

precise to within ± 0.05 B.M. and the θ values to within $\pm 2^\circ$.¹⁶

The μ values for the two complexes clearly show that the ligand field is stronger in $[\text{Co}(\text{NCO})_4]^{-2}$ than in $[\text{Co}(\text{N}_3)_4]^{-2}$ in agreement with the analysis

(16) While in previous papers^{2,3} in this series we have attributed the θ values to interionic interactions of an antiferromagnetic character, Piggis (*Trans. Faraday Soc.*, **56**, 1553 (1960)) has observed that small adventitious distortions of the tetrahedra could also cause small θ 's. However, the Curie-Weiss moment is the value which μ_{eff} will reach at temperatures sufficiently high to make the Weiss constants and the splitting of the ground state which are responsible for it negligible, whatever their origin. It thus represents the magnetic moment the Co(II) would exhibit in the particular complex if the ligand field were perfectly tetrahedral and/or there were no interionic interactions.

of the spectral data. This follows from equation (3)²

$$\mu_{\text{obs}} = \mu_{\text{SO}} - \frac{15.56\lambda'}{\Delta} = 3.89 - \frac{15.56\lambda'}{\Delta} \quad (3)$$

λ' represents the effective value of the spin-orbit coupling constant in the ground state, and should be $< 178 \text{ cm.}^{-1}$, the free-ion value.¹⁷ From the magnetic moments and Δ values, the values of λ' given in Table II were computed. The uncertainties assigned allow for uncertainties of 200 cm.^{-1} in the Δ values and 0.05 B.M. in the μ values. It is seen that the λ' values are substantially below the free ion value.

(17) J. Owen, *Proc. Roy. Soc. (London)*, **A227**, 183 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY AND THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE, MASS.]

Magnetic Investigations of Spin-free Cobaltous Complexes. VI.¹ Complexes Containing Phosphines and the Position of Phosphines in the Spectrochemical Series

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Thorough study of the magnetic moments and the visible spectra of the complexes $[\text{Co}(\text{R}_3\text{P})_2\text{X}_2]$ ($\text{R} = \text{C}_6\text{H}_5$, $\text{X} = \text{Cl}$, Br , I ; $\text{R} = \text{C}_6\text{H}_{11}$, $\text{X} = \text{Br}$, I) and of salts of two representatives of a new type of anionic complex, $[\text{Co}((\text{C}_6\text{H}_5)_3\text{P})\text{Br}_3]^-$ and $[\text{Co}((\text{C}_6\text{H}_5)_3\text{P})\text{I}_3]^-$ are reported. The effect of low-symmetry components in the ligand fields upon the magnetic and spectral properties are reported and discussed and by comparison of the new data with previously reported data on other tetrahedral Co(II) complexes, it is shown that the two phosphines occupy a position in the spectrochemical series adjacent to toluidine and N_3^- .

Introduction

As shown in earlier papers^{1,2,3} in this series, the fact that magnetic moments of tetrahedral Co(II) complexes are related to the ligand field strength Δ , by the equation

$$\mu_{\text{obs}} = \mu_{\text{so}} - \frac{15.59\lambda'}{\Delta} = 3.89 - \frac{15.59\lambda'}{\Delta} \quad (1)$$

in which μ_{obs} is the observed moment, $\mu_{\text{so}} = 3.89$ B.M. is the spin-only moment, λ' is the effective value of the spin-orbit coupling constant in the complexed Co(II) ion and Δ measures the strength of the ligand field, means that magnetic moment measurements can provide a basis for determining values of Δ . Absolute Δ values could be determined if λ' values were independently known, but this is seldom the case. Hence, by assuming that the λ' values vary slowly and regularly with Δ , relative Δ values can be obtained.

The ordering of ligands according to the relative strengths of their contributions to ligand fields, the spectrochemical series, recently has been given as⁴

$\text{I}^- < \text{Br}^- < -\text{SCN}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- \sim \text{ONO}^- < \text{HCOO}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < -\text{NCS}^- < \text{glycine}^- < \text{EDTA}^{4-} < \text{py} \sim \text{NH}_3 < \text{en} \sim \text{den} \sim \text{tren} < \text{dipy} < o\text{-phen} < \text{NO}_2^- \ll -\text{CN}^-$

It is recognized that this ordering is not inviolate,

(1) Part V: F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961).

(2) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959).

(3) R. H. Holm and F. A. Cotton, *ibid.*, **32**, 1168 (1960).

