Five-Coordination. VI. Low-Spin Cobalt(II) Complexes with Bidentate Ligands[1-3]

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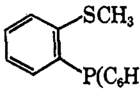
Abstract: Stable, crystalline complexes containing the five-coordinate $[CoL_2X]^+$ species, where X = Cl, Br, or I and L is one of the bidentate ligands diphenyl(*o*-methylthiophenyl)phosphine (I, SP), diphenyl(*o*-methylselenophenyl)phosphine (II, SeP), or diphenyl(*o*-diphenylarsinophenyl)phosphine (III, AP), have been isolated and characterized by magnetism and conductivity measurements, electronic and infrared spectra, and elemental analyses. All of the complexes are deep red and possess one unpaired electron (μ_{eff} = 2.1–2.5 BM). The electronic spectra exhibit three distinct bands below 22,000 cm^{-1} which may be assigned to ligand-field transitions.

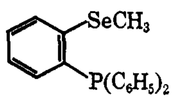
Research interest and activity in five-coordinate complexes has accelerated dramatically during the past 4 years. Whereas five-coordination is now fairly common for nickel(II), when polydentate ligands containing π-bonding donor atoms, such as arsenic, phosphorus, sulfur, or selenium, are used,[3-6] well-characterized examples of five-coordinate complexes of a d^7 ion have not been observed so frequently. One authentic, low-spin example is $[Co(HPPh_2)_3Br_2]$.[7] Also, Venanzi and co-workers[8] have prepared five-coordinate cobalt(II) complexes where a trigonal-bipyramidal structure is imposed by the rigid tetradentate ligand tris(*o*-diphenylphosphinophenyl)phosphine. Other possible low-spin, five-coordinate cobalt(II) examples are $[(C_{14}H_{13}P)_3CoX_2]$ (X = Br and I; $C_{14}H_{13}P$ = 2-phenylisophosphindoline),[9] $[Co(triarsine)X_2]$ (X = Br and I),[10] $[Co(isonitriles)_5]^{2+}$,[11] and a series of green $[CoL_2X]ClO_4$ (X = Cl, Br and I) complexes with the bidentate ligand 1,2-bis(diphenylphosphino)ethane.[12] The electronic spectra of these compounds, which would differentiate the five-coordinate possibility from the more common four- and six-coordinate complexes better than analytical or conductivity data, have unfortunately not been reported fully. The magnetic moments of all the above Co(II) five-coordinate compounds fall in the range of 2.0 to 2.5 BM. These values should be compared with a range of 1.8 to 2.0 BM for low-spin, octahedral Co(II) complexes and 2.3 to 2.9 BM for low-spin, planar Co(II) complexes.[13]

Recently, bulky ligands which contain decidedly electronegative donor atoms, *i.e.*, nitrogen and oxygen, have been used to give the first high-spin, five-coordinate cobalt(II) complexes (μ_{eff} = ~4.5 BM).[14-22] The ligands which produce such complexes are Schiff bases derived from salicylaldehyde and N,N-substituted ethylenediamines,[15] bis(3-aminopropyl)amines,[16] or methylamine;[17] aliphatic polyamines with bulky terminal groups;[18-21] and the monodentate ligand diphenylmethylarsine oxide.[22] Very recently, two high-spin, five-coordinate cobalt(II) complexes of thiourea were reported, *i.e.*, $[Co(tu)_3X_2]$ (X = Cl and Br).[23]

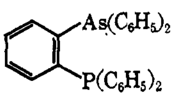
This paper describes three different series of low-spin, five-coordinate cobalt(II) complexes obtained during our investigations with bidentate ligands containing one phosphorus and one sulfur, selenium, or arsenic donor atom, *i.e.*, diphenyl(*o*-methylthiophenyl)phosphine, (SP, I), diphenyl(*o*-methylselenophenyl)phosphine (SeP, II), and diphenyl(*o*-diphenylarsinophenyl)phosphine (AP, III).



I (SP)



II (SeP)



III (AP)

Experimental Section

Syntheses of the Ligands. Diphenyl(*o*-methylthiophenyl)phosphine. Liquid *o*-bromothioanisole (38.5 g, 0.19 mole), prepared as described previously,[4a] in dry ether (200 ml) was treated dropwise over a period of 2 hr with 1-butyllithium (125 ml of a 1.5 *N* solution in hexane, 0.19 mole) at 0° under nitrogen with vigorous stirring. After stirring for an additional hour at 0°, chlorodiphenylphosphine

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[2] Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstract No. H-64.

[3] Part V: G. S. Benner and D. W. Meek, *Inorg. Chem.*, **6**, 1399 (1967).

[4] (a) G. Dyer and D. W. Meek, *ibid.*, **4**, 1398 (1965); (b) G. Dyer and D. W. Meek, *ibid.*, **6**, 149 (1967).

[5] G. S. Benner, W. E. Hatfield, and D. W. Meek, *ibid.*, **3**, 1544 (1964).

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[19] Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966).

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[21] M. Di Vaira and P. L. Orioli, *Chem. Commun.*, 590 (1965).

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(42 g, 0.19 mole) in 125 ml of ether was added over a period of 3 hr. The resulting white precipitate was then hydrolyzed with 0.2 *N* hydrochloric acid (125 ml), and, after stirring for some time to ensure that all inorganic matter had dissolved, the white crystalline ligand was collected (yield 43 g, 74%), washed with water, ethanol, and ether, and dried in a desiccator.

Anal. Calcd for $C_{19}H_{17}PS$: C, 74.00; H, 5.56; S, 10.38. Found: C, 74.28; H, 5.76; S, 10.60.

Diphenyl(*o*-methylselenophenyl)phosphine. Liquid *o*-bromoselenoanisole (10 g, 0.04 mole), prepared as described previously,[4b] dissolved in a mixture of hexane and anhydrous ether (50 ml each) was treated at −78° with 1-butyllithium (0.032 mole in 20 ml of hexane) under nitrogen with vigorous stirring. The mixture was stirred for an additional 30 min at −78°, and then chlorodiphenylphosphine (8.8 g, 0.04 mole) in 50 ml of ether was added over a period of 30 min. The resulting mixture was stirred while it warmed to room temperature, and then it was hydrolyzed with 60 ml of water. All the solid material dissolved, and the pale yellow organic layer was separated, washed with water, dried with calcium chloride, filtered, and concentrated under nitrogen to a volume of 50 ml. Absolute ethanol (100 ml) was then added, and the distillation was continued until an oil remained; it was heated to 120° at 0.5 mm pressure. Hot absolute ethanol dissolved the residual oil and when the solution was cooled to 0°, 3.55 g (0.01 mole, 31% based on 1-butyllithium) of colorless crystals separated. A sample was recrystallized from a dichloromethane–ethanol mixture.

Diphenyl(*o*-diphenylarsinophenyl)phosphine. This ligand was prepared as described previously.[24]

Preparation of the Complexes. **$[Co(AP)_2Cl](ClO_4)$.** A solution of cobalt(II) chloride (0.476 g of $CoCl_2 \cdot 6H_2O$, 2 mmoles) and cobalt(II) perchlorate (0.734 g of $Co(ClO_4)_2 \cdot 6H_2O$, 2 mmoles) in ethanol (20 ml) was added to a solution of diphenyl(*o*-diphenylarsinophenyl)phosphine (AP, 1.96 g, 4 mmoles) in dichloromethane (25 ml). The resulting dark red solution was concentrated to half its original volume, and the red compound which separated was purified by dissolving it in dichloromethane (30 ml), filtering the solution, and adding warm acetone (70 ml). The complex crystallized slowly over a period of 6 hr (yield 1.38 g, 59%).

$[Co(AP)_2Br](ClO_4)$. A solution of AP ligand (2.94 g, 6 mmoles) in dichloromethane (30 ml) was added with stirring to a warm solution of $CoBr_2 \cdot 6H_2O$ (0.98 g, 3 mmoles) and $Co(ClO_4)_2 \cdot 6H_2O$ (1.10 g, 3 mmoles) in acetone (100 ml). The red precipitate was collected after 6 hr and recrystallized two times by dissolving it in boiling dichloroethane (100 ml), filtering the solution, adding a little petroleum ether (bp 60–110°), and allowing the solution to stand a short time. The solvated crystals were then heated at 100° under high vacuum (yield 1.90 g, 52%).

$[Co(AP)_2I](ClO_4)$. A solution of cobalt iodide[25] (0.25 mmole) and $Co(ClO_4)_2 \cdot 6H_2O$ (0.092 g, 0.25 mmole) in 1-butanol (5 ml) was added to a warm solution of AP (0.49 g, 1 mmole) in chlorobenzene (20 ml). The deep maroon crystals were deposited after a few minutes. The product was recrystallized by dissolving it in dichloromethane (15 ml) and dichloroethane (15 ml), filtering the solution, and adding petroleum ether (15 ml, bp 60–110°). The resulting dense crystals were heated at 56° *in vacuo* (yield 0.32 g, 50%).

$[Co(AP)_2Cl](SnCl_3)$. A solution of anhydrous cobalt chloride (0.13 g, 1 mmole) and anhydrous stannous chloride (0.38 g, 2 mmoles) in boiling 1-butanol (10 ml) was added to AP (0.49 g, 1 mmole) in boiling 1-butanol (15 ml). The red crystals, which separated rapidly, were collected when the mixture had cooled to room temperature (yield 0.51 g, 78%).

$[Co(AP)_2Br](SnBr_3)$. This compound was prepared as the above chloride except that $CoBr_2 \cdot 6H_2O$ (0.327 g, 1 mmole) and anhydrous stannous bromide (0.556 g, 2 mmoles) were used instead of the chloride salts (yield 0.58 g, 78%).

$[Co(SeP)_2Br]ClO_4$. A cold solution of cobalt(II) bromide (0.082 g of $CoBr_2 \cdot 6H_2O$, 0.25 mmole) and cobalt(II) perchlorate (0.092 g of $Co(ClO_4)_2 \cdot 6H_2O$, 0.25 mmole) in 5 ml of 1-butanol was added to diphenyl(*o*-methylselenophenyl)phosphine (SeP, 0.355 g, 1 mmole) in warm (70°) 1-butanol (5 ml). The crystalline compound separated rapidly from the intensely red solution which was stirred at 45° for 5 min. After 1 hr, the crystals were washed twice with 1-butanol by decantation, then collected (yield 0.37 g, 82%), and recrystallized by dissolving them in dichloromethane (15 ml), adding 1-butanol (15 ml), filtering, and concentrating the solution at room temperature under vacuum for 2 hr.

$[Co(SP)_2Br](ClO_4)$. This compound was prepared as above, using diphenyl(*o*-methylthiophenyl)phosphine (SP, 0.308 g, 1 mmole) instead of SeP, except that during the stirring at 45°, it was necessary to seed the solution with a minute crystal of the above $[Co(SeP)_2Br]ClO_4$ complex. The red crystals, which separated rapidly, were collected after 10 min, washed with 1-butanol (yield 0.34 g, 80%), and recrystallized as above, except that a few crystals of $[Co(SP)_2Br]ClO_4$ must be retained and added during the concentration procedure to induce crystallization.

Characterization Measurements. The spectral, magnetic, and conductance measurements were obtained as described previously.[3-5] Dr. C. S. Springer, Jr., recorded the infrared spectra in the 600–250 cm^{-1} region on a Perkin-Elmer Model 521 spectrophotometer.

Results and Discussion

The physical properties and analytical data of the five-coordinate cobalt(II) compounds which were obtained are listed in Table I. The band maxima and extinction coefficients of the electronic absorption spectra are given in Tables II and III.

An equimolar mixture of cobalt(II) halide and cobalt(II) perchlorate in ethanol or 1-butanol yielded the deep red, crystalline complexes $[CoL_2X](ClO_4)$ (X = Cl, Br, or I), when mixed with the appropriate ligand (L = SP, SeP, or AP) in dichloromethane. To induce crystallization of the SP complexes, it was necessary, in the first instance, to seed the solutions with the corresponding SeP complexes. The bromo and iodo AP complexes had a strong tendency to crystallize as solvates from dichloromethane and other solvents, but heating the compounds at 100° under high vacuum removed the solvent molecules without causing a change in the solid-state electronic absorption spectrum. The possibility of perchlorato coordination was excluded by a careful study of the infrared spectra of the solid compounds; the perchlorate bands at ~1100 and ~625 cm^{-1} of T_d ClO_4^- groups showed no evidence of splitting.[26]

We have prepared analogous five-coordinate complexes of nickel(II) with the three bidentate ligands,[27,28] and, since cobalt(I) is isoelectronic with nickel(II), we tried to reduce the $[CoL_2X]ClO_4$ complexes with hydrazine, sulfur dioxide, and anhydrous stannous chloride. No reduction occurred with any of the reagents; however, under certain conditions stannous chloride produced crystalline $Co(AP)_2Cl_2 \cdot SnCl_2$ complexes. Subsequently, the $Co(AP)_2X_2 \cdot SnX_2$ (X = Cl or Br) compounds were obtained more readily from a solution of the appropriate cobalt(II) halide, the anhydrous tin(II) halide, and the ligand in 1-butanol. The $SnCl_3^-$ group can function as a ligand, so it was of interest to determine if the unknown Co–$SnCl_3^-$ bonds were present in these complexes. An infrared peak at ~330 cm^{-1} has been assigned as characteristic of a coordinated $SnCl_3^-$ group.[29] The infrared spectrum of $Co(AP)_2Cl_2 \cdot SnCl_2$ shows a number of absorptions in this region, but the peaks are present also in the spec-

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[24] P. Nicpon and D. W. Meek, *Inorg. Chem.*, **6**, 145 (1967).

[25] Cobalt(II) iodide was used as a freshly prepared 0.1 *M* solution in 1-butanol, obtained by mixing 1-butanol solutions of $Co(NO_3)_2 \cdot 6H_2O$ and sodium iodide and filtering off the sodium nitrate.

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

[27] T. D. DuBois and D. W. Meek, *ibid.*, **6**, 1395 (1967).

[28] M. O. Workman, G. Dyer, and D. W. Meek, *ibid.*, **6**, 1543 (1967).

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Table I. Analytical Data and Physical Properties of the Five-Coordinate Cobalt(II) Complexes[a]

Compound	Λ_M,[b] cm²/ohm mole	μ_{eff}, BM	C,[c] %		H,[c] %		P,[c] %		Other,[c] %	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Co(AP)_2Cl]ClO_4$[d]	86	2.26	61.30	61.22	4.12	4.17	5.27	5.21	6.05	6.17 (Cl)
$[Co(AP)_2Cl]SnCl_3$	85	2.20	55.42	55.15	3.72	3.84			10.91	11.02 (Cl)
$[Co(AP)_2Br]ClO_4$	80	2.18	59.10	59.10	3.97	4.12	5.08	4.82		
$[Co(AP)_2Br]SnBr_3$	77	2.14	48.81	49.37	3.27	3.24			21.62	22.63 (Br)
$[Co(AP)_2I]ClO_4$	78	2.14	56.90	56.64	3.82	4.12	4.59	4.56		
$[Co(SP)_2Br]ClO_4$[e]	88	2.20	53.37	53.44	4.00	4.12	7.24	7.20	7.49	7.71 (S)
$[Co(SeP)_2Br]ClO_4$[f]	77	2.54	48.10	48.27	3.61	3.84	6.52	6.40	16.64	16.53 (Se)

[a] All of the complexes are deep red. [b] For approximately 10^{-3} *M* solutions in nitromethane at 25°; uni-univalent electrolytes have molar conductance values in the range 75–95. [c] Phosphorus content was determined colorimetrically in this laboratory; other microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. [d] AP, diphenyl(*o*-diphenylarsinophenyl)phosphine, $Ph_2P(o\text{-}C_6H_4AsPh_2)$. [e] SP, diphenyl(*o*-methylthiophenyl)phosphine, $Ph_2P(o\text{-}C_6H_4SCH_3)$. [f] SeP, diphenyl(*o*-methylselenophenyl)phosphine, $Ph_2P(o\text{-}C_6H_4SeCH_3)$.

trum of the $[Co(AP)_2Cl]ClO_4$ complex. Therefore, these infrared peaks are attributed to absorptions by the $[Co(AP)_2Cl]^+$ cation, and the $Co(AP)_2Cl_2\cdot SnCl_2$ compound is the $SnCl_3^-$ salt, $[Co(AP)_2Cl]SnCl_3$. Additional evidence that the SnX_3^- groups are not coordinated was obtained from the fact that $[Co(AP)_2Cl]ClO_4$ crystallized instantly from solution when $[Co(AP)_2Cl]SnCl_3$ was treated with lithium perchlorate. The electronic band maxima and extinction coefficients of both the perchlorate and trichlorostannate(II) compounds were identical. It appears, therefore, that anhydrous stannous halides do not reduce cobalt(II) to cobalt(I) nor do they form stable Co–SnX_3 bonds in the cobalt–AP complexes.

All of the five-coordinate cobalt(II) compounds are dark red crystals, and they are stable toward air, water, and all organic solvents used. They are uni-univalent electrolytes in nitromethane solution (Table I), and the iodomethane test[30] indicated that all the arsine and phosphine groups are coordinated. It is concluded that the cations should be formulated as five-coordinate, both in solution and in the solid state, since the electronic absorption spectra are nearly identical in both phases.

Corresponding five-coordinate nickel(II) complexes, *e.g.*, $[NiL_2Br](ClO_4)$ (where L = SP, SeP, or AP) have also been prepared by two synthetic methods.[27,28] As with cobalt(II), the intensely purple, five-coordinate $[NiL_2X]ClO_4$ complexes may be prepared from an equimolar mixture of the corresponding nickel halide and nickel perchlorate. In addition, the $[NiL_2X]^+$ species are formed instantly when halide ion is added to the yellow, planar $[NiL_2](ClO_4)_2$ complexes in nonaqueous solvents. The latter synthetic route was unavailable for the cobalt complexes since the planar $[CoL_2](ClO_4)_2$ complexes could not be isolated.

The five-coordinate $[NiL_2X]ClO_4$ complexes do not appear to have trigonal-bipyramidal structures since the electronic absorption spectra are not characteristic of the known trigonal-bipyramidal complexes with similar donor atoms.[3–6] The alternative regular structure is a square pyramid, and this structure is tentatively proposed for both the nickel(II) and cobalt(II) complexes, with the halide ion probably occupying the apical position and the two bidentate ligands forming the square base (Figure 1a). Although crystal-field stabilization favors a square pyramid with the angle L_{ax}–Ni–L_{base} (α in Figure 1a) equal to 90°, the covalent character of these metal–ligand bonds (low *B* values) should favor a trigonal-bipyramidal structure;[3,5,31] an intermediate structure might be preferred. In fact, a vast majority of the known square-pyramidal transition metal complexes have $\alpha > 90°$.

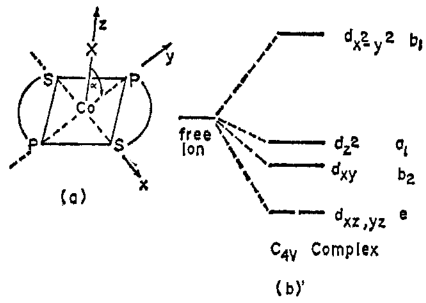

Figure 1. (a) The postulated arrangement of ligand atoms in the five-coordinate complex $[Co(SP)_2X]ClO_4$. The sulfur and phosphorus atoms are placed *trans* to each other arbitrarily. (b) The d-orbital energy-level splitting in a strong ligand field of C_{4v} symmetry. Actually, the highest microsymmetry possible in these complexes is C_{2v}.

The magnetism and electronic spectra of the cobalt(II) complexes can be interpreted in terms of a square-pyramidal arrangement of donor atoms. The magnetic moments (Table I, μ_{eff} = ~2.1–2.5 BM) indicate that these cobalt complexes contain one unpaired electron with considerable orbital contribution. Low-spin, square-pyramidal cobalt(II) compounds may be expected to possess magnetic values intermediate between the ranges for low-spin octahedral (μ_{eff} = 1.8–2.0 BM) and planar (μ_{eff} = 2.3–2.9 BM) cobalt(II) complexes,[13] in agreement with the observed values (Table I). Since the $[CoL_2X]^+$ complexes possess a doublet ground state, the magnitude of the interactions between the metal's d electrons and the ligand field is evidently much greater than interelectronic repulsions; in such a case the splitting of the d-orbital energy levels approximates that shown in Figure 1b. The d_{z^2} orbital

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(30) G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4433 (1961).

