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The Coordination Properties of Tris(dimethylamino)phosphine Sulfide

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Tris(dimethylamino)phosphine sulfide (TDPS), $[(CH_3)_2N]_3PS$, forms stable coordination compounds with both class a and class b metals. The spectral parameters of the tetrahedral, paramagnetic $[Co(TDPS)_4](ClO_4)_2$ and $Co(TDPS)_2X_2$ (X = Cl, Br, I) complexes show that the ligand field strength of $[(CH_3)_2N]_3PS$ is comparable to both $[(CH_3)_2N]_3PO$ and $(CH_3)_3PS$, whereas the β values are comparable to $(CH_3)_3PS$ and significantly lower than for $[(CH_3)_2N]_3PO$. These results are interpreted in terms of the electronic properties of the P=S linkage and the steric requirements of the bulky dimethylamino groups. Typical complexes of some heavy metals such as Hg(II), Ag(I), and Pd(II) were isolated and characterized to confirm the class b behavior of the ligand. Tris(dimethylamino)phosphine sulfide reduces copper(II) to copper(I), which then forms the colorless $[Cu(TDPS)_4]ClO_4$ complex. The ligand is oxidized in the process and gives the stable, colorless $[(CH_3)_2N]_3PSSP[N(CH_3)_2]_3^{2+}$ cation.

Introduction

In contrast to numerous metal complexes of phosphine oxides[1] and arsine oxides,[2] very few phosphine sulfide complexes[3] had been reported prior to the initial investigations on the coordination properties of P=S and P=Se ligands in this laboratory.[4-6] In spite of the limited results of previous investigators,[3] our initial results[4-6] indicated that tertiary phosphine sulfides and selenides form numerous stable complexes with metals that normally bond with easily polarized donor atoms, *e.g.*, "class b" or "soft" metallic ions, using the designations of Ahrland, Chatt, and Davies[7] and Pearson,[8] respectively. For example, $R_3P{=}S$ and $R_3P{=}Se$ molecules (R = methyl, ethyl, phenyl, and *p*-tolyl) form stable complexes with Pd(II), Pt(II), Hg(II), Cd(II), and Pb(II),[4-6,9] and they spontaneously reduce Cu(II) to Cu(I) and Au(III) to Au(I).[6,10]

Several attempts to prepare complexes of the first-transition-series metals such as Co(II), Ni(II), and Fe(II) with $R_3P{=}S$ ligands had been unsuccessful.[3,4-6,9] However, Wilkins, *et al.*,[11] recently reported that trimethylarsine sulfide complexes of Fe(II), Mn(II), Co(II), and Ni(II) were isolated. One might have attributed the isolation of the above arsine sulfide complexes to the facts that although phosphorus and arsenic have similar electronegativities,[12] the size[13] and relative double-bonding[14] differences should make the As=S group more polar and basic than the P=S unit. In an attempt to increase the basic character of the P=S group and to prepare a liquid tertiary phosphine sulfide for use as a nonaqueous solvent near room temperature, the molecule $[(CH_3)_2N]_3P{=}S$ was synthesized and investigated as a ligand toward "hard"[8] metallic ions. This paper describes the tris(dimethylamino)phosphine sulfide (TDPS) complexes of Co(II) and Ni(II), as well as the complexes of some representative heavy metals.[15]

Experimental Section

Synthesis of the Ligand.—Tris(dimethylamino)phosphine sulfide (TDPS) was prepared from the reaction of dimethylamine

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[14] R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965, Chapter 3.

[15] After most of this study had been completed, C. J. Wilkins informed us, in Dec 1967, that they had isolated cobalt(II) halide complexes of $(CH_3)_3P{=}S$. The results with $(CH_3)_3P{=}S$ were published recently: A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc.*, *A*, 2039 (1968).

and thiophosphoryl chloride (eq 1) in 74% yield[16]; bp 65–68° (1.0 mm), lit. bp 61° (0.1 mm),[17] 63° (1.2 mm).[18] The ligand was also prepared[18] by refluxing tris(dimethylamino)phosphine with a stoichiometric amount of sulfur in toluene, 84% yield, bp 64–66° (1.0 mm). The infrared spectra of both samples of TDPS were identical and were comparable to the published spectrum.[19] A proton nmr spectrum of the TDPS sample showed a sharp doublet at τ 7.32 ($DCCl_3$ solution with TMS as an internal standard) with $J_{P-H} = 11.0$ cps and $J_{C^{13}-H} = 136$ cps; lit. values, τ[17,20] 7.38, $J_{P-H} = 11.3$[17] and 10.8[20] cps, and $J_{C^{13}-H} = 136$ cps.[21]

$$Cl_3PS + 6(CH_3)_2NH \longrightarrow [(CH_3)_2N]_3PS + 3(CH_3)_2NH_2Cl \quad (1)$$

