complexes are clearly examples of carbon monoxide bonded to nickel in a +2 formal oxidation state.

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The Stereochemistry of Four-Coordinate Bis(imidodiphosphinato)metal(II) Chelate Complexes

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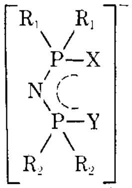
A series of bivalent metal complexes of the type $[\text{X-PR}_2\text{NPR}_2\text{-X}]_2\text{M}^{\text{II}}$ have been synthesized: M = Fe, Co, Ni, Zn, Pd, and Pt (X = S, R = CH_3, C_6H_5), M = Co, Ni (X = NH, R = C_6H_5), M = Co(X = O, R = C_6H_5). The sulfur complexes of Fe(II), Co(II), and Ni(II) include the first characterized tetrahedral four-coordinate complexes of these metals containing an MS_4 core. The ligand field spectral and magnetic data are discussed.

Introduction

There has been considerable interest in determining what factors influence the stereochemistry of four-coordinate metal(II) chelate complexes. The utility of employing bidentate chelates in which either the donor functions or the degree of steric overcrowding at the donor sites can be changed has been elegantly demonstrated.[3-8] Monomeric sterically unencumbered[7] chelates of nickel(II) with various donor sets have been found to be planar while those which are sterically overcrowded are usually[9,10] either fully tetrahedral ($S = 1$) or are involved in a planar ⇄ tetrahedral equilibrium. A series of β-difunctional ligands of the type **1**, where $R_1 = R_2 = CH_3$, C_6H_5 and X = Y = S, O, NH, have been synthesized.[11] This potentially large and versatile set of ligands can be named from the generic root "imidodiphosphinate" to simplify the collective nomenclature of the resulting metal complexes. This ligand system is ideally suited to studying the effect of the variation of the donor sets X and Y and the terminal substituents R_1 and R_2. While the earlier reports [11a] indicated that some metal complexes of these ligands could be prepared, no other information was given. This communication deals with the synthesis of bis-chelate complexes of the "imidodiphosphinates" and the establishment of their structures in both the solid and solution phases.



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Experimental Section

General Data.—Microanalyses were performed by Midwest Microlab Inc., Indianapolis, Ind., and at MIT by Mrs. Nancy F. Alvord. Molecular weights were determined osmometrically in dry benzene, toluene, or ethanol-free chloroform.

All melting points were determined using a hot-stage microscope.

The magnetic susceptibilities of the solid samples were determined using $HgCo(SCN)_4$ as a calibrant[12] either by the Gouy method, in double-ended glass Gouy tubes, or by the Faraday method. The diamagnetic susceptibility for $K[((C_6H_5)_2PS)_2N]$ was determined directly by the Gouy method, while those for the other ligands were obtained using Pascal's constants.[13] The values used were the following ($\times 10^{-6}$): $((C_6H_5)_2PS)_2N^-$, 198.8; $((CH_3)_2PS)_2N^-$, 188.4; $((C_6H_5)_2PNH)_2N^-$, 185.8; $((C_6H_5)_2PO)_2N^-$, 178.0. The magnetic susceptibilities of samples in solution were determined by the Evans[14] method.

Electronic spectra were recorded on a Cary (Model 14) spectrometer in dry methylene chloride. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer. Nuclear magnetic resonance spectra were recorded on Varian Associates T-60 and A-60 spectrometers.

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(9) Some sterically overcrowded ligands which form bis complexes with nickel(II) do not distort to a tetrahedral structure but in fact distort to a "stepped ligand structure" in which the steric strain is relieved but an essentially planar donor atom set is maintained.[10] The factors which cause this to occur in preference to a tetrahedral structure are not understood.

(10) Bis(3-methyl-1-phenyl-5-*p*-tolylformazyl)nickel(II) has a "stepped" structure: D. Dale, *J. Chem. Soc. A*, 278 (1967).

(11) (a) A. Schmidpeter, R. Böhm, and H. Groeger, *Angew. Chem.*, **76**, 860 (1964); (b) A. Schmidpeter and H. Groeger, *Z. Anorg. Allg. Chem.*, **345**, 106 (1966); (c) A. Schmidpeter and H. Groeger, *Chem. Ber.*, **100**, 3979 (1967); (d) A. Schmidpeter and J. Ebeling, *ibid.*, **101**, 815 (1968); (e) E. Fluck and F. L. Goldman, *ibid.*, **96**, 3091 (1963).

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Where sensitive materials were involved, manipulations were carried out in an inert atmosphere.

Materials.—Chlorodiphenylphosphine was obtained from the Stauffer Chemical Co. Tetramethyldiphosphine disulfide was obtained from Strem Chemicals, Inc. The other "imidodiphosphinates," $((C_6H_5)_2PS)_2NH$, $K[((C_6H_5)_2PS)_2N]$, $[((C_6H_5)_2PCl)_2N]Cl$, $[((C_6H_5)_2PNH_2)_2N]Cl$, $((C_6H_5)_2PO)_2NH$, $K[((C_6H_5)_2PO)_2N]$, and $((CH_3)_2PS)_2NH$, were prepared by the published procedures.[11]

