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Three-Coordinate Copper(I) Complexes of Tertiary Phosphine Sulfide, Phosphine Selenide, and Arsine Sulfide Ligands¹

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A series of stable, trigonal-planar, three-coordinate copper(I) cations, $[\text{CuL}_3]^+$, have been isolated and characterized by elemental analyses, conductance, infrared spectra, X-ray powder patterns, and the single-crystal structure determination of $[\text{Cu}(\text{CH}_3)_3\text{PS}]_3\text{ClO}_4$.⁴ The values of the $\nu(\text{P}-\text{S})$ stretching frequency for the tris-ligand complexes decrease in the range of 13–36 cm^{-1} from the values of the corresponding free ligands. Infrared spectral studies on acetone solutions of the complexes $[\text{CuL}_3]^+$ ($\text{L} = (\text{CH}_3)_x(\text{C}_6\text{H}_5)_{3-x}\text{PS}$) show an increasing tendency toward dissociation as the number of methyl groups decreases. In addition to the tris-ligand complexes, a series of neutral complexes of formula CuLX ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) was obtained and characterized. Several structural types are proposed for the latter series of complexes.

Introduction

Tertiary phosphine sulfide ligands form rather stable complexes with "class b" or soft metal ions.^{5–12} Copper(I) forms several different types of compounds with phosphine sulfides, e.g., cations composed of three ligands,⁴ cations containing two chelating biphosphine disulfide ligands,^{6,8,13} and neutral complexes of stoichiometry CuLX .^{9,14}

Until recently the coordination number in copper(I) complexes was generally assumed to be 2 (linear) or more often 4 (tetrahedral) in the presence of soft donor atoms.¹⁵ Although the number of structural determinations of Cu(I) complexes is still small, a definitive example of linear coordination is known for $[\text{CuCl}_2]^-$ ¹⁶ while examples of tetrahedral coordination are known for the monomers L_2CuX ($\text{L} = \text{Ph}_3\text{P}$, $\text{X} = \text{a doubly coordinating anion such as } \text{NO}_3^- \text{ or } \text{BH}_4^-$),¹⁷ for the dimer $[(\text{Ph}_3\text{P})_2\text{CuN}_3]_2$,¹⁸ and for higher

polymers such as the tetramer $[\text{Cu}(\text{AsMe}_3)\text{I}]_4$.¹⁹ Recently three-coordinate Cu(I) complexes were proposed to explain molecular weight and nmr data obtained for solutions of $(\text{R}_3\text{P})_2\text{CuX}$ and $(\text{R}_3\text{P})_3\text{CuX}$ compounds.^{15,20,21} Support for this contention was furnished when definitive examples of trigonal-planar or distorted trigonal-planar, tricoordination were found for Cu(I) with the X-ray structure determinations of $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{ClO}_4$,⁴ $[\text{Cu}(\text{Me}_3\text{PS})\text{Cl}]_3$,¹⁴ $(\text{Ph}_3\text{P})_3\text{Cu}_2\text{Cl}_2$,²² and $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$ ($\text{etu} = \text{ethylenethiourea}$).²³ Toward copper(I), trimethylphosphine sulfide can function either as a terminal⁴ or as a bridging ligand.¹⁴

To provide more information on the structural types and the coordination numbers preferred by copper(I) with phosphine sulfide ligands, the following investigation was undertaken. An extensive series of cationic complexes of the type $[\text{CuL}_3]\text{BF}_4$ (where L is a tertiary phosphine sulfide or selenide or a tertiary arsine sulfide) was isolated and characterized by elemental analyses, conductance, infrared spectra, and X-ray powder pattern data. A preliminary report of this work has appeared.²⁴ A series of neutral complexes of the formula CuLX ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) was also obtained and characterized. In the solid state all of the tris-ligand complexes are thought to possess a trigonal-planar structure similar to that of $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{ClO}_4$. In acetone solution only a few of the complexes retain the tris-ligand structures. Most of them undergo some loss of ligand, and the extent of ligand dissociation depends markedly on L. Several structural features are proposed for the CuLX compounds on the basis of X-ray structure determinations^{14,25} and infrared spectra.

Experimental Section

Reagents and Equipment. All solvents were reagent grade and were used without additional purification. Conductance measurements were obtained using a calibrated Lab Line 11200 conductivity

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(4) P. G. Eller and P. W. R. Corfield, *Chem. Commun.*, 105 (1971).

(5) E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1959 (1960).

(6) D. W. Meek and P. E. Nicpon, *J. Amer. Chem. Soc.*, 87, 4951 (1965).

(7) P. E. Nicpon and D. W. Meek, *Chem. Commun.*, 398 (1966).

(8) P. E. Nicpon, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1966.

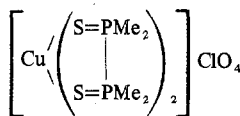
(9) J. A. W. Dalziel, A. F. le C. Holding, and B. E. Watts, *J. Chem. Soc. A*, 358 (1967).