(4) T. M. Dunn, "Modern Coördination Chemistry," J. Lewis and R. G. Wilkins, editors, Interscience Publishers, New York, N. Y., 1960, p. 266. This reference also cites much of the original literature pertaining to the spectrochemical series.

there being some, usually small, variations from metal to metal as a result of differing amounts of sigma and pi bonding, variations of covalence in ground and excited states, etc.⁵ Conspicuously absent from this series are heavy atom donors such as those containing sulfur, phosphorus, arsenic, selenium and tellurium. The only attempt to place molecules containing some of these donors in the spectrochemical series has been made by Chatt, Gamlin and Orgel,⁶ who have examined complexes of the type *trans*-[L, piperidine PtCl₂]. By varying the ligand L in these complexes, they have inferred from the consequent spectral changes that the ligand field strengths decrease in the order $\text{P}(\text{OCH}_3)_3 > \text{P}(n\text{-C}_3\text{H}_7)_3 > \text{piperidine} > \text{As}(n\text{-C}_3\text{H}_7)_3 > \text{S}(\text{C}_2\text{H}_5)_2 > \text{Se}(\text{C}_2\text{H}_5)_2 > \text{Te}(\text{C}_2\text{H}_5)_2$

It will be noted that there is little indication of how this series can be leaved into the major one given above.

In this paper we describe magnetic and spectral studies of Co(II) complexes of the types $[\text{Co}(\text{R}_3\text{P})_2\text{X}_2]$ and $[\text{Co}(\text{R}_3\text{P})\text{X}_3]^-$ which have been made with the objective of obtaining information about the relative positions of the ligands R_3P relative to the ligands X in the spectrochemical series. Other results of the studies reported here concern the interrelation of the spectral properties and the magnetic properties, the origin of Weiss constants in these complexes and the effect of the differences in the positions of the two kinds of ligands in a particular complex in the spectrochemical series upon the degree of splitting of the spectral bands. It may be noted that the com-

(5) R. J. P. Williams, *J. Chem. Soc.*, 8 (1956).

(6) T. Chatt, G. A. Gamlin, L. E. Orgel, *ibid.*, 1047 (1959).

pounds studied here are Co(II) analogs of the Ni(II) complexes containing both phosphines and halide ions,⁷ and the comparison of the effects of low symmetry components in the ligand fields in the two cases upon both magnetic and spectral properties is of interest.

Experimental

Bis-(triphenylphosphine)-dihalocobalt(II)— $[(C_6H_5)_3P]_2CoX_2$, $X = Cl^-, Br^-, I^-$.—These three compounds were prepared by slowly mixing hot absolute ethanol solutions of the anhydrous cobaltous halide and triphenylphosphine. The complexes began to precipitate before the mixing was complete. After complete mixing the hot solutions were allowed to cool for about two minutes, filtered while still warm, and the crystalline products washed several times alternately with absolute ethanol and ethyl acetate. The products then were dried in vacuum over phosphorus pentoxide. The chloride complex was dark blue, the bromide blue-green and the iodide brown. $((C_6H_5)_3P)_2CoI_2$ is reported by Issleib and Mitscherling⁸ to have brown and green modifications with the same magnetic moment at room temperature. Only the brown form was isolated in this work.

Anal. Calcd. for $C_{36}H_{30}CoCl_2P_2$: C, 66.07; H, 4.62; Co, 9.01. Found: C, 66.25; H, 4.76; Co, 8.97. Calcd. for $C_{36}H_{30}Br_2CoP_2$: C, 58.17; H, 4.07; Co, 7.93. Found: C, 58.32; H, 4.07; Co, 7.81. Calcd. for $C_{36}H_{30}CoI_2P_2$: C, 51.64; H, 3.61; Co, 7.04. Found: C, 51.96; H, 3.71; Co, 6.92.

Tricyclohexylphosphine.—This compound was prepared by the method of Issleib and Brack.⁹

Bis-(tricyclohexylphosphine)-dibromocobalt(II).—A solution of tricyclohexylphosphine (4.20 g., 0.015 mole), in hot absolute ethanol (8 ml.) was added to a solution of cobaltous bromide (1.65 g., 0.0075 mole) also in hot absolute ethanol (11 ml.). Blue crystals formed from the deep blue solution on cooling. The solid product was filtered, washed with a small quantity of ice-cold absolute ethanol and dried in vacuum. Yield of crude product: 3.54 g., 61%. The compound was recrystallized from hot absolute ethanol (80 ml.) with a recovery of 64%, giving an overall yield of 40%. M.p. (uncorr.) was 199° compared to 205° previously⁹ reported.

Anal. Calcd. for $C_{36}H_{66}Br_2CoP_2$: C, 55.46; H, 8.53; P, 7.95. Found: C, 55.64; H, 8.42; P, 7.96.

The compound is soluble in the cold in benzene, chlorobenzene, methylene chloride, chloroform and acetone. It is slightly soluble in cold alcohols and much more so on heating in these solvents. Blue solutions are formed in each case. The compound is insoluble in carbon tetrachloride, cyclohexane and ligroin (90–100°).

Bis-(tricyclohexylphosphine)-diiodocobalt(II).—Dark green crystals were obtained in 67% overall yield by a method similar to that for the bromo complex. M.p. (uncorr.) was 220.5° compared to 221–223° reported previously.⁹

Anal. Calcd. for $C_{36}H_{66}CoI_2P_2$: C, 49.49; H, 7.62; P, 7.09. Found: C, 49.07; H, 7.40; P, 6.95.

$[(C_2H_5)_4N][Co(C_6H_5)_3PBr_3]$.—A butanol solution of cobalt(II) bromide was prepared by dissolving 5.82 g. (0.02 mole) of $Co(NO_3)_2 \cdot 6H_2O$ in 100 ml. of 1-butanol. 4.76 g. (0.04 mole) of finely ground KBr was added to the butanol solution and the mixture refluxed for several hours. The mixture was then cooled, filtered and the filtrate brought to the boil. A boiling solution of 4.14 g. (0.02 mole) of tetraethylammonium bromide and 5.26 g. (0.02 mole) of triphenylphosphine in 100 ml. of 1-butanol was then added to the boiling $CoBr_2$ solution, and this solution set aside to cool overnight. A crop of 4.65 g. (33.7%) of dark blue crystals was removed by suction filtration and dried in vacuum overnight; m.p., 228°; molar conductance of $10^{-3} M$ solution in CH_3NO_2 at 27°; 85 ohm⁻¹.

Anal. Calcd. for $C_{26}H_{35}Br_3CoNP$: C, 46.0; H, 5.06; Co, 8.52; N, 2.02; P, 4.49. Found: C, 45.8; H, 5.15; Co, 8.57; N, 1.97; P, 4.54.

(7) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

(8) K. Issleib and B. Mitscherling, *Z. anorg. u. allgem. Chem.*, **304**, 73 (1960).

(9) K. Issleib and A. Brack, *ibid.*, **277**, 258 (1954).

$[(n-C_4H_9)_4N][Co(C_6H_5)_3PI_3]$.—This was prepared in ethyl acetate by a method quite similar to that for the bromide. The green crystals were obtained in 68% yield, m.p. 141°; molar conductance of $10^{-3} M$ solution in CH_3NO_2 at 30°; 72 ohm⁻¹.

Anal. Calcd. for $C_{34}H_{51}CoI_3NP$: C, 43.2; H, 5.40; Co, 6.24; N, 1.48; P, 3.28. Found: C, 42.8; H, 5.34; Co, 6.21; N, 1.60; P, 3.37.

We were unable to prepare the $(CH_3)_4N^+$ salt of $[Co(C_6H_5)_3PCl_3]^-$ using the same general method with *n*-butanol, glacial acetic acid or ethyl acetate as solvents; the products were always $Co[(C_6H_5)_3P]_2Cl_2$ and $[(CH_3)_4N]_2[CoCl_4]$ in varying proportions depending on solvent. Neither could any reaction be effected by mixing and heating these two products.

Magnetic Measurements.—These were made by the Gouy method as previously described.^{1,2,3}

Spectral Measurements.—Solution spectra were measured using Cary model 11 and model 14 recording spectrophotometers. Reflectance spectra were taken using a Beckman DU spectrophotometer equipped with the standard Beckman reflectance attachment. Finely powdered, USP magnesium carbonate was used as the blank.

Results and Discussion

Preparations.—The compounds prepared and studied in this work are of two types. Those of the type $[Co(R_3P)_2X_2]$ are represented by the three triphenylphosphine compounds in which $X = Cl, Br, I$ and by the two tricyclohexylphosphine compounds in which $X = Br$ and I . At the time this work was begun none of the compounds in the former group had been reported, but subsequently Sacco¹⁰ has reported their preparation and approximate values of their magnetic susceptibilities, and Issleib and Mitscherling⁸ have reported the iodide in two forms, green and brown. The cyclohexylphosphine complexes were reported by Issleib and Brack⁹ in 1954, but no magnetic data were given. For none of these compounds have spectral data been reported heretofore. The anions in the salts $[(C_2H_5)_4N][Co\{(C_6H_5)_3P\}Br_3]$ and $[(n-C_4H_9)_4N][Co\{(C_6H_5)_3P\}I_3]$ are examples of a new type of mixed phosphine-halide Co(II) complex, although similar $[Co(amine)X_3]^-$ anions have been prepared in which the amine is pyridine^{11,12} or benzimidazole.¹³

Magnetic Moments.—The magnetic susceptibilities of each of the seven compounds have been measured in replicate at three temperatures, ~300, ~195 and ~77°K. Each susceptibility value has been corrected for diamagnetism using Pascal's constants¹⁴ and for temperature independent paramagnetism (TIP), taking the latter to be 500×10^{-6} c.g.s. units, which should be correct to within at least 20% in any particular compound.¹⁵ The values so corrected are denoted X_{300}^{corr} . in Table I. The reciprocals of these corrected

(10) A. Sacco and M. Freni, *Ist. Lomb. Sc. e. Lett.*, **94**, 221 (1960).

