Five-Coordination. VIII. Low-Spin Transition Metal Complexes with an Open-Chain Tetradentate Phosphorus–Sulfur Ligand[1]

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The new open-chain tetradentate ligand 1,3-bis(diphenylphosphinopropylthio)propane, $(C_6H_5)_2P(CH_2)_3S(CH_2)_3S(CH_2)_3P$-$(C_6H_5)_2$, forms five-coordinate $[M(C_{33}H_{38}P_2S_2)X]ClO_4$ complexes (where M = Ni, Pd, Pt, Co), in addition to the square-planar $[M(C_{33}H_{38}P_2S_2)](ClO_4)_2$ complexes (where M = Ni, Pd, Pt). Spectrophotometric titrations of the four-coordinate d^8 complexes with iodide ion, as well as the conductance behavior of the isolated materials, substantiate formation of the $M(C_{33}H_{38}P_2S_2)X^+$ complexes. The five-coordinate nickel(II) complexes are intensely purple and exhibit a trigonal-bipyramidal structure, whereas the five-coordinate palladium(II) and platinum(II) complexes are orange and apparently possess a square-pyramidal structure. All of these four- and five-coordinate d^8 ions are diamagnetic. The analogous series of maroon, five-coordinate $[Co(C_{33}H_{38}P_2S_2)X]Y$ complexes (where X = Cl, Br, I and Y = $B(C_6H_5)_4$; X = Cl and Y = ClO_4) possess one unpaired electron (μ_{eff} = 2.05 ± 0.08 BM). The magnetic and spectral properties of the different series of complexes are correlated principally with those of the bidentate phosphorus–sulfur ligand diphenyl(*o*-methylthiophenyl)-phosphine.

Introduction

Five-coordination can no longer be considered unusual for nickel(II). For example, numerous five-coordinate, trigonal-bipyramidal nickel(II) complexes with the "tripod-like" ligands $P[o\text{-}C_6H_4P(C_6H_5)_2]_3$,[3] $As[o\text{-}C_6H_4As(C_6H_5)_2]_3$,[4,5] $P(o\text{-}C_6H_4SCH_3)_3$,[6] $P(o\text{-}C_6H_4\text{-}SeCH_3)_3$,[7] $P[CH_2CH_2CH_2As(CH_3)_2]_3$,[8] $As[CH_2CH_2CH_2\text{-}As(CH_3)_2]_3$,[9] and $N[CH_2CH_2N(CH_3)_2]_3$[10,11] have been reported during the past 4 years. However, of these seven tetradentate ligands, only $P[o\text{-}C_6H_4P(C_6H_5)_2]_3$ and $As[o\text{-}C_6H_4As(C_6H_5)_2]_3$ form five-coordinate palladium(II) and platinum(II) complexes. In these two cases the strong complexing tendency of the phosphine and arsine donor atoms probably imposes the *rigid* trigonal structure of the ligands on the metal ion, resulting in maximum chelation energy when all four donor atoms are coordinated to the same metal. However, with the more flexibile tetradentate ligands listed above, the prevailing tendency is for palladium(II) and platinum(II) to form square-planar complexes. In the latter cases the potentially tetradentate ligands function as bidentates or tridentates, in addition to behaving as tetradentates when they form polynuclear species by bridging between two metals.[12,13]

Following our observations that similar phosphorus–sulfur ligands yielded different five-coordinate structures with Ni(II),[6,12,13] it was of interest to investigate the coordination properties of a *flexible* tetradentate ligand containing essentially the same type of donor atoms. For this purpose the flexible, open-chain ligand 1,3-bis(diphenylphosphinopropylthio)propane, $(C_6H_5)_2P(CH_2)_3S(CH_2)_3S(CH_2)_3P(C_6H_5)_2$, was designed and synthesized so that the structures of the resulting complexes would reflect the preferred coordination number and geometry of the metallic ion with a given set of donor atoms. Such a ligand could wrap around a metal in several different ways, so the structures of the resulting complexes should be controlled by electronic rather than by steric effects.