(10) W. E. Stinkard and D. W. Meek, *Inorg. Chem.*, 8, 1811 (1969).

(11) M. G. King and G. P. McQuillan, *J. Chem. Soc. A*, 898 (1967).

(12) P. M. Boorman and K. J. Reimer, *Can. J. Chem.*, 49, 2926 (1971).

(13) P. W. R. Corfield, personal communication, 1973, has shown by a X-ray structure determination of



that both ligands are chelated to give a tetrahedral arrangement of sulfur atoms around copper, as proposed in ref 6.

(14) (a) J. A. Tiethof, J. K. Stalick, P. W. R. Corfield, and D. W. Meek, *J. Chem. Soc., Chem. Commun.*, 1141 (1972); (b) J. A. Tiethof, J. K. Stalick, and D. W. Meek, *Inorg. Chem.*, 12, 1170 (1973).

(15) W. T. Reichle, *Inorg. Chim. Acta*, 5, 325 (1971), and references contained therein.

(16) M. G. Newton, H. D. Caughman, and R. G. Taylor, *Chem. Commun.*, 1227 (1970).

(17) S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, 10, 1322 (1971), and references contained therein.

(18) R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, 10, 1289 (1971).

(19) A. F. Wells, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 94, 447 (1936).

(20) S. J. Lippard and J. J. Mayerle, *Inorg. Chem.*, 11, 753 (1972).

(21) E. L. Muettterties and C. W. Alegrianti, *J. Amer. Chem. Soc.*, 92, 4114 (1970).

(22) D. F. Lewis, S. J. Lippard, and P. S. Welcker, *J. Amer. Chem. Soc.*, 92, 3805 (1970).

(23) M. S. Weininger, G. W. Hunt, and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1140 (1972).

(24) J. A. Tiethof, A. T. Hetevy, P. E. Nicpon, and D. W. Meek, *Inorg. Nucl. Chem. Lett.*, 8, 841 (1972).

(25) P. W. R. Corfield, personal communication, 1973; the structure of $[\text{Cu}(\text{Me}_3\text{PS})\text{SCN}]_n$ consists of a linear chain formed by bridging thiocyanate units. A somewhat weaker interaction of SCN^- between chains causes part of the copper atoms to be pseudo four-coordinate.

cell, an Industrial Instruments Inc. Model RC162B conductivity bridge operating at 1000 Hz, and $\sim 10^{-3}$ M solutions of the complexes in nitromethane or acetone that had been dried with Linde 4A molecular sieves. Infrared spectra were recorded on a Beckman IR-9 or on a Perkin-Elmer 337 spectrophotometer with the solid samples suspended in Nujol mulls between polished KBr plates. Infrared spectra of the solutions were obtained in the 560–650-cm⁻¹ region using polyethylene cells (Barnes Engineering Co.). Proton nmr measurements were taken on a Varian A-60A instrument with TMS as an internal standard. X-Ray powder patterns were obtained on a Norelco camera, and the samples were placed in a 0.3-mm Lindemann glass capillary. Single-crystal X-ray diffraction photographs were taken on a Supper precession camera. Molecular weights of the complexes in acetone solutions were determined by Galbraith Laboratories, Inc., Knoxville, Tenn., using vapor pressure osmometry. Elemental analyses were determined by Galbraith Laboratories, Inc., and M.H.W. Laboratories, Garden City, Mich. Melting points were obtained on a hot-stage microscope and are uncorrected.

Synthesis of the Ligands.²⁶ Triphenylarsine sulfide (Ph₃AsS)^{26a} and triphenylphosphine selenide (Ph₃PSe)^{26b} were prepared according to literature procedures. All of the phosphine sulfides were prepared by treating the commercially available phosphines with recrystallized elemental sulfur. The detailed procedure is described below for trimethylphosphine sulfide (Me₃PS). Trimethylphosphine (10 g, 0.13 mol) was placed in a flask containing degassed benzene (150 ml) under nitrogen. Sulfur (5 g, 0.156 mol) was added in 1-g portions with cooling and agitation. The solvent was removed on a rotary evaporator, and the residue was dissolved in warm methanol. The resultant solution was filtered and allowed to cool and the crystalline product was collected. Additional material was obtained when the volume of the filtrate was reduced; yield 11.3 g, 80%; mp 157°, $\nu(\text{P}=\text{S}) = 564 \text{ cm}^{-1}$ (lit. values, 155.5–156° and 570 cm⁻¹).^{26c,d} Properties of the other phosphine sulfides are listed below and the literature values are given in parentheses: triethylphosphine sulfide (Et₃PS), mp 94.5–96° and $\nu(\text{P}=\text{S}) 536 \text{ cm}^{-1}$ (94.5–95.5° and 535 cm⁻¹);^{26c} triisopropylphosphine sulfide (*i*-Pr)₃PS, mp 36–37° and $\nu(\text{P}=\text{S}) 539 \text{ cm}^{-1}$ (35° and 537 cm⁻¹);^{26e} dimethylphenylphosphine sulfide (Me₂PhPS), mp 43–45° and $\nu(\text{P}=\text{S}) 586 \text{ cm}^{-1}$ (47–47.5°^{26f} and 585 cm⁻¹^{26c}); triphenylphosphine sulfide (Ph₃PS), mp 158° and $\nu(\text{P}=\text{S}) 637 \text{ cm}^{-1}$ (160° and 637 cm⁻¹); tris(dimethylamino)phosphine sulfide ($\{\text{Me}_2\text{N}\}_3\text{PS}$), bp 80–82° (2 mm); nmr: doublet at $\tau 7.35$ with $J_{\text{P-H}} = 11.0 \text{ Hz}$ and $J_{13\text{C-H}} = 136 \text{ Hz}$ ($\tau 7.38$,^{26g} $J_{\text{P-H}} = 11.3 \text{ Hz}$ ^{26g} and $J_{13\text{C-H}} = 136 \text{ Hz}$ ^{26h}).