(11) A. Reitzenstein, *Z. anorg. u. allgem. Chem.*, **18**, 290 (1898).

(12) A. V. Babaeva and I. B. Baranovskii, *Zhur. Neorg. Khim.*, **4**, 1931 (1959); *Russ. J. Inorg. Chem.*, **4**, 874 (1959).

(13) M. Goodgame, M.I.T., unpublished experiments.

(14) See, for example, "Magnetochemistry," 2nd ed., by P. W. Selwood, Interscience Publishers, Inc., New York, N. Y., 1956, pp. 91.

(15) According to B. Figgis (private communication to F.A.C.) and J. Van Vleck (private communication to P. Cossee) the TIP in tetrahedral Co(II) is given by $8N\beta^2/\Delta = 2.09/\Delta$ where Δ is the separation of the 4A_2 ground state and the 4T_2 (first excited) state in cm⁻¹. For Δ values from 3500–5000 cm⁻¹ the TIP values are $400\text{--}600 \times 10^{-6}$ c.g.s. units. P. Cossee [Thesis, Leiden, 1956; *J. Inorg. Nuclear Chem.*, **8**, 483 (1958); paper with A. E. van Arkel in course of publication, *Phys. Chem. Solids*] has found values in the range $350\text{--}580 \times 10^{-6}$ c.g.s. units for Co(II) in various oxide lattices.

molar susceptibilities were then plotted *vs.* absolute temperature and values of μ and θ in the Curie-Weiss equation, $\mu = 2.84[X(T - \theta)]^{1/2}$ evaluated. These are also listed in Table I. In all cases, the $1/X$ *vs.* T plots were straight lines within errors corresponding to 0.05 B.M. or less.

TABLE I
MAGNETIC DATA AND CALCULATED MOMENTS FOR MIXED
PHOSPHINE-HALIDE COMPLEXES OF Co(II)

Compound	Temp. (°K.)	χ_M^{corr} $\times 10^{18}$	Dia- mag- netic ^a corr. $\times 10^6$	μ, θ B.M. (°K.)
[Co{(C ₆ H ₅) ₂ P) ₂ Cl ₂]	299.6	8092	386	4.41 +2
	193.2	12590	386	
	75.2	30920	386	
	301.2	8060	386	
	197.0	12420	386	
[Co{(C ₆ H ₅) ₂ P) ₂ Br ₂]	302.2	8169	418	4.52 -1
	195.7	12600	418	
	79.0	30500	418	
	300.7	8392	418	
	195.2	13100	418	
[Co{(C ₆ H ₅) ₂ P) ₂ I ₂]	295.6	8770	436	4.62 -6
	189.0	13670	436	
	75.0	32720	436	
	298.4	8582	436	
	194.2	13000	436	
[Co{(C ₆ H ₁₁) ₂ P) ₂ Br ₂]	299.7	8371	482	4.61 0
	193.4	13140	482	
	76.0	32970	482	
	296.7	8394	482	
	195.2	13000	482	
[Co{(C ₆ H ₁₁) ₂ P) ₂ I ₂]	298.9	8655	510	4.63 -8
	198.7	13070	510	
	81.2	31980	510	
	300.9	8601	510	
	196.2	13110	510	
[(C ₆ H ₅) ₄ N][Co{(C ₆ H ₅) ₂ P) ₂ Br ₂]	299.2	8423	372	4.50 +1
	196.2	13140	372	
	79.0	32330	372	
	299.0	8416	372	
	199.0	13040	372	
[(n-C ₄ H ₉) ₄ N][Co{(C ₆ H ₅) ₂ P) ₂ I ₂]	299.4	8730	516	4.63 -4
	196.2	13330	516	
	75.7	32680	516	
	298.4	8614	516	
	194.7	13200	516	
	75.2	32340	516	

^a In c.g.s. units. ^b Computed from χ_M^{corr} as explained in text.

On the basis of equation 1, these conclusions can be drawn from the magnetic moments recorded in Table I. (1) In every case, when the moments of stoichiometrically analogous complexes, differing only in which halogen they contain, are compared, the moments decrease, meaning that Δ increases in the order $I^- < Br^- < Cl^-$. This, of course is in good agreement with the generally accepted spectrochemical series (*vide supra*) and with the results previously obtained by the magnetic investigation² of $[CoX_4]^{2-}$ complexes. (2) It can be seen that there are no significant differences in the orbital contributions to the magnetic moments of corresponding complexes containing tricyclohexylphosphine and triphenylphosphine, although

Streuli¹⁶ recently has shown that these two phosphines stand at opposite ends of the basicity scale for a large number of R_3P species with respect to the hydrogen ion. Presumably, however, with both of these very bulky ligands, changes in relative magnitudes of steric strains when the reference acid changes from H^+ to CoX_2 may be quite sufficient to swamp an intrinsic basicity effect even of the order of 10^7 in K_a , since this corresponds to only ~ 10 kcal./mole at $300^\circ K$. Another factor which may well be significant is pi bonding which may occur in the cobalt complexes but not in the protonated species. It should be noted that inductive effects which would cause an increase in basicity toward a purely sigma bonding ion (*e.g.*, H^+) would tend to decrease the pi acceptor strength of the $d\pi$ orbitals of phosphorus. Thus with an ion engaging in both sigma and pi bonding (*e.g.*, $Co(II)$) the overall change in effective basicity of the ligand might turn out to be small. (3) By comparison of the present results with those previously reported^{2,3} for a variety of other tetrahedral complexes of $Co(II)$ it is possible to place the phosphines in the spectrochemical series relative to a number of other ligands. However, because previously^{2,3} corrections for TIP were not made direct comparison of previous and present results would be misleading. In order to make the desired comparisons we have recalculated the magnetic moments of a number of the complexes previously studied, assuming that TIP equals 500×10^{-6} c.g.s. units, and the results are given in Table II. Comparison of the moments in Tables I and II suggests that the ordering of the various ligands included therein must be approximately

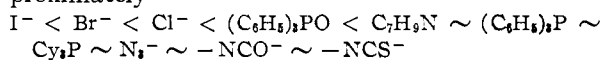


TABLE II
CURIE-WEISS MAGNETIC MOMENTS AND WEISS CONSTANTS
FOR SOME TETRAHEDRAL COBALT (II) COMPLEXES (WITH
TIP CORRECTION)

Species	Compound	Ref. ^a	μ , B.M.	θ , °K.
[CoI ₄] ³⁻	(C ₆ H ₅) ₂ [CoI ₄]	2	4.88	-13
[Co((C ₆ H ₅) ₂ PO) ₂ I ₂]	3	4.82	-10
[CoBr ₄] ³⁻	(C ₆ H ₅) ₂ [CoBr ₄]	2	4.75	-8
	(C ₆ H ₅) ₂ [CoBr ₄]	2	4.70	-3
[Co((C ₆ H ₅) ₂ PO) ₂ Br ₂]	3	4.69	-6
[Co((C ₆ H ₅) ₂ PO) ₂ Cl ₂]	3	4.63	-6
[Co(C ₇ H ₉ N) ₂ I ₂]	3	4.63	-4
[CoCl ₄] ³⁻	(C ₆ H ₅) ₂ [CoCl ₄]	2	4.65	-7
	[(C ₆ H ₅) ₂ AsCH ₃] ₂ [CoCl ₄]	2	4.63	-4
	Cs ₂ CoCl ₆	2	4.52	-4
[Co((C ₆ H ₅) ₂ PO) ₂ I ₂] ⁺	[Co((C ₆ H ₅) ₂ PO) ₂](ClO ₄) ₂	3	4.53	+1
[Co(C ₇ H ₉ N) ₂ Br ₂]	3	4.54	-8
[Co(C ₇ H ₉ N) ₂ Cl ₂]	3	4.54	-6
[Co(N ₃) ₄] ³⁻	((C ₆ H ₅) ₂ As) ₂ [Co(N ₃) ₄]	1	4.47	-6
[Co(NCO) ₄] ³⁻	[(C ₆ H ₅) ₂ (n-C ₄ H ₉)P] ₂ [Co(NCO) ₄]	1	4.44	-8
[Co(NCS) ₄] ³⁻	[(CH ₃) ₄ N] ₂ [Co(NCS) ₄]	17	4.40	-7
	Hg[Co(NCS) ₄]	17	4.32	-4

^a These references are to the source of the susceptibility data.

Several other features of the magnetic data and their treatment merit brief comment. Throughout the above discussion it has been assumed that

(16) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

(17) F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, in press.

