

lines in the spectrum. A second test for planarity comes from the measured moments of inertia, since the out-of-plane contributions to the moments are measured by  $\Sigma m_i c_i^2 = \frac{1}{2}(I_a + I_b - I_c)$ , where  $m_i$  is the mass of the  $i$ th atom,  $c_i$  is its out-of-plane distance, and the  $I$  values are the three moments of inertia.

Table I. Observed and Calculated Transition Frequencies

Transition	$\nu_{\text{obsd}}$ , Mc.	$\nu_{\text{calcd}}$ , Mc.	$\nu_{\text{calcd}} - \nu_{\text{obsd}}$ , Mc.
$1_{11} \rightarrow 2_{12}$	12,003.38	12,033.29	-0.09
	...	12,009.09	...
$1_{01} \rightarrow 2_{02}$	12,933.70	12,933.48	-0.22
	12,938.12	12,938.43	+0.31
	14,261.14	14,260.99	-0.15
$1_{10} \rightarrow 2_{11}$	14,264.27	14,264.23	-0.04
	17,889.99	17,890.04	+0.05
$2_{12} \rightarrow 3_{13}$	17,898.63	17,898.98	+0.35
	18,941.14	18,941.18	+0.04
$2_{02} \rightarrow 3_{03}$	18,949.25	18,949.53	+0.28
	19,698.00	19,698.21	+0.21
$2_{21} \rightarrow 3_{22}$	19,704.74	19,704.99	+0.25
	20,455.35	20,455.24	-0.11
$2_{20} \rightarrow 3_{21}$	20,460.58	20,460.45	-0.13
	21,254.34	21,254.33	-0.01
$2_{11} \rightarrow 3_{12}$	21,259.80	21,259.50	-0.30
	23,666.77	23,667.28	+0.51
$3_{13} \rightarrow 4_{14}$	23,680.03	23,679.56	-0.47
	24,563.32	24,563.72	+0.40
$3_{03} \rightarrow 4_{04}$	24,576.08	24,575.99	-0.09
	26,107.30	26,108.58	+1.28
	...	26,117.96	...

The observed microwave spectrum of ethylene carbonate was quite rich, with many observable transitions from molecules in excited vibrational states. Particularly prominent in the spectrum were closely spaced doublets of considerably greater intensity than the other lines. The frequencies of these were measured, and they were found to fit rigid rotor patterns for low-J,

Table II. Calculated Rotational Constants and Moments of Inertia<sup>a</sup>

	Lower frequency set	Higher frequency set
$A$ , Mc.	8044.3	8045.1
$B$ , Mc.	3847.46	3847.95
$C$ , Mc.	2718.61	2720.38
$I_a$ , a.m.u. Å. <sup>2</sup>	62.824	62.818
$I_b$ , a.m.u. Å. <sup>2</sup>	131.353	131.337
$I_c$ , a.m.u. Å. <sup>2</sup>	185.895	185.774
$\frac{1}{2}(I_a + I_b - I_c)$ , a.m.u. Å. <sup>2</sup>	4.141	4.191

<sup>a</sup> Conversion factor:  $I_a = 5.05377 \times 10^8/A$ , corresponding to  $C^{12} = 12$  atomic weight scale.

R-branch transitions. From their intensity, they must be considered to arise from the two lowest vibrational states split by tunneling. The measured frequencies are listed in Table I together with the frequencies cal-

culated from the derived rotational constants given in Table II.

The data provide two independent kinds of evidence that ethylene carbonate has a nonplanar ring in the gas phase and that the reported symmetry difference between the gas and solid phases is not present. First, the appearance of doublets of similar intensity for the rotational transitions can be explained only by the assumption of a nonplanar ground state with tunneling through the barrier at the planar configuration. Secondly, the observed out-of-plane contribution to the moments of inertia is too large to arise from the hydrogen atoms only. If a C-H bond length of 1.096 Å. and tetrahedral angles are assumed,  $\frac{1}{2}(I_a + I_b - I_c)$  can be calculated to be 3.229 a.m.u. Å.<sup>2</sup>. Propiolactone, which does have a planar ring with the same number of out-of-plane hydrogen atoms, has been shown<sup>4</sup> to have  $\frac{1}{2}(I_a + I_b - I_c) = 3.242$  a.m.u. Å.<sup>2</sup> in the ground state. The values of 4.141 and 4.191 measured for ethylene carbonate must contain an appreciable contribution from the heavier atoms since they would otherwise represent impossibly large hydrogen distances or angles.