Preparations. Bis(imidotetraphenyldithiodiphosphino-*S,S*)iron(II).—The addition of excess $[(C_2H_5)_4N]_2[FeCl_4]$ (*ca.* 1.1 g, 2.6 mmol) to a solution of $K[((C_6H_5)_2PS)_2N]$ (0.974 g, 2.0 mmol) in methanol (100 ml) under an inert atmosphere caused the immediate formation of a pale green precipitate. The product was separated by filtration, washed with methanol (three 25-ml portions), and dried. Recrystallization from CH_2Cl_2–heptane gave very pale green crystals (0.70 g, 73.3%), mp 285–286°. *Anal.* Calcd for $C_{48}H_4OFeN_2P_4S_4$: C, 60.31; H, 4.23; Fe, 6.15; N, 2.93. Found: C, 60.42; H, 4.23; Fe, 5.98; N, 2.97. λ_{max} (cm^{-1}): 3220, 4049, 5000 (sh); ϵ (l. mol^{-1} cm^{-1}): 142, 134, ~81. Nmr ($CDCl_3$): −0.06 (b), 4.40 (b). The complex is paramagnetic in both solid (5.17 BM Gouy, 5.20 BM Faraday) and solution (4.80 BM, CH_2Cl_2). The solid is air stable, but in solution the complex is rapidly oxidized.

Bis(imidotetramethyldithiodiphosphino-*S,S*)iron(II).—A mixture of $((CH_3)_2PS)_2NH$ (0.804 g, 4.0 mmol) and sodium methoxide (4.0 mmol) in methanol (100 ml) was treated with excess $[(C_2H_5)_4N]_2[FeCl_4]$ (1.1 g, 2.6 mmol) under a nitrogen atmosphere. The solution was concentrated to *ca.* 50 ml which caused the product to separate. It was collected and recrystallized, as above, from CH_2Cl_2–heptane yielding (0.30 g, 32.9%) colorless crystals, mp 186–188° with sublimation. *Anal.* Calcd for $C_8H_{24}FeN_2P_4S_4$: C, 21.06; H, 5.31; Fe, 12.24. Found: C, 21.04; H, 5.17; Fe, 11.65. λ_{max} (cm^{-1}): 3100, 4098, 5000 (sh); ϵ (l. mol^{-1} cm^{-1}): 101, 108, ~70. Nmr ($CDCl_3$): −8.3 (width at half-height *ca.* 200 Hz). The complex is paramagnetic in both solid (5.25 BM) and solution (4.99 BM, CH_2Cl_2). The complex is air sensitive as a solid and in solution.

Bis(imidotetraphenyldithiodiphosphino-*S,S*)cobalt(II).—This complex was prepared as outlined above from $K[((C_6H_5)_2PS)_2N]$ and $CoCl_2 \cdot 6H_2O$ in 80% yield. It was obtained as green, air-stable crystals, mp 304–309°. *Anal.* Calcd for $C_{48}CoH_{40}N_2P_4S_4$: C, 60.30; H, 4.23; N, 2.93. Found: C, 60.51; H, 4.19; N, 2.73. λ_{max} (cm^{-1}): 8772 (sh), 10,309, 12,706, 14,045, 15,348; ϵ (l. mol^{-1} cm^{-1}): 55, 233, 199, 163. The complex is paramagnetic as a solid (4.54 BM).

Bis(imidotetramethyldithiodiphosphino-*S,S*)cobalt(II).—The complex was prepared as outlined above from $((CH_3)_2PS)_2NH$, sodium methoxide, and $[(C_2H_5)_4N]_2[CoBr_2Cl_2]$ in 58% yield. The blue-green crystals are air stable, mp 202–204°. *Anal.* Calcd for $C_8CoH_{24}N_2P_4S_4$: C, 20.90; H, 5.33; N, 6.10; mol wt 459.63. Found: C, 21.14; H, 5.34; N, 5.82; mol wt 432 ($CHCl_3$). λ_{max} (cm^{-1}): 5780, 7246, 13,333, 14,225, 15,924; ϵ (l. mol^{-1} cm^{-1}): 138, 164, 406, 554, 347. Nmr ($CHCl_3$): −10.7 (width at half-height *ca.* 76 Hz). The complex is paramagnetic both in solid form (4.68 BM) and in solution (4.50 BM, CH_2Cl_2).

Bis(imidotetramethyldithiodiphosphino-*S,S*)nickel(II).—This complex was prepared, in 57% yield, from $((CH_3)_2PS)_2NH$, sodium methoxide, and $[(C_2H_5)_4N]_2[NiCl_4]$ in a manner similar to the preparation of the analogous iron complex. The green crystals are air stable, mp 194–195° with sublimation. *Anal.* Calcd for $C_8H_{24}N_2NiP_4S_4$: C, 20.92; H, 5.28; N, 6.10; mol wt 459.15. Found: C, 20.80; H, 5.48; N, 5.76; mol wt 402 ($CHCl_3$). λ_{max} (cm^{-1}): 8700, 10,700, 12,750, 14,000, 16,000 (sh); ϵ (l. mol^{-1} cm^{-1}): 34, 56, 204, 171, ~118. Nmr ($CDCl_3$): −0.3 (b). The magnetic moment is 3.40 (solid) and 3.20 BM ($CHCl_3$ in solution).

Bis(imidotetraphenyldithiodiphosphino-*S,S*)nickel(II).—This complex has been reported briefly by Schmidpeter, *et al.* The brown crystals, mp 289–290° (lit.[11a] mp 265–266° dec), were obtained by a modification of the published procedure from $K[((C_6H_5)_2PS)_2N]$ and $[(C_2H_5)_4N]_2[NiCl_4]$. *Anal.* Calcd for $C_{48}H_{40}N_2NiP_4S_4$: C, 60.32; H, 4.23; N, 2.93; mol wt 955.73. Found: C, 60.24; H, 3.80; N, 2.72; mol wt 846 ($CHCl_3$). λ_{max} (cm^{-1}) 8772, 10,309, 12,706, 14,045, 15,384; ϵ (l. mol^{-1} cm^{-1}): 36, 55, 233, 199, 168. Nmr ($CDCl_3$): 1.35, triplet (2); 2.67, doublet (2); 3.37, triplet (1). The magnetic moment is 3.40 BM in the solid and 3.08 BM in solution (CH_2Cl_2).

Bis(imidotetraphenyldithiodiphosphino-*S,S*)nickel(II)–Pyridine.—A small amount of pyridine was added dropwise to a warm, saturated solution of $[((C_6H_5)_2PS)_2N]_2Ni$ (~0.03 g/ml) in CH_2Cl_2. On mixing the solution, immediately deep red-orange crystals deposited on standing. The orange crystals were collected, washed with CH_2Cl_2 and then with pentane, and air dried, dec pt ~200°, mp 286–287. *Anal.* Calcd for $C_{53}H_{41}N_3NiP_4S_4$: C, 61.51; H, 4.39; N, 4.06. Found: C, 61.44; H, 4.72; N, 3.97.

Bis(imidotetraphenyldithiophosphino-*S,S*)nickel(II)–2-Pyridine.—This complex was prepared by dissolving $[((C_6H_5)_2PS)_2N]_2Ni$ in a minimum of warm pyridine. As the solution was cooled to room temperature the color changed from red to light green. Sufficient pentane was added to cause precipitation of a pale green solid which was collected, washed with pentane, and air dried, mp 282°. *Anal.* Calcd for $C_{58}H_{50}N_4NiP_4S_4$: C, 62.53; H, 4.53; N, 5.03. Found: C, 62.21; H, 3.83; N, 5.14.

Bis(imidotetraphenyldithiodiphosphino-*S,S*)zinc(II).—This complex was prepared as outlined above from $((C_6H_5)_2PS)_2NH$, sodium methoxide, and excess $[(C_2H_5)_4N]_3[ZnCl_5]$ in 88% yield. The stable white crystals melt at 301–302°. *Anal.* Calcd for $C_{48}H_{40}N_2P_4S_4Zn$: C, 59.90; H, 4.20; N, 2.91. Found: C, 59.24; H, 4.13; N, 2.88. Nmr ($CDCl_3$): 1.17, multiplet; 2.33, multiplet.

Bis(imidotetramethyldithiodiphosphino-*S,S*)zinc(II).—This complex was prepared similarly from $((CH_3)_2PS)_2NH$ in 90.5% yield as air-stable white crystals, mp 196–198° with sublimation. *Anal.* Calcd for $C_8H_{24}N_2P_4S_4Zn$: C, 20.63; H, 5.19; N, 6.01. Found: C, 20.87; H, 5.26; N, 5.64. Nmr ($CDCl_3$): 8.17, doublet (J_{P-CH_3} = 12.0 Hz).

Bis(imidotetraphenyldithiodiphosphino-*S,S*)platinum(II).—Excess $K[((C_6H_5)_2PS)_2N]$ (1.20 g, 2.5 mmol) in warm methanol (100 ml) was treated with a solution of $K_2[PtCl_4]$ (0.435 g, 1.1 mmol) in warm water (50 ml). The cloudy solution was digested for 0.5 hr at 80°. The product was separated, washed with water (three 25-ml portions), and dried in air. Recrystallization from CH_2Cl_2–heptane gave yellow crystals (0.73 g, 64%), mp 285–294°. *Anal.* Calcd for $C_{48}H_{40}N_2P_4PtS_4$: C, 52.79; H, 3.70; N, 2.57. Found: C, 52.74; H, 3.72; N, 2.49. λ_{max} (cm^{-1}): 25,000; ϵ (l. mol^{-1} cm^{-1}): 249. Nmr ($CDCl_3$): 2.13, multiplet; 2.63, multiplet.

Bis(imidotetramethyldithiodiphosphino-*S,S*)platinum(II).—A solution of $((CH_3)_2PS)_2NH$ (0.40 g, 2.0 mmol) and sodium methoxide (2.0 mmol) in warm methanol (50 ml) was treated with a solution of $K_2[PtCl_4]$ (0.42 g, 1.0 mmol) in warm water (25 ml). The mixture was evaporated to dryness and extracted with CH_2Cl_2 (50 ml). Addition of heptane and concentration of the solution caused the crude product to separate. It was collected and subjected to sublimation (80° (0.1 mm)) to remove the unreacted $((CH_3)_2PS)_2NH$. Recrystallization from CH_2Cl_2–heptane gave yellow crystals, mp 197–204° with sublimation. *Anal.* Calcd for $C_8H_{24}N_2P_4PtS_4$: C, 16.13; H, 4.07; N, 4.70; mol wt 595.55. Found: C, 16.15; H, 4.07; N, 4.48; mol wt 643 ($CHCl_3$). λ_{max} (cm^{-1}): 28,329; ϵ (l. mol^{-1} cm^{-1}): 455. Nmr ($CDCl_3$): 8.13, doublet (J_{P-CH_3} = 12.0, $J_{^{195}Pt-CH_3}$ = 32 Hz).