A methyl iodide derivative of TDPS was prepared by refluxing $[(CH_3)_2N]_3P{=}S$ with an excess of methyl iodide in nitromethane. A white precipitate was obtained by addition of ether and it was recrystallized twice from a nitromethane–THF mixture to yield white needles, mp 119–120°. The proton nmr spectrum of $[((CH_3)_2N)_3PSCH_3]^+I^-$ showed two sharp doublets at τ 7.06 ($N-CH_3$) and τ 7.46 ($S-CH_3$) (D_3CNO_2 solution with TMS as an internal standard) with J_{P-H} (of the $N(CH_3)_2$ group) = 11.2 cps and J_{P-H} (of the SCH_3 group) = 15.5 cps. The relative area of the two doublets was approximately 6:1 as expected for alkylation on the sulfur atom.

Preparation of the Complexes.—All preparations and handling of the complexes were done under a dry nitrogen atmosphere. Solvents, except anhydrous ether, were dried and freshly distilled before use. All metal salts used were anhydrous. The acetonitrile–metal perchlorate complexes were used as sources of anhydrous metal perchlorates and were prepared by the method reported by van Leeuwen.[22]

$[Co(TDPS)_4](ClO_4)_2$.—This complex was prepared by adding 5.0 g (0.025 mol) of TDPS to 0.50 g (0.001 mol) of the pink acetonitrile complex $[Co(CH_3CN)_6](ClO_4)_2$. There was an instantaneous color change from pink to bluish green. The reaction mixture was stirred overnight, and then a few milliliters of ether was added to complete precipitation. The precipitate was collected on a filter and washed thoroughly with ether, yield 50%.

$[Co(TDPS)_2X_2]$.—The cobalt halide complexes were prepared by dissolving 2 mmol of the appropriate anhydrous metal halide in approximately a tenfold excess of TDPS, the solutions were filtered, and ether (hexane for the iodide) was added just to the point of initiating precipitation. The mixture was allowed to stand for several minutes, the solid was collected, and the resulting crystals were washed with hexane. Yields were 50, 70, and 93% for the chloride, bromide, and iodide complexes, respectively.

$[Ni(TDPS)_4](ClO_4)_2$.—The nickel perchlorate complex was prepared in the same manner as the cobalt perchlorate complex; yield 94%. In this case there was an instantaneous color change, from the light purple color of $[Ni(CH_3CN)_6](ClO_4)_2$ complex to a reddish brown, on addition of the ligand.

$[Cu(TDPS)_4]ClO_4$.—The copper(I) perchlorate complex was prepared by adding approximately a tenfold excess of TDPS to the light blue copper(II)–acetonitrile complex $[Cu(CH_3CN)_4](ClO_4)_2$. The solution became almost colorless within 10 sec after adding the ligand. The reaction mixture was stirred for 1 hr and then the precipitate was collected on a filter. Addition of a small amount of ether to the clear filtrate gave white crystalline flakes of the Cu(I) complex; yield 40%. The initial precipitate was washed with THF to remove any traces of $[Cu(TDPS)_4]ClO_4$ and then recrystallized once from nitromethane–ether to give colorless crystals. This material was subsequently identified as the perchlorate salt of the oxidized ligand, *i.e.*, $[((CH_3)_2N)_3PS_2P(N(CH_3)_2)_3](ClO_4)_2$. *Anal.* Calcd for $C_{12}H_{36}N_6Cl_2O_8P_2S_2$: C, 24.42; H, 6.16; Cl, 12.05; S, 10.88. Found: C, 24.41, 24.56; H, 6.16, 6.21; Cl, 12.09, 12.20; S, 11.12, 11.03.

Copper Chloride Reaction.—A copper-containing complex was prepared by stirring anhydrous cupric chloride in approximately a tenfold excess of TDPS for 4 hr. The mixture was then filtered to give an orange precipitate and a brown solution. All attempts to obtain solid material from the brown filtrate were unsuccessful. The orange precipitate was washed three times with 15-ml portions of nitromethane to give a brown residue and a deep red solution. Bright red crystals were obtained from the solution on addition of ether.

Identical red crystals were also obtained in much better yield from the reaction of a slurry of the acetonitrile–copper(II) chloride complex in acetonitrile with an excess of TDPS. The color changed from brownish yellow to deep red when TDPS was added and all of the material dissolved. Addition of ether initiated precipitation of the red crystals, which were identified as $\{[(CH_3)_2N]_3PS_2P[N(CH_3)_2]_3\}\{Cu_2Cl_6\}$. *Anal.* Calcd for $C_{12}H_{36}N_6Cl_6Cu_2P_2S_2$: C, 19.74; H, 4.97; Cl, 29.13. Found: C, 19.67; H, 5.04; Cl, 29.06.