Preparation of the Metal Complexes. The molar conductivity values, $\nu(\text{P}=\text{S})$, elemental analyses, and melting points, if determined, are given in Table I.

A. $[\text{Cu}(\text{Ph}_3\text{AsS})_3]\text{BF}_4$, Method I. A hot ethanol solution of Ph₃AsS (1.00 g, 2.96 mmol in 45 ml) was added with stirring to an ethanol solution (20 ml) of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.34 g, 0.99 mmol) that had been saturated with sulfur dioxide. On mixing the solutions, the color turned to a pale yellow and a white solid began to crystallize. After cooling the mixture to ambient temperature and then to 0°, the white solid was collected (1.01 g, 0.88 mmol). A portion of the solid (0.65 g) was recrystallized by dissolving it in hot ethanol and cooling to 4°. The resulting large white plates were collected, washed with ethanol and ether, and dried under vacuum; yield 0.53 g.

B. $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{BF}_4$. An ethanol solution (14 ml) of Me₃PS (0.39 g, 3.6 mmol) was added over a 10-min period to a stirred ethanol solution (8 ml) of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.32 g, 0.99 mmol). On mixing the solutions the color changed from blue-green to a pale green and a white solid precipitated. After cooling the mixture to 4°, the solid was collected and recrystallized by dissolving it in hot ethanol and cooling the solution to 4°; yield 0.37 g.

C. $[\text{Cu}(\{\text{Me}_2\text{N}\}_3\text{PS})_3]\text{BF}_4$. The complex $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (0.19 g, 0.61 mmol) prepared by the method described for $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$,^{26h} was added to an ethanol solution (15 ml) of $\{\text{Me}_2\text{N}\}_3\text{PS}$ (0.40 g, 1.95 mmol). The mixture was stirred until the $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ dissolved and then the solvent was removed on a rotary evaporator. Recrystallization was accomplished by dissolving the solid in hot ethanol-ether (1:4) and cooling the solution to -15°. The resulting white needles were collected, washed with ether, and dried *in vacuo*; yield 0.33 g.

(26) (a) W. T. Reichle, *Inorg. Chem.*, **1**, 650 (1962); (b) P. E. Nicpon and D. W. Meek, *Inorg. Syn.*, **10**, 157 (1967); (c) R. A. Zingaro, *Inorg. Chem.*, **2**, 192 (1963); (d) F. N. Hooge and P. J. Christen, *Recl. Trav. Chim. Pays-Bas*, **77**, 911 (1958); (e) A. H. Cowley and J. L. Mills, *J. Amer. Chem. Soc.*, **91**, 2915 (1969); (f) H. J. Harwood and K. A. Poilart, *J. Org. Chem.*, **28**, 3430 (1963); (g) R. Keat and R. A. Shaw, *J. Chem. Soc.*, 4802 (1965); (h) G. Marvel and G. Martin, *C. R. Acad. Sci.*, **255**, 2095 (1962).

D.-H. $[\text{CuL}_3]\text{BF}_4$, L = Et₃PS, (*i*-Pr)₃PS, Me₂PhPS, Ph₃PS, Ph₃PSe. These complexes were prepared following method I and recrystallized from the solvents indicated: L = Ph₃PS and Ph₃PSe, ethanol; L = Et₃PS and (*i*-Pr)₃PS, an ethanol-ether mixture; L = Me₂-PhPS, methanol.

I. $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{NO}_3$. This complex was prepared following method I using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and recrystallized from acetone.

J. $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{ClO}_4$, Method II. Solid LiCl (25 mg, 0.59 mmol) was stirred with an acetonitrile solution (7 ml) of $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{BF}_4$ (0.3 g, 0.63 mmol) for 30 min. The resultant white solid was collected, washed with ether, and dried *in vacuo*; yield 35 mg.

K.-M. $\text{Cu}(\text{Me}_3\text{PS})\text{X}$, X = Br, I, SCN. These complexes were prepared following method II using LiBr, NaI, and LiSCN, respectively.