Bis(imidotetraphenyldithiodiphosphino-*S,S*)palladium(II).—A mixture of $PdCl_2$ (0.185 g, 1.04 mmol) and excess LiCl were boiled for 2 min in methanol (100 ml) and filtered into a solution of $K[((C_6H_5)_2PS)_2N]$ (1.01 g, 2.08 mmol) in methanol (50 ml). The product separated immediately as an orange suspension and was digested for several minutes at ~80°. It was collected, dried, and recrystallized from CH_2Cl_2–heptane to give orange crystals, mp 312–315°, in 91% yield. *Anal.* Calcd for $C_{48}H_{40}$-

$N_2P_4PdS_4$: C, 57.45; H, 4.03; N, 2.79. Found: C, 57.11; H, 3.95; N, 2.65. λ_{max} (cm^{-1}): 21,739; ϵ (l. mol^{-1} cm^{-1}): 708. Nmr ($CDCl_3$): 2.25, multiplet; 2.82, multiplet.

Bis(imidotetramethyldithiodiphosphino-*S,S*)palladium(II).—A mixture of $PdCl_2$ (0.354 g, 2.0 mmol) and excess LiCl were boiled for 2 min in methanol (50 ml) and filtered into a solution of $Na[((CH_3)_2PS)_2N]$ (4 mmol) in 50 ml of methanol. The solution was evaporated to dryness and the solids were extracted with CH_2Cl_2 and the resulting orange solution was concentrated to *ca.* 25 ml and sufficient heptane was added to induce crystallization. The product was collected and recrystallized from CH_2Cl_2–heptane to give orange crystals, mp 210–211° with sublimation (0.7 g, 69%). *Anal.* Calcd for $C_8H_{24}N_2P_4PdS_4$: C, 18.96; H, 4.78; N, 5.53; mol wt 506.86. Found: C, 18.88; H, 4.59; N, 5.26; mol wt 492 ($CHCl_2$). λ_{max} (cm^{-1}): 22,727; ϵ (l. mol^{-1} cm^{-1}): 669. Nmr ($CDCl_3$): 8.10, doublet (J_{P-CH_3} = 12.0 Hz).

Bis(imidotetraphenyldiiminodiphosphino-*NH,NH*)cobalt(II).—A solution of $[((C_6H_5)_2PNH_2)_2N]Cl$ (0.65 g, 1.45 mmol) and sodium methoxide (2.90 mmol) in 75 ml of methanol was treated with a solution of excess $[(C_2H_5)_4N]_2[CoBr_2Cl_2]$ (~1.0 g) in 50 ml of methanol. The deep blue solution was evaporated to dryness and extracted with cold benzene (~50 ml). To this extract ~15 ml of heptane was added and the solution was concentrated. The resulting solid was collected, washed with methanol (~50 ml), and dried. Recrystallization from benzene–heptane gave deep blue crystals (0.40 g, 63%), dec above 123°. *Anal.* Calcd for $C_{48}CoH_{44}N_6P_4$: C, 64.93; H, 5.01; N, 9.47; mol wt 887.79. Found: C, 64.52; H, 5.12; N, 9.20; mol wt 836 ($CHCl_3$). λ_{max} (cm^{-1}): 6623, 7937, 9174, 15,949, 18,215, 18,587; ϵ (l. mol^{-1} cm^{-1}): 68, 80, 126, 225, 307, 223. Nmr ($CDCl_3$): 0.27, broad (3); 4.05, broad (2). The complex is paramagnetic both in the solid (4.91 BM) and in solution (4.79 BM, CH_2Cl_2).

Bis(imidotetraphenyldiiminodiphosphino-*NH,NH*)nickel(II).—An excess of $[(C_2H_5)_4N]_2[NiCl_4]$ (~3.5 g) was added to a solution of $[((C_6H_5)_2PNH_2)_2N]Cl$ (6.04 g, 13.3 mmol) and potassium *tert*-butoxide (2.98 g, 26.6 mmol) in dry *tert*-butyl alcohol (200 ml). After stirring for 5 hr the resulting purple solid was collected and dried. The solid material was extracted with cold benzene (~50 ml). Heptane (~15 ml) was added and the solution was concentrated until crystallization occurred. The solid was collected and recrystallized from benzene–heptane to give purple crystals (3.5 g, 59%), mp 201–203°. *Anal.* Calcd for $C_{48}H_{44}N_6NiP_4$: C, 64.95; H, 5.01; N, 9.47; mol wt 887.57. Found: C, 64.47; H, 5.00; N, 9.20; mol wt 795 ($CHCl_3$). λ_{max} (cm^{-1}) at 23.5°: 6570, 11.428, 12,195, 18,018; ϵ (l. mol^{-1} cm^{-1}): 29, 46, 41, 103. Nmr ($CDCl_3$): 2.27, broad multiplet (10); 3.27, broad (1). The complex is diamagnetic both as a solid and in solution.

Bis(imidotetraphenyldiphosphino-*O,O*)cobalt(II).—A mixture of $((C_6H_5)_2PO)_2NH$ (0.64 g, 1.53 mmol) and sodium methoxide (1.53 mmol) in methanol (50 ml) was treated with excess $[(C_2H_5)_4N]_2[CoBr_2Cl_2]$ (~1.0 g). The solution was evaporated to dryness and extracted with CH_2Cl_2 (~25 ml). Heptane (~10 ml) was added and the solution concentrated until crystallization occurred. The solid was collected, washed with methanol (two 25-ml portions), dried, and recrystallized from CH_2Cl_2–heptane to give deep blue crystals (0.50 g, 37%), mp 229–232°. *Anal.* Calcd for $C_{48}CoH_{40}N_2O_4P_4$: C, 64.56; H, 4.53; N, 3.14; mol wt 891.71. Found: C, 64.66; H, 4.95; N, 3.26; mol wt 993 ($CHCl_3$). λ_{max} (cm^{-1}): 6493, 7092, 16,000, 16,949, 18,349, 20,000; ϵ (l. mol^{-1} cm^{-1}): 32, 57, 191, 193, 128, 84. Nmr ($CDCl_3$): 2.94, broad (3); 3.27, broad (2). This complex is paramagnetic both in the solid (4.88 BM) and in solution (4.72 BM, CH_2Cl_2).

