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Copper(I) and Copper(II) Complexes of Tetramethyldiphosphinedisulfide. I. Structural Characterization of the Dinuclear, Molecular Complex of Copper(I) Chloride

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The potentially bidentate ligand, tetramethyldiphosphinedisulfide $(CH_3)_4P_2S_2$, *has been found to react with copper(II) chloride dihydrate,* $CuCl_2 \cdot 2H_2O$, *in ethanol at room temperature to yield, as the major product, a white compound. This is apparently the same substance reported in 1965 by Meek and Nicpon and formulated by them as* $[Cu(S_2P_2Me_4)_2][CuCl_2]$. *An X-ray crystallographic investigation has shown that the white substance is a molecular, dinuclear compound (which may, of course, dissociate or otherwise rearrange in solution) in which each Cu(I) is surrounded by a tetrahedral array of three sulfur atoms and one chlorine atom. The* $Me_4P_2S_2$ *ligands have a gauche rotational configuration and each one chelates to one Cu(I) atom to form a five-membered ring. The* $Me_4P_2S_4CuCl$ *halves of the molecule are joined by two bridging sulfur atoms, one from each half, thus forming a planar* Cu_2S_2 *rhombic ring. The entire molecule has as its only symmetry element an inversion center. The principal crystallographic data are: space group,* $P2_1/n$; $a = 7.998(1)$ Å; $b = 9.688(2)$ Å; $c = 14.473(3)$ Å; $\beta = 104.90(1)°$; $V = 1083.7(3)$ Å^3; $Z = 2$.

Introduction

Despite the fact that, on the one hand, sulfur as a ligand atom is of major, widespread importance and, on the other, phosphine oxides, and P=O groups in other compounds, are also important ligands, the literature on complexes containing P=S groups as ligands is remarkably sparse. Indeed the first coordination compound containing such a ligand, Ph_3PS, was reported only in 1960.[1] In that limited investigation only the palladium complex, $PdCl_2(Ph_3PS)_2$, its Ph_3PSe analog and $SnCl_4(Ph_3PSe)_2$ were reported. An attempt to prepare $SnCl_4(Ph_3PS)_2$, as well as attempts to prepare Ph_3PS complexes of BF_3, Co^{2+}, Hg^{2+} and Cu^{2+} were unsuccessful. This work implied that the prospects for obtaining an extensive series of phosphine sulfide (or selenide) complexes seemed doubtful.

Subsequently, however, there have been many further reports.[2–11] Of special interest here are certain results of Meek and Nicpon.[12,13] These workers have shown that Me_3PS is a better ligand than Ph_3PS. They then extended their studies to the potentially bidentate ligands, $Me_2P(S)–P(S)Me_2$ and its tetraethyl analog. They found these diphosphine disulfides to be good ligands for Cu(I); these complexes were prepared by reactions of the ligands with Cu(II) compounds, specifically, $Cu(ClO_4)_2$ and $CuCl_2$. From the perchlorate, compounds with the composition $(R_4P_2S_2)_2CuClO_4$ were obtained. Conductance data led Meek and Nicpon to conclude that these compounds are uni–univalent electrolytes. Thus, the ability of the $R_4P_2S_2$ ligand to function as a bidentate chelating ligand was indicated. The product obtained with $Me_4P_2S_2$ and $CuCl_2$, of composition $(Me_4P_2S_2)CuCl$, was formulated as $[(Me_4P_2S_2)_2Cu][CuCl_2]$ on the basis of electrolytic conductance data.