(31) R. J. Gillespie, *ibid.*, 4679 (1963).

Table II. Electronic Spectral Data for the $[CoL_2Br]ClO_4$ Complexes

	$[Co(AP)_2Br]ClO_4$		$[Co(SeP)_2Br]ClO_4$		$[Co(SP)_2Br]ClO_4$	
	λ_{max}, cm^{-1}	ϵ[a]	λ_{max}, cm^{-1}	ϵ[a]	λ_{max}, cm^{-1}	ϵ[a]
ν_1	6,670	66.4	7,410	64.5	7,330	59.3
ν_2	12,500 (sh)[b]	72.3	11,600	495	11,740	419
	14,600	142				
ν_3	21,050	1,733	20,080	1246	20,320	1091
ν_4	30,030	12,445	29,410 (sh)	7614	27,780 (sh)	5703
ν_5	34,480 (sh)	14,480	38,460 (sh)	17,318	. . .	

[a] ε, molar extinction coefficients. [b] sh, shoulder on a more intense absorption.

Table III. Electronic Spectral Data for the $[Co(AP)_2X]ClO_4$ Complexes

	$[Co(AP)_2Cl]ClO_4$		$[Co(AP)_2Br]ClO_4$		$[Co(AP)_2I]ClO_4$	
	λ_{max}, cm^{-1}	ϵ[a]	λ_{max}, cm^{-1}	ϵ[a]	λ_{max}, cm^{-1}	ϵ[a]
ν_1	6,600	71.3	6,670	66.4	6,450	67.8
ν_2	12,750 (sh)[b]	154.2	12,500 (sh)	72.3	11,900 (sh)	95.3
	14,500	240	14,600	142	14,220	219
ν_3	21,380	1,880	21,050	1,733	20,325	1712
					22,573	1230
ν_4	29,400	13,319	30,030	12,445	29,762	14,205
ν_5	34,600 (sh)	16,870	34,480 sh	14,480	. . .	
ν_6	37,300 (sh)	19,600	. . .		. . .	

[a] ε, molar extinction coefficients. [b] sh, shoulder on a more intense absorption.

then contains one electron, and the ground state of the complex is $^2A_1(G)$. Of course, the representation in Figure 1b is an oversimplification, but it is remarkable how well the observed spectra can be interpreted from this scheme.

One may question whether the strong absorption bands (ε 1200–1800) (Tables II and III) at 18,000–20,000 cm^{-1} in the electronic spectra of these five-coordinate cobalt and nickel complexes[27,28] are due to ligand-field or to charge-transfer transitions. The former possibility would normally be excluded because of the high intensities. However, Venanzi and coworkers[6,32] have found very intense bands (ε ~5000) at ~17,000 cm^{-1} in the trigonal-bipyramidal $[Ni(As(o\text{-}C_6H_4AsPh_2)_3)X]^+$ and $[Ni(P(o\text{-}C_6H_4PPh_2)_3)X]^+$ chromophores. The presence of aryl ligands is not a prerequisite for such strong absorptions as Benner and Meek[3,5] also observed high intensities (ε ~2000) for diamagnetic, trigonal-bipyramidal nickel(II) complexes with the aliphatic ligands $P(CH_2CH_2CH_2AsMe_2)_3$ and $As(CH_2CH_2CH_2AsMe_2)_3$. In all of these cases, the bands are assigned more appropriately to the $^1A_1 \rightarrow {}^1E(D)$ ligand-field transition rather than to charge-transfer transitions.

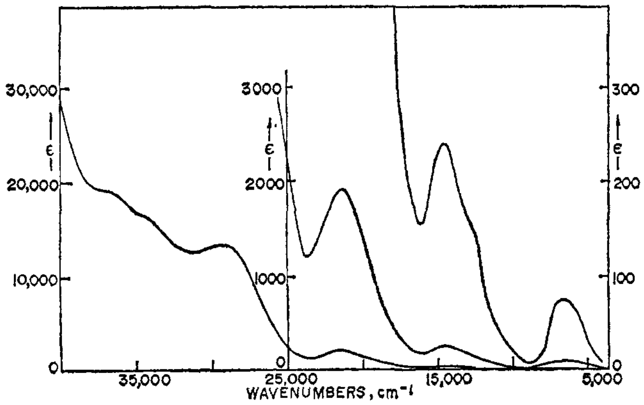

Figure 2. The electronic absorption spectrum of $[Co(AP)_2Cl]ClO_4$ dissolved in dichloromethane; note the three different ranges of extinction coefficients in the plot.

Jørgensen[33] has suggested that the high intensities of the visible bands may result from an electron transfer from a filled orbital of nearly constant optical electronegativity, χ_{opt}, to the σ-antibonding orbital (a_1, d_{z^2}) of the trigonal-bipyramidal complexes. However, even the lowest energy absorption bands of $[Co(QP)X]ClO_4$ and $[Fe(QP)X]ClO_4$[34] in the near-infrared region have moderate intensities.[8] We believe that, despite their high intensities, the low-energy bands of the five-coordinate complexes result *predominantly* from ligand-field transitions. For example, changes in the anionic ligand in either the trigonal-bipyramidal nickel complexes or these square-pyramidal cobalt complexes cause the bands to shift as predicted from the spectrochemical series, and not those expected from charge-transfer transitions. This effect is demonstrated effectively by the spectra in Figure 1 of ref 27. Also, it is extremely unlikely that the absorption bands at 6670 and 12,000–14,000 cm^{-1} in the $[Co(AP)_2Br]ClO_4$ complex (Figure 2) are due to charge-transfer transitions.

Interpretation of the electronic spectra of the cobalt(II) complexes is aided by a comparison with the spectra of analogous nickel(II) compounds. For diamagnetic

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(32) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1967); G. Dyer and L. M. Venanzi, *ibid.*, 2771 (1967).

(33) (a) C. K. Jørgensen, *Coord. Chem. Rev.*, 1, 164 (1966); (b) C. K. Jørgensen, *Intern. Rev. Halogen Chem.*, 1, 1 (1967).

(34) QP, $P(o\text{-}C_6H_4PPh_2)_3$.

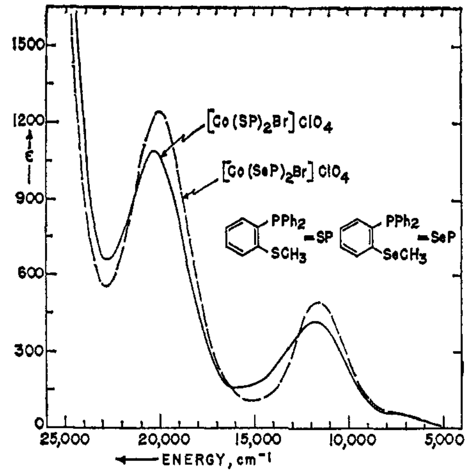

Figure 3. The near-infrared and visible regions of the electronic spectra of (———) $[Co(SP)_2Br]ClO_4$ and (- - - -) $[Co(SeP)_2Br]ClO_4$ dissolved in dichloromethane.

C_{4v} nickel(II) complexes, the first ligand-field transition is expected at $\sim$20,000 cm^{-1} on the basis of the energy-level diagram calculated recently by Ciampolini.[35] In fact, two strong absorptions are observed in the $[Ni(ligand)_2X]ClO_4$ complexes (where ligand = one of the bidentate ligands AP, SP, or SeP).[28] The lowest energy one ($\sim$19,000 cm^{-1}) is assigned to the $a_1 \rightarrow b_1$ ligand-field transition (Figure 1b), and the second one is assigned to a charge-transfer transition involving the lone-pair electrons on phosphorus (forming the P–Ni σ bond) and the empty b_1 orbital of nickel.[28]