$Pd(TDPS)_2Cl_2$.—This complex was prepared by dissolving Na_2PdCl_4 (0.56 g, 0.002 mol) with 2.0 g (0.01 mol) of TDPS in THF. The solution was concentrated and addition of a small amount of ether caused precipitation of red crystals. The complex was recrystallized once from THF–ether in the presence of excess ligand; yield 55%. (Recrystallizing the above compound in the absence of excess ligand resulted in the formation of $(Pd(TDPS)Cl_2)_2$.)

$Ag(TDPS)NO_3$.—The silver nitrate complex was prepared by stirring a suspension of $AgNO_3$ (0.34 g, 2 mmol) with 1.6 g (8 mmol) of ligand in 50 ml of tetrahydrofuran. White needles (0.66 g, 90%) were obtained from the THF solution by concentrating the solution and adding a small amount of diethyl ether.

$[Ag(TDPS)_2]ClO_4$.—This complex was prepared by adding a solution of silver perchlorate (0.42 g, 1 mmol) in THF to 10 mmol (2.0 g) of TDPS in ether with rapid stirring. A white precipitate formed immediately; this was collected and recrystallized three times from THF–ether in the presence of excess ligand to give long white needles; yield 64%.

$(Hg(TDPS)Br_2)_2$.—This complex was prepared by dissolving mercuric bromide (0.72 g, 2 mmol) with 10 mmol of TDPS in 40 ml of THF. Addition of ether caused precipitation of white crystals; these were recrystallized three times from THF–ether in the presence of excess ligand; yield 60%.

Nickel Halide Complexes.—Several attempts were made to prepare nickel halide complexes similar to those of the cobalt halides. Although nickel chloride and bromide gave bright blue and green solutions, respectively, no crystalline complex could be isolated from the solutions.

Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 337 grating spectrophotometer using Nujol mulls between potassium bromide plates. Electronic spectra of the complexes in nitromethane solution were obtained using a set of matched 1-cm quartz cells and in the solid state using Nujol mulls supported on filter paper[23] with a Cary Model 14 recording spectrophotometer. The proton nmr spectra were taken at 37° on a Varian A-60 spectrometer.

Conductance Measurements.—The measurements were performed at 23° with an Industrial Instruments Model RC-16B conductivity bridge on approximately 10^{-3} *M* nitromethane solutions.

Magnetic Measurements.—Magnetic moments were determined at 23° ± 1° using a Faraday magnetic susceptibility balance. The magnetic measurements were performed at two different field strengths to check for ferromagnetic impurities. The observed susceptibility values were corrected for diamag-

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TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE TRIS(DIMETHYLAMINO)PHOSPHINE SULFIDE COMPLEXES

Compound	Color	Λ_M,[a] cm²/ohm mol	μ_{eff}, BM	% C Calcd	% C Found	% H Calcd	% H Found	% X[b] Calcd	% X[b] Found
$TDPSCH_3^+I^-$	White	94.5	Diamag	24.93	25.16	6.28	6.36	37.63	37.73
$[Co(TDPS)_4](ClO_4)_2$	Green	164	4.59	27.74	27.57	6.98	6.91	6.82	6.86
$Co(TDPS)_2Cl_2$	Blue	23.8	4.54	27.69	27.49	6.98	7.18	13.63	13.96
$Co(TDPS)_2Br_2$	Turquoise	24.1	4.57	23.65	23.50	5.94	5.90	26.23	26.45
$Co(TDPS)_2I_2$	Dark green	25.9	4.64	20.49	20.46	5.16	4.97	36.09	35.91
$[Ni(TDPS)_4](ClO_4)_2$	Brown	c	3.58	27.74	27.55	6.98	7.13	6.82	6.73
$[Cu(TDPS)_4]ClO_4$	White	112	Diamag	30.50	30.29	7.62	7.65	3.81	3.96
$Pd(TDPS)_2Cl_2$	Red	13.5	Diamag	25.38	25.41	6.39	6.54	12.49	12.48
$Ag(TDPS)NO_3$	White	38.2	Diamag	19.74	19.70	4.97	5.01	15.31 (N)	15.14 (N)
$[Ag(TDPS)_2]ClO_4$	White	75.2	Diamag	24.11	23.58	6.08	6.06	5.95	5.50
$[Hg(TDPS)Br_2]_2$	White	18.1	Diamag	12.97	12.95	3.26	3.36	28.76	28.10

[a] Solutions were ~10^{-3} M in nitromethane. [b] Halogen, or where indicated, nitrogen. [c] Decomposes in solution.