Bis(imidotetraphenyldiphosphino-*O,O*)nickel(II).—A mixture of $((C_6H_5)_2PO)_2NH$ (0.834 g, 2.0 mmol) and nickel acetate tetrahydrate (0.278 g, 1.0 mmol) was refluxed for 20 min in *n*-butyl alcohol (100 ml). The solution was then filtered and evaporated to dryness. The resulting solid was extracted with benzene (~50 ml). Heptane (~15 ml) was added and the solution concentrated until crystallization occurred. The solid was collected, dried, and recrystallized slowly from benzene–heptane to give golden crystals (0.27 g, 30%), mp 291–292°. *Anal.* Calcd for $C_{48}H_{40}N_2NiO_4P_4$: C, 64.66; H, 4.53; N, 3.14; mol wt 891.49. Found: C, 64.61; H, 4.28; N, 3.02; mol wt 1880 (benzene). λ_{max} (cm^{-1}): 11,364, 17,857, 22,727; ϵ (l. mol^{-1} cm^{-1}) based on the dimer: 20, 20, 115. This complex is paramagnetic both in the solid (3.50 BM per nickel atom) and in solution (3.38 BM per nickel atom).

Results and Discussion

The "imidodiphosphinate" complexes have β-difunctional ligands which are sterically unencumbered about the donor atoms. This general class of ligands has the distinct advantage that the uncomplexed ligands are readily obtainable and that various permutations both of substituents at the phosphorus atoms and of donor sets can be easily achieved. The ligands are thus ideally suited to studying variations in stereochemistry of the metal complexes both as a function of the metal ion, with constant ligand structure, and as a function of the changes in the ligand substituents and donor atoms with a given metal. The relevant information concerning the structures of some selected complexes of iron (II), cobalt(II), nickel(II), copper(II), zinc(II), palladium(II), and platinum(II) in both the solid and in solution are presented in the following sections.

Iron(II) Complexes.—The complexes $[((C_6H_5)_2PS)_2N]_2Fe^{II}$ and $[((CH_3)_2PS)_2N]_2Fe^{II}$ were readily prepared as off-white crystals. Both complexes are moderately stable as solids but oxidation and decomposition are rapid in solution. No attempt has been made to characterize the oxidation products. Because of the extreme sensitivity to oxygen no reliable solution molecular weight data have been obtained. The complexes are, however, similar to the cobalt(II) and nickel(II) complexes and are presumed to be monomeric.[15]

All the manipulations for the spectral and magnetic studies were carried out in an efficient glove box under an inert atmosphere.

The magnetic moments for both the solids and the solutions agree quite well. The moments lie in the range 5.0–5.4 BM found for high-spin iron(II) complexes. A spin-only value of 4.90 BM would be expected for a tetrahedral iron(II) complex and with a reasonably small admixture of an orbital contribution to the moment arising from mixing in of the $^5T_2$ level by spin–orbit coupling, the moments might be expected to lie in the range 5.1–5.3 BM. However, no unambiguous structural information can be made on this basis because although planar bonding arrangements for four-coordinate iron(II) complexes are rare, the planar FeO_4 unit[16] in the mineral gillespite $BaFeSi_4O_{10}$ gives a high-spin moment of 5.12 BM.

The most convincing evidence for the structure of these iron(II) complexes is obtained from their electronic

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(15) After the submission of this manuscript an X-ray structure determination on a single crystal of $[((CH_3)_2PS)_2N]_2Fe^{II}$, while not isomorphous with $[((CH_3)_2PS)_2N]_2Ni^{II}$, shows that the iron atom is structurally coordinated to four sulfurs: M. R. Churchill and J. Wormald, *Chem. Commun.*, 703 (1970).

(16) R. G. Burns, M. G. Clark, and A. J. Stone, *Inorg. Chem.*, **5**, 1268 (1966).

spectra. The spectra for both complexes show a very broad, split, moderately intense ligand field transition centered at ~3500 cm^{-1} (Figure 1). These spectra are quite similar to those found for tetrahedral Fe(II) ions

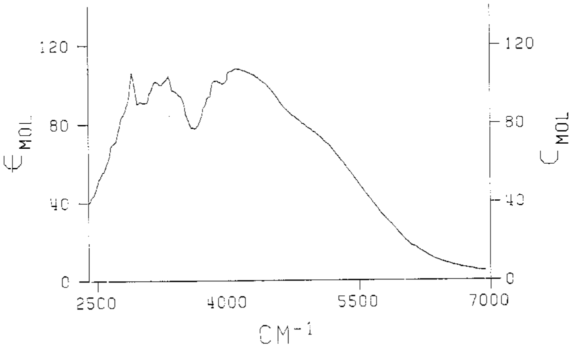

Figure 1.—The absorption spectrum of $[((CH_3)_2PS)_2N]Fe^{II}$ in CH_2Cl_2 solution. The spectrum above 4000 cm^{-1} was recorded in a 1-cm quartz cell on a Cary 14 spectrometer. The spectrum below 4000 cm^{-1} was recorded in a 0.5-mm quartz cell on a Perkin-Elmer 337 spectrometer.

