

plexes of the *n*-Pr series indicates that weak axial effects perturb Δ to an extent comparable to that in the unsubstituted complex. It is concluded that steric inhibition of association is the dominant effect in the diminution or complete loss of solution paramagnetism by the N-methyl complexes.

The small red shifts in the spectra of the alkyl-substituted complexes point out the general situation accounting for the ease in obtaining paramagnetism in the N-alkylsalicylaldimine complexes. In bis-(salicylaldimine)-Ni(II) the spin-allowed visible band (presumably $^1A_g - ^1B_{3g}$) occurs at 555 $m\mu$, and neither this complex^{2,3} nor its 3-isopropyl variant becomes fully paramagnetic in pyridine. Upon replacing the imine hydrogen by the more strongly electron releasing methyl group, the visible band in chloroform is shifted ~ 1700 cm^{-1} to lower energies and Δ becomes negative in pyridine. These results are anticipated by the weak field model¹¹ in D_{2h} symmetry. In the salicylaldimines the in-plane ligand field provided by the O_2N_2 donor set and modified by the nitrogen substituent is such that Δ is more or less perturbed by weak axial effects. It would be of interest to assess the criticality of this range of field strengths by comparison with other ligands providing D_{2h} symmetry, but sufficient data on other systems are not yet available.

It is a general conclusion of symmetry arguments that the d^8 configuration in each of the three common planar symmetries should possess in some range of ligand parameters a triplet ground state. An important point at issue in the study of any series of quadricoordinate Ni(II) complexes is whether

or not a triplet ground state can be stabilized strictly as a result of the in-plane ligand field strengths. This is evidently not possible with the N-alkylsalicylaldimine complexes in solution nor with certain Ni(II) β -diketone complexes³¹ whose paramagnetism is the result of molecular association. Attempts in this work to alter the ligand field strength sufficiently to cause a change in spin state resulted in diamagnetic solids when the medium to strong electron withdrawing groups $CH_2C_6H_5$, $CH(C_6H_5)_2$ and CH_2CF_3 were appended to nitrogen. Only $-CH_2CF_3$ affected the visible spectrum, and the small red shift seems curious if the field retains D_{2h} symmetry. However, it has been found possible to produce extensive population of the triplet state in both the solid and solution when the nitrogen substituent is aromatic.³⁰ These complexes will be the subject of a forthcoming part of this series.

The results of this investigation together with the earlier significant findings on Ni(II) bis-(β -diketone) complexes³¹ emphasize the necessity for the consideration of solute association in solution and specific associative interactions in the solid among those factors which may lessen the tetragonal character of the ligand field and hence promote the relative stability of a triplet state.

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The Electronic Structures of Tetrahedral Cobalt(II) Complexes

BY F. A. COTTON,^{1a} D. M. L. GOODGAME^{1b} AND M. GOODGAME

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Thorough spectral and magnetic studies of the tetrahedral Co(II) species $[CoI_4]^{2-}$, $[CoBr_4]^{2-}$, $[CoCl_4]^{2-}$, are reported. New data on some other tetrahedral species are also given, and from these and previously reported data the following general conclusions, *inter alia*, about tetrahedral Co(II) complexes and their electronic structures are drawn. (1) The order of ligands in the spectrochemical series, as deduced from the Δ values, agrees well with the established order and several additional ligands are now accurately or approximately located in the general order. (2) From the Racah parameters (B'), and from the spin-orbit coupling constants (λ'), we obtain two more or less independent lines of evidence that appreciable overlap of metal and ligand orbitals occurs in these complexes. (3) $[CoX_4]^{2-}$ ions probably are not obtained, or only partially obtained, in aqueous solutions of Co(II), even when saturated with HX or LiX (X = Cl, Br, I). (4) $Co(OH)_2$ dissolves in concentrated alkali metal hydroxide to give one or more tetrahedral species, which probably are $[Co(OH)_4]^{2-}$ and/or $[Co(OH)_3(H_2O)]^-$.

Introduction

Previous papers from this Laboratory have reported spectral and magnetic data concerning the electronic structures of tetrahedral complexes of cobalt(II) and discussed the analysis and interpretation of these data for several groups of compounds.²⁻⁶ There is also a number of papers from

other laboratories containing experimental and theoretical contributions to this subject. Many of these⁷⁻¹⁷ will be discussed later in this paper.

(1) (a) Alfred P. Sloan Foundation Fellow. (b) Now in the Department of Chemistry, Imperial College of Science and Technology, London.

(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) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2983 (1960).

(5) F. A. Cotton and M. Goodgame, *ibid.*, **83**, 1777 (1961).

(6) F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco, *ibid.*, **83**, 4157 (1961).

(7) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

(8) C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

(9) T. Dreisch and W. Trommer, *Z. physik. Chem.*, **B97**, 37 (1937).

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

(11) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(12) B. N. Figgis and R. S. Nyholm, *ibid.*, 338 (1959).

(13) B. N. Figgis, *Trans. Faraday Soc.*, **56**, 1553 (1960).

TABLE I
 FORMULAE, PROPERTIES AND ANALYTICAL PURITY OF THE COMPLEXES

Compound	Color	M.p., °C. ^b	Yield, %	Analytical data ^a							
				C		H		N, As or Cs		Halogen	
				Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$[(n-C_4H_9)_4N]_2[CoCl_4]$	Blue	182.5	97	56.04	56.05	10.45	10.58	4.22	4.09
$Cs_3[CoCl_4]Cl^c$	Blue	62.92	62.80	27.63	27.92
$[(n-C_4H_9)_4N]_2[CoBr_4]$	Pale blue	104.5	90	44.44	44.51	8.28	8.40	3.50	3.24	37.14	37.02
$[(n-C_4H_9)_4N]_2[CoI_4]$	Pale green	139	84	36.68	36.55	6.98	6.90	2.66	2.66
$[(C_6H_5)_2CH_3As]_2[CoI_4]$	Pale green	166.5	90	37.75	37.88	3.00	3.06	12.39	12.33	41.98	42.11
$[C_9H_3N]_2[CoI_4]$	Pale green	160 dec.	75	26.47	26.14	2.12	1.95	3.35	3.39	61.30	61.39

^a Microanalyses by S. M. Nagy, M.I.T. and Schwarzkopf Microanalytical Laboratories, Long Island, New York. ^b Uncorrected. ^c Cobalt: found, 9.13; calcd., 9.28.

This paper has two purposes. First, we wish to report new magnetic and spectral data, especially for the very important tetrahalo complexes. Secondly, we wish to present a critical summary of magnetic and spectral data and derived parameters descriptive of the electronic structures for these and various other tetrahedral cobalt(II) complexes in order to give an over-all picture of our present knowledge and understanding of the subject.

Experimental

Preparation of Compounds. Tetra-*n*-butylammonium Tetrahalocobaltate(II) Complexes.—The compounds $[n-Bu_4N]_2[CoX_4]$, X = Cl, Br, I, were prepared by the following general method. The tetra-*n*-butylammonium halide and cobalt halide were mixed in 2 to 1 molar ratio in hot absolute ethanol. For the chloro- and bromo-complexes, hot benzene was added to the ethanol solutions until crystallization of the compound began, while for the iodo-complex, ethyl acetate was used as the precipitating agent. Good yields (~90%) of the crystalline complexes were obtained. Tetra-*n*-butylammonium tetrachlorocobaltate(II) was recrystallized from acetone (57% recovery). Further details of the compounds are given in Table I.

Analytical data, melting points and approximate yields of all of the compounds used in the studies described here are collected in Table I.

Deuteriochloroform was purchased from Volk Radiochemical Company.

Spectral Measurements.—A Cary Model 14 recording spectrophotometer was used for all measurements. Mulls were prepared using hexachlorobutadiene (C_4Cl_6) or Nujol by hand grinding in an agate mortar. Ordinary chloroform and dichloromethane absorb too strongly to be useful at wave lengths longer than 2200 $m\mu$ whereas $CDCl_3$ is useful to at least 2600 $m\mu$. Similarly, concentrated NaOH in H_2O cuts out at ~1350 $m\mu$ while NaOD in D_2O is useful to ~1800 $m\mu$.

Magnetic Measurements.—These were made with a Gouy balance using $HgCo(NCS)_4$ for calibration as previously described.^{2,5,6}

Results

The Tetrahalo Ions, $[CoX_4]^{2-}$. Spectral Studies.

—The first attempt to study the spectra of these ions was reported by Dreisch and Trommer⁹ who used solutions of the cobalt halides in concentrated aqueous hydrohalic acids. Their results have been used, in the absence of any others for ν_2 , to estimate the ligand field strengths^{7,8} in these

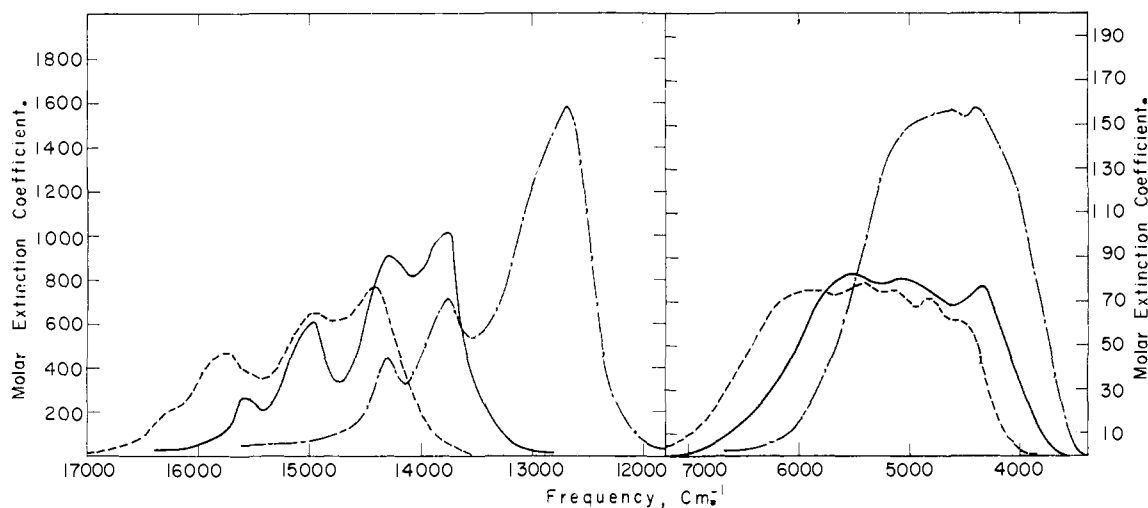


Fig. 1.—Spectra of the $(n-Bu_4N)_2[CoX_4]$ salts: -----, X = Cl; dissolved in CH_2Cl_2 containing 0.1M $(n-Bu_4N)Cl$; ———, X = Br, dissolved in CH_2Cl_2 containing 0.1M $(n-Bu_4N)Br$; - · - · - ·, X = I, dissolved in $CHCl_3$ containing 0.1M $(n-Bu_4N)I$.

Methyltriphenylarsonium Tetraiodocobaltate (II).—This compound was prepared by the method of Gill and Nyholm.¹¹

Quinolinium Tetrahalocobaltate (II) Complexes.—The preparation of these compounds has been described previously.²

(14) D. S. McClure, *Phys. and Chem. Solids*, **3**, 311 (1957).

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

(16) S. Buffagni and T. M. Dunn, *Nature*, **188**, 937 (1960).

(17) D. R. Stephens and H. G. Drickamer, *J. Chem. Phys.*, **35**, 429 (1961).

ions. While there is no doubt that the main features of the assignment and analysis of the older spectral data for the $[CoX_4]^{2-}$ ions, as given by Orgel⁷ and by Ballhausen and Jørgensen,⁸ are correct,² the need for more accurate and reliable data with which to test and correlate theoretical treatments of the spectral and magnetic properties of tetrahedral cobalt(II) complexes is quite evident.

TABLE II
SPECTRAL DATA FOR TETRAHALOCOBLT IONS^a

Compound	State	Doublets					
(Bu ⁿ ₄ N) ₂ CoCl ₄	Hexachlorobutadiene mull	22000		18900	18100	17300	
	CH ₂ Cl ₂			18900(9)		17300sh	
	CH ₂ Cl ₂ + 0.1 M (Bu ⁿ ₄ N)Cl			18830(10)			
(QH) ₂ CoCl ₄	Hexachlorobutadiene mull	22100	19400	18800	18150		
	Nujol mull						
	MeNO ₂ 0.01 M	22100(2)	19600sh	18760(9,4)			
Cs ₂ CoCl ₄	Hexachlorobutadiene mull	22030	19650sh	18830	18200sh	17240	
	Co ³⁺ in 12 N HCl						
	Co ³⁺ in saturated LiCl						
(Bu ⁿ ₄ N) ₂ CoBr ₄	Hexachlorobutadiene mull	23400	22900	21800	21500	21150	20800
	CH ₂ Cl ₂				21400(10)		
	CH ₂ Cl ₂ + 0.1 M (Bu ⁿ ₄ N)Br						17920
	CDCl ₃ 0.001 M						
(QH) ₂ CoBr ₄	Hexachlorobutadiene mull		22900		21500	21100	20600
	MeNO ₂ 0.01 M						
	Co ³⁺ in 48% HBr						
	Co ³⁺ in saturated LiBr						
(Bu ⁿ ₄ N) ₂ CoI ₄	Reflectance						
	Hexachlorobutadiene mull						
	CHCl ₃						
	CHCl ₃ + 0.1 M (Bu ⁿ ₄ N)I						
(QH) ₂ CoI ₄	Reflectance						
	Hexachlorobutadiene mull		19700 ^a	19000 ^a	17900		
	MeNO ₂	21100 ^a	20000 ^a		18300		
	Acetone 0.001 M						
(Me(C ₂ H ₅) ₂ As) ₂ CoI ₄	Reflectance						
	Hexachlorobutadiene mull	21000 ^a	19800 ^a	19050 ^a	18020	16500	15700
	MeNO ₂ 0.001 M				18100(10)	~16300sh	
	Acetone 0.001 M				18350(8)	~16300sh	
	Co ³⁺ in conc. HI						
	Co ³⁺ in satd. LiI						

^a All frequencies in cm.⁻¹; molar extinction coefficients are given in parentheses. ^b 5900–6250 cm.⁻¹ obscured by solvent

All of the spectral data collected in this work are presented in Table II, and the values chosen for the energies of ν_2 and ν_3 , together with the values of Δ , B' and β derived therefrom are given in Table III. A few remarks concerning the choice of the former and the method of computing the latter must be made. Selection of single energy values for ν_2 and ν_3 is necessarily arbitrary to a degree. Figure 1 shows some of the recorded spectra and serves to illustrate the points now to be discussed. It will first be noted that the ν_2 bands are broad and exhibit a great deal of fine structure. Some splitting is to be expected as a result of spin-orbit coupling, and Stahl-Brada and Low¹⁵ have published the theoretical results. As already noted for the [Co(N₃)₄]²⁻ and [Co(NCO)₄]²⁻ cases,⁵ the separation of the highest and lowest energy sub-bands of ν_2 is considerably greater than the value of $\delta\lambda$ (the calculated value¹⁵), even taking for λ the full free-ion value of 178 cm.⁻¹. For the tetrahalo ions there is the further complication that more than the three peaks expected because of splitting by spin-orbit coupling are present. The most likely explanation of these observations is one suggested by McClure,¹⁸ which is that dynamic Jahn-Teller effects in the excited states are responsible for the number and energy spread of the components of these bands. In view of these considerations there seems at present no more sophisticated way of selecting energies for the ν_2 bands, using observations on isotropic samples at room temperature, than by taking the center of

(18) D. S. McClure, R.C.A. Laboratories, private communication. Dr. McClure also has considerable experimental evidence in the form of highly resolved, polarized spectra of Cu³⁺ in several zinc calconides to support his proposal.

gravity of the total intensity, and this has been done by visual estimation. The values are accurate to within at least ± 200 cm.⁻¹. For the ν_3 bands the same effects with, evidently, the same explanations are encountered and a similar procedure has been adopted for selecting the energies. Those sub-bands on the high energy side of ν_3 with maxima less than about 1/10 those of the strongest peaks were excluded in the energy estimations. On the other hand as before⁵ they were included in estimating the oscillator strengths of the ν_3 bands, since they borrow most of their intensity from the stronger neighboring bands.

The values of Δ and B' were calculated from the energies of ν_2 and ν_3 using the equations of Tanabe and Sugano,¹⁹ which are derived using a Hamiltonian which does not include spin-orbit coupling. In order to obtain a general view of the energy level pattern given by such a treatment in the range of Δ and B' values of interest for real tetrahedral complexes of Co(II), the Tanabe and Sugano matrices were solved on an IBM 704 digital computer for the range of Δ 2500–5000 cm.⁻¹ with B' equal to 710 cm.⁻¹ and C' equal to 3290 cm.⁻¹. The results for levels below 30,000 cm.⁻¹ are presented in Fig. 2.²⁰

The oscillator strengths of the ν_2 and ν_3 bands of the tetrahalo ions were evaluated graphically and are given in Table IV.

Magnetic Studies.—In this work, the magnetic susceptibilities of three salts containing the [CoI₄]²⁻ ion, one containing the [CoBr₄]²⁻ ion and two containing the [CoCl₄]²⁻ ion have been measured

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

(20) We are indebted to Dr. W. D. Horrocks, Jr., for carrying out these computations.

ν ₂ Band					ν ₃ Band				
16230sh	15750		14900	14300	5920	5400	5100	4780	
16260sh	15770(450)	15600sh	15000(630)	14310(750)	b	5440(78)	5180(75)	4820(71)	
16200sh	15750(469)	15600sh	14950(646)	14310(765)	b	5428(82)	5152(80)	4812(74)	
16230sh	15720	15430	14900	14200	6140		5260	4980	
	Broad absorption 15700-13500				6110	5550	5280sh	4975	4650
16250sh	15870(375)	15450sh	14930(555)	14290(600)	6120(67)	5470(70)	5180(69)	4820(66)	
16200sh		15600	14900sh	14290	6128	5592	5313	4981	4726
16400sh	16080(272)		15040(422)	14490(463)	6170	5630			
16400sh	16060(357)	15630sh	15150(539)	14530(583)					
	15530	14900	14200	13700	5460	4880		4390	
	15600(250)	14950(600)	14290(890)	13740(1000)	5540	5000			
	15530(300)	14990(600)	14310(900)	13790(1000)	5500(97)	4980(99)		~4350(97)	
					5556(82)	5050(80)		4370(76)	
	15500	14930	14040	13666	5560	5080		4550	
16130(117)	15600(313)	14970(550)	14180(845)	13700(783)	7010(13)	Broad absorption 5780-4650(~75)			
	15700(244)	15100(372)	14360(599)	13830(628)	6920sh	5750(63)	5360sh	4620(17)	
	15700(350)	15080(529)	14360(855)	13840(913)		5780(92)			
15400sh			13400sh	12600					
	14300	13800		12750		Broad absorption 5000-4100			
15200(400)	14430sh	13900(690)	13300(890)			Broad absorption centering at 5700(~96)			
	14290(444)	13760(707)		12710(1593)		Broad absorption centering at 4700(155) with shoulder at 4170			
15000(384)	14450sh		13400(1055)						
15050sh		Broad absorption 13700-12000							
15200sh	14120		13500	12950	12270	Broad absorption 5550-4350			
14970sh	14245(570)	13643(960)	13245(970)	12660(1120)		6540(50)	Broad absorption 5350-3950(~150)		
15400sh			13330sh	12500					
	14300	13700	13120	12500		Broad absorption 5200-4550			
15060(492)	14250(720)		13460(1146)						
15000(372)	14450sh		13400(1040)						
	14370(373)	13750(482)	13200sh	12680(1023)					
	14340(485)	13700(595)	13160sh	12670(1366)			5620(77)		

absorption. * Shoulder on side of charge transfer band.

at three temperatures, usually on several different samples of each compound. These susceptibility values then were corrected for diamagnetism and temperature-independent paramagnetism (t.i.p.) to provide the fully corrected molar susceptibilities, χ_M^{corr} , which are listed, together with the corrections, in Table V. Reciprocals of these corrected molar susceptibilities then were plotted against temperature and, from the resulting straight lines, the magnitudes of μ and θ were obtained. The t.i.p. corrections were calculated from the Δ values in Table VII, taking the mean Δ value where a range is given, using the relation¹³ t.i.p. = $2.09/\Delta$.

Finally, in Table VI, we have tabulated all of the results obtained in the present study together with results recalculated by the present procedure (*i.e.*, using a t.i.p. correction) from the earlier data of Holm and Cotton.²

The $[\text{Co}(\text{OH})_4]^{2-}$ or $[\text{Co}(\text{OH})_3(\text{H}_2\text{O})]^-$ Ion.—It has long been known that $\text{Co}(\text{OH})_2$ is slightly amphoteric, dissolving in very concentrated aqueous alkali metal hydroxides to give deep blue solutions. We have studied the spectra of these solutions and the results, shown in Fig. 3, demonstrate clearly that a tetrahedral complex, or conceivably several, is present. Using OH^- ion in H_2O it was not possible to record ν_2 in its entirety because of strong interference by the vibrational absorption of the solvent and the OH^- , but this difficulty was circumvented by using a deuterated solvent system prepared from metallic sodium and 99.5% D_2O . The observed extinction coefficients of ν_2 and ν_3 are appreciably lower than those for the corresponding bands in other $[\text{CoX}_4]^{2-}$ species, *e.g.*, the tetrahalo ions. Although it is

quite possible that the observed values represent the true molar absorbances of the tetrahedral species present, we have no evidence to prove this. It is also possible that the observed extinction coefficients are low because some significant fraction (as high, possibly, as half) of the cobalt(II) is present in octahedral environments. This would not be detectable from the spectrum since (1) the extinction coefficients for the three absorption bands of octahedral species are only of the order of 10, and (2) the absorption bands of octahedral species likely to be present in this system would very probably occur at about the same frequencies as the strong ones due to the tetrahedral species. In support of these statements we may cite the work of Ballhausen and Jørgensen⁸ who reported that the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion has its two high energy bands at $\sim 16,000$ and $\sim 20,000$ cm^{-1} (with extinctions of only ~ 5) and its low energy band at ~ 8000 cm^{-1} .

In view of the conclusion which will be drawn later that even in the most concentrated aqueous hydrohalic acids and lithium halide solutions complete conversion of $\text{Co}(\text{II})$ to $[\text{CoX}_4]^{2-}$ species probably does not occur, we feel that these concentrated base solutions cannot necessarily be assumed to contain $[\text{Co}(\text{OH})_4]^{2-}$ as the only tetrahedral $\text{Co}(\text{II})$ complex. It seems possible that some significant amount of $[\text{Co}(\text{OH})_3(\text{H}_2\text{O})]^-$ may also be present.

NOTE ADDED IN PROOF.—Subsequent to the acceptance of this paper for publication we came upon the paper of S. Gordon and J. M. Schreyer, *J. Am. Chem. Soc.*, **74**, 3169 (1952). These authors presented data which led them to conclude that the blue species is a trihydroxo complex. However, their results are also consistent with the presence

TABLE III

SUMMARY OF SPECTRAL AND MAGNETIC DATA AND DERIVED ELECTRONIC STRUCTURE PARAMETERS FOR THE TETRAHALO-COBALT(II) COMPLEXES

Compound and state ^a	Experimental data			Calculated parameters			
	ν_2 , cm. ⁻¹	ν_1 , cm. ⁻¹	μ , B.M.	Δ , cm. ⁻¹	B' , cm. ⁻¹	β	λ' , cm. ⁻¹
[CoCl ₄] ²⁻							
Co(ClO ₄) ₂ in HCl/H ₂ O	5900	14,750	..	3426	691	0.715	..
Co(ClO ₄) ₂ in LiCl/H ₂ O	5900	14,750	..	3426	691	.715	..
(QH) ₂ [CoCl ₄] in CH ₃ NO ₂	5600	14,700	4.60	3214	711	.735	147
(<i>n</i> -Bu ₄ N) ₂ [CoCl ₄] in CH ₂ Cl ₂	5260	14,700	4.72	3010	729	.754	161
(<i>n</i> -Bu ₄ N) ₂ [CoCl ₄] in CH ₂ Cl ₂ + 0.1 <i>M</i> (<i>n</i> -Bu ₄ N)Cl	5250	14,700	4.72	3003	729	.754	160
(QH) ₂ [CoCl ₄] in C ₄ Cl ₆ mull	5700	14,600	4.60	3275	698	.722	147
(QH) ₂ [CoCl ₄] in Nujol mull	5650	14,600	4.60	3246	701	.725	148
(<i>n</i> -Bu ₄ N) ₂ [CoCl ₄] in C ₄ Cl ₆ mull	5220	14,700	4.72	2985	731	.756	159
Cs ₃ [CoCl ₄]Cl in C ₄ Cl ₆ mull	5580	14,800	4.53	3200	719	.744	132
[CoBr ₄] ²⁻							
Co(ClO ₄) ₂ in HBr/H ₂ O	5750	14,000	..	3316	653	.675	..
Co(ClO ₄) ₂ in LiBr/H ₂ O	5780	14,000	..	3335	652	.674	..
(<i>n</i> -Bu ₄ N) ₂ [CoBr ₄] in CH ₂ Cl ₂	5000 ^b	14,300	4.77	2857	715	.739	162
(<i>n</i> -Bu ₄ N) ₂ [CoBr ₄] in CH ₂ Cl ₂ + 0.1 <i>M</i> (<i>n</i> -Bu ₄ N)Br	5000 ^b	14,300	4.77	2857	715	.739	162
(QH) ₂ [CoBr ₄] in CH ₃ NO ₂	5210 ^b	14,000	4.68	2987	683	.706	152
(<i>n</i> -Bu ₄ N) ₂ [CoBr ₄] in C ₄ Cl ₆ mull	4880	14,200	4.77	2790	715	.739	158
(QH) ₂ [CoBr ₄] in C ₄ Cl ₆ mull	5080	13,800	4.69	2910	677	.700	148
[CoI ₄] ²⁻							
Cl(ClO ₄) ₂ in HI/H ₂ O	..	13,200
Co(ClO ₄) ₂ in LiI/H ₂ O	5620	13,200	..	2350	605	.626	..
(QH) ₂ [CoI ₄] in CH ₃ NO ₂	4930	13,200	4.77	2830	643	.665	160
(<i>n</i> -Bu ₄ N) ₂ [CoI ₄] in CHCl ₃	5700	13,800	4.86	3300	642	.664	205
(<i>n</i> -Bu ₄ N) ₂ [CoI ₄] in CH ₃ Cl + 0.1 <i>M</i> (<i>n</i> -Bu ₄ N)I	4700	13,200	4.86	2688	640	.662	169
(<i>n</i> -Bu ₄ N) ₂ [CoI ₄] in C ₄ Cl ₆ mull	4540	13,500	4.86	2590	685	.708	165
(QH) ₂ [CoI ₄] in C ₄ Cl ₆ mull	4700	13,000	4.77	2690	642	.664	152
((C ₆ H ₅) ₂ MeAs) ₂ [CoI ₄] in C ₄ Cl ₆ mull	4700	13,000	4.69	2690	642	.664	142

^a Abbreviations: HX/H₂O = satd. aqueous HX; LiX/H₂O = satd. aqueous LiX; QH = quinolinium ion; CHCl₃ also represents CDCl₃; C₄Cl₆ = hexachlorobutadiene. ^b Exact position doubtful because of solvent absorption on low energy side.

TABLE IV

OSCILLATOR STRENGTHS FOR THE [CoX₄]²⁻ IONS

Compound	Solvent	$f\nu_2^a$	$f\nu_2$	$f\nu_3/f\nu_2$	$\frac{4\nu_3}{\nu_2}$
(<i>n</i> -Bu ₄ N) ₂ [CoI ₄]	CHCl ₃ ^b + 0.1 <i>M</i> (<i>n</i> -Bu ₄ N)I	8.12×10^{-3}	11.1×10^{-4}	7.17	12.6
(<i>n</i> -Bu ₄ N) ₂ [CoBr ₄]	CH ₂ Cl ₂	5.89×10^{-3}		8.38	11.44
	CDCl ₃		7.10×10^{-4}		
(<i>n</i> -Bu ₄ N) ₂ [CoCl ₄]	CH ₂ Cl ₂	5.09×10^{-3}	7.21×10^{-4}	7.07	11.18

^a Including intensity of small bands on high energy side of the strongest peaks. ^b CDCl₃ used for ν_2 band to eliminate solvent absorption.

of a mixture of tri- and tetrahydroxo species, and perhaps even with the predominance of a tetrahydroxo species if one takes a less optimistic view of the accuracy of activity corrections in very concentrated OH⁻ solutions. Of course their tacit suggestion, by use of the formula [Co(OH)₃(H₂O)₃]⁻, that the trihydroxo species is octahedral can be dismissed according to the arguments presented in this paper.

Because solutions sufficiently concentrated for accurate measurements of the moment of the Co(II) could not be prepared and because of the uncertainty about the state of all Co(II) in solution, no magnetic measurements were made on these solutions.

Discussion

Solvent Effects on Spectra of [CoX₄]²⁻ Ions.—As we have noted in the introduction, the only previously reported study which could be used as a comprehensive source of spectral data for the [CoX₄]²⁻ ions is that of Dreisch and Trommer,³ who

studied solutions of the Co(II) halides in concentrated aqueous hydrohalic acids. It has been optimistically assumed^{7,8} that the spectra so obtained are those of the [CoX₄]²⁻ species but there has been no proof of this. The studies reported here show, in fact, that the spectra so obtained are not those of the [CoX₄]²⁻ ions.

In addition to repeating Dreisch and Trommer's work using concentrated hydrohalic acids we also have used saturated aqueous solutions of the lithium halides in a further attempt to effect complete conversion of the Co(II) to [CoX₄]²⁻ species, but again, as shown below, this does not appear to be possible.

It will be seen from Table II that the absorption spectra of the various salts and solutions, which might all be supposed to contain the same [CoX₄]²⁻ species, exhibit certain differences, and the aqueous systems particularly are consistently

TABLE V
MAGNETIC DATA FOR SALTS OF THE TETRAHALO $[\text{CoX}_4]^{2-}$
IONS

Temperature, °K.	Specimen no. ^a	Dia- magnetic corr., ^b c.g.s.u. $\times 10^6$	T.i.- p., ^c c.g.s.u. $\times 10^6$	$\chi_{\text{M}}^{\text{corr.}} \times 10^6$, c.g.s. units ^d	μ , B.M. ^e	θ , °K. ^e
[[$(n\text{-C}_4\text{H}_9)_4\text{N}$] ₂][CoI ₄]						
296.9	(1)	-612	800	9,720	4.88	-7
194.5	(1)			14,770		
73.2	(1)			36,910		
298.8	(1)			9,344	4.83	-9
194.5	(1)			14,450		
73.2	(1)			35,375		
297.7	(2)			9,677	4.88	-7
194.5	(2)			14,645		
72.7	(2)			37,040		
[CH ₃ (C ₆ H ₅) ₂ As] ₂ [CoI ₄]						
297.7	(1)	-533	800	8,719	4.64	-7
194.5	(1)			13,175		
73.7	(1)			33,260		
298.6	(1)			9,100	4.70	-7
194.5	(1)			13,510		
74.2	(1)			33,570		
300.4	(2)			8,922	4.69	-7
194.5	(2)			13,550		
73.2	(2)			34,190		
298.2	(3)			9,101	4.71	-8
194.5	(3)			13,540		
72.7	(3)			34,010		
[C ₆ H ₅ N] ₂ [CoI ₄]						
296.8	(1)	-392	800	9,230	4.79	-10
194.8	(1)			13,760		
73.1	(1)			34,290		
296.4	(2)			8,961	4.72	-9
195	(2)			13,360		
73	(2)			33,050		
297.7	(2)			9,120	4.75	-10
195	(2)			13,590		
73.2	(2)			33,790		
[[$(n\text{-C}_4\text{H}_9)_4\text{N}$] ₂][CoBr ₄]						
298.2	(1)	-548	750	9,144	4.76	-10
194.2	(1)			13,635		
73.7	(1)			34,210		
299.4	(1)			9,219	4.78	-10
194.7	(1)			13,839		
73.7	(1)			34,417		
[[$(n\text{-C}_4\text{H}_9)_4\text{N}$] ₂][CoCl ₄]						
300.4	(1)	-508	700	8,928	4.72	-12
194.7	(1)			13,158		
73.7	(1)			33,547		
298.8	(1)			9,028	4.72	-12
194.7	(1)			13,152		
73.2	(1)			32,550		
Cs ₂ [CoCl ₄]Cl						
299.1	(1)	-135	700	8,528	4.56	-3
194.7	(1)			13,004		
74.2	(1)			33,424		
298.6	(1)			8,623	4.56	-4
194.7	(1)			12,915		
73.7	(1)			32,764		

^a Different numbers indicate that the specimens were from different preparations or, at least, from separately recrystallized batches. Repetition of the same specimen number at the same (or nearly the same) temperature indicates a repacking of the tube. ^b Diamagnetic corrections were estimated from Pascal's constants as tabulated in P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 92 ff. ^c Temperature-independent paramagnetism was calculated from the expression¹⁸ $8N\beta^2/\Delta = 2.09/\Delta$ where Δ is in cm^{-1} . ^d $\chi_{\text{M}}^{\text{corr.}}$ means the measured molar susceptibility corrected for both diamagnetism and t.i.p. ^e Calculated from the equation $\mu = 2.84 [\chi_{\text{M}}^{\text{corr.}} (T - \theta)]^{1/2}$.

different from the others. These differences are suitably represented by the values of ν_2 , ν_3 , Δ and B' given in Table III, and it will be convenient in the following discussion to refer to these rather than to the raw data.

As we have done previously in dealing with the spectra of tetrahedral Ni(II) complexes²¹ we begin

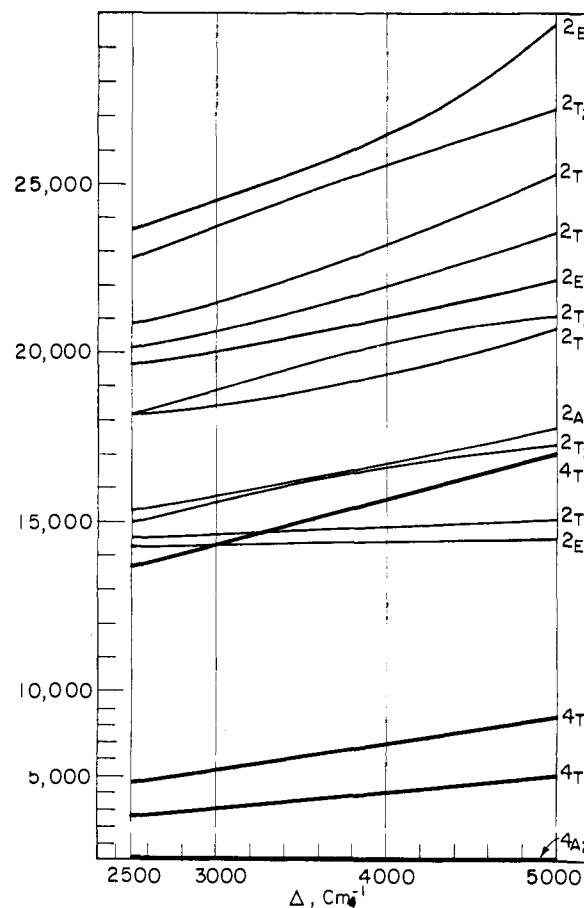


Fig. 2.—Energy levels for tetrahedrally coordinated Co(II) as obtained from Tanabe and Sugano's¹⁹ secular equations. Only levels lying below 30,000 cm^{-1} are included. The Racah parameters were taken as $B = 710 \text{ cm}^{-1}$, $C = 3290 \text{ cm}^{-1}$. Note the change in the ordinate scale at 10,000 cm^{-1} . The quartet levels are shown with heavier lines than those for the doublet levels.

with the assumption that the spectra of the solid compounds are the true spectra of the $[\text{CoX}_4]^{2-}$ ions. It will be seen in Tables II and III that the several salts containing a given $[\text{CoX}_4]^{2-}$ ion have

(21) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

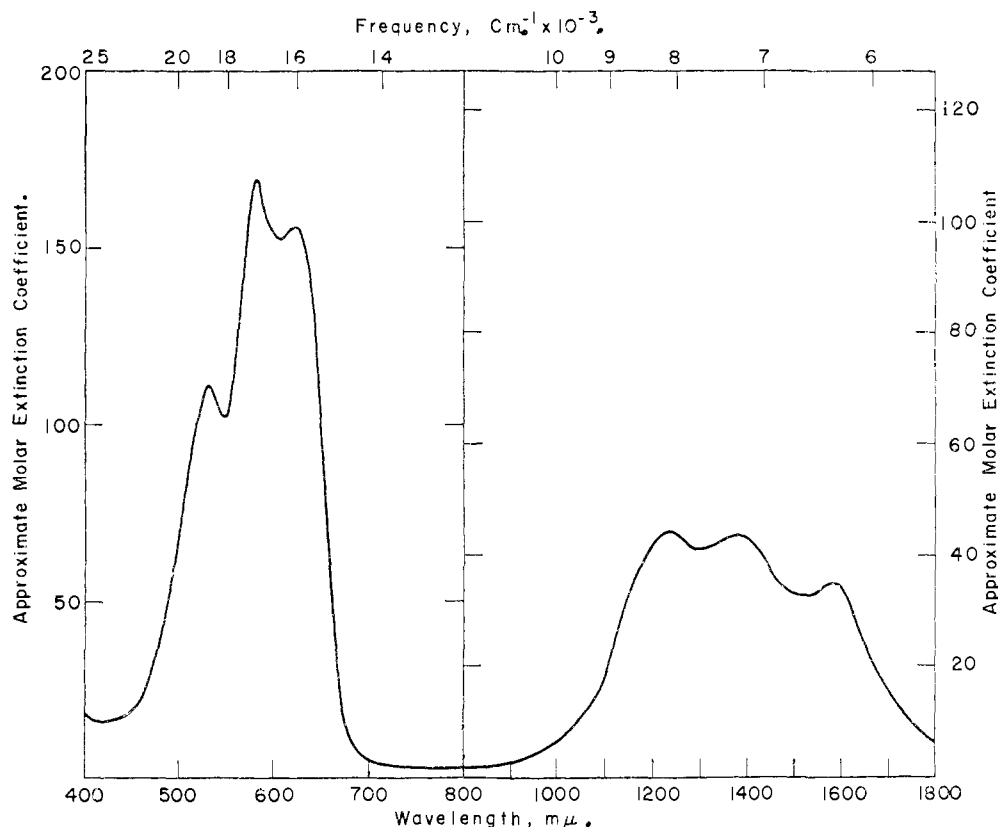


Fig. 3.—The visible and near infrared spectrum of Co(II) in ~ 50 wt. % aqueous NaOH (out to ~ 1350 $m\mu$) and in $\sim 50\%$ NaOD in D_2O (from ~ 1350 to 1800 $m\mu$). The molar extinction coefficients are only approximate ($\pm 20\%$) since the Co(II) concentrations are only approximately 0.005 M .

essentially the same spectra: the differences in the Δ values obtained do not exceed $\sim 4\%$ with the exception of those for the several $[CoCl_4]^{2-}$ compounds.

It was found that the spectra of these compounds in organic solvents such as nitromethane, chloroform and dichloromethane often, though not always, showