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### Magnetic Investigations of Spin-free Cobaltous Complexes. V. Tetra-azido and Tetracyanato Cobaltate(II) Ions

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The electronic spectra between 0.4 and 2.0 microns and the magnetic susceptibilities between 70 and 300°K. of the tetra-azido- and tetra-isocyanatocobaltate(II) ions,  $[\text{Co}(\text{N}_3)_4]^{-2}$  and  $[\text{Co}(\text{NCO})_4]^{-2}$ , are reported. These results are interpreted using ligand field theory to show the following structural and electronic features of these complex ions: (1) they are tetrahedral; (2) in  $[\text{Co}(\text{NCO})_4]^{-2}$  it is almost certainly the nitrogen atoms which are bound to the Co(II); (3)  $-\text{NCO}^-$  lies toward the stronger end in the spectrochemical series but toward the weaker end in the nephelauxetic series relative to  $\text{N}_3^-$ ; (4) the metal-ligand bonds possess covalent character; (5) the spin-orbit coupling constants of Co(II) in these complexes are ~80% of the free-ion value.

#### Introduction

To extend the program of study of the magnetic properties of spin-free cobaltous complexes,<sup>2-4</sup> we have investigated the tetra-azido and the tetracyanato complexes,  $[\text{Co}(\text{N}_3)_4]^{-2}$  and  $[\text{Co}(\text{NCO})_4]^{-2}$ . The existence of the former was reported recently<sup>5</sup>; the latter has been known for some time<sup>6</sup> though no recent investigations of it have been reported.<sup>7</sup> In conjunction with the magnetic study, the electronic spectra have also been examined. The electronic spectra together with the magnetic data leave no doubt that these anions are tetrahedral and permit us to evaluate certain parameters of the electronic structures. The methods by which the spectral and magnetic data may be analyzed to yield a considerable amount of information about the electronic structure of the metal ion and its interaction with the ligands are presented and applied to these two complex ions. This kind of analysis is applicable to any tetrahedral complex and the methods described here will be applied subsequently to a number of others. However, because of the relatively strong ligand fields in these two species,

the spectral band expected for all tetrahedral Co(II) complexes in the 1-2 micron range occurs near the high energy end of the range, thus making its observation and measurement unusually convenient.

#### Experimental

**Materials.**—Tetraphenylarsonium tetra-azidocobaltate (II) was prepared and recrystallized from acetone/carbon tetrachloride as directed by Senise.<sup>5</sup>

*Anal.* Co, 5.86; C, 57.40; H, 3.81. M.p. 153.5 (lit.,<sup>5</sup> 153-154°).

The potassium tetracyanatocobaltate (II) was prepared by adding a hot solution of potassium cyanate (32.4 g., 0.4 mole) in water (30 ml.) to a hot solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (29.1 g., 0.1 mole) in ethanol (140 ml.). On cooling, a mixture of deep blue crystals with a pink powder was formed. This was filtered off and the blue compound dissolved out with acetone and then reprecipitated from the hot acetone with dioxane. It was immediately filtered off and dried in vacuum. The yield was 5.4 g. of dark blue crystals.

*Anal.* Calcd. for  $\text{C}_4\text{CoK}_2\text{N}_4\text{O}_4$ : C, 15.74; Co, 19.31; N, 18.36. Found: C, 15.59; Co, 19.30; N, 18.46. About 0.2% hydrogen was also found due, presumably, to the slightly hygroscopic nature of the compound.

The new compound butyltriphenylphosphonium tetracyanatocobaltate(II) was prepared by adding a solution of 3.8 g. of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 4 ml. of water to 50 g. of  $\text{KCNO}$  in 30 ml. of cold water; 8 g. of butyltriphenylphosphonium bromide in 30 ml. of hot water was added, and the blue precipitate filtered, washed with water, and dried *in vacuo*. The yield was 7.9 g. of dark blue crystals, m. p., 120.5-121.5°. *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{18}\text{CoN}_4\text{O}_4\text{P}_2$ : C, 66.59; H, 5.59; N, 6.47; P, 7.15. Found: C, 66.65; H, 5.47; N, 6.74; P, 7.08.