doped into ZnS[17] and CdS[18] lattices where Δ_t was estimated to be 3300 and 2860 cm^{-1}, respectively. It has been experimentally observed that the extinction coefficients of the ligand field transitions in tetrahedral complexes of bivalent ions of the first transition series are usually a factor of a 100 times more intense than the octahedral ones. For a tetrahedral iron(II) complex a single transition is expected at fairly low energies. With the exception of β-diketone, β-thioketone, and β-ketoamino[8] ligands, Δ_t values for most ligands[19] lie in the range 3000–6000 cm^{-1} in their tetrahedral iron(II) complexes, are usually 5–25% greater than the values for tetrahedral cobalt(II), and have extinction coefficients in the range ~60–150 l. mol^{-1} cm^{-1}.

The absorption band found for these bis(imidodithiodiphosphino) iron(II) complexes is then most reasonably assigned to the $^5E \rightarrow {}^5T_2$ transition for a tetrahedral FeS_4 unit. The effect of spin–orbit coupling[17,20] on the $^5T_2$ level would be expected to give rise to three transitions each separated by not more than 200–300 cm^{-1}. The additional splitting and breadth is presumably due to a lowering of the symmetry in the complex to D_{2d}. On the basis of this assignment, Δ_t for these ligands can be estimated to be *ca.* 3500–4500 cm^{-1} and lies close to Δ_t values[19] found for the halides. In view of these data and of the noted stereochemical trends[8] found for bivalent first-row metals with other β-difunctional ligands these complexes represent the *first authentic examples* of *tetrahedral* FeS_4 units in a simple coordination compound. Two other simple FeS_4 complexes have been claimed, $[(CH_3CS)_2CH]_2Fe^{II}$ [21] and $(F_2PS_2)_2Fe^{II}$.[22] The former complex cannot be prepared[8] by the published procedure and its existence is questionable. The latter complex with a magnetic moment of 5.2 BM which is not structurally diagnostic may be tetrahedral. The only other documented example of an FeS_4 unit is in the nonheme iron protein rubredoxin which has one iron atom per molecule. Jensen and coworkers have presented preliminary results[23] of an X-ray structural determination of the red oxidized form of rubredoxin which shows that the configuration of sulfur atom about the iron atom is essentially tetrahedral. The colorless form (reduced by dithionite and presumably containing iron(II)) has lattice parameters essentially unchanged and is felt to have the same tetrahedral configuration.

Cobalt(II) Complexes.—The complexes are readily prepared from a tetrahalocobaltate(II) salt and the appropriate ligand salt. They are all air stable both in the solid and in solution. Molecular weight measurements indicate that they are all monomeric in solution. The relevant spectral and magnetic data are collected in Table I. The moments of the complexes are consistent with tetrahedral geometry in the solid and in solution.

TABLE I

SUMMARY OF SPECTRAL AND MAGNETIC DATA FOR COBALT COMPLEXES, CoL_2

L	ν_2,[a] cm^{-1}	ν_3,[a] cm^{-1}	Δ_t, cm^{-1}	B', cm^{-1}	μ_{eff}, BM	
					Solid	Soln
$((C_6H_5)_2PS)_2N$	6613	14,258	4027	586	4.54	*b*
$((CH_3)_2PS)_2N$	6576	14,399	3831	632	4.68	4.50
$((C_6H_5)_2PO)_2N$	6877	17,376	3959	825	4.88	4.72
$((C_6H_5)_2PNH)_2N$	8180	17,650	4635	795	4.91	4.79

[a] Weighted averages of the several maxima. [b] Compound too insoluble for accurate measurement.

The optical spectra of all of the complexes are characteristic of those found[24] in tetrahedral cobalt(II) complexes. There are two bands in each spectrum, one in the range 5700–9100 cm^{-1} which corresponds to ν_2 ($^4A_2 \rightarrow {}^4T_1(F)$) and one in the range 13,300–20,000 cm^{-1} which corresponds to ν_3 ($^4A_2 \rightarrow {}^4T_1(P)$). The spectrum of $[((CH_3)_2PS)_2N]_2Co^{II}$ is shown in Figure 2. Here, as

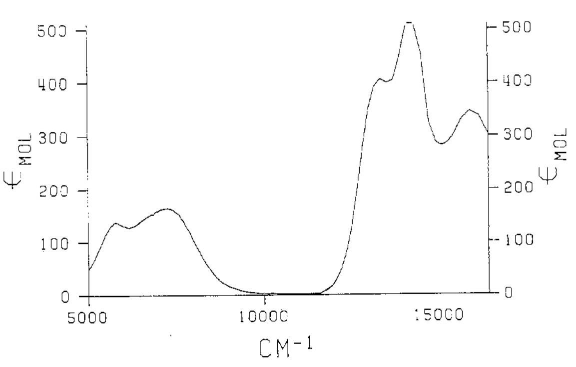

Figure 2.—The absorption spectrum of $[((CH_3)_2PS)_2N]_2Co^{II}$ in CH_2Cl_2 solution.

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[17] W. Low and M. Weger, *Phys. Rev.*, **118**, 1130 (1960).

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[21] K. Knauer, P. Hemmerich, and J. D. W. van Voorst, *Angew. Chem., Int. Ed. Engl.*, **6**, 262 (1967).