TABLE III
 SPECTRAL DATA FOR THE MIXED PHOSPHINE-HALIDE COMPLEXES OF Co(II)

Compound	Medium	$m\mu$	Observed bands ^a Cm. ⁻¹	ϵ^b
Co[(C ₆ H ₅) ₂ P] ₂ Cl ₂	CH ₂ COCl ₂ 2 × 10 ⁻³ M	581	17,200	235
		638	15,700	290
		682	14,700	310
	Solid	Broad, weak, absorption, ~1.0-1.6 μ ; see text		
		650	15,800	..
Co[(C ₆ H ₅) ₂ P] ₂ Br ₂	CH ₂ Cl ₂ (10 ⁻³ M)	769	13,000	..
		640(sh)	15,600	~740
		665	14,900	970
		755	13,100	610
		985	10,200	80
	Solid	1300	7,700	95
		1620	6,200	110
Co[(C ₆ H ₅) ₂ P] ₂ I ₂	CH ₂ Cl ₂ (10 ⁻³ M)	667	15,000	..
		781	12,800	..
		646	15,500	370
		687	14,500	750
	Solid	727	13,800	920
		790	12,700	470
[Co{(C ₆ H ₁₁) ₂ P} ₂ Br ₂]	CH ₂ Cl ₂ 2 × 10 ⁻³ M	~710(sh)	14,200	..
		750	13,400	..
		820	12,200	..
	Solid	625	16,000	513
		665	15,000	577
		705	14,200	542
[Co{(C ₆ H ₁₁) ₂ P} ₂ I ₂]	CH ₂ Cl ₂ 2 × 10 ⁻³ M	630	15,800	..
		680	14,700	..
		720	13,900	..
		~610(sh)	~16,400(sh)	..
		~650(sh)	~15,400(sh)	..
	Solid	674	14,800	749
		728	13,700	463
		744	13,400	468
		350	28,600	..
		~380(sh)	~26,300(sh)	..
		~400(sh)	~25,000(sh)	..
[(C ₂ H ₅) ₄ N] ⁺ [Co{(C ₆ H ₅) ₂ P]Br ₂] ⁻	10 ⁻³ M in CH ₃ NO ₂	515	19,400	..
		~580(sh)	~17,200	..
		690	14,500	..
		~745(sh)	~13,400	..
		645	15,500	653
	Solid	~685(sh)	~14,600(sh)	~440
		695	14,400	563
		730	13,700	580
		545(sh)	18,300	..
		~580(sh)	~17,200	..
[(<i>n</i> -C ₄ H ₉) ₄ N] ⁺ [Co{(C ₆ H ₅) ₂ P]I ₂] ⁻	10 ⁻³ M in CH ₃ NO ₂	640	15,600	..
		683	14,600	..
		720(sh)	13,900	..
		732	13,700	..
	Solid	700	14,300	648
		720	13,900	689
		760	13,200	880
		790	12,700	890
Solid	590(w)	16,900	..	
	645(w)	15,500	..	
	730(sh)	13,700	..	
	790	12,700	..	

^a Sh = shoulder; w = weak. ^b Molar extinction coefficient at band maximum ($\epsilon = D/lc$) for solution spectra.

the presence of low symmetry components in the ligand field resulting from the presence of different, often very disparate, ligands in the coordination sphere could be ignored and the mixed complexes

treated as though they are truly tetrahedral with a cubic ligand field whose strength is some kind of an average of the contributions of the various ligands. We believe that this approach is justifi-

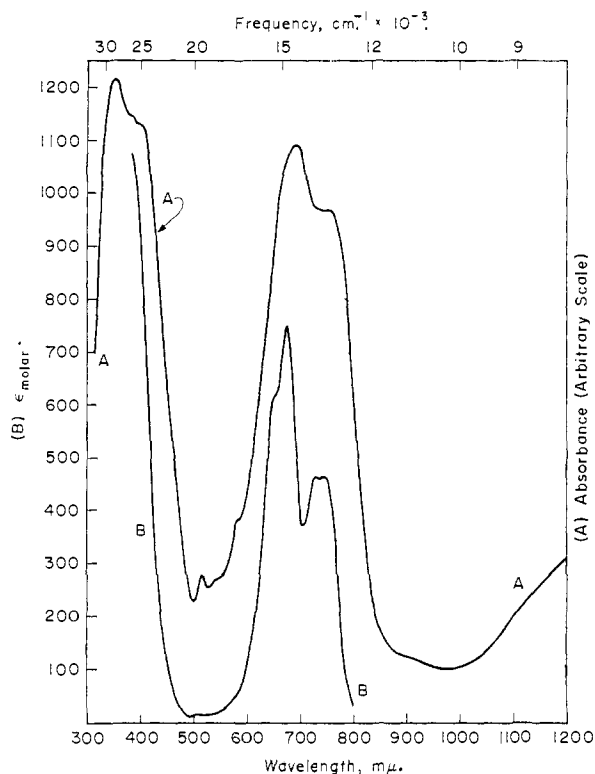


Fig. 1.—The visible spectrum of $[\text{Co}(\text{Cy}_3\text{P})_2\text{I}_2]$: (A) the reflectance spectrum in which ordinates are only relative; (B) the absorption spectrum of a 0.002 M solution in CH_2Cl_2 .