TABLE II

ELECTRONIC SPECTRAL DATA (cm^{-1}) OF TRIS(DIMETHYLAMINO)PHOSPHINE SULFIDE COMPLEXES

Complex	Solution ν_3	Solution ν_2[a]	Solid (Nujol mull) ν_3	Solid (Nujol mull) ν_2
$[Co(TDPS)_4](ClO_4)_2$	15,250 (480)[b]	6944 (115)		
	14,290 (570)	5473 (124)	14,370	
	12,630 (140)			
$Co(TDPS)_2Cl_2$	17,000 sh	7010 (51)	16,580	6830
	16,360 sh	5130 (66)	14,770	4940
	15,720 (388)		13,480	
	14,710 sh			
$Co(TDPS)_2Br_2$	16,970 sh	6850 (61)	15,770	6250
	16,100 sh	4900 (60)	14,370	4860
	15,150 (550)		13,070	
	14,610 sh			
$Co(TDPS)_2I_2$	15,150 sh	6600 (86)	14,710	5850
	14,390 (790)		13,600	4710
	13,820 sh		12,570	
$[Ni(TDPS)_4](ClO_4)_2$	14,400 (179)	8658 (34)		
	13,080 (163)			
	10,000 (35)			
$Pd(TDPS)_2Cl_2$	26,670 (2920)		27,160	
			20,160 sh	

[a] The absorption peak maxima in the 13,000–17,000 and 5000–7000-cm^{-1} ranges are assigned as the ν_3 and ν_2 multiplets for tetrahedral Co(II) and Ni(II) complexes. [b] Molar extinction coefficients are in parentheses.

netism of the ligands using Pascal's constants[24] as well as temperature-independent paramagnetism ($2.09/\Delta$)[25] for the cobalt complexes. The diamagnetic contribution of TDPS was determined from the experimental molar susceptibility of the methyl iodide derivative after subtracting Pascal's constants for CH_3 and I^-. The experimental diamagnetic correction for TDPS was -105.5×10^{-6} cgsu, whereas the value calculated from Pascal's constants[24] was -146.7×10^{-6} cgsu.

Results

The physical properties and analytical data for the $[(CH_3)_2N]_3PS$ (TDPS) complexes are given in Table I. Conductance measurements show that the TDPS–cobalt halide complexes dissociate somewhat in nitromethane, but they probably can be classified as molecular CoL_2X_2 species in the solid state; the cobalt perchlorate complex is a 1:2 electrolyte. The electronic spectra of all of the cobalt complexes (Table II) exhibit visible (ν_3, ${}^4A_2 \rightarrow {}^4T_1(P)$) and near-infrared ($\nu_2$, ${}^4A_2 \rightarrow {}^4T_1(F)$) absorptions with extinction coefficients typical of known tetrahedral and pseudotetrahedral cobalt(II) compounds. Spectral parameters for the cobalt(II) complexes of TDPS, as well as other tetrahedral and pseudotetrahedral cobalt(II) complexes, are presented in Table III. The magnetic susceptibility values are consistent with tetrahedral Co(II) complexes (Table I).

The ligand field strength modulus, Δ, and the effective value of the Racah interelectronic repulsion term, B', for the TDPS cobalt complexes were determined from the relationships[26,27]

$$\nu_1 = \Delta$$

$$\nu_2 = 1.5\Delta + 7.5B' - Q$$

$$\nu_3 = 1.5\Delta + 7.5B' + Q$$

$$Q = {}^1/_2[(0.6\Delta - 15B')^2 + 0.64\Delta^2]^{1/2}$$

The value for the ν_3 transition was determined from the solid-state spectra of the $Co(TDPS)_2X_2$ complexes and from the solution spectrum of the $[Co(TDPS)_4](ClO_4)_2$ complex according to a method outlined by Drago.[28] The maximum for the ν_3 band of the [Co-