Experimental Section

Reagents.—Reagent grade 1,4-dioxane was dried over sodium wire for several days and then distilled (bp 101°) from molten sodium under a dry nitrogen atmosphere. Reagent grade tetrahydrofuran was refluxed over calcium hydride for 24 hr and then fractionated (bp 65°). Reagent grade butanol was refluxed over barium oxide and then distilled (bp 116.5°) from magnesium ribbon. Technical grade dichloromethane was refluxed over calcium chloride and then distilled (bp 40°) from fresh calcium chloride. Nitromethane was washed with 5% aqueous sulfuric acid and 5% aqueous sodium bicarbonate, dried over anhydrous calcium chloride, and fractionated (bp 101°). Acetonitrile was refluxed over calcium hydride, decanted, and then distilled (bp 81°) from a small amount of P_4O_{10}. Diphenylphosphine was distilled two times from molecular sieves, the center fraction (bp 96° (~0.25 mm)) being collected each time. Trimethylene sulfide was refluxed over anhydrous barium oxide and then fractionated (bp 94°) from fresh BaO. Spectrograde solvents, absolute ethanol, reagent grade acetone, and other reagent grade materials were used without further purification.

Synthesis of 1,3-Bis(diphenylphosphinopropylthio)propane.—All glassware was dried overnight at 110° and assembled with a dry nitrogen purge while still hot. All reagents were weighed and transferred in a nitrogen-atmosphere drybox and all steps of the reaction were performed under dry nitrogen.

To 80.3 g (0.431 mol) of diphenylphosphine in 800 ml of refluxing dioxane was added dropwise 27.6 g (0.431 mol in 268 ml of hexane) of *n*-butyllithium (required 1 hr). The hexane solvent was removed by distillation and the resulting reaction mixture, which contained a large amount of yellow crystals, was refluxed for 1 hr.[14] Then 32.0 g (0.431 mol) of trimethylene sulfide (in

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TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA ON NICKEL(II), COBALT(II), PALLADIUM(II),
AND PLATINUM(II) COMPLEXES OF 1,3-BIS(DIPHENYLPHOSPHINOPROPYLTHIO)PROPANE

Complex	Color	Yield, %	Λ_M,[a] cm²/ ohm mol	μ_{eff},[e] BM	Analyses,[b] % — C — Calcd	Found	— H — Calcd	Found	— S — Calcd	Found	— Halogen[c] — Calcd	Found
[Ni(C₃₃H₃₈P₂S₂)](ClO₄)₂[d]	Red	86	251 (148)	Diamagnetic	48.44	48.52	4.68	4.81	7.83	7.90	8.67	8.63
[Ni(C₃₃H₃₈P₂S₂)](ClO₄)₂·C₃H₆O	Burgundy	86	258 (154)	Diamagnetic	49.34	49.18	5.06	5.10	7.32	7.51	8.09	8.20
[Ni(C₃₃H₃₈P₂S₂)Cl]ClO₄·0.5CH₂Cl₂	Deep blue	85	152	Diamagnetic	50.50	50.85	4.93	5.06	8.05	8.15	13.35	12.88
[Ni(C₃₃H₃₈P₂S₂)Br]ClO₄	Deep blue	88	150 (87)	Diamagnetic	49.62	49.40	4.80	4.86	8.03	8.23	(8.88)	(8.93)
[Ni(C₃₃H₃₈P₂S₂)I]ClO₄	Deep green	96	152	Diamagnetic	46.85	46.65	4.53	4.53	7.58	7.37	(8.38)	(8.54)
[Co(C₃₃H₃₈P₂S₂)Cl]ClO₄	Maroon	93	151	2.13 ± 0.01	52.52	52.74	5.07	5.04	8.50	8.67	9.40	9.18
[Co(C₃₃H₃₈P₂S₂)Cl]B(C₆H₅)₄	Maroon	55	92.0	2.13 ± 0.01	70.24	70.29	6.00	6.13	6.58	6.78	3.64	3.86
[Co(C₃₃H₃₈P₂S₂)Br]B(C₆H₅)₄	Maroon	69	91.8 (63)	1.98 ± 0.01	67.20	67.10	5.74	5.80	6.29	6.10	7.84	7.64
[Co(C₃₃H₃₈P₂S₂)I]B(C₆H₅)₄	Purple	69	114	2.04 ± 0.01	64.24	64.40	5.49	5.57	6.02	5.84	11.91	11.71
[Pd(C₃₃H₃₈P₂S₂)](ClO₄)₂	Light yellow	97	259	Diamagnetic	45.78	45.64	4.42	4.57	7.41	7.62	8.19	8.45
[Pd(C₃₃H₃₈P₂S₂)I]I	Deep red	87	(78)	Diamagnetic	43.04	{42.94 / 43.06}	4.16	{4.33 / 4.31}	6.96	{6.82 / 6.82}	27.56	{27.30 / 27.38}
[Pt(C₃₃H₃₈P₂S₂)](ClO₄)₂	White	86	262	Diamagnetic	41.50	41.35	4.01	4.13	6.71	6.89	7.42	7.37
[Pt(C₃₃H₃₈P₂S₂)I]ClO₄	Bright yellow	28	(147)	Diamagnetic	40.35	40.73	3.90	4.03	6.53	6.50	(7.22)	(7.46)