fied for tetrahedral $\text{Co}(\text{II})$ complexes, although it is not generally appropriate. For example, with tetrahedral $\text{Ni}(\text{II})$ it has been shown that low symmetry components in the ligand field have a profound effect upon the magnetic behavior.⁷ This is because the ground state of $\text{Ni}(\text{II})$ in a tetrahedral environment is an orbital triplet (split by L-S coupling of course) and it thus owes its orbital moment mainly to orbital momentum resident in the ground orbital multiplet. Any splitting of the components of this multiplet by the low symmetry field is thus very effective in destroying the orbital contribution. With $\text{Co}(\text{II})$ in a tetrahedral environment the ground state is an orbital singlet and orbital momentum is introduced only by L-S coupling with higher states. Although the upper triplet orbital states in $\text{Co}(\text{II})$ appear from the spectra (*vide infra*) to suffer as much splitting as do analogous states in corresponding tetrahedral nickel (II) complexes,⁷ the effect on the orbital momentum in the ground states is bound to be small so long as these splittings are small compared with the primary splittings caused by the cubic component of the ligand field.

It is known, however, that splitting in the upper states of tetrahedral $\text{Co}(\text{II})$ will cause splitting of the M_s components of the ground state,¹⁸

(18) The precise relationship between the upper state splittings and the ground state splittings poses a tricky theoretical problem which has been treated only for the case of a trigonal distortion. Some calculations which have been reported appear to be in error and the correct, or most nearly correct value of the numerical coefficient seems to be that of Meijer and Gerritsen.¹⁹

and Figgis²⁰ has shown that these small ground state splittings will give rise to Weiss constants in the temperature dependence of the susceptibilities. In all of the compounds studied in this work the presence of different ligands guarantees the existence of the ground state splittings, but a check of observed Weiss constants against theory is possible only for the two $[\text{Co}((\text{C}_6\text{H}_5)_3\text{P})\text{X}_3]^-$ species, because when the symmetry is lower than axial, as in all the other cases, no simple relationship can be expected. For the two $[\text{Co}((\text{C}_6\text{H}_5)_3\text{P})\text{X}_3]^-$ species we may confidently expect from the relative positions of $(\text{C}_6\text{H}_5)_3\text{P}$, Br^- and I^- in the spectrochemical series that the trigonal component in the field would be greater for the iodide, and this is in agreement with the observation of a larger Weiss constant in the iodide. However, this one favorable comparison between theory and experiment is hardly conclusive and studies of other $[\text{CoLX}_3]^-$ species have been undertaken.

Electronic Spectra.—Table III records the visible spectra of all complexes studied in this work. The absorption is due to the transition usually called ν_3 , which is a ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ transition in pure T_d symmetry. This band is normally a complex multicomponent one^{1,21-23} because of the effects of spin-orbit coupling in splitting up the ${}^4\text{T}_1(\text{P})$ state and in coupling it to close-lying doublet states. In the phosphine complexes studied here these bands are still more complex than usual and clearly show that the ${}^4\text{T}_1(\text{P})$ state is split by the order of 10^3 wave numbers by the distortion of the ligand fields from the T_d symmetry. In order to illustrate the appearance of these further splittings the reflectance and solution spectra of $[\text{Co}(\text{Cy}_3\text{P})_2\text{I}_2]$ are shown in Figure 1. In all cases both reflectance spectra and solution spectra were taken in order to detect any gross changes in electronic or geometrical structure which might occur on solution. In no case was any significant difference in the two spectra observed except for the typically lower resolution in the reflectance spectra.

In addition to showing the presence and indicating the order of magnitude of the splittings of the ${}^4\text{T}_1(\text{P})$ state by the lower symmetry, the spectral data may also be used to arrange the five ligands occurring in these complexes in their relative order in the spectrochemical series. Inspection of the data in Table III shows that this order is



in agreement with the order deduced above from the magnetic data but necessarily less rigorously certain because of the complex character of the spectral bands.

In a few cases broad absorptions corresponding to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})(\nu_2)$ transitions were observed. In general such absorption was so broad that no

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precise energy values could be ascertained from them, although in truly tetrahedral complexes they provide fairly precise information.

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Organic Anions as Bridging Groups in Oxidation-Reduction Reactions

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A kinetic study has been made of the reactions of Cr^{++} with complex ions of the type $(\text{NH}_3)_5\text{Co(III)L}$ where L is acid succinate, methyl succinate (half-ester), acetate, acid fumarate, methyl fumarate (half-ester) and the three isomeric forms of phthalic acid. The data are interpreted on the basis that adjacent attack of Cr^{++} takes place in all cases except for acid fumarate, methyl fumarate and terephthalic acid. In these three cases, there is conjugation between the carboxylate group at the remote end and that bearing the Co(III) center, and it is postulated that Cr^{++} attacks the remote end. In these special cases, the rates of reaction are greater than in the others and, furthermore, a term in the rate law is observed which is first order in (H^+) . The role of H^+ is interpreted as being that of adding to the carbonyl adjacent to the Co(III), thus improving conjugation between the Cr^{++} on the remote end and the Co(III) group.