**Magnetic Measurements.**—The magnetic susceptibilities were measured at various temperatures using a Gouy bal-

(1) Alfred P. Sloan Foundation Fellow.

(2) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959); **32**, 1168 (1960).

(3) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

(4) M. Goodgame and F. A. Cotton, *J. Phys. Chem.*, in press.

(5) P. Senise, *J. Am. Chem. Soc.*, **81**, 4196 (1959).

(6) C. W. Blomstrand, *J. prakt. Chem.*, [2] **3**, 221 (1871).

(7) P. Pascal, *Bull. soc. chim. France*, [4] **15**, 19 (1914).

ance as previously described.<sup>2-4</sup> The Gouy tube was calibrated with Mohr's salt (taking  $\chi_g$  as  $31.67 \times 10^{-6}$  c.g.s. units at 299°). The calibration was checked by measuring the susceptibility of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  for which a value of  $\chi_g$  equal to  $6.01 \pm 0.05 \times 10^{-6}$  c.g.s. units was obtained. This agrees satisfactorily with the values  $6.05 \times 10^{-6}$ ,<sup>8</sup>  $6.14 \times 10^{-6}$ <sup>9</sup> and  $5.95 \times 10^{-6}$ <sup>10</sup> given in the literature. The experimental results and derived quantities are recorded in Table I. The diamagnetic corrections used were  $-500 \times 10^{-6}$ ,  $-120 \times 10^{-6}$  and  $-511 \times 10^{-6}$  c.g.s. units per mole for the  $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Co}(\text{N}_3)_4]$ ,  $\text{K}_2\text{Co}(\text{NCO})_4$  and  $[(\text{C}_6\text{H}_5)_3(\eta\text{-C}_4\text{H}_9)\text{P}]_2[\text{Co}(\text{NCO})_4]$  respectively.

The gram susceptibility of  $\text{K}_2[\text{Co}(\text{NCO})_4]$  was reported by Pascal<sup>7</sup> as  $8.10 \times 10^{-6}$  c.g.s. units at an unspecified temperature. From this datum,  $\mu_{\text{eff}}$  assuming a temperature of 20° would be 4.38 B.M., which agrees with our result (4.39 B.M. at about 20°, calculated making no correction for TIP).

**Electronic Spectra.**—The spectra were measured using a Beckman DK recording spectrophotometer for solutions and a Beckman DU spectrophotometer equipped with the standard reflectance attachment for powders.

### Discussion

**Electronic Spectra.**—We shall first discuss the electronic spectra since certain information derived therefrom will be required in the treatment and interpretation of the magnetic data. In a tetrahedral field, the  $^4\text{F}$  ground term of  $\text{Co}(\text{II})$  is split to give the following states, in increasing order of energies:  $^4\text{A}_2$ ,  $^4\text{T}_2$ ,  $^4\text{T}_1(\text{F})$ . In addition, there is a  $^4\text{T}_1(\text{P})$  state originating from the  $^4\text{P}$  term of the free ion. We denote the frequencies ( $\text{cm}^{-1}$ ) of the transitions  $^4\text{A}_2 \rightarrow ^4\text{T}_2$ ,  $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{F})$  and  $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{P})$  respectively as  $\nu_1$ ,  $\nu_2$  and  $\nu_3$ . From Tanabe and Sugano's results<sup>11</sup> we can derive these convenient expressions for these frequencies

$$\begin{aligned} \nu_1 &= \Delta \\ \nu_2 &= 1.5\Delta + 7.5B' - Q \\ \nu_3 &= 1.5\Delta + 7.5B' + Q \\ Q &= \frac{1}{2}[(0.6\Delta - 15B')^2 + 0.64\Delta^2]^{1/2} \end{aligned} \quad (1)$$