Aside from a general interest in the ligand properties of the $R_4P_2S_2$ molecules, our interest in the particular compound $(Me_4P_2S_2)CuCl$ was aroused because of the plausible suggestion that it might contain the $CuCl_2^-$ ion. Although this linear ion has often been postulated, there is only one report of direct evidence for its existence[14] and an additional documented example would have been of interest. An attempt was therefore made to prepare the compound in crystalline form and ascertain its structure by X-ray crystallography. That attempt was successful and is described in this paper. In the course of preparing the substance in a form suitable for crystallographic investigation we observed that in addition to the white substance a brown product could be obtained in small quantities and in crystalline form. This is probably the same compound mentioned by Nicpon[13] although we were unaware of this unpublished observation until much later when a copy of Nicpon's doctoral thesis was made available to us by Professor Meek. That substance was also identified and structurally characterized, as described in the following paper.[15]

Experimental

Preparation

Copper(II) chloride dihydrate (0.5 g) was dissolved in 70 ml absolute ethanol. Separately, an equimolar solution of $Me_4P_2S_2$ (0.55 g) in 50 ml tetrahydrofuran plus 20 ml CH_2Cl_2 was prepared. These solutions were poured into the two sides of a U-tube having a medium porosity sintered glass disk at its midpoint. The solutions were able to mix slowly, at 22° C, through the disk. After about an hour a mixture of brown crystals and white crystals had formed on the disk, the white crystals being far more abundant. Further observation showed that when the brown substance remained in contact with the reaction mixture, it was converted into a white material in a few hours. Crystals of both the brown and the white substances were separated by filtration, dried by brief pumping and mounted in capillaries for X-ray study.

Collection of X-ray Data

A crystal of dimensions $0.010 \times 0.0047 \times 0.050$ cm was selected and mounted on a Syntex $P\bar{1}$ computer-controlled, four-circle diffractometer, equipped with a graphite-crystal monochromator in the incident beam. The unit cell was found to be monoclinic and least-squares refinement of fifteen centered reflections produced the orientation matrix for data collection and gave the following unit cell dimensions: a = 7.998(1) Å; b = 9.688(2) Å; c = 14.473(3) Å; β = 104.90(1)°; V = 1083.7(3) $Å^3$. Systematic absences subsequently evident in the set of intensity data indicated that the space group is $P2_1/n$, a nonstandard setting of $P2_1/c$. The calculated density is 1.747 gcm^{-3} if the cell is assumed to contain four formula units, $(CH_3)_4P_2S_2CuCl$; this agrees well with a density of 1.752 (± 0.005) gcm^{-1} measured by flotation.

Intensity data were collected in the range $0° < 2\Theta \leqq 55°$ using Mo Kα radiation. The Θ–2Θ scan technique with a variable scan rate from 4–24°/min was used. The scan range was from 2Θ(Mo Kα_1) $-0.9°$ to 2Θ(Mo Kα_2) $+0.9°$. Additional details about data collection have been described elsewhere.[16] In order to check the stability of the crystal and the X-ray diffractometer, four reflections were selected as standards and their intensities were recorded periodically. No significant variations in these intensities were observed.

A total of 3242 reflections was collected and the usual data reduction procedures[17] were applied. The parameter p, used in the calculation of standard deviations on intensities $[\sigma(F_o^2)]$, was assigned the value 0.06. Although the linear absorption coefficient was not especially high (μ = 29.24 cm^{-1} for Mo Kα radiation), in order to get the most accurate atomic parameters, absorption corrections have been made. The faces of the crystal were identified by the indices $0\bar{1}0$, $\bar{1}01$, $10\bar{1}$, 101, $\bar{1}0\bar{1}$, $11\bar{1}$ and $\bar{1}11$. A numerical correction gave transmission factors varying from 73% to 91% with an average of 85%.

Solution and Refinement of the Structure[17]

A Patterson function was calculated and the copper atom was located on the Harker plane of 1/2–2X; 1/2; 1/2–2Z. The structure was solved by the usual combination of least-squares refinements and difference Fourier syntheses. In the least-squares refinements only those 1488 reflections were used for which $F_o^2 > 3\sigma(F_o^2)$. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weight w is $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from the International Tables[18] and anomalous dispersion corrections[19] were included for all atoms except carbon and hydrogen atoms.

After all nonhydrogen atoms in the asymmetric unit, *i.e.*, Cu, Cl, 2S, 2P and 4C atoms, had been located, anisotropic refinement was carried to convergence, which resulted in the following discrepancy indices: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.065$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.11$. A difference electron density map then revealed some of the hydrogen atoms, namely two on C(1), two on C(2), one on C(3) and one on C(4). The positions of the remaining six hydrogen atoms were calculated assuming tetrahedral geometry about the carbon atoms and C–H bond lengths of 0.95 Å.

Two more cycles of refinement were carried out in which all nonhydrogen atoms were refined anisotropically and the positional coordinates of the hydrogen atoms were refined, while the temperature parameter for each hydrogen atom was fixed at an isotropic value of 5.0 $Å^2$. This lead to the discrepancy indices $R_1 = 0.041$ and $R_2 = 0.052$. Finally, two cycles, in which the isotropic thermal parameters for the hydrogen atoms were also allowed to vary, were carried out; in these cycles there was a total of 139 variable parameters so that the ratio of data to variables was slightly greater than 10. The final R values were: R_1 = 0.040 and R_2 = 0.051. For only three parameter pairs (all on the chlorine atom) did the correlation coefficients slightly exceed 0.5. Parameter changes in the final cycle were all less than 0.25 times the esd of the parameter.

A final difference map, calculated using all the reflections included in the refinement, had no peak with a density in excess of 0.5 $eÅ^{-3}$ with the exception of one maximum with a density of 1.7 $eÅ^{-3}$ at a distance of 0.92Å from the Cu atom and trans to a trigonal sulfur atom. This peak had roughly twice the density of peaks due to the hydrogen atoms that were found. However, on a difference map calculated using only the 126 reflections for which $\lambda^{-1}\sin\Theta < 0.250$ this peak disappeared while the peaks due to the hydrogen atoms remained. We conclude that this peak is an artifact.

Of the 1488 reflections used in the refinement, there were only 20 for which $||F_o|-|F_c||$ slightly exceeded $3\sigma(F_o^2)$. No dependence of the $\Sigma w(|F_o|-|F_c|)^2$ values on the indices, on $(\sin\Theta)/\lambda$ or on $|F_o|$ was noted. The standard deviation in an observation of unit weight was 1.11.

The F_o and the final F_c values are presented in Table I. The final refined positional and thermal parameters are listed in Table II.

TABLE I. The Observed and Final Calculated Structure Factor Amplitudes Listed as $10F_o|$ and $10F_c|$, in Electrons.

[illegible]

TABLE II. Positional and Thermal Parameters and their Standard Deviations.[a]
The Form of the Thermal Ellipsoid is $\exp[-(\beta_{11}k^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Atom	x	y	z	B isotropic	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	−0.0295(1)	0.08567(8)	0.09733(6)		0.0340(3)	0.00583(5)	0.00450(4)	0.0019(1)	0.00244(8)	0.00049(5)
Cl	−0.1073(3)	0.3029(2)	0.1204(1)		0.0373(5)	0.0061(1)	0.0069(1)	0.0032(2)	0.0100(2)	0.0008(1)
S1	0.0053(2)	−0.0434(1)	0.2353(1)		0.0209(3)	0.0057(1)	0.00283(7)	−0.0018(1)	0.0006(1)	−0.00029(8)
S2	−0.2195(2)	−0.0580(1)	−0.0256(1)		0.0120(1)	0.0059(1)	0.00322(7)	0.0000(1)	0.0003(1)	0.00122(8)
P1	−0.0263(2)	−0.2314(1)	0.18115(9)		0.0096(2)	0.0050(1)	0.00241(6)	0.0006(1)	0.0008(1)	0.00042(7)
P2	−0.2455(2)	−0.2237(1)	0.05140(9)		0.0091(2)	0.0047(1)	0.00282(6)	−0.0003(1)	0.0006(1)	0.00022(7)
C1	−0.0822(9)	−0.3578(7)	0.2586(5)		0.018(1)	0.0070(7)	0.0037(3)	−0.0013(8)	0.0018(6)	0.0014(4)
C2	0.1526(9)	−0.2968(8)	0.1437(6)		0.014(1)	0.0122(9)	0.0053(4)	0.0048(9)	0.0032(6)	0.0007(5)
C3	−0.250(1)	−0.3827(7)	−0.0122(5)		0.026(2)	0.0066(7)	0.0035(3)	−0.0035(9)	0.0001(6)	−0.0009(4)
C4	−0.4339(9)	−0.2156(9)	0.0966(6)		0.011(1)	0.014(1)	0.0059(4)	0.0009(9)	0.0023(6)	0.0024(6)
H1	−0.119(8)	−0.430(6)	0.228(4)	3(1)						
H2	−0.176(8)	−0.324(6)	0.277(4)	3(1)						
H3	0.019(9)	−0.368(7)	0.313(5)	4(1)						
H4	0.180(9)	−0.260(8)	0.092(5)	5(2)						
H5	0.148(9)	−0.391(9)	0.137(5)	6(2)						
H6	0.262(9)	−0.277(7)	0.187(6)	6(2)						
H7	−0.143(9)	−0.386(7)	−0.044(4)	4(1)						
H8	−0.345(9)	−0.386(7)	−0.052(5)	5(2)						
H9	−0.259(8)	−0.457(6)	0.029(4)	4(1)						
H10	−0.417(9)	−0.137(9)	0.139(6)	7(2)						
H11	−0.444(9)	−0.285(7)	0.130(5)	4(1)						
H12	−0.518(9)	−0.211(7)	0.045(5)	5(2)						

[a] Numbers in parentheses are estimated standard deviations in the last significant digit.

Results

The structure is made up of dinuclear molecules, one of which is shown in Fig. 1. These dinuclear units lie on crystallographic inversion centers; there are two of them in each unit cell. Table III presents interatomic distances and Table IV gives bond angles. Table V gives the equations of some mean planes and the dihedral angles between them.

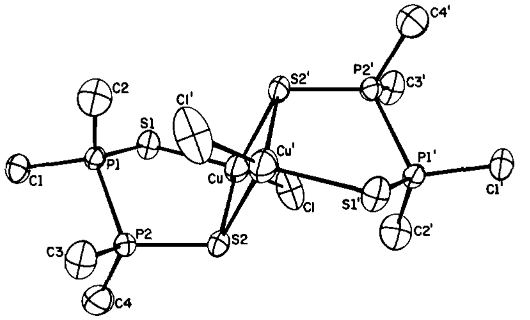

Figure 1. The structure of the centrosymmetric dinuclear molecule showing the atom numbering scheme. Atoms with primed labels are related by the inversion center to those with the corresponding unprimed numbers. Each atom is represented by its thermal ellipsoid, scaled to enclose 50% of the electron density.

TABLE III. Bond Distances, Angstroms.[a]

		Average Value
Cu–Cl	2.244(2)	
Cu–S1	2.311(2)	
Cu–S2	2.453(2)	
Cu–S2′	2.486(2)	
P1–S1	1.973(2)	
P2–S2	1.995(2)	
P1–P2	2.217(2)	
Cu–Cu′	3.406(2)	
P1–C1	1.772(7)	1.787(3)
P1–C2	1.792(6)	
P2–C3	1.790(6)	
P2–C4	1.793(7)	
C1–H1	0.84(6)	0.92(2)
C1–H2	0.92(6)	
C1–H3	0.98(7)	
C2–H4	0.91(7)	
C2–H5	0.91(9)	
C2–H6	0.96(8)	
C3–H7	1.07(7)	
C3–H8	0.82(9)	
C3–H9	0.96(6)	
C4–H10	0.96(8)	
C4–H11	0.86(6)	
C4–H12	0.86(8)	

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[a] Numbers in parentheses are estimated standard deviations in the last significant digit.