In this paper we report the results of detailed kinetic studies of the reactions of Cr^{++} with some complex ions of the class $(\text{NH}_3)_5\text{Co(III)-L}$ where L is an organic ion containing one or more carboxylic groups. Some early, rather rough kinetic studies¹ with systems of this type showed that large differences in rate are observed for different bridging groups and suggested that for certain of them, the reducing agent can attack at a site remote from the oxidizing center, the electron being conducted through the bridging group. This feature particularly encouraged us to undertake the present study, which includes some of the systems studied earlier, but others as well, chosen with a view to learning something about the subject of electron conduction through bridging groups. In the course of this work some novel kinetic effects have been uncovered, and strong evidence for electron conduction through several bonds in a molecule has been adduced; in fact, the experiments which provide proof of remote attack and which have already been published in part^{2,3} grew out of the present work.

Experimental

Materials.—The salt $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}(\text{ClO}_4)_3$ was used as the source of the radical $\text{Co}(\text{NH}_3)_5$ which is common to all the oxidizing agents studied. The salt was prepared from $\text{Co}(\text{NH}_3)_5\text{CO}_3(\text{NO}_3)_4$ by treating a hot solution of the carbonato salt with concentrated perchloric acid. The crystals recovered on cooling were subjected to a second treatment with perchloric acid.

The general method for the preparation of most of the organic acid complexes referred to here consists in heating a solution containing $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{++}$, the organic acid and (usually) the sodium salt for *ca.* 2 hr. at 70°. Acid and salt are in large excess, and the concentrations are as high as tolerated. Substitution is rapid enough and the equilibrium is sufficiently favorable in most of the systems so that substantial conversion of the aquo to the acido ion takes place. The perchlorate salt in each case is readily precipitated by adding perchloric acid. The difficulties that arise are in the

separation of the product desired from the aquopentammine-cobalt (III) perchlorate and the organic acid which in many cases is only sparingly soluble. Cation exchange resins are especially useful in separating the acido ions from the aquopentammine cobaltic ion. Good samples of the compounds with L = acetate, acid succinate, acid maleate, acid fumarate, acid phthalate and acid isophthalate were obtained without much difficulty in the general way described. However, a good preparation of the acid terephthalate complex was not obtained. The principal component of the cobalt-containing preparation appeared to be the salt of the binuclear complex, and only *ca.* 20% of it was comprised by the substance taken to be the acid terephthalato complex. An attempt to prepare the simple complex from the binuclear one by controlled hydrolysis did not lead to improved yields. We also failed to obtain a good preparation of the muconato complex. The product resulting from the attempted preparation appeared to contain a number of components, which presumably are complexes of the various isomeric muconate forms. To get appreciable substitution in this system (as well as some others which have since been encountered), a much more prolonged period of heating is required than the approximate 2 hr. which suffice for the majority of complexes prepared for the present work.

All of the complexes containing dibasic acids precipitate from acid solution as the acid salts, a feature which is very useful in assessing the purity of the sample.

In every case, the purity of the sample was checked by titration with alkali. This is a direct method of establishing the equivalent weight of the compound when the ligand is an acido group. For most of the preparations described as "good" in the previous paragraph, the equivalent weight thus determined agreed with that calculated for the anhydrous perchlorate within 2%. The bisuccinato complex is an exception, and the agreement here was only within 4%. Another exception is the bifumarato perchlorate. The equivalent weight determined for this substance agrees accurately with the formula $\text{Co}(\text{NH}_3)_5\text{C}_4\text{O}_4\text{H}_2(\text{ClO}_4)_2 \cdot \frac{1}{2}\text{HClO}_4$, as does the analysis for N, Cl and H (obsd. 13.4, 17.4, 0.30%; calcd., 13.8, 17.4, 0.30%). Analyses for N and Cl were made on the other compounds as well. These agree satisfactorily with the formulas as described, except in the case of the bisuccinato salt. Here again the deviations from theoretical were somewhat outside the expected errors of analysis.

Methyl half ester complexes of the fumarato, maleato and succinato complexes were prepared by reaction of the acid salts with diazomethane. The diazomethane in ether solution⁵ is added slowly to a solution of the salt in 40% aqueous ethanol using approximately 20% excess. The approach of the end of the reaction can be noted by observing the rate at which successive portions of the diazomethane solution are

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