[22] F. N. Tebbe, H. W. Roesky, W. C. Rode, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 3578 (1968).

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[24] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, **83**, 4690 (1961).

is the case for the tetrahalocobaltate spectra, the predicted[25] number of bands arising from spin-orbit coupling is not observed. The values of Δ_t for the sulfur-containing chromophores compare quite well with those obtained from the iron(II) spectra as well as the values of 3500–3160 cm^{-1} for Co(II) ions doped into ZnS[17] and CdS[18] lattices. Using this and the previously tabulated[24] values for Δ_t it is possible to obtain the following spectrochemical series for cobalt(II) chromophores: $I^- < Br^- < Cl^- < (C_6H_5)_3PO \sim ((CH_3)_2PS)_2N^- \sim ((C_6H_5)_2PO)_2N^- \sim ((C_6H_5)_2PS)_2N^- \sim NCO^- < OH^- < NCS^- < ((C_6H_5)_2PNH)_2N^-$.

The complex $[((CH_3)_2PS)_2N]_2Co^{II}$ is isomorphous with the analogous nickel complex $[((CH_3)_2PS)_2N]_2Ni^{II}$ which has been shown[26] to have a tetrahedral NiS_4 unit by a single-crystal X-ray structural determination. Apart from some dithiophosphates[27] and dithiophosphinates,[28] The sulfur-containing bis(imidodithiodiphosphino)cobalt(II) complexes are the only examples of well-characterized tetrahedral cobalt(II) systems having a CoS_4 core. All of the "imidodiphosphinate" complexes of cobalt(II) show well-defined Curie behavior in $CHCl_3$ solution down to −60° which indicates that little if any of a planar ($S = {}^1/_2$) form is in equilibrium with the high-spin ($S = {}^3/_2$) tetrahedral form at these temperatures and the complexes to all intents are fully tetrahedral in this temperature range.

Nickel(II) Complexes.—The two complexes $[((CH_3)_2PS)_2N]_2Ni^{II}$ and $[((C_6H_5)_2PS)_2N]_2Ni^{II}$ are readily prepared as air-stable crystalline solids. Both complexes are monomeric in solution. The solution high-spin moments of 3.20 and 3.08 BM are somewhat lower that that of 3.40 BM found for the solids but nevertheless are indicative of tetrahedral nickel(II) stereochemistry.

The ligand field spectra of the complexes (Figure 3) are very similar to those found[7,29] for a variety of nickel(II) tetrahedral chromophores. The band at 12,700–15,000 cm^{-1} is most reasonably assigned to ν_3 ($^3T_1(F) \rightarrow {}^3T_1(P)$). There are two other moderately intense features in the range 5000–11,000 cm^{-1}, at 8700 and at 10,500 cm^{-1}, one of which is presumably ν_2 ($^3T_1 \rightarrow {}^3A_2$). In view of the value of $\Delta_t \approx 4150$ cm^{-1} obtained for Ni(II) ions doped into a CdS[17] lattice and the Δ_t values found for these ligands with Fe(II) and Co(II) (see the previous sections), it seemed reasonable to expect that Δ_t for the nickel complexes would lie between 4000 and 4500 cm^{-1} such that one might reasonably expect ν_2 to occur close to 8000 cm^{-1}.

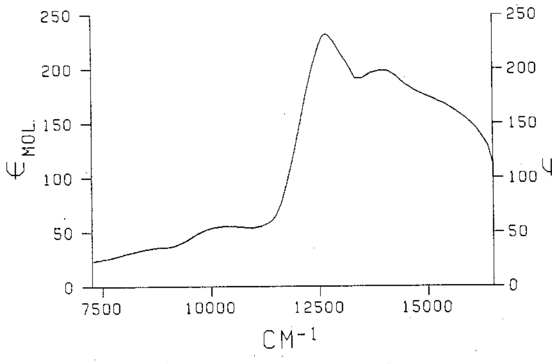
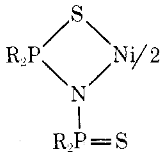


Figure 3.—The absorption spectrum of $[((C_6H_5)_2PS)_2N]Ni^{II}$ in CH_2Cl_2 solution.

This information clearly indicated that the nickel complexes contained a tetrahedral chromophore. It *does not show* that the donor set is comprised of four sulfur atoms. Another reasonable alternative, namely, the ligand chelating as an iminothiophosphinate with an NiS_2N_2 core, 2, could not be excluded. However,



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an X-ray determination[26] on $[((CH_3)_2PS)_2N]_2Ni^{II}$ proved that the complex is sulfur bonded and that it is *tetrahedral* in the solid state. In fact it is the *only* nickel(II) complex which attains a tetrahedral configuration under ambient conditions in both the solid and in solution. This fact is rather surprising since the ligand system is clearly not sterically overcrowded at the donor sites and the reason for the preference of a tetrahedral over a planar configuration is not clear.