TABLE IV. Bond angles, Degrees.[a]

Cl–Cu–S1	110.81(7)
Cl–Cu–S2	119.76(8)
Cl–Cu–S2′	116.48(7)
S1–Cu–S2	103.52(6)
S1–Cu–S2′	111.79(7)
S2–Cu–S2′	92.82(5)
P1–S1–Cu	100.48(7)
Cu–S2–Cu′	87.18(5)
P2–S2–Cu	100.71(7)
P2–S2–Cu′	110.87(7)
S1–P1–P2	107.32(8)
C1–P1–S1	114.2(3)
C1–P1–P2	106.4(2)
C1–P1–C2	107.4(4)
C2–P1–S1	114.8(3)
C2–P1–P2	106.1(3)
P1–P2–S2	109.09(8)
C3–P2–P1	108.2(3)
C3–P2–S2	113.4(2)
C3–P2–C4	108.5(4)
C4–P2–P1	104.4(3)
C4–P2–S2	112.8(3)
H1–C1–P1	110(4)
H2–C1–P1	107(4)
H3–C1–P1	106(4)
H1–C1–H2	104(5)
H1–C1–H3	117(5)
H2–C1–H3	112(5)
H4–C2–P1	120(5)
H5–C2–P1	112(5)
H6–C1–P1	114(5)
H4–C2–H5	109(7)
H4–C2–H6	95(6)
H5–C2–H6	106(7)
H7–C3–P2	110(4)
H8–C3–P2	107(6)
H9–C3–P2	108(4)
H7–C3–H8	113(6)
H7–C3–H9	117(5)
H8–C3–H9	102(7)
H10–C4–P2	106(5)
H11–C4–P2	113(4)
H12–C4–P2	103(5)
H10–C4–H11	106(6)
H10–C4–H12	117(7)
H11–C4–H12	111(7)

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[a] Numbers in parentheses are estimated standard deviations in the last significant digit.

Discussion

The $Me_4P_2S_2$ molecules in this compound serve as chelating, bidentate ligands. They form puckered five-membered rings including the copper atoms.

Each copper(I) atom achieves a coordination number of four with distorted tetrahedral geometry of the

TABLE V. Least Squares Planes.[a]

Plane	Atoms	Equation	Dihedral Angle	
1	Cu, S1, S2, P1, P2	$-7.269x+2.716y+7.554z-1.3089=0$	1 and 2 1 and 3 1 and 4	11.7° 6.1° 101.5°
2	Cu, S1, S2	$-7.006x+4.306y+5.797z-1.1397=0$	2 and 3 2 and 4	17.3° 113.2°
3	S1, S2, P1, P2	$-7.455x+1.707y+7.744z-1.5244=0$	3 and 4	96.6°
4	Cu, S2, Cu′, S2′	$1.217x-7.782y+7.218z=0$	–	

B Distances (Å) of Atoms from Least Squares Planes

Plane 1		Plane 4	
Cu	−0.127	S1	0.185
S1	0.313	S2	−0.186
S2	−0.064	P1	−0.322
P1	−0.379	P2	0.323
P2	0.257	C1	0.482
C1	1.207	C2	−2.062
C1	0.271	C3	−0.411
C2	−2.145	C4	2.096
C3	−0.626		
C4	1.996		

[a] x, y and z are fractional monoclinic coordinates.

surrounding ligands. This is possible because one sulfur atom in each $Me_4P_2S_2$ molecules serves as a bridge between two copper atoms. The bonds from the copper atoms to the bridging sulfur atoms are considerably longer (~0.15 Å) than those to the nonbridging sulfur atoms.

The central four-membered ring consisting of alternating Cu and S atoms is rigorously planar because of the crystallographic inversion center. There is a slight distortion from full rhombic (C_{2h}) symmetry because the Cu–S(2) and Cu–S(2)′ are not quite equal.

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