in which  $\Delta$  is the modulus of the ligand field strength and  $B'$  is the effective value of the Racah inter-electronic repulsion integral. It has also been shown by Low<sup>12</sup> that each of the three upper states will be split by spin orbit coupling, with the splitting in the two  $\text{T}_1$  states

$$T_1 \begin{cases} -\frac{9}{4}\lambda' > \frac{15}{4}\lambda' \\ +\frac{6}{4}\lambda' > \frac{9}{4}\lambda' \\ +\frac{15}{4}\lambda' > \frac{9}{4}\lambda' \end{cases} \quad (2)$$

The transitions  $\nu_2$  and  $\nu_3$  have been observed in each of the complexes reported here. The experimental data are collected in Table I. While the solution spectra will be the basis for subsequent discussion because of their superior resolution, the reflectance spectra of the  $\nu_3$  bands in each case are important because they show that, allowing for the poorer resolution of the reflectance spectra, there is no significant change in the complex ions upon solution in the solvents used.

Turning first to the  $\nu_3$  bands, we note that each one consists of three reasonably strong components.

(8) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

(9) S. Sugden, *ibid.*, 161 (1952).

(10) C. J. Gorter and W. J. de Haas, *Comm. Kammerlingh Onnes Lab.*, Leiden, No. 210 d, p. 39 (1930).

(11) Y. Tanabe and S. Sugano, *J. Phys. Soc., Japan*, 9, 753 (1954).

(12) R. Stahl-Brada and W. Low, *Phys. Rev.*, 113, 775 (1959).

TABLE I  
ELECTRONIC SPECTRA OF THE  $[\text{Co}(\text{N}_3)_4]^{2-}$  AND  $[\text{Co}(\text{NCO})_4]^{2-}$  IONS

Medium	$m\mu$	$\text{cm}^{-1}$	$\epsilon$	Compound
Acetone	615	16,260	450	$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Co}(\text{N}_3)_4]$
	655	15,270	820	
	685	14,600	900	
Nitromethane	618	16,180	430	$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Co}(\text{N}_3)_4]$
	660	15,150	760	
	690	14,490	800	
$\text{CHCl}_3$	1385	7,220		$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Co}(\text{N}_3)_4]$
	1560	6,410		
	~1700	~5,880	sh	
$\text{CH}_3\text{NO}_2$	1365	7,330	150	$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Co}(\text{N}_3)_4]$
	1480	6,760	157	
	{ 1675	5,970	122	
	{ 1725	5,800	116	
Acetone	1370	7,300	140	$[(\text{C}_6\text{H}_5)_3(\eta\text{-C}_4\text{H}_9)\text{P}]_2[\text{Co}(\text{NCO})_4]$
	1520	6,580	150	
	~1700	~5,880	~130	
Solid (reflectance)	~625	16,000	sh	$[(\text{C}_6\text{H}_5)_3(\eta\text{-C}_4\text{H}_9)\text{P}]_2[\text{Co}(\text{NCO})_4]$
	690	14,500	..	
	>1200	<8,300	..	
$\text{CH}_3\text{CN}$	581	17,210	456	$\text{K}_2\text{Co}(\text{NCO})_4$
	612	16,340	725	
	633	15,800	750	
	1315	~7,600	112	
	1450	~6,900	112	
	1540	~6,500(sh)	100	
Solid (reflectance)	520	19,200	vw, sh	$[(\text{C}_6\text{H}_5)_3(\eta\text{-C}_4\text{H}_9)\text{P}]_2[\text{Co}(\text{NCO})_4]$
	590	17,000	sh	
	630	15,900	..	
	>1200	<8,300	..	
Acetone	580	17,240	465	$[(\text{C}_6\text{H}_5)_3(\eta\text{-C}_4\text{H}_9)\text{P}]_2[\text{Co}(\text{NCO})_4]$
	610	16,400	740	
	631	15,850	770	
	1300	~7,700	122	
	1460	~6,850	126	
	1550	~6,450(sh)	106	