[a] Molar conductance values on approximately 10^{-3} M solutions in acetonitrile at 23.5°. The values in parentheses are for ~10^{-3} M nitromethane solutions at 23.5°. Typical values for 1:1 and 2:1 electrolytes in CH₃NO₂ are 80–95 and 160–190, whereas the values in CH₃CN are 135–155 and 250–310 cm² ohm/mol. [b] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. [c] Values in parentheses are the percentage total halogen reported as per cent chlorine. [d] Phosphorus analysis: calcd, 7.57; found, 7.70. [e] The magnetic susceptibilities of the Ni(II) complexes were determined at two different applied field strengths in the range 4800–7800 G. The values reported for the Co(II) complexes are average values from three different field strengths. The effective moments did not vary more than 0.01 BM among the three field strengths.

100 ml of dioxane) was added over a period of 2 hr while the reaction mixture was refluxed. The resulting light yellow mixture, which contained a small amount of white solid, was refluxed for 1 additional hr before 43.5 g (22.0 ml 0.215 mol) of 1,3-dibromopropane was added over a period of 5 hr. The final reaction mixture, which contained solid lithium bromide, was refluxed for 2 hr as 600 ml of dioxane was removed by distillation. On addition of 250 ml of anhydrous deaerated diethyl ether, a large amount of lithium bromide crystallized and the resulting mixture was stirred overnight.

The reaction mixture was hydrolyzed with 250 ml of deaerated water, the ether and water layers were separated, and the water layer was extracted with three 75-ml portions of diethyl ether. The combined ether portions were dried over anhydrous sodium sulfate, decanted onto molecular sieves, and the diethyl ether–dioxane solvent mixture was removed by distillation. Heating was controlled carefully by means of an oil bath.

The resulting colorless oil was heated at 120° (0.5 mm) for 8 hr and then at 140° (0.5 mm) for 4 hr to remove diphenylphosphine and other volatile by-products. The entire sample was dissolved in diethyl ether and filtered to remove any remaining lithium bromide.

The solvent was again removed by distillation and the resulting oil was heated to 100° (0.5 mm), cooled, and then weighed (98.5 g or 81%). Infrared spectra of the oil were consistent with the functional groups of the proposed tetradentate ligand. Of major importance was the absence of PH, SH, P=O, S=O, and POH absorptions,[15] which are strong and would have arisen from incomplete and/or side reactions during the synthesis. Attempts to induce crystallization of the oil[16] were unsuccessful so a stock solution was prepared by dissolving the material in freshly distilled dichloromethane. Aliquots of the stock solution were used in the syntheses of the coordination compounds.

The ligand was also synthesized in lower yield from potassium diphenylphosphide, which was prepared from metallic potassium and chlorodiphenylphosphine in dioxane.[14]

Synthesis of Complexes.—All preparative manipulations with the uncoordinated ligand were performed under a nitrogen at-

mosphere to prevent its possible oxidation. The metal complexes were collected on a sintered glass funnel, washed with ethanol, recrystallized from a 1:1 mixture of dichloromethane and ethanol or 1-butanol, dried with a stream of dry nitrogen, and finally dried in vacuo over anhydrous calcium chloride. The reported yields (Table I) are of the recrystallized products.

Nickel(II) Complexes.—Solutions containing 1 mmol of "NiXClO₄," which were prepared conveniently in situ by mixing equimolar amounts of Ni(ClO₄)₂·6H₂O and NiX₂·6H₂O (X = Cl, Br, I) in ethanol, were treated with 1 mmol (0.561 g) of the ligand (C₃₃H₃₈P₂S₂) dissolved in 10 ml of dichloromethane. Crystals of the appropriate nickel complex separated on evaporation of dichloromethane from the solvent mixture.

Palladium(II) and Platinum(II) Complexes.—The appropriate Na₂MCl₄ (M = Pd, Pt) compound (0.5 mmol) was dissolved in absolute ethanol and treated with 1 mmol (0.561 g) of ligand dissolved in 10 ml of dichloromethane. The resulting light yellow solutions were filtered and treated dropwise with 3 ml of a saturated ethanol solution of lithium perchlorate; solid compounds separated immediately on adding the perchlorate.