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TABLE III

SPECTRAL PARAMETERS FOR TETRAHEDRAL AND PSEUDOTETRAHEDRAL COBALT COMPLEXES

Compound[a]	ν_3, cm^{-1}	ν_2, cm^{-1}	Δ, cm^{-1} [b]	B', cm^{-1}	$\beta = B'/B$[c]	μ_{eff}, BM[d]	$-\lambda$, cm^{-1} [e]	Ref
$Co(TDPS)_4(ClO_4)_2$	14,270	6208	3620	642	0.66	4.59	162	*f*
$Co(HMPA)_4(ClO_4)_2$	16,150	6590	3640	774	0.80	4.58	150	*g*
$Co((C_6H_5)_3PO)_4(ClO_4)_2$	16,300	6240	3680	787	0.81	4.53	147	*h*
$Co((CH_3)_3PS)_4(ClO_4)_2$	14,400	6690	3890	630	0.65	4.31	105	*i*
$CoCl_4^{2-}$	14,700	5460	3130	710	0.73	4.59	145	*h*
$CoBr_4^{2-}$	14,000	4980	2850	695	0.72	4.69	153	*h*
CoI_4^{2-}	13,250	4600	2645	665	0.69	4.77	155	*h*
$Co(TDPS)_2Cl_2$	15,290	5880	3390	733	0.76	4.54	144	*f*
$Co((C_6H_5)_3PO)_2Cl_2$	15,500	5710	3270	760	0.79	4.63	156	*j*
$Co((CH_3)_3PS)_2Cl_2$	14,990	5810	3340	720	0.74	4.32	92	*i*
$Co(TDPS)_2Br_2$	14,680	5560	3210	708	0.73	4.57	145	*f*
$Co((C_6H_5)_3PO)_2Br_2$	15,300	5560	3180	754	0.78	4.69	164	*j*
$Co((CH_3)_3PS)_2Br_2$	14,540	5700	3280	700	0.72	4.41	111	*i*
$Co(TDPS)_2I_2$	13,840	5280	3050	665	0.68	4.64	147	*f*
$Co((C_6H_5)_3PO)_2I_2$	14,500	5340	3056	711	0.74	4.79	177	*k*
$Co((CH_3)_3PS)_2I_2$	13,710	5650	3260	640	0.66	4.42	110	*i*

[a] Values for tetrahalocobalt complexes are average values for a number of cations.[h] [b] Values are ±200 cm^{-1}. [c] B(free ion) = 967 cm^{-1}. [d] Values are ±0.05 BM. [e] Values are ±20 cm^{-1}; λ(free ion) = −172 cm^{-1}. [f] This work. [g] J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2,** 572 (1963). [h] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83,** 4690 (1961). [i] See ref 15. [j] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83,** 4157 (1961). [k] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *Inorg. Chem.*, **1,** 239 (1962).

$(TDPS)_4](ClO_4)_2$ complex was located at approximately the same position in both the solid state and in solution, so both the ν_2 and ν_3 values for the calculations were taken from the spectrum of $[Co(TDPS)_4](ClO_4)_2$ in nitromethane. Fortunately the ν_2 bands in the $Co(TDPS)_2X_2$ complexes were sufficiently resolved in the solid-state spectra to use, since both ν_2 and ν_3 are shifted to higher energy in nitromethane as a result of solvation. The value for the ν_2 transition was determined by averaging the energy of the two broad bands observed in the 7000–5000-cm^{-1} region.

Discussion

The infrared spectra of all of the $[(CH_3)_2N]_3P{=}S$ complexes are very similar and, except for three absorptions at 720, 740, and 565 cm^{-1}, are essentially unchanged from that of the uncoordinated ligand. The two peaks at 720 and 740 cm^{-1} seem to be split apart further (up to 60 cm^{-1}) in the complexes and the P=S stretching frequency (565 cm^{-1} in the free ligand) is shifted to lower energy by 15–20 cm^{-1}. The entire infrared spectrum of $[((CH_3)_2N)_3PSCH_3]^+I^-$ also is very similar to those of the metal complexes. We interpret the shift of the P=S frequency as indicating that coordination has occurred through the sulfur atom in the ligand, since coordination through the nitrogen should raise the P=S stretching frequency. Moreover, refluxing the free ligand with excess methyl iodide gave only the monomethylated derivative with the methyl group attached to sulfur. (The P=S frequency is also reduced 20 cm^{-1} in this case.) The alkylation of $[(CH_3)_2N]_3P{=}S$ at sulfur was proven by the nmr spectrum. The methyl iodide reaction seems to indicate that the lone pair of electrons on nitrogen is not available for bonding and that the nitrogen atoms do not possess appreciable nucleophilic character. This behavior is consistent with previous observations[29] that the nitrogen atom of a phosphoramidate group is not very basic. To rationalize the reduced basicity of the $P{-}NR_2$ group, one might consider that the nitrogen lone pair was involved in $p_\pi{-}d_\pi$ bonding with the empty d orbitals of phosphorus or that it was located in a sterically unfavorable situation.[30] In any case, the coordination of $[(CH_3)_2N]_3P{=}S$ undoubtedly occurs *via* the thiophosphoryl group.