It is unlikely that these can all be identified with substrates of the  $^4\text{T}_1(\text{P})$  level produced by spin-orbit coupling, because the separations are too large if we make the reasonable assumption that  $\lambda'$  will be about  $150 \text{ cm}^{-1}$  or less *vide infra*. In conformity with the procedure of Stahl-Brada and Low,<sup>12</sup> we assume that the highest energy component represents a transition to a doublet state which acquires intensity by spin-orbit coupling interaction with  $^1\text{T}_1(\text{P})$ , and we then assign the middle peaks to the highest transition, and the lowest energy peaks to the unresolved transitions to the two lower energy components of  $^4\text{T}_1(\text{P})$ . In this way, using equations 2, we place  $\nu_3$  at  $14,900 \text{ cm}^{-1}$  in  $[\text{Co}(\text{N}_3)_4]^{2-}$  and at  $16,100 \text{ cm}^{-1}$  in  $[\text{Co}(\text{NCO})_4]^{2-}$ .

Turning to the  $\nu_2$  bands, it is seen that in each case there are three components, although for  $[\text{Co}(\text{NCO})_4]^{2-}$  the resolution was rather poor. Here we assign these to the several components produced in the  $^4\text{T}_1(\text{F})$  state by spin-orbit coupling and using the relations (2) we place  $\nu_2$  at  $6750 \text{ cm}^{-1}$  in  $[\text{Co}(\text{N}_3)_4]^{2-}$  and at  $7150 \text{ cm}^{-1}$  in  $[\text{Co}(\text{NCO})_4]^{2-}$ . We now solve equations 1 using the values given above for  $\nu_2$  and  $\nu_3$  and obtain the values of  $\Delta$  and  $B'$  shown in Table II.

The spectral data thus provide two important pieces of information about the ligands in these complexes. First, it is seen from the values of  $\Delta$  that  $-\text{NCO}$  lies to the stronger end of the spectrochemical series<sup>13</sup> compared to  $\text{N}_3^-$ , whereas the  $\beta$

(13) For a general discussion and references to the original literature, see T. M. Dunn in "Modern Coordination Chemistry," J. Lewis

TABLE II  
PARAMETERS OF THE SPECTRA AND ELECTRONIC STRUCTURES  
OF Co(II) IN  $[\text{Co}(\text{N}_3)_4]^{-2}$  AND  $[\text{Co}(\text{NCO})_4]^{-2}$

	$[\text{Co}(\text{N}_3)_4]^{-2}$	$[\text{Co}(\text{NCO})_4]^{-2}$
$\nu_2$ , $\text{cm.}^{-1}$	6,750	7,150
$\nu_3$ , $\text{cm.}^{-1}$	14,900	16,100
$\Delta$ , $\text{cm.}^{-1}$	3,920	4,150
$B'$ , $\text{cm.}^{-1}$	658	720
$\beta$ ( $= B'/B^a$ )	0.680	0.745
TIP, c.g.s. units $\times 10^6$	533	504
Oscillator strengths:		
$f(\nu_2)$	$1.49 \times 10^{-3}$	$1.37 \times 10^{-3}$
$f(\nu_3)$	$8.58 \times 10^{-3}$	$6.70 \times 10^{-3}$
$f(\nu_3)/f(\nu_2)$	$6 \pm 1$	$5 \pm 1$
$\mu$ , B.M.	4.47	4.32
$\lambda'$ , $\text{cm.}^{-1}$	$146 \pm 20$	$115 \pm 20$

<sup>a</sup> B (free ion) = 967  $\text{cm.}^{-1}$ .

values show that  $\text{N}_3^-$  lies to the stronger end of the nephelauxetic series<sup>13</sup> compared to  $-\text{NCO}$ .