As the ring approaches planarity, the intensities of the infrared transitions that are inactive in the  $C_{2v}$  limit must become weaker. If the ring is more nearly planar in the liquid and vapor states it may be that the intensity of these bands falls below the observable limit even though they are not forbidden by symmetry.

*Acknowledgment.* This research was made possible by support extended by the Robert A. Welch Foundation.

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Received August 30, 1965

## Metal Complexes of Tertiary Phosphine Sulfides<sup>1</sup>

Sir:

A variety of interesting phosphine oxide<sup>2</sup> complexes have been investigated during the past 7 years. Since tertiary phosphine sulfides possess unshared pairs of electrons on the sulfur atom and have approximately the same structures as analogous phosphine oxides, one would expect tertiary phosphine sulfides also to form stable transition metal complexes. In fact, Zingaro, *et al.*,<sup>3,4</sup> demonstrated that phosphine sulfides

(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research through Grant No. 1518-A1,3.

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possessed donor properties similar to the phosphine oxides in forming addition compounds with halogens. However, a thorough search of the literature revealed only two cursory and rather negative reports of phosphine sulfide-metal complexes.<sup>5,6</sup>

In contrast to the limited results of previous investigators,<sup>5,6</sup> we have prepared several different metal coordination complexes with a series of tertiary phosphine sulfides. For example, trimethylphosphine sulfide,  $(\text{CH}_3)_3\text{P}=\text{S}$ , forms white crystalline complexes with Cu(I), Cd(II), Hg(II), and Zn(II) salts by the direct reaction of the appropriate metal salt with the ligand in absolute ethanol. The analytical and conductance data for the bis(trimethylphosphine sulfide) complexes of  $\text{ZnI}_2$ ,  $\text{CdI}_2$ , and  $\text{HgCl}_2$  are reported below. *Anal.* Calcd. for  $\text{C}_6\text{H}_{18}\text{I}_2\text{P}_2\text{S}_2\text{Zn}$ : C, 13.46; H, 3.39; I, 47.40. Found: C, 13.69; H, 3.37; I, 47.37; yield, 70%;  $\Lambda_m$ , 7.8.<sup>7</sup> Calcd. for  $\text{C}_6\text{H}_{18}\text{CdI}_2\text{P}_2\text{S}_2$ : C, 12.37; H, 3.11; I, 43.57. Found: C, 12.58; H, 3.11; I, 43.47; yield, 90%;  $\Lambda_m$ , 12.0.<sup>7</sup> Calcd. for  $\text{C}_6\text{H}_{18}\text{Cl}_2\text{HgP}_2\text{S}_2$ : C, 14.77; H, 3.72; Cl, 14.54. Found: C, 14.69; H, 3.72; Cl, 14.24; yield, 99%;  $\Lambda_m$ , 8.9.<sup>7</sup>

The conductance data indicate that the complexes are essentially nonelectrolytes<sup>7</sup>; thus they may be represented as  $\text{ML}_2\text{X}_2$ .

The position of the  $\text{P}=\text{S}$  band in the infrared spectrum of each of the complexes is shifted to lower energy compared with the position of the peak in the uncomplexed ligand, in agreement with the expected behavior of a  $\text{P}=\text{S}$  group bonded directly to the metal. The  $\text{P}=\text{S}$  band is assigned unambiguously at  $565\text{ cm}^{-1}$  in  $(\text{CH}_3)_3\text{P}=\text{S}$  and at 535, 538, and  $528\text{ cm}^{-1}$  in the  $\text{ZnL}_2\text{I}_2$ ,  $\text{CdL}_2\text{I}_2$ , and  $\text{HgL}_2\text{Cl}_2$  complexes, respectively.

Diphosphine disulfides,  $\text{R}_2\text{P}(\text{S})\text{P}(\text{S})\text{R}_2$ , present the intriguing possibility that both  $\text{P}=\text{S}$  groups could coordinate to the same metallic ion to form a five-membered chelate ring containing no carbon atoms. Diphosphine disulfides only recently have been shown to exist in the *trans* form in the solid state.<sup>8,9</sup> As is generally the case with chelate formation, in which two donor groups are joined by a single bond, formation of a chelate with a  $\text{R}_2\text{P}(\text{S})\text{P}(\text{S})\text{R}_2$  molecule would require that the complex be sufficiently stable to permit the ligand to overcome the barrier to rotation about the  $\text{P}-\text{P}$  bond in solution.