N, O. $\text{Cu}(\text{Ph}_3\text{PS})\text{Br}$, $\text{Cu}(\text{Me}_2\text{PhPS})\text{Cl}$. These complexes were prepared in ethanol following method II. The infrared spectra of $\text{Cu}(\text{Ph}_3\text{PS})\text{Br}$ resembled the one reported previously.⁹

P. $\text{Cu}(\text{Ph}_3\text{PS})\text{Cl}$. A hot ethanol solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.76 g, 4.0 mmol) was stirred with Ph₃PS (3.97 g, 13.0 mmol) until all the solid had dissolved. Addition of stannous chloride (0.44 g, 4 mmol) in ethanol caused a pale precipitate to form and the solution to turn colorless. The resulting solid was collected and dried *in vacuo*; mp 172° (lit.⁹ mp 168°).

Solution Infrared Studies. Infrared measurements were taken on acetone solutions of Me₃PS, Me₂PhPS, Ph₃PS, and the corresponding $[\text{CuL}_3]\text{BF}_4$ complexes. The spectra were recorded in the 560–650-cm⁻¹ region on a Beckman IR-9 spectrophotometer using matched polyethylene cells (~ 0.5 -mm thickness). Concentrations of the free phosphine sulfide ligands were determined from the A_{max} of the $\nu(\text{P}=\text{S})$ band. The A_{max} vs. concentration curves for standardized ligand solutions were obtained and used for calibration. The complexes were studied in the concentration range of 0.008–0.07 M.

Results and Discussion

Three-Coordinate, Cationic $[\text{CuL}_3]^+$ Complexes. The triligand complexes $[\text{CuL}_3]\text{BF}_4$ were prepared (1) by treating $[\text{Cu}(\text{H}_2\text{O})_6]\text{BF}_4$ either with the phosphine sulfide in the presence of a reducing agent (*e.g.*, SnCl₂ or SO₂) or with an excess of the ligand in the cases of trialkylphosphine sulfides,²⁷ or (2) by treating $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ with stoichiometric amounts of the ligands. The latter method appears to be generally applicable and is preferred since no reducing agent is required and no phosphine sulfide is consumed.

The white crystalline products are uni-univalent electrolytes, analyze consistently for three phosphine sulfide ligands (Table I),²⁸ and exhibit infrared peaks characteristic of an uncoordinated, T_d BF_4^- ion.^{29,30} A single-crystal, X-ray structure determination of $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{ClO}_4$ showed that it consists of discrete $[\text{Cu}(\text{Me}_3\text{PS})_3]^+$ and ClO_4^- ions with approximately trigonal-planar coordination of sulfur atoms about the Cu(I) ion.⁴

For the present study the tetrafluoroborate salts were prepared rather than the perchlorate salts for laboratory safety reasons. However, structural differences between the two salts should be minimal. Indeed, the X-ray powder pattern of $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{ClO}_4$ is indistinguishable from that of $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{BF}_4$, indicating that the two salts are isomorphous with almost identical cell dimensions. A similar situation exists for $[\text{Cu}(\text{Ph}_3\text{PS})_3]\text{BF}_4$ and $[\text{Cu}(\text{Ph}_3\text{PS})_3]\text{ClO}_4$, but the powder pattern of $[\text{Cu}(\{\text{Me}_2\text{N}\}_3\text{PS})_3]\text{BF}_4$ does not resemble that of $[\text{Cu}(\{\text{Me}_2\text{N}\}_3\text{PS})_4]\text{ClO}_4$. As an additional variation of anions, the complex $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{NO}_3$ was prepared. It

(27) Although the specific oxidation products in these reactions have not usually been determined, it is known that $(\text{Me}_2\text{N})_3\text{PS}$ is oxidized by both bromine and Cu(II) to $[(\text{Me}_2\text{N})_3\text{P}-\text{S}-\text{S}-\text{P}(\text{NMe}_2)_3]^{2+}$ [W. E. Slinkard and D. W. Meek, *Chem. Commun.*, 361 (1969)], which is analogous to the oxidation product of thiourea, $[(\text{H}_2\text{N})_2\text{C}-\text{S}-\text{S}-\text{C}(\text{NH}_2)_2]^{2+}$.

(28) When liquid $(\text{Me}_2\text{N})_3\text{PS}$ was used as both ligand and solvent, Cu^{2+} was reduced to Cu(I), and the tetrakis complex $[\text{CuL}_4]\text{ClO}_4$ was isolated, owing to the large mole ratio of $(\text{Me}_2\text{N})_3\text{PS}$ to Cu present.¹⁰

(29) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970.

(30) F. Cariatì and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).