In an attempt to prepare [Pd(C₃₃H₃₈P₂S₂)I]ClO₄, 1 mmol of NaClO₄ and 1 mmol of NaI in ethanol were mixed with an ethanol–dichloromethane (1:1) solution of [Pd(C₃₃H₃₈P₂S₂)]Cl₂ (1 mmol). On evaporation of dichloromethane, only Pd(C₃₃H₃₈-P₂S₂)I₂ was isolated. The Pd(C₃₃H₃₈P₂S₂)I₂ complex was recrystallized from ethanol.

However, by mixing an ethanol–dichloromethane (1:1) solution of [Pt(C₃₃H₃₈P₂S₂)]Cl₂ (1 mmol) with 1 mmol of NaI and 1 mmol of NaClO₄ in ethanol, [Pt(C₃₃H₃₈P₂S₂)I]ClO₄ was obtained on evaporation of the dichloromethane from the solvent mixture.

Cobalt(II) Complexes.—Acetone solutions of cobalt(II) tetraphenylborate were prepared in situ by mixing a solution (5 ml) of Co(NO₃)₂·6H₂O (0.146 g, 0.5 mmol) with a solution (5 ml) of sodium tetraphenylborate (0.342 g, 1 mmol); the solutions were concentrated to 5 ml and the sodium nitrate was removed by filtration. Solutions of "CoXB(C₆H₅)₄" were then treated with 0.561 g (1 mmol) of the ligand dissolved in a mixture of 1-butanol (10 ml) and dichloromethane (10 ml). Crystals of the [Co(C₃₃H₃₈-P₂S₂)X]B(C₆H₅)₄ compounds were deposited from solution when the acetone and dichloromethane were evaporated.

The [Co(C₃₃H₃₈P₂S₂)Cl]ClO₄ complex was prepared as the analogous nickel(II) complex except that 1-butanol (rather than ethanol) was used as the solvent. Several attempts to prepare the four-coordinate Co(C₃₃H₃₈P₂S₂)Y₂ complexes (where Y = B-(C₆H₅)₄ or ClO₄) were unsuccessful.

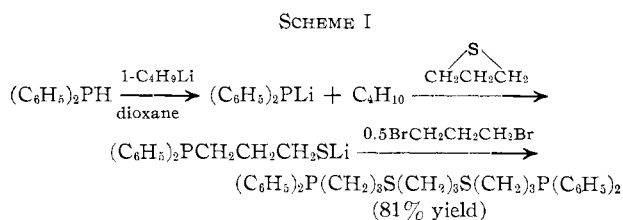**Characterization Measurements.**—The conductance, mag-

(15) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1959.

(16) Attempts to obtain solid derivatives such as the phosphine oxide, sulfide, or methyl iodide generally yielded only intractable oils. However, after chromatography on alumina and evaporation of the solvent, a viscous oil was obtained for the phosphine sulfide derivative. *Anal.* Calcd for C₃₃H₃₈P₂S₄: C, 63.57; H, 6.13; S, 20.48. Found: C, 64.35; H, 6.24; S, 20.11. We thank W. Slinkard for this experiment.

netic, and spectral data were obtained as described previously.[7,12,13]

Results and Discussion

Ligand Synthesis.—The three steps involved in the synthesis of 1,3-bis(diphenylphosphinopropylthio)propane (illustrated in Scheme I) can be done consecutively without isolating each of the intermediates.

Scheme I

$$(C_6H_5)_2PH \xrightarrow[\text{dioxane}]{\text{1-}C_4H_9Li} (C_6H_5)_2PLi + C_4H_{10} \xrightarrow{\overset{S}{\underset{CH_2CH_2CH_2}{\diagup\diagdown}}}$$

$$(C_6H_5)_2PCH_2CH_2CH_2SLi \xrightarrow{0.5BrCH_2CH_2CH_2Br}$$

$$(C_6H_5)_2P(CH_2)_3S(CH_2)_3S(CH_2)_3P(C_6H_5)_2$$

(81% yield)

In the first step, diphenylphosphine is converted almost quantitatively and cleanly to lithium diphenylphosphide by butyllithium. The $LiP(C_6H_5)_2$ then opens the cyclic thioether in a reaction analogous to the cleavage of cyclic ethers by alkali metal organophosphides.[17,18] In the cases of cyclic ethers Issleib has proven that the intermediates are $R_2P(CH_2)_nOM$ (M = Li, Na, K) compounds; therefore, $(C_6H_5)_2PCH_2CH_2-CH_2SLi$ is the logical species in this case. Since alkali metal mercaptides are excellent nucleophiles, this intermediate reacts cleanly in the third step with 1,3-dibromopropane to give the tetradentate ligand in 81% over-all yield.

Four-Coordinate d^8 Complexes.—The following data indicate that all four donor atoms of 1,3-bis(diphenylphosphinopropylthio)propane, $(C_6H_5)_2P(CH_2)_3S(CH_2)_3-S(CH_2)_3P(C_6H_5)_2$, are coordinated in the square-planar $[M(C_{33}H_{38}P_2S_2)](ClO_4)_2$ complexes (M = Ni, Pd, Pt): (1) the magnetism and electronic spectra are consistent with four-coordinate, square-planar complexes; (2) the conductance data (Table I) are indicative of di-univalent electrolytes; (3) the conductivity of nitromethane solutions of the Pd(II) and Pt(II) complexes does not increase when methyl iodide is added;[19] (4) the possibility of perchlorate coordination is excluded since the infrared bands for ionic ClO_4^- at ~625 and 1100 cm^{-1} are not split;[20] and (5) electrochemical oxidation of the complexes occurs well above the oxidation potential of the free ligand. Even though excess ligand was used with Pd(II) and Pt(II) in attempts to prepare the bis complexes $M(\text{ligand})_2^{2+}$, the only compounds isolated correspond to $M(\text{ligand})^{2+}$ cations. If there was significant strain imposed on the ligand in forming a square-planar complex, only two or three of the four donors would have been expected to coordinate when excess ligand was present. Therefore, any strain in the three alkyl chelate rings or any steric interactions between *cis*-diphenylphosphino groups in the square-planar complexes must be smaller than the energy gained in forming the additional chelate

rings. In fact, molecular models indicate that the ligand can fit easily around the square-planar d^8 ions. Shifts in the electronic absorption spectra due to coordination by polar solvent molecules are negligible for $Pd(C_{33}H_{38}P_2S_2)^{2+}$; however, the red nickel complex exhibits a bathochromic shift to purple in acetonitrile, in nitromethane, and, to a much lesser extent, in acetone. It was somewhat surprising then that a stable crystalline acetone solvate was isolated (Table I). Since the carbonyl stretching frequency (1710 cm^{-1}) is not significantly lower than that of liquid acetone (1718 cm^{-1}),[21] the acetone molecule probably is incorporated into the crystal lattice and, at most, interacts only slightly with the nickel(II) ion.

Five-Coordinate d^8 Complexes.—Spectrophotometric titrations of the square-planar $M(C_{33}H_{38}P_2S_2)^{2+}$ complexes with $(n\text{-}C_7H_{15})_4NI$ in dichloromethane (Figure 1) give sharp breaks at a 1:1 mole ratio, indicating formation of the five-coordinate $M(C_{33}H_{38}P_2S_2)I^+$ species. For isolating these nickel complexes, it is simpler to mix solutions of the ligand directly with an equimolar mixture of nickel perchlorate and the appropriate nickel halide.
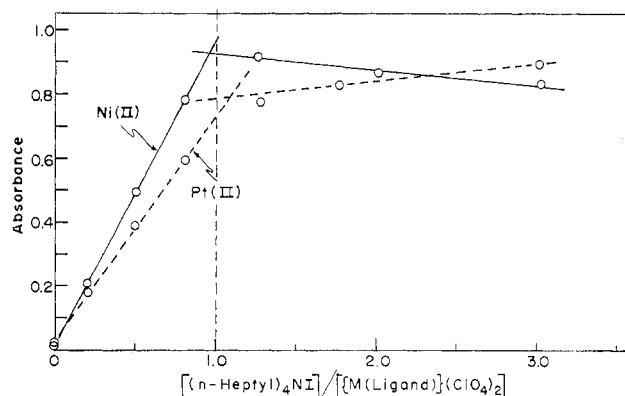

Figure 1.—Plots of absorbance of the metal complexes against increasing mole ratios of $(n\text{-}C_7H_{15})_4NI$ in dichloromethane: ———, $[Ni(C_{33}H_{38}P_2S_2)](ClO_4)_2$ at 675 mμ; ------, $[Pt(C_{33}H_{38}P_2S_2)](ClO_4)_2$ at 400 mμ.