We have prepared several metal complexes with the tetramethyl- and tetraethyldiphosphine disulfides as ligands. These are the first known examples of complexes which contain a chelating diphosphine disulfide. The copper(I) perchlorate complexes  $[\text{Cu}(\text{ligand})_2]\text{ClO}_4$  were prepared from both  $(\text{CH}_3)_2\text{P}(\text{S})\text{P}(\text{S})(\text{CH}_3)_2$  and  $(\text{C}_2\text{H}_5)_2\text{P}(\text{S})\text{P}(\text{S})(\text{C}_2\text{H}_5)_2$  by the reaction of the appropriate ligand with copper(II) perchlorate. The cupric ion is reduced rapidly to copper(I) in the presence of the diphosphine disulfides. We have not yet identified the oxidized product.

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(6) J. Philip and C. Curran, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p. 28L.

(7) The conductance measurements were done on  $\sim 10^{-3}\text{ M}$  acetonitrile solutions. A uni-univalent electrolyte should give a value in the range 140–155; a bi-univalent electrolyte should be  $\sim 280$ –310.

(8) P. J. Wheatly, *J. Chem. Soc.*, 523 (1960); S. N. Dutta and M. M. Woolfson, *Acta Cryst.*, 14, 178 (1961).

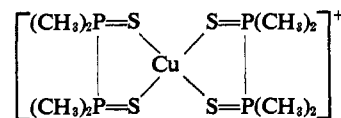
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For preparation of bis(tetraethyldiphosphine disulfide)copper(I) perchlorate, the ligand (2.42 g., 10 mmoles) in 20 ml. of warm absolute ethanol was added with stirring to a solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1.85 g., 5 mmoles) in 10 ml. of absolute ethanol. A light yellow solution resulted immediately upon mixing the two solutions and a white compound crystallized from the cooled solution. The crystals were collected on a sintered glass funnel, washed with ethanol and ether, and dried over  $\text{P}_4\text{O}_{10}$  *in vacuo*. The complex was recrystallized from 1-butanol; yield 2.70 g., 83%. *Anal.* Calcd. for  $\text{C}_{16}\text{H}_{40}\text{ClCuO}_4\text{P}_4\text{S}_4$ : C, 29.67; H, 6.23; S, 19.80; Cl, 5.47. Found: C, 29.55; H, 6.28; S, 20.09; Cl, 5.69. The bis(tetramethyldiphosphine disulfide)copper(I) perchlorate was prepared similarly. *Anal.* Calcd. for  $\text{C}_8\text{H}_{24}\text{ClCuO}_4\text{P}_4\text{S}_4$ : C, 17.94; H, 4.49; Cl, 6.62; P, 23.15. Found: C, 17.56; H, 4.34; Cl, 6.59; P, 23.19. Both complexes are uni-univalent electrolytes in acetonitrile ( $\Lambda_m = 147.0$  and  $149.7$ , respectively).

Ethanol solutions of the cupric halides are also rapidly reduced in the presence of the diphosphine disulfides. White crystalline compounds which correspond to the composition  $\text{Cu}(\text{ligand})\text{X}$  are isolated from the solutions. For example, a solution of tetraethyldiphosphine disulfide (2.42 g., 10 mmoles) in 10 ml. of absolute ethanol was added to 0.85 g. (5 mmoles) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 10 ml. of absolute ethanol. After stirring for 20 min., addition of anhydrous diethyl ether induced crystallization. The white platelets were collected on a sintered glass funnel, washed with ether (in which the ligand is very soluble), and dried over  $\text{P}_4\text{O}_{10}$  *in vacuo*; yield, 1.65 g., 96%. *Anal.* Calcd. for  $\text{C}_8\text{H}_{20}\text{ClCuP}_2\text{S}_2$ : C, 28.15; H, 5.91; Cl, 10.39; P, 18.15. Found: C, 28.28; H, 5.78; Cl, 10.32; P, 18.06.

The conductance data on the cuprous halide complexes are typical of uni-univalent electrolytes in acetonitrile and indicate that the complexes should be formulated as  $[\text{CuL}_2][\text{CuX}_2]$ .

The greatly increased complexity of the infrared spectra of the  $(\text{CH}_3)_2\text{P}(\text{S})\text{P}(\text{S})(\text{CH}_3)_2$  complexes, compared with the spectrum of the free ligand, clearly demonstrates that the coordinated molecule has undergone a structural rearrangement from the *trans* form and that it no longer possesses a center of symmetry. That is, the infrared spectra indicate a *cis*  $>\text{P}(\text{S})-\text{P}(\text{S})<$  atom arrangement of the ligand in the complexes. Therefore, the Cu(I) cations are represented as



in which the Cu(I) ion probably is surrounded by a tetrahedron of four sulfur atoms.

(10) Public Health Service Predoctoral Fellow, 1965–1966.

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Received July 30, 1965