Table I. Characterization Data for the Copper(I) Complexes

| Complex | m.p., °C | M in CH_3NO_2 (ohms ⁻¹ cm ² mole ⁻¹) | Elemental Analyses | | | | Infrared Bands (cm ⁻¹) | | Other Diagnostic Infrared Bands | |
|---|------------------------|--|--------------------|-------------|--------------|-------------|---------------------------------------|---------------------|------------------------------------|-------------|
| | | | %C Calcd. | %C Found | %H Calcd. | %H Found | % other Calcd. | % other Found | | ν (P-S) |
| [Cu(Me ₃ PS) ₃]BF ₄ | 194.5-196 ^a | 86 ^b | 22.93 | 22.79 | 5.73 | 5.80 | 16.05 | 15.83(F) | 540 (s) | 24 |
| [Cu(St ₃ PS) ₃]BF ₄ | 122-125 | 72 | 35.90 | 35.95 | 7.44 | 7.41 | 12.50 | 12.41(F) | c | |
| [Cu(1-Pr ₃ PS) ₃]BF ₄ | 142-155 | 74 | 44.59 | 44.03 | 8.73 | 8.57 | 13.23 | 13.52(S) | c | |
| [Cu(Me ₂ PHFS) ₃]BF ₄ | 110.5-112.5 | 71 | 43.66 | 43.49 | 5.00 | 5.00 | 11.46 | 11.58(F) | 553(vs) | 33 |
| [Cu(Ph ₃ PS) ₃]BF ₄ | 201 ^a | 69 ^d | 62.71 | 63.04 | 4.35 | 4.60 | 7.35 | 7.07(F) | 602(vs) | 35 |
| [Cu([Me ₂ N]PFS) ₃]BF ₄ | 98-99.5 | 90 | 29.37 | 29.51 | 7.40 | 7.85 | 10.32 8.63 | 8.8 (F) 8.8 (Cu) | 533 | 13 |
| [Cu(Ph ₃ PSe) ₃]BF ₄ | a | 69 | 55.24 | 55.33 | 3.86 | 3.98 | 5.41 | 5.22(Cu) | 546(vs) ^e | 15 |
| [Cu(Ph ₃ AsS) ₃]BF ₄ | 180-181.5 | 74 | 56.39 | 56.12 | 3.92 | 3.80 | 6.54 | 6.50(F) | 473(vs) ^f | 23 |
| [Cu(Me ₃ PS) ₃]NO ₃ | a | 62 | 24.02 | 23.80 | 6.05 | 6.06 | 3.11 | 2.93(N) | 537(s), 547(s) | 17, 27 |
| [Cu(Me ₃ PS)(Cl) ₂] | | g | 17.40 | 17.57 | 4.38 | 4.42 | 17.12 | 17.29(Cl) | 520(s) | 44 |
| Cu(Me ₃ PS)Br | | g | 14.32 | 14.29 | 3.61 | 3.51 | 38.58 | 38.41(Br) | 524(s) | 40 |
| Cu(Me ₃ PS)I | | g | 12.07 | 12.18 | 3.04 | 2.90 | 42.50 | 42.31(I) | 519(s) | 45 |
| [Cu(Me ₃ PS)(SCN)] | | g | 20.91 | 20.80 | 3.95 | 4.04 | 6.10 | 5.92(N) | 543, 547(s) | 17, 21 |
| Cu(Me ₂ PHFS)Cl | | g | 35.69 | 35.59 | 4.12 | 4.31 | 13.17 | 12.98(Cl) | 534, 546(s) | 52, 40 |

a) decomposed in a sealed capillary.

b) conductance in acetone = 145.

c) ν (P-S) band obscured by other bands.

d) conductance in acetone = 119.

e) ν (P-Se)

f) ν (As-S)

g) Insufficiently soluble for conductance measurements.

NO_3^- : $\nu_1=1055$ (vw), $\nu_2=831$ (w), $\nu_3=1340$ (vs).
 sym (P-C)=698(s), asym (P-C)=767(m)^{1ed}
 sym (P-C)=697(s), asym (P-C)=762(m)^{1ed}
 sym (P-C)=692(s), asym (P-C)=756(m)^{1ed}
 sym (P-C)=704(s)^{2e}; ν (C≡N)=2108, 2119(s)

is substantially more soluble in common solvents and decomposes more rapidly on standing than the analogous BF_4^- and ClO_4^- salts. Although NO_3^- tends to coordinate more often than ClO_4^- and BF_4^- , the conductivity of the nitrate compound in nitromethane and the appearance of infrared bands assignable to ionic nitrate²⁹ support its formulation as $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{NO}_3$.

The infrared spectra of the $[\text{CuL}_3]\text{BF}_4$ complexes are essentially composites of the spectra of the ligands and the BF_4^- ion. They show the phosphorus-sulfur stretching vibration (or $\nu(\text{As-S})$, or $\nu(\text{P-Se})$) shifted to a lower energy in the complexes. The shifts of $\nu(\text{P-S})$ are -13 to -36 cm^{-1} while the shifts of $\nu(\text{As-S})$ and $\nu(\text{P-Se})$ are smaller. These trends in the shifts have been observed previously with other metals^{5-9,11,12} and presumably reflect a decreased P-S bond order when sulfur is bonded to a metal. We have observed a direct correlation between the $\nu(\text{P-S})$ and the P-S bond distance for $(\text{CH}_3)_3\text{PS}$ derivatives.¹⁴