The oscillator strengths of  $\nu_2$  and  $\nu_3$  in each of the complexes have been estimated to within  $\pm 10\%$  by graphical integration. These results are also included in Table II. In treating the  $\nu_3$  bands we have included the area under the highest energy component because it presumably borrows most of its intensity from the genuine quartet components. These oscillator strength data may be analyzed using the theory developed by Ballhausen and Liehr.<sup>14</sup> These authors have shown<sup>14</sup> first that for a purely ionic complex in which the band intensities would be attributable to d-p mixing, the ratio of  $f(\nu_3)$  to  $f(\nu_2)$  should be given by  $4\nu_3/\nu_2$ . From Table II we see that these ratios for  $[\text{Co}(\text{N}_3)_4]^{-2}$  and  $[\text{Co}(\text{NCO})_4]^{-2}$  should be 8.84 and 9.00, respectively, whereas the observed values are lower by vastly more than experimental error. This appears to offer definite evidence that there is appreciable covalence in the metal ligand bonds in these complexes. Ballhausen and Liehr<sup>14</sup> have presented an equation relating the mixing coefficients,  $\alpha$ , for the metal and ligand  $T_2$  sigma orbitals and the sigma overlap integral with  $f(\nu_3)$  with which the degree of covalence might be estimated semiquantitatively within the limits of the fairly severe approximations used to derive the relation. We have not undertaken to do this here however.

In the foregoing discussion the  $\text{CNO}^-$  complex has been assumed to be the isocyanato compound  $[\text{Co}(\text{NCO})_4]^{-2}$ . This assumption is based on the position of the  $\text{NCO}$  ion as it occurs in this complex in the spectrochemical series. It appears to lie so far to the strong field end that the possibility of its coordinating through oxygen in this case seems very unlikely.

**Magnetic Moments.**—The moment of 4.32 B.M. for the  $[\text{Co}(\text{NCO})_4]^{-2}$  ion obtained from the measurements on the potassium salt seems much too low since the only way to reconcile it with the spectral data is to assign a value of only 115  $\text{cm.}^{-1}$  to  $\lambda'$ . Such a low spin-orbit coupling constant is far out of line with those in all other complexes we have

and R. Wilkins, editors, Interscience Publishers, Inc., New York, N. Y., 1960.

(14) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spect.*, **2**, 342 (1958); Erratum, **4**, 190 (1960).

studied. We believe that the small size of the cation may cause significant distortion of the complex in the crystal. In order to test this belief that the value 4.32 B.M. was not representative and to obviate the problem of the small cation, the new salt  $[(\text{C}_6\text{H}_5)_3(\text{C}_4\text{H}_9)\text{P}]_2[\text{Co}(\text{NCO})_4]$  was prepared and studied. It was found to have a magnetic moment of  $4.44 \pm 0.05$  B.M. which we believe to be more truly representative of that for the undistorted  $[\text{Co}(\text{NCO})_4]^{-2}$  ion. It is this latter value which will be used exclusively in the subsequent discussion.

TABLE III  
MAGNETIC SUSCEPTIBILITIES OF THE  $[\text{Co}(\text{N}_3)_4]^{-2}$  AND  
 $[\text{Co}(\text{NCO})_4]^{-2}$  SALTS AND THEIR MAGNETIC MOMENTS

Temp., K.	Speci- men no.	$\chi_M^{\text{corr}} \times 10^6$ , c.g.s. units	$\mu$ , B.M.	$\theta$ , °K.
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Co}(\text{N}_3)_4]$ :				
299	1	8,020	4.47	-6
195	1	12,420		
72	1	31,680		
297	2	7,860		
194	2	12,310		
72	2	31,250		
301	3	8,080		
$\text{K}_2[\text{Co}(\text{NCO})_4]$ :				
300	4	7,500	4.32	-8
194	4	11,260		
72	4	28,290		
301	5	7,518		
193	5	11,420		
72	5	28,500		
$[(\text{C}_6\text{H}_5)_3(\text{C}_4\text{H}_9)\text{P}]_2[\text{Co}(\text{NCO})_4]$ :				
297	6	7,983	4.44	-8
195	6	12,060		
73	6	30,130		
297	6	8,085		
195	6	12,180		
73	6	30,140		

The magnetic moments of the anions  $[\text{Co}(\text{N}_3)_4]^{-2}$  and  $[\text{Co}(\text{NCO})_4]^{-2}$  may be used to estimate the relative positions of the azide and the N-coordinated cyanate ions in the spectrochemical series according to the procedure outlined in earlier papers.<sup>1,2</sup> However, in the present instance we have introduced a refinement not previously used, namely, the correction of all molar susceptibility values for the temperature independent paramagnetism (TIP) as well as for diamagnetism. The  $\chi_M^{\text{corr}}$  values in Table III are the measured values with both of these corrections. The diamagnetic corrections are given in the experimental section; the TIP's were calculated by the formula of Van Vleck<sup>15</sup> and Figgis,<sup>16</sup> and are listed in Table II. The reciprocals of these  $\chi_M^{\text{corr}}$  values were plotted against the absolute temperature and from the best straight line the values of  $\mu$  and  $\theta$  in the Curie-Weiss equation,  $\mu = 2.84 [\chi_M^{\text{corr}}(T-\theta)]^{1/2}$  were computed. The points so plotted defined straight lines to well within the experimental errors; the  $\mu$  values are believed to be

(15) According to J. Van Vleck (private communication to P. Cossee) and B. Figgis, *Trans. Faraday Soc.*, **56**, 1553 (1960), the TIP in tetrahedral Co(II) is given by  $8N\beta^2/\Delta = 2.09/\Delta$ , where  $\Delta$  is in  $\text{cm.}^{-1}$ .

precise to within  $\pm 0.05$  B.M. and the  $\theta$  values to within  $\pm 2^\circ$ .<sup>16</sup>

The  $\mu$  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<sup>2,3</sup> in this series we have attributed the  $\theta$  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  $\theta$ 's. However, the Curie-Weiss moment is the value which  $\mu_{\text{eff}}$  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)<sup>2</sup>

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

$\lambda'$  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.<sup>17</sup> From the magnetic moments and  $\Delta$  values, the values of  $\lambda'$  given in Table II were computed. The uncertainties assigned allow for uncertainties of 200  $\text{cm.}^{-1}$  in the  $\Delta$  values and 0.05 B.M. in the  $\mu$  values. It is seen that the  $\lambda'$  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.<sup>1</sup> 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  $[\text{Co}(\text{R}_3\text{P})_2\text{X}_2]$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ;  $\text{R} = \text{C}_6\text{H}_{11}$ ,  $\text{X} = \text{Br}$ ,  $\text{I}$ ) 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  $\text{N}_3^-$ .

### Introduction

As shown in earlier papers<sup>1,2,3</sup> in this series, the fact that magnetic moments of tetrahedral Co(II) complexes are related to the ligand field strength  $\Delta$ , 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  $\mu_{\text{obs}}$  is the observed moment,  $\mu_{\text{so}} = 3.89$  B.M. is the spin-only moment,  $\lambda'$  is the effective value of the spin-orbit coupling constant in the complexed Co(II) ion and  $\Delta$  measures the strength of the ligand field, means that magnetic moment measurements can provide a basis for determining values of  $\Delta$ . Absolute  $\Delta$  values could be determined if  $\lambda'$  values were independently known, but this is seldom the case. Hence, by assuming that the  $\lambda'$  values vary slowly and regularly with  $\Delta$ , relative  $\Delta$  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 as<sup>4</sup>

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

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 Coordination 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.<sup>5</sup> 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,<sup>6</sup> who have examined complexes of the type *trans*-[L, piperidine PtCl<sub>2</sub>]. 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  $\text{R}_3\text{P}$  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).