That the isolated $[M(C_{33}H_{38}P_2S_2)X]ClO_4$ complexes are five-coordinate in nitromethane solution is illustrated by Figure 2 where the equivalent conductivity of a complex is plotted against the square root of its equivalent concentration.[22] The slopes of all of the five-coordinate complexes agreed with that of a uni-univalent standard, tetraethylammonium bromide. To exclude the possibility that the coordinated halide ion had displaced one of the four ligand donor atoms, the $[M(C_{33}H_{38}P_2S_2)X]ClO_4$ complexes (M = Ni, Pd, Pt) were treated with methyl iodide in nitromethane. No increase in conductance was noted over a 24-hr period. If one of the donor atoms of the tetradentate ligand had been detached from the metal on coordination of the halide, the methyl iodide would have formed a

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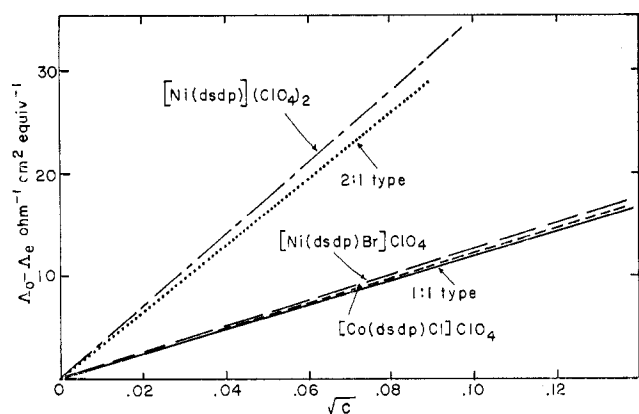
Figure 2.—A plot of the equivalent conductivity of the four-coordinate [Ni(C$_{33}$H$_{38}$P$_2$S$_2$)](ClO$_4$)$_2$ and the five-coordinate [Ni(C$_{33}$H$_{38}$P$_2$S$_2$)Br]ClO$_4$ and [Co(C$_{33}$H$_{38}$P$_2$S$_2$)Cl]ClO$_4$ complexes against the square root of their equivalent concentrations. The abbreviation dsdp is the tetradentate ligand C$_{33}$H$_{38}$P$_2$S$_2$.

Figure 3.—Electronic absorption spectra: ————, [Ni-C$_{33}$H$_{38}$P$_2$S$_2$)Cl]ClO$_4$; — — —, trigonal-bipyramidal [Ni(TSP)-Cl]ClO$_4$; —·—·, square-pyramidal Ni(DSP)Br$_2$; - - - -, [Ni(SP)$_2$Br]-(ClO$_4$)$_2$. The solvent was dichloromethane. TSP, DSP, and SP are the phosphorus–sulfur ligands P(o-C$_6$H$_4$SCH$_3$)$_3$, C$_6$H$_5$P-(o-C$_6$H$_4$SCH$_3$)$_2$, and (C$_6$H$_5$)$_2$P(o-C$_6$H$_4$SCH$_3$), respectively.

Figure 4.—Most probable trigonal-bipyramidal structures for the [Ni(C$_{33}$H$_{38}$P$_2$S$_2$)X]ClO$_4$ complexes.

quaternary salt of the uncoordinated donor and an increase in conductance would have been observed.[19]

The isolated complexes are not susceptible to air oxidation either in the solid state or in nonaqueous solutions. Infrared bands characteristic of C–H, P–CH$_2$, and P–aryl and of ionic perchlorate were checked carefully on each complex.[15,20] No SH, PH, S=O, or P=O infrared absorptions were detected in any of the complexes.

In lieu of direct X-ray data, the coordination geometry of these five-coordinate complexes has been deduced by correlating the observed electronic spectra with the spectra of other five-coordinate complexes of known structure and containing similar donor atoms. Fortunately, for this correlation two recent three-dimensional X-ray determinations[23,24] have confirmed the trigonal-bipyramidal and square-pyramidal structures for [Ni(TSP)Cl]ClO$_4$ and Ni(DSP)I$_2$, respectively.[13,25] Figure 3 shows the remarkable similarity between the spectra of [Ni(C$_{33}$H$_{38}$P$_2$S$_2$)Cl]ClO$_4$ and the known trigonal-bipyramidal [Ni(TSP)Cl]ClO$_4$.[23] The electronic spectra of all of the Ni(C$_{33}$H$_{38}$P$_2$S$_2$)X$^+$ cations are quite similar, so they all are assigned trigonal-bipyramidal structures. Unfortunately, the electronic spectral data are not precise enough to differentiate among the trigonal-bipyramidal isomers that are possible with this ligand. The nmr spectra are very complicated and have not been useful for determining which trigonal-bipyramidal isomer is preferred. Either of the two isomers represented in Figure 4 would be compatible with the electronic spectra. An X-ray investigation of the structure has been initiated to determine which isomer actually is formed.