Ligand Dissociation in Solution. The $[\text{CuL}_3]^+$ complexes undergo varying degrees of dissociation and exchange in non-aqueous solutions at ambient temperatures. Mixtures of $[\text{Cu}(\text{Me}_3\text{PS})_3]^+$ and Me_3PS in acetone at 37° undergo rapid exchange and show only one sharp methyl doublet in the proton nmr at an average chemical shift.³¹ The methyl resonance occurs at τ 7.98 in $[\text{Cu}(\text{Me}_3\text{PS})_3]^+$ and at τ 8.26 in free Me_3PS , while the value of $J_{\text{P-H}}$ remains nearly unchanged, *i.e.*, 13.6 and 13.3 Hz, respectively. Plots of mole fraction of added ligand *vs.* the value of δ_{CH_3} observed for solutions of $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{BF}_4$ and Me_3PS are linear. This supports the contention that only one principal metal-SPMe₃ species is present in the case of Me_3PS , presumably the 3:1 cation.

To identify the nature of the species present in solution, infrared studies have proven more useful than nmr studies. The $\nu(\text{P=S})$ bands of coordinated and free ligand are distinguishable in the spectra of Ph_3PS , Me_2PhPS , and Me_3PS in acetone solutions. Four absorptions in the region 600–650 cm^{-1} are present in a solution spectrum of $[\text{Cu}(\text{Ph}_3\text{PS})_3]\text{BF}_4$ as shown in Figure 1. From a comparison of this spectrum with the solid-state spectrum of $[\text{Cu}(\text{Ph}_3\text{PS})_3]\text{BF}_4$, it is concluded that the peaks at 603 and 622 cm^{-1} are the $\nu(\text{P=S})$ and X-sensitive phenyl peaks, respectively, of coordinated Ph_3PS . The remaining two peaks at 640 and 614 cm^{-1} are the analogous peaks of free Ph_3PS . The solution spectrum of free Ph_3PS in this region is also shown in Figure 1. Thus, the 3:1 complex is substantially dissociated in acetone at a 10^{-2} M concentration (calculated to be $\sim 75\%$ of one L from CuL_3^+). Equilibrium concentrations of Ph_3PS were determined from the absorbance maxima of the $\nu(\text{P=S})$ peak at 640 cm^{-1} . Dissociation equilibrium constants were then calculated from the measured concentrations of free ligand assuming equilibrium 1. The equilibrium constants are



0.027, 0.0012, and $<10^{-4}$ for $[\text{Cu}(\text{Ph}_3\text{PS})_3]\text{BF}_4$, $[\text{Cu}(\text{Me}_2\text{PhPS})_3]\text{BF}_4$, and $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{BF}_4$, respectively. Molar conductance values in acetone are consistent with uni-univalent electrolytes. The validity of equilibrium 1 was confirmed for $[\text{Cu}(\text{Ph}_3\text{PS})_3]\text{BF}_4$; various amounts of excess Ph_3PS (0.00–0.03 *M*) were added to the complex, and equilibrium constants were determined assuming (1). The values were

(31) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1966, Chapter 9.

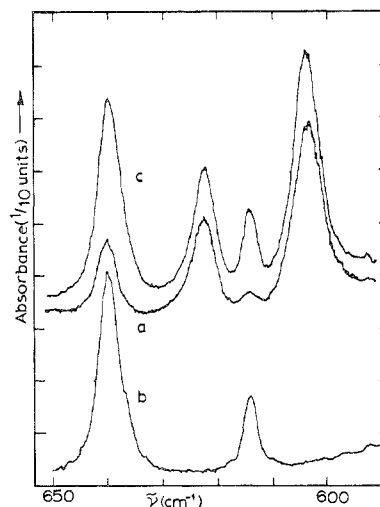


Figure 1. The infrared spectra in acetone in the $\nu\text{-P-S}$ region: (a) $[\text{Cu}(\text{Ph}_3\text{PS})_3]\text{BF}_4$, 0.0078 *M*; (b) free ligand Ph_3PS , 0.0239 *M*; (c) $[\text{Cu}(\text{Ph}_3\text{PS})_3]\text{BF}_4$, 0.0078 *M*, with added Ph_3PS , 0.0239 *M*.

equal within experimental error.³² One of these spectra is given in Figure 1c.

Infrared spectra of acetone solutions of $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{BF}_4$ showed essentially *no dissociation* of a ligand; also, the spectra with added Me_3PS showed no detectable *association* of a fourth ligand. The rapid exchange between $[\text{Cu}(\text{Me}_3\text{PS})_3]^+$ and free Me_3PS observed by nmr could occur *via* a low concentration of either a four-coordinate or a two-coordinate species that was undetectable by the infrared studies. Thus, in solution, as well as in the solid state, there is a definite preference for tricoordination (and perhaps even two-coordination) rather than four-coordination.