Three ligand-field bands are observed for $[Co(SP)_2X]^+$ and $[Co(SeP)_2X]^+$ below 22,000 cm^{-1} (Figure 3). Since the magnetic data indicate a strong ligand field, the three bands are tentatively assigned to the one-electron transitions $b_2 \rightarrow a_1$, $e \rightarrow a_1$, and $a_1 \rightarrow b_1$, in order of increasing energy. The spectra of the $[Co(AP)_2X]^+$ series are quite similar, except that the middle band ($\sim$13,000 cm^{-1}) is split into two components, indicating that the degeneracy of the e level has been removed. Therefore, the AP complexes appear to be distorted from C_{4v} symmetry. Of all the ligands used, clearly AP has the largest steric requirements, and a distorted square-pyramidal structure is quite likely. Support for the above assignments is provided by the fact that the splitting between the a_1 and b_1 orbital levels in both nickel(II) and cobalt(II) C_{4v} complexes should be comparable; the bands at 20,080 and 18,550 cm^{-1} for $[Co(SeP)_2Br]^+$ and $[Ni(SeP)_2Br]^+$ (Figure 4), respectively, are in excellent agreement with expectations.

As with nickel,[28] the strong transition at 28,000–30,000 cm^{-1} (Figure 2) in all three series of cobalt(II) complexes is assigned to the $\sigma P \rightarrow b_1$ ligand–metal electron transition. The alternative possibility, $\sigma P \rightarrow a_1$, is excluded on the basis that a common band is present in both series of cobalt and nickel spectra. The $\sigma P \rightarrow a_1$ transition is forbidden in the nickel case. The ionization potentials of triphenylphosphine and triphenylarsine are comparable (7.36 ev for PPh_3 and 7.34 ev for $AsPh_3$)[36] and lower than for the sulfur and selenium donor atoms.[37] Since the phosphorus donor is the only one held constant throughout the entire series of cobalt(II) complexes, the nearly constant value of ν_4 (Tables II and III) suggests a σ phosphorus→cobalt electron transition. In addition, the lower energy of the band in the nickel(II) complexes ($\sim$28,000 *vs.* $\sim$30,000 cm^{-1} in Co(II) complexes) is consistent with the larger optical electronegativity of nickel(II).[38]

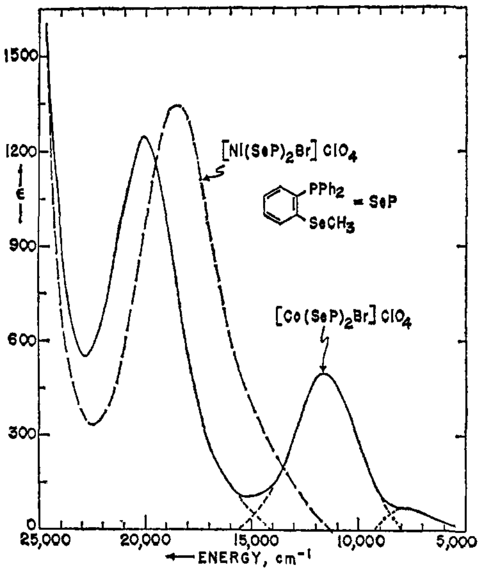

Figure 4. The near-infrared and visible portions of the electronic absorption spectra of (——) $[Co(SeP)_2Br]ClO_4$ and (- - - -) $[Ni(SeP)_2Br]ClO_4$ dissolved in dichloromethane.

The easily polarized donor atoms used in this study (*i.e.*, P, As, S, and Se) cause a marked reduction in the *B* parameter and lead to low-spin ground states. The small values of *B*, or the large nephelauxetic effects, have been ascribed to covalent bonding and correlated with increased extinction coefficients.[4b,39] Probably the most important contribution to the increased intensity of the "d–d" transitions in five-coordinate complexes, compared with planar and octahedral cases, is the absence of a center of inversion. The bands at $\sim$20,000 cm^{-1} in both the nickel(II) and cobalt(II) series also probably gain intensity from the charge-transfer band at $\sim$28,000–30,000 cm^{-1}, owing to strong mixing between odd and even orbitals. Such mixing between ligand-field and charge-transfer bands is operative even if they are separated by 10,000 cm^{-1}.[33b]

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