As can be seen from Figure 2, the two copper atoms are bridged by the two thiocyanates to form an eight-membered ring which is only approximately planar. The deviation from planarity manifests itself in the displacement of the copper atoms by .28 Å above and below the plane determined by the two thiocyanate anions. Similar atomic arrangements were observed in the structures of $[AGSCNP(n\text{-}C_3H_7)_3]$[16] and α-$[Pt_2(SCN)_2Cl_2(P(C_3H_7)_3)_2]$,[17] although in these cases the deviation of the eight-membered ring from planarity is considerably smaller.

The copper atoms are in a four-coordinate environment, surrounded by one nitrogen, one sulfur and two phosphorus atoms. The two Cu—P bond lengths of 2.27±.01 Å and 2.24±.01 Å and the Cu—N distance of 2.02±.02 Å are normal for these types of coordinated ligands.[18a,b,c] The Cu—S bond length of 2.46±.01 Å is longer than a normal Cu—S single bond of 2.39 Å.[19] Metal-sulfur bond lengths of this magnitude have been observed in other structures containing bridging thiocyanates,[17,18a]

The coordination geometry around the copper atoms is quite irregular and at best can be described as an extremely distorted tetrahedron. We note that the distortion from idealized tetrahedral geometry is particularly evident in the bond angles P_1—Cu_1—P_2, P_2—Cu_1—N_1, P_1—Cu_1—S_1' and S_1'—Cu_1—N_1 which deviate markedly from the expected angle of 109.5°, and in the long Cu—S bond distance. It is tempting to suggest that the non-bonded repulsions between the carbon and nitrogen atoms of the two thiocyanates (N_1—C_1' and N_1'—C_1; interatomic distance, 3.19±.02 Å; see Figure 2) are responsible for the observed Cu_1—S_1' bond length. However, this does not appear to be the case since in the molecule μ-diazido-tetrakis-(triphenylphosphine)dicopper(I)[8] the shortest inter N—N distance is 3.05±.02 Å and, if this distance were maintained in the present structure, the resulting Cu_1—S_1' distance would have been 2.30 Å. We, therefore, conclude that the long Cu_1—S_1' distance is due primarily to weak interaction between the copper and sulfur atoms.

Table IV. Distances of Central Atom from Bounding Faces the Polyhedron



Complex	Plane	X	Y	Distance (Å)
$[CuNCS(PCH_3(C_6H_5)_2)_2]_2$	$N_1P_1P_2$	N	—	0.48
	$S_1'N_1P_1$	N	S'	0.99
	$S_1'N_1P_2$	N	S'	0.74
	$S_1'P_1P_2$	—	S'	0.75
$[CuN_3(P(C_6H_5)_3)_2]_2$	$N_1P_1P_2$	N_1	—	0.60
	$N_3N_1P_1$	N_1	N_3	0.94
	$N_3N_1P_2$	N_1	N_3	0.77
	$N_3P_1P_2$	—	N_3	0.58
$C_6H_5C{\equiv}CCuP(CH_3)_3$ [a]	$C_1P_1P_2$	C_1	—	0.62
	$C_9C_1P_1$	C_1	C_9	0.94
	$C_9C_1P_2$	C_1	C_9	0.77
	$C_9P_1P_2$	—	C_9	0.59

[a] The copper atom is the one labeled Cu(2) in the structure; see ref. 20.

In describing the distortion of the coordination sphere from idealized tetrahedral geometry, one additional factor has to be considered, this being the distance of the central atom from the bounding faces of the polyhedron. In Table IV we list those distances for three four-coordinate structures of Cu^I. These can be compared with a distance of .73 Å calculated for a hypothetical molecule in which all bond lengths are 2.20 Å and all bond angles are 109.5°. Detailed examination of Table IV reveals the similarity in the coordination geometry around the copper atom in the two complexes $[CuN_3(P(C_6H_5)_3)_2]_2$[8] and $C_6H_5C{\equiv}CCuP(CH_3)_3$[20,21] and the difference between these two structures and that of $[CuNCS(PCH_3(C_6H_5)_2)_2]_2$. This difference manifests itself in the fact that in the thio-

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(16) A. Turco, C. Panattoni, and E. Frasson, *Nature*, *187*, 772 (1960).

(17) P. G. Owston, and J. M. Rowe, *Acta Cryst.*, *13*, 253 (1960).

(18) a) J. Garaj, *Inorg. Chem.*, *8*, 304 (1969); b) G. G. Messmer and G Palenik, *Can. J. Chem.*, *47*, 1440 (1969); c) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, *6*, 2223 (1967).

(19) L. Pauling «Nature of the Chemical Bond» 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 246, 410.

(20) P. W. R. Corfield, H. M. M. Shearer, *Acta Cryst.*, *21*, 957 (1966).

(21) The structure of $CuNO_3(P(C_6H_5)_3)_2$ (Ref 18b) is probably very similar to the two structures $C_6H_5C{\equiv}CCuP(CH_3)_3$ and $[CuN_3(P(C_6H_5)_3)_2]_2$.

(22) Infrared spectra were recorded on a Beckman IR-9 spectrophotometer.

Table V. Significant Least Squares Planes in $[CuNCS(PCH_3(C_6H_5)_2)_2]_2$ [a]

Best Plane Equation through Atoms P_1, P_2, N_1, C_1(NCS), S_1
$2.69X-10.74Y+3.46Z+1.45=0$
Distances of Atoms (in Å) from Plane

P_1	.005(5)	N_1	−.14(1)		
P_2	.010(5)	C_1(NCS)	−.08(2)	S_1	.014(5)

Best Plane Equation through Atoms of P_1R_1
$6.55X+2.41Y+4.82Z-2.3=0$
Distances of Atoms (in Å) from Plane

C_1	.01(2)	C_3	.01(2)	C_5	.00(2)
C_2	−.02(2)	C_4	.00(2)	C_6	.00(2)

Best Plane Equation through Atoms of P_1R_2
$4.19X-10.86Y-2.90Z+3.08=0$
Distances of Atoms (in Å) from Plane

C_1	.02(2)	C_3	.00(2)	C_5	.00(2)
C_2	.00(2)	C_4	−.02(2)	C_6	−.01(2)

Best Plane Equation through Atoms of P_2R_1
$4.46X-8.50Y+6.21Z-.48=0$
Distances of Atoms (in Å) from Plane

C_1	.01(2)	C_3	−.02(2)	C_5	.00(2)
C_2	.01(2)	C_4	−.04(2)	C_6	.05(3)

Best Plane Equation through Atoms of P_2R_2
$9.36X-.059Y-7.23Z-2.62=0$
Distances of Atoms (in Å) from Plane

C_1	.03(3)	C_3	.02(3)	C_5	.02(3)
C_2	−.03(2)	C_4	−.01(3)	C_6	−.02(3)

[a] The least square planes are given in terms of triclinic coordinates (see ref. 9).

cyanato complex, the copper atom is much closer to one of the bounding faces of the polyhedron. We note that this face is the one determined by the least squares plane through atoms P_1, P_2, N_1, C_1(NCS), S_1 (Table V). One might, therefore, suggest that the thiocyanato complex can be described as derived from trigonal pyramidal geometry. However, we argue against this description since the distance of the copper atom from the closest lying bounding plane, although short (.48 Å), is more than one-half of the distance expected for the idealized tetrahedral geometry. We therefore conclude that the coordination gometry around the copper atom in this complex can best be described as a squashed tetrahedron. We also suggest that this relatively short distance is a direct manifestation of the weak Cu_1–S_1' interaction.

The methyldiphenylphosphine ligands appear normal. The average phosphorus to phenyl carbon distance is 1.80 Å and the average angle around the phosphorus atoms is 109.4°. The phenyl rings are planar as expected (Table V) and the individual carbon-carbon distances range from 1.33 Å to 1.46 Å with a mean value of 1.39 Å. The average C–C–C angle in the rings is 120.0’ The thiocyanate anion is linear as expected and the N–C and C–S distances of 1.14±.02 Å and 1.64±.02 Å respectively are similar to those observed in other structures containing bridging thiocyanates.[8,17,18a]

Molecular weight determination in $CHCl_3$ suggests that the predominant species in solution is a three-coordinate monomer with a presumably trigonal planar geometry. In the thiocyanate $C{\equiv}N$ stretching region,[22] a solid sample shows one sharp band centered at 2103 cm^{-1}. In $CHCl_3$ solution the band splits into a broad doublet (2084 cm^{-1}, 2112 cm^{-1}) which might indicate the presence of both N and S bonded thiocyanate. This interesting observation and some other related structural problems of Cu^I complexes containing phosphine ligands are currently under investigation.

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