The perchlorate and nitrate complexes also exhibit infrared bands characteristic of these anions. The strong perchlorate bands at ~1090 and 625 cm^{-1} show no signs of splitting; thus, the ClO_4^- ions retain their Td symmetry and are assumed to be uncoordinated.[31] The silver nitrate complex is one case of nitrate coordination and it will be discussed later.

The position of $[(CH_3)_2N]_3P{=}S$ in the spectrochemical series relative to other ligands in tetrahedral cobalt(II) complexes is $I^- < Br^- < Cl^- < [(CH_3)_2N]_3PS \sim [(CH_3)_2N]_3PO \sim (C_6H_5)_3PO < (CH_3)_3PS$, whereas the β values give the following nephelauxetic series: $(CH_3)_3PS \sim [(CH_3)_2N]_3PS \sim I^- < Br^- \sim Cl^- < [(CH_3)_2N]_3PO \sim (C_6H_5)_3PO$ (Table III). In the $Co(TDPS)_2X_2$ complexes the energy values of the elec-

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[29] J. I. G. Cadogan, *J. Chem. Soc.*, 1079 (1957).

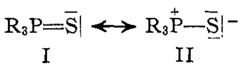
[30] The importance of $d_\pi{-}p_\pi$ bonding between phosphorus and nitrogen is indicated by recent X-ray structural results on $[PN(N(CH_3)_2)_2]_4$ [G. J. Bullen, *J. Chem. Soc.*, 3193 (1962)] and $[PN(N(CH_3)_2)_2]_6$ [A. J. Wagner and A. Vos, *Acta Cryst.*, **B24**, 1423 (1968)]. The exocyclic P–N bond distances in the two compounds are 1.67 Å, *i.e.*, significantly shorter than the P–N single-bond value of 1.77 Å. A short exocyclic P–N bond (1.614 ± 0.002 Å) was also observed in the octamethylpyrophosphoramide ligand when it was coordinated to copper(II) [M. D. Joesten, M. S. Hussain, P. G. Lenhert, and J. H. Venable, Jr., *J. Am. Chem. Soc.*, **90**, 5623 (1968)]. Moreover, in all three examples cited above, the nearly planar nature of the exocyclic dimethylamino group is consistent with sp^2 hybridization around nitrogen and significant P–N double bonding. However, the degree to which $d_\pi{-}p_\pi$ bonding restricts rotation of the dimethylamino group around the P–N bond is questionable on the basis of limited proton nmr data. The low-temperature (−60°) nmr spectra of $(C_6H_5)_2PN(CH_3)_2$ and $(C_6H_5)_2P(S)N(CH_3)_2$ showed no tendency of the N-methyl doublet (due to P–H coupling) to undergo further splitting. Any P–N double bonding would present a rotational barrier for the $-N(CH_3)_2$ group and the two methyl groups would be magnetically nonequivalent. This experiment does not totally exclude P–N π interaction, but its importance in a barrier to the free rotation of an $N(CH_3)_2$ group at room temperature must be small.

[31] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 1091 (1965), and references contained therein.

tronic transitions decrease from chloride to bromide to iodide and are consistent with ligand field theory.

Comparison of the parameters Dq and β for the $[(CH_3)_2N]_3PS$ complexes shows one surprising result. That is, the calculated Dq value of $[(CH_3)_2N]_3PS$ is lower than the Dq value of $(CH_3)_3PS$. The β values for both $(CH_3)_3PS$ and $[(CH_3)_2N]_3PS$ are comparable in the Co(II) complexes, indicative of similar polarizability and covalency effects in the Co–S bonding. Wilkins, *et al.*,[11,15] have observed that similar tertiary oxo and thioxo ligands of group V elements produce similar ligand field effects. The spectral data in Table III show that $[(CH_3)_2N]_3PO$ and $[(CH_3)_2N]_3PS$ also give comparable Dq values; however, the β values are significantly lower in the $[(CH_3)_2N]_3PS$ complexes, as expected for the more polarizable thioxo group.

The permanent dipole moments of R_3PS molecules are 10–12% larger than for analogous R_3PO compounds.[32] It is difficult to assess whether the larger dipole moments of the R_3PS molecules are due primarily to the longer P–S bond or to a greater relative contribution from resonance form II. In comparing $(CH_3)_3PS$ with



$$\underset{\text{I}}{R_3P{=}\overline{S}|} \longleftrightarrow \underset{\text{II}}{R_3\overset{+}{P}{-}\overline{\underline{S}}|^-}$$

$[(CH_3)_2N]_3PS$, the increased inductive character of the dimethylamino group should make resonance form II relatively more important in $[(CH_3)_2N]_3PS$; hence the σ-donor strength of $[(CH_3)_2N]_3PS$ should exceed that of $(CH_3)_3PS$.[33] The spectral data of the cobalt(II) complexes (Table III) show just the opposite behavior.