The differences observed in the dissociation constants can be rationalized in the following way: (1) ligand bulkiness should decrease the stability of the 3:1 complex; (2) increased polarity and basicity of the donor atom should increase the stability of the Cu-S bond. Either effect would produce the observed *dissociation trend*, *i.e.*, $\text{Cu}(\text{Ph}_3\text{PS})_3^+ > \text{Cu}(\text{Me}_2\text{PhPS})_3^+ > \text{Cu}(\text{Me}_3\text{PS})_3^+$. Although sufficient data are not available to evaluate the role of steric effects, as Lippard and Mayerle²⁰ have done for copper-phosphine complexes, a separate infrared and Raman study on the Cu-S vibrations supports the importance of a more basic sulfur atom in Me_3PS .³³

Many of the complexes could not be studied satisfactorily using infrared or nmr measurements; thus, apparent molecular weights were determined to ascertain the following order of *dissociation tendencies* in acetone:³⁴ $\text{Cu}(\{\text{Me}_2\text{N}\}_3\text{PS})_4^+ > \text{Cu}(\text{Ph}_3\text{PS})_3^+ \sim \text{Cu}(\{\text{Me}_2\text{N}\}_3\text{PS})_3^+ \sim \text{Cu}(\text{i-Pr})_3\text{PS}_3^+ > \text{Cu}(\text{Ph}_3\text{AsS})_3^+ > \text{Cu}(\text{Me}_3\text{PS})_3^+ \sim \text{Cu}(\text{Et}_3\text{PS})_3^+$

The Neutral Complexes, CuLX . Although the cationic complexes $[\text{CuL}_3]^+$ do not react with excess ligand to form significant amounts of $[\text{CuL}_4]^+$, many of them react readily

(32) Although the equilibrium most certainly involves dissociation to a 2:1 complex, it is not certain whether the resulting complex is $[\text{CuL}_2]^+$ or $[\text{CuL}_2(\text{solvent})]^+$. In cases of more strongly coordinating solvents (*e.g.*, MeCN) even $\text{Cu}(\text{Me}_3\text{PS})_3^+$ dissociates, presumably due to solvent coordination.

(33) J. Kincaid, K. Nakamoto, J. A. Tiethof, and D. W. Meek, *Spectrochim. Acta, Part A*, in press.

(34) In cases in which solution infrared, molecular weight and conductivity data are all available (*i.e.*, for complexes of Me_3PS and Ph_3PS), apparent molecular weights are somewhat higher than predicted by infrared and conductivity. However, the relative discrepancy, which is presumably due to ion-pairing effects, is nearly the same for the complexes Ph_3PS and Me_3PS .

with halides and the thiocyanate ion to give rather insoluble complexes of empirical formula CuLX. The first CuLX complex was prepared originally by treating a cuprous halide with excess Ph_3PS .⁹ It is apparent from this work that CuLX complexes (X = Cl, Br, I, SCN) of several phosphine sulfides can be prepared by different routes, presumably because of the strong affinity of Cu(I) for halides^{35,36} and pseudohalides.

The CuLX compounds are insoluble in common organic solvents. Coordinating solvents such as DMF lead to rapid decomposition, as evidenced by the appearance of a blue-green color. An infrared spectrum of an acetonitrile solution of $\text{Cu}(\text{Me}_3\text{PS})\text{Cl}$ shows a very complicated spectrum in the $\nu(\text{P-S})$ region, suggesting that several different complexes of Me_3PS are present. The insolubility of the CuLX complexes suggests that they are polynuclear. Polymerization could reasonably occur *via* halide and/or sulfur bridges.

Assuming that the magnitude of $\nu(\text{P-S})$ depends on the coordination environment around sulfur, the data in Table II suggest at least three groupings for the CuLX compounds. Compounds in class I have $\Delta\nu(\text{P-S})$ approximately double that of the 3:1 complexes, in which only nonbridging sulfur donors are present. Coordination *via* one electron pair on sulfur shifts $\nu(\text{P-S}) \sim 24\text{--}35 \text{ cm}^{-1}$, and it may be expected that bridging (or coordination *via* two electron pairs on sulfur) would shift the $\nu(\text{P-S})$ even further to lower energy. Thus, we propose that the compounds $\text{Cu}(\text{Me}_3\text{PS})\text{X}$ (X = Cl, Br, I) contain sulfur-bridged phosphine sulfide ligands. Complexes of class II have $\Delta\nu(\text{P-S})$ approximately equal to that of the 3:1 complexes and are represented by $\text{Cu}(\text{Ph}_3\text{PS})\text{Cl}$ and $\text{Cu}(\text{Me}_3\text{PS})\text{SCN}$. On the basis of the infrared argument, these complexes would have nonbridging phosphine sulfides. The compounds in class III, $\text{Cu}(\text{Ph}_3\text{PS})\text{Br}$ and $\text{Cu}(\text{Me}_2\text{PhPS})\text{Cl}$, have rather complex infrared spectra in the $\nu(\text{P-S})$ region. These latter complexes may have *both* bridging and nonbridging sulfur donors.