The nuclear magnetic resonance spectrum of $[((CH_3)_2PS)_2N]_2Ni^{II}$ shows a single broad resonance at τ −0.3 while that for $[((C_6H_5)_2PS)_2N]_2Ni^{II}$ shows a separation of the phenyl proton resonances, τ 1.35 triplet (2) meta, 2.67 doublet (2) ortho, and 3.37 triplet (1) para, which is indicative of a small imbalance of spin density in the ligands presumably as a result of ligand to metal π bonding in this tetrahedral complex. The temperature dependence of the solution magnetic susceptibility of $[((CH_3)_2PS)_2N]_2Ni^{II}$ in $CHCl_3$ solution in the range −48 to +60° is shown in Figure 4. The Curie behavior in

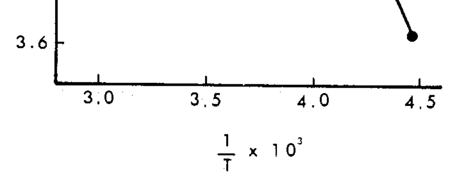

Figure 4.—The temperature dependence of the magnetic susceptibility of $[((CH_3)_2PS)_2N]_2Ni^{II}$ in $CHCl_3$–TMS solution in the range +60 to −48°.

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[26] M. R. Churchill, J. Cooke, J. Wormald, A. Davison, and E. S. Switkes, *J. Amer. Chem. Soc.*, **91**, 6518 (1969).

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

the range +60 to +12° is consistent with the complex existing in solution as a tetrahedral species. The maxima in the χ_m *vs.* $1/T$ curve at +12° and the subsequent decrease in the value of χ_m as $1/T$ increases is most readily interpreted in terms of the onset of the equilibrium: tetrahedral ($S = 1$) $\rightleftarrows$ planar ($S = 0$). However, even at −50° this equilibrium lies largely on the side of the high-spin species. A large number of cases of this type of equilibria have been found with other β-difunctional ligands.[3-8]

The lavender complex $[((C_6H_5)_2PNH)_2N]_2Ni^{II}$ is an air-stable diamagnetic solid. It is presumably planar. The mull spectrum shows one band at 19,800 cm^{-1} with a low-energy shoulder at 17,500 cm^{-1}. The solution spectrum shows, in addition to the strong band at ~18,000 cm^{-1} which is most likely due to the transition $(d_{x^2-y^2})^2 \rightarrow (d_{x^2-y^2})^1(d_{xy})^1$ in the planar complex, much weaker bands at ~6500 and ~12,000 cm^{-1}. These weak bands can be assigned to a small amount of the tetrahedral isomer existing in equilibrium with the planar form. This conclusion is confirmed by the temperature dependence of the spectra shown in Figure 5 in the range +20 to +60°. As the temperature is raised, the bands assigned to the tetrahedral isomer gain in intensity while that for the planar isomer shows a concomitant decrease.

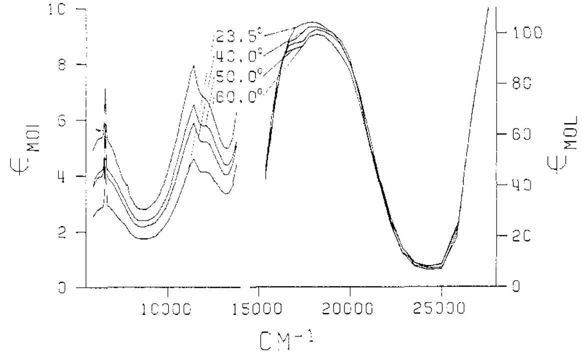

Figure 5.—The temperature dependence of the absorption spectrum of $[((C_6H_5)_2PNH)_2N]_2Ni^{II}$ in $CHCl_3$ solution in the range 23.5–60°.

The pale yellow complex $\{[((C_6H_5)_2PO)_2N]_2Ni^{II}\}_n$ appears to be associated in solution probably as a dimer. The solid moment per nickel atom is 3.50 BM and the solution moment is 3.38 BM. Thus for this ligand with nickel(II) unlike cobalt(II) the marked tendency of β-difunctional oxygen-containing ligand complexes to associate is realized.

Unlike other four-coordinate sulfur complexes, $[((C_6H_5)_2PS)_2N]_2Ni^{II}$ forms both a red monoadduct and a pale green diadduct with pyridine. The latter is only stable in the presence of excess pyridine and in solution readily dissociates to the presumably five-coordinate species $[((C_6H_5)_2PS)_2N]_2Ni^{II} \cdot py$.

Other Metal(II) Complexes.—The planar diamagnetic complexes $[(R_2PS)_2N]_2M^{II}$ (R = CH_3, C_6H_5; M = Pd, Pt) are readily prepared. The position of the first spin-allowed transitions when compared[30] to other MS_4 chromophores for these metals does not indicate any unusually weak ligand fields. The zinc complexes are readily prepared and are undoubtably tetrahedral. Attempts to prepare the complexes $[(R_2PS)_2N]_2Cu^{II}$ (R = CH_3, C_6H_5) lead to reduction to the copper(I) species. The previously reported complexes $[((C_6H_5)_2PO)_2N]_2Cu^{II}$ and $[((C_6H_5)_2PNH)_2N]_2Cu^{II}$ are presumed to be planar.

Summary

The ligand field spectral data of the imidodithiodiphosphinates with a number of MS_4 chromophores do not indicate the presence of unusually weak ligand fields. There are no steric factors present in the ligands which might destabilize a planar configuration with respect to a tetrahedral one. The existence of fully tetrahedral $[(R_2PS)_2N]_2Ni^{II}$ (R = C_6H_5, CH_3) and the observation of a square-planar $\rightleftarrows$ tetrahedral equilibrium for $[((C_6H_5)_2PHN)_2N]_2Ni^{II}$ is totally unexpected and not fully understood. The tetrahedral stereochemistry of Fe(II) and Co(II) while rare for these metals with sulfur donors is not as surprising in view of the nickel results.

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