Any ligand–ligand interaction between adjacent coordinated $[(CH_3)_2N]_3PS$ molecules would reduce the effective ligand field and lead to a smaller Dq value. Accurate molecular models show that the dimethylamino groups are certainly larger than methyl groups; thus ligand–ligand interactions would be more pronounced in $[(CH_3)_2N]_3PS$ and may account for its low Dq values. A steric interaction has been suggested previously for coordinated amides[34] and nitriles[35] where the observed Dq values did not increase with increasing N substitution and relative basicities toward the reference acids iodine and phenol. The steric argument might also explain why $[(CH_3)_2N]_3PS$ and $[(CH_3)_2N]_3PO$ exhibit comparable Dq values toward Co(II). That is, the shorter Co–O and O–P bond distances for coordinated $[(CH_3)_2N]_3PO$ would increase the ligand–ligand repulsions compared to the $[(CH_3)_2N]_3PS$ case, and the effective field would be lower than expected for the oxo ligand.

The magnetic moments of the $Co(TDPS)_2X_2$ complexes produce a regular trend and are in good agreement with a tetrahedral structure. The orbital contribution of the $^4T_2$ state to the total magnetic moment is expected to increase from chloride to iodide, as observed (Table I). The magnetic moment of $[Co(TDPS)_4](ClO_4)_2$, however, seems abnormally high; in fact the value (4.59 BM) is higher than that for $(CH_3)_3PS$ or the oxo ligands. From the spectral correlations of $(CH_3)_3PS$ and TDPS, a magnetic value closer to 4.31 BM was expected (Table III). Wilkins, *et al.*,[11,15] have attributed the low magnetic moments of the $(CH_3)_3PS$–Co(II) complexes to the higher covalency (and correspondingly lower spin–orbit coupling) in the metal–sulfur bond as compared to the metal–oxygen bond of analogous oxo ligands. Comparison of the CoL_2X_2 series of complexes ($L = (CH_3)_3PS$, $[(CH_3)_2N]_3PS$) shows that the moments of the $Co(TDPS)X_2$ complexes are consistently higher than those for the $(CH_3)_3PS$ series (Table III). The implication from these data is that delocalization (or covalent-bonding) effects are less important for $[(CH_3)_2N]_3PS$ than for $(CH_3)_3PS$.

The rule of average environment states that, for a set of mixed ligands, the cubic field magnitude is the weighted average of the cubic ligand fields associated with each of the complete sets of ligands separately.[36] From the spectral data of the tetrahedral CoX_4^{2-} and $[Co(TDPS)_4](ClO_4)_2$ complexes it is possible to check the applicability of the "average field" in the $Co(TDPS)_2X_2$ complexes. The spectral results are given in Table IV; the calculated and observed ligand field values for the $Co(TDPS)_2X_2$ complexes agree very well. The same relationship of average environment was also applied to the magnetic moment and B' values. Here the calculated and observed values are, in general, within the limits of experimental error.

TABLE IV

AVERAGE LIGAND FIELD APPROXIMATION FOR $Co(TDPS)_2X_2$ COMPLEXES

	Calcd[a]			Obsd		
X	Δ, cm⁻¹	B', cm⁻¹	μ_{eff}, BM	Δ, cm⁻¹	B', cm⁻¹	μ_{eff}, BM
Cl	3375	676	4.59	3390	733	4.54
Br	3235	669	4.64	3210	708	4.57
I	3132	653	4.68	3050	665	4.64

[a] Values calculated by averaging those for CoX_4^{2-} from ref 20 and the values for $[Co(TDPS)_4](ClO_4)_2$ obtained in this study.

The electronic absorption spectrum of $[Ni(TDPS)_4](ClO_4)_2$ in a 1:1 mixture of TDPS–nitromethane is typical of other tetrahedral nickel(II) complexes. Unfortunately, the solid-state spectrum of the complex could not be obtained for comparison owing to its rapid decomposition in air, even when coated with Nujol. The magnetic moment (3.59 BM) is at the low end of the range observed (3.49–4.00 BM) for tetrahedral nickel(II) complexes. The low moment for $[Ni(TDPS)_4](ClO_4)_2$ is probably due to a distortion from a strictly tetrahedral structure. A similar explanation was given for the magnetic moment of NiI_4^{2-},[37] whereby the structural distortion causes considerable splitting and separation of the ground-state multiplet that exists for a Td nickel(II) complex. The combined magnetic and

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[32] R. Carlson and D. W. Meek, unpublished data, 1968; H. Goetz, F. Nerdel, and K. H. Wiechel, *Ann. Chem.*, **665**, 1 (1963).

[33] C. R. Noller, "Textbook of Organic Chemistry," W. B. Saunders Co., Philadelphia, Pa., 1966, p 380.

[34] R. S. Drago, D. W. Meek, M. J. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

[35] H. F. Henneike, Jr., and R. S. Drago, *ibid.*, **7**, 1908 (1968).

[36] B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, Inc., New York, N. Y., 1966, p 236.

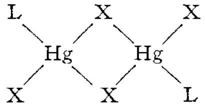
[37] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

spectral data are consistent with a tetrahedral structure for $[Ni(TDPS)_4](ClO_4)_2$, and it is one of the few known cationic tetrahedral nickel complexes.

The stoichiometry, infrared spectra, and low conductance value of the $Ag(TDPS)NO_3$ complex all suggest that the nitrate group is coordinated. The infrared spectrum of $Ag(TDPS)NO_3$ in a Nujol mull shows two sharp, medium-intensity peaks at 1035 and 1030 cm^{-1}, which are assigned to the $-ONO_2$ symmetric stretch of coordinated nitrate groups. However, the infrared spectrum cannot be used to differentiate between monodentate and bidentate NO_3^- groups, owing to overlap of strong ligand bands in the 1500–1200-cm^{-1} region.

The conductance value (Table I) of the silver perchlorate complex is typical of a uni-univalent electrolyte, and since its infrared spectrum shows only ionic perchlorate groups,[31] the silver ion is assumed to be two-coordinate.

The mercury bromide complex is a nonelectrolyte (Table I); in order to have a four-coordinate mercuric ion that is consistent with the elemental analyses, the complex is formulated as a dimer. The infrared spectrum shows that the TDPS ligand retains its normal bonding, so bromide bridges between the two mercuric ions are suggested. Dimeric



complexes are known with phosphines and phosphine selenide ligands.[38] The $Hg(TDPS)Br_2$ complex was always recrystallized in the presence of excess TDPS ligand, but no $Hg(TDPS)_2Br_2$ complex was isolated.

The copper(I) complex $[Cu(TDPS)_4]ClO_4$ was obtained from the spontaneous reduction of $[Cu(CH_3CN)_4](ClO_4)_2$ by excess TDPS. The conductance and magnetic data, elemental analysis, and infrared spectrum all support a four-coordinate copper(I) complex. It is not unusual for copper(II) to be reduced to copper(I) by alkylphosphine sulfides.[4,6] Copper(I) complexes of R_3PS ligands were previously isolated from ethanol or 1-butanol by Nicpon;[4,6] the oxidized species in those cases could easily have been the alcohol solvent. Often in the present study no solvent, other than excess TDPS, was used; thus it was of interest to identify the material that was oxidized when Cu(II) was reduced spontaneously to Cu(I) in $[(CH_3)_2N]_3PS$. We[39] have shown that the ligand itself is oxidized by Cu(II) to form the $[(CH_3)_2N]_3PSSP[N(CH_3)_2]_3^{2+}$ cation. The same cation also is formed in good yield by bromine oxidation of $[(CH_3)_2N]_3PS$ in the absence of metal salts. Such a cation would result from the oxidation of $[(CH_3)_2N]_3P{=}\overline{S}|$ to the positive free radical $[(CH_3)_2N]_3P{=}\overline{S}\cdot^+$, followed by rapid coupling.

The proton nmr spectra of the perchlorate and tribromide salts of $[(CH_3)_2N]_3PS_2P[N(CH_3)_2]_3^{2+}$ show a sharp doublet centered at τ 7.10 and 7.02, with the J_{P-H} values of 11.3 and 11.5 cps, respectively (D_3CCN solution with TMS as an internal standard). The above values are to be compared with τ 7.32 and $J_{P-H} =$ 11.0 cps for $((CH_3)_2N)_3P{=}S$ itself. The nmr spectra show that all of the dimethylamino groups are equivalent and bonded to phosphorus. The J_{P-H} coupling constants and the downfield shift of the methyl doublet are comparable to those observed for the methyl iodide derivative of $((CH_3)_2N)_3P{=}S$, $[((CH_3)_2N)_3PSCH_3]^+I^-$. The infrared spectra also suggest that little change has occurred in the dimethylamino groups, but a major change in the bond order of the phosphorus–sulfur bond is apparent.

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(38) M. G. King and G. P. McQuillan, personal communication, 1968.

(39) W. E. Slinkard and D. W. Meek, *Chem. Commun.*, 361 (1969)