Single-crystal X-ray structural determinations of $[\text{Cu}(\text{Me}_3\text{PS})\text{Cl}]_3$ ¹⁴ and $[\text{Cu}(\text{Me}_3\text{PS})\text{SCN}]_\infty$ ²⁵ support the above groupings based on the infrared spectra. The chloride complex is a trimer containing three-coordinate Cu(I), terminal chlorides, and bridging phosphine sulfides. The thiocyanate complex is an infinite chain of three-coordinate copper atoms and bridging thiocyanate groups with only terminal-bonded phosphine sulfide ligands.²⁵ The success of these two predictions

(35) R. G. Solomon and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 1889 (1973).

(36) W. H. Quinn and J. H. Tsai, *Advan. Inorg. Chem. Radiochem.*, **12**, 217 (1969).

Table II. Shifts of $\nu(\text{P-S})$ to Lower Energy in the Copper(I) Complexes as Compared to the Free Ligand (cm^{-1})

| L | In CuLX complexes | | | In $[\text{Cu-L}_3]\text{BF}_4$ Complexes |
|--------------------------|-------------------|--------|--------------|---|
| | X = Cl | X = Br | X = I SCN | |
| Me_3PS | 44 | 40 | 45 | 24 |
| Ph_3PS | 32 | 36, 48 | | 35 |
| Me_2PhPS | 42, 52 | | | 33 |

might suggest further structural predictions based on values of $\Delta\nu(\text{P-S})$; however, caution is warranted. For example, all the compounds $\text{Cu}(\text{Me}_3\text{PS})\text{X}$ (X = Br, Cl, I) have rather similar infrared spectra and solubility properties, but the bromide and iodide complexes *do not* have the trimeric structure of the chloride analog. Crystals of $\text{Cu}(\text{Me}_3\text{PS})\text{Br}$ were found from X-ray precession photographs and density measurements to have the space group $P2_1/c$ with eight formula units in the unit cell. This eliminates the trimeric possibility for $\text{Cu}(\text{Me}_3\text{PS})\text{Br}$ and for $\text{Cu}(\text{Me}_3\text{PS})\text{I}$, which is isomorphous with $\text{Cu}(\text{Me}_3\text{PS})\text{Br}$ on the basis of X-ray powder patterns. However, these facts do not exclude other polymeric structures and do not negate the principal conclusions from the infrared spectra, since only the mode of sulfur bonding and the polynuclear nature of the complexes are proposed.

Conclusions

Three-coordinate, trigonal-planar copper(I) is an important coordination number and structural basis for complexes of soft donors, *e.g.*, sulfur in phosphine sulfides and phosphorus in phosphines. Until recently, three-coordinate copper(I) was considered a novel structural phenomenon,^{37,38} however, recent structural results with tertiary phosphine,^{22,39} tertiary phosphine sulfide,^{14,25} and thiourea²³ complexes, indicate that tricoordination must be considered an important aspect of copper(I) chemistry.

Registry No. $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{BF}_4$, 38294-37-0; $[\text{Cu}(\text{Et}_3\text{PS})_3]\text{BF}_4$, 38294-39-2; $[\text{Cu}(i\text{-Pr}_3\text{PS})_3]\text{BF}_4$, 38294-41-6; $[\text{Cu}(\text{Me}_2\text{PhPS})_3]\text{BF}_4$, 38294-12-1; $[\text{Cu}(\text{Ph}_3\text{PS})_3]\text{BF}_4$, 38294-14-3; $[\text{Cu}(\text{Me}_2\text{N})_3\text{PS}]_3\text{BF}_4$, 51838-85-8; $[\text{Cu}(\text{Ph}_3\text{PSe})_3]\text{BF}_4$, 38294-35-8; $[\text{Cu}(\text{Ph}_3\text{AsS})_3]\text{BF}_4$, 38294-15-4; $[\text{Cu}(\text{Me}_3\text{PS})_3]\text{NO}_3$, 51838-86-9; $[\text{Cu}(\text{Me}_3\text{PS})\text{Cl}]_3$, 38656-77-8; $\text{Cu}(\text{Me}_3\text{PS})\text{Br}$, 51838-88-1; $\text{Cu}(\text{Me}_3\text{PS})\text{I}$, 51838-90-5; $[\text{Cu}(\text{Me}_3\text{PS})\text{SCN}]$, 51838-92-7; $\text{Cu}(\text{Me}_2\text{PhPS})\text{Cl}$, 51838-94-9.

(37) D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1957).

(38) N. C. Baenziger, J. R. Doyle, and H. L. Haight, *Inorg. Chem.*, **3**, 1535 (1964).

(39) (a) V. G. Albano, P. L. Bellon, G. Ciani, and M. Manassero, *J. Chem. Soc., Dalton Trans.*, 171 (1972); (b) N. C. Baenziger, G. F. Richards, and J. R. Doyle, *Inorg. Chem.*, **3**, 1529 (1964); (c) P. Ganis, U. Lepore, and G. Paiaro, *Chem. Commun.*, 1054 (1969).