Since the five-coordinate nickel(II) complexes may be prepared readily from the square-planar [Ni(C$_{33}$-

H$_{38}$P$_2$S$_2$)](ClO$_4$)$_2$ complexes and since the related bidentate ligand (C$_6$H$_5$)$_2$P(o-C$_6$H$_4$SCH$_3$) forms square-pyramidal [Ni(SP)$_2$X]ClO$_4$ complexes,[13] it was anticipated that C$_{33}$H$_{38}$P$_2$S$_2$ would also yield square-pyramidal complexes in which the two sulfur atoms would be constrained to *cis* positions. However, the nickel(II) complexes apparently rearrange to a trigonal-bipyramidal structure on addition of a halide ion. This suggests that the trigonal-bipyramidal structure is favored over a square-pyramidal one with this ligand. Ligand field stabilization considerations predict the opposite stability order.[26]

The Pd(C$_{33}$H$_{38}$P$_2$S$_2$)I$_2$ complex is a uni-univalent electrolyte and is five-coordinate in nitromethane (Table I). However, on the basis of spectrophotometric titrations and molecular weight measurements, it exists as a mixture of five- and six-coordinate species in dichloromethane and chloroform. In contrast to the Pd(C$_{33}$H$_{38}$P$_2$S$_2$)$^{2+}$ cation, the analogous platinum-(II) cation apparently forms only the five-coordinate Pt(C$_{33}$H$_{38}$P$_2$S$_2$)I$^+$ species. The latter cation was isolated as the perchlorate salt, but it dissociates extensively into Pt(C$_{33}$H$_{38}$P$_2$S$_2$)$^{2+}$ and iodide in nitromethane (Table I).

The electronic absorption spectra of the five-coordinate M(C$_{33}$H$_{38}$P$_2$S$_2$)I$^+$ cations (M = Pd, Pt) have symmetrical peaks at 20,300 cm^{-1} (ϵ 1060) and 25,000 cm^{-1} (ϵ 2080), respectively. These spectra are not characteristic of the known trigonal-bipyramidal As(o-C$_6$H$_4$As(C$_6$H$_5$)$_2$)$_3$ and P(o-C$_6$H$_4$P(C$_6$H$_5$)$_2$)$_3$$^{3-5}$ complexes of Pd(II) and Pt(II), and since the spectra resemble

(23) The authors thank Professor R. Eisenberg for determining the structure of [Ni(TSP)Cl]ClO$_4$ and for the structural data which show a symmetrical C$_{3v}$ Ni(TSP)Cl$^+$ cation for this complex.

(24) D. W. Meek and J. A. Ibers, unpublished data, 1968. The structure has dicrete square pyramidal Ni(DSP)I$_2$ molecules in which the phosphorus, nickel, one sulfur, and two iodide atoms form the basal plane and the other sulfur atom is the apex.

(25) The abbreviations TSP and DSP refer to the tetradentate P(o-C$_6$H$_4$-SCH$_3$)$_3$ and the tridentate C$_6$H$_5$P(o-C$_6$H$_4$SCH$_3$)$_2$ ligands, respectively.

(26) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

those of the square-pyramidal [Pd(TPAS)Cl]ClO$_4$[27,28] and [Ni(SP)$_2$X]ClO$_4$ complexes,[13] a square-pyramidal structure is tentatively assigned to the Pd(II) and Pt(II) five-coordinate cations of C$_{33}$H$_{38}$P$_2$S$_2$. As with the above trigonal-bipyramidal complexes of nickel(II), due to the two types of donor atoms in the tetradentate ligand, there are several isomers possible for a square-pyramidal complex. Some likely structures are represented in Figure 5.
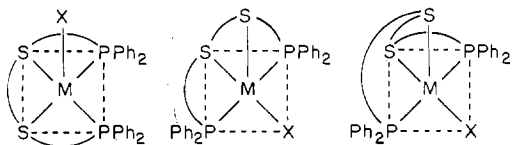

Figure 5.—Some possible structures for square-pyramidal [M(C$_{33}$H$_{38}$P$_2$S$_2$)X]ClO$_4$ complexes (M = Pd, Pt).

The d^8 complexes of the flexible tetradentate ligand (C$_6$H$_5$)$_2$P(CH$_2$)$_3$S(CH$_2$)$_3$S(CH$_3$)$_2$P(C$_6$H$_5$)$_2$ indicate that the relative stability of square-pyramidal Pt(II) and Pd(II) complexes is greater than that for Ni(II) complexes. This may be a general trend resulting from electronic properties of the soft sulfur and phosphorus donor atoms. Ligand-field stabilization is greater for a square pyramid than for a trigonal bipyramid.[26] Clearly, the magnitude of the ligand-field effects is greater in palladium and platinum complexes than for analogous nickel complexes. Thus, electronic effects appear to predominate in the C$_{33}$H$_{38}$P$_2$S$_2$–Pt(II) and –Pd(II) complexes, whereas opposing forces may be important in these five-coordinate nickel complexes. Until X-ray studies are completed on both [Ni(C$_{33}$H$_{38}$P$_2$S$_2$)Br]ClO$_4$ and [Pd(C$_{33}$H$_{38}$P$_2$S$_2$)Br]ClO$_4$, subtle steric interactions of either the fifth donor atom or of *cis*-diphenylphosphino groups cannot be discounted in the nickel case.

In any case, more systematic variations of donor atoms in flexible ligands and X-ray structural data are required before a definitive evaluation of the relative importance of electronic and steric factors on five-coordinate structures should be attempted.

Cobalt(II) Complexes.—Cobalt(II) readily forms maroon, crystalline, five-coordinate complexes with 1,3-bis(diphenylphosphinopropylthio)propane. The low

conductivities of the tetraphenylborate salts (Table I) are due to the low ionic mobility of the tetraphenylborate anion. It should be noted that the molar conductance of [Co(C$_{33}$H$_{38}$P$_2$S$_2$)Cl]ClO$_4$ is in excellent agreement with the corresponding five-coordinate nickel(II) complex (Table I).

The electronic spectra of both M(C$_{33}$H$_{38}$P$_2$S$_2$)X$^+$ series (M = Co, Ni) produce the normal spectrochemical shift to lower energy, *i.e.*, Cl > Br > I. The spectra of the cobalt complexes are similar to those of the [Co(SP)$_2$X]ClO$_4$ series.[29] The magnetic susceptibility values (Table I) indicate one unpaired electron with a small orbital contribution. The effective magnetic moments for these complexes are similar to those of the analogous [Co(SP)$_2$Br]ClO$_4$ and [Co(AP)$_2$X]ClO$_4$ (where X = Cl, Br, I) complexes,[29] and the value for [Co(C$_{33}$H$_{38}$P$_2$S$_2$)Cl]ClO$_4$ is 0.22 BM greater than that of [Co(QP)Cl]ClO$_4$[3] which possesses a distorted trigonal-bipyramidal structure.[30] The values of the [Co(C$_{33}$H$_{38}$P$_2$S$_2$)X]ClO$_4$ complexes are in excellent agreement with those reported for the [Co(dpe)$_2$X]X complexes (where X = Cl, Br, I; dpe = 1,2-bis(diphenylphosphino)ethane). The latter were assigned square-pyramidal structures on the basis of their electron paramagnetic resonance spectra.[31] Preliminary electron paramagnetic resonance data on our C$_{33}$H$_{38}$P$_2$S$_2$ complexes give g values in the same range as those reported for the [Co(dpe)$_2$X]X series. A square-pyramidal structure provides the most consistent correlation of the electronic and magnetic data. The ligand-field electronic transitions are assigned as in the [Co(SP)$_2$X]ClO$_4$ complexes.[29]

Attempts to oxidize the five-coordinate cobalt(II) complexes with air, nitrosyl chloride, bromine, and controlled-voltage coulometry resulted in decomposition of the original complexes. All attempts to isolate definitive cobalt complexes after oxidation were unsuccessful.

(27) TPAS is the tetraarsine ligand o-phenylenebis(o-dimethylarsinophenylmethylarsine).

(28) T. L. Blundell and H. M. Powell, *J. Chem. Soc., A*, 1650 (1967).

(29) G. Dyer and D. W. Meek, *J. Am. Chem. Soc.*, **89**, 3983 (1967).

(30) T. L. Blundell, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 763 (1967).

(31) W. D. Horrocks, G. R. Van Hecke, and D. D. Hall, *Inorg. Chem.*, **6**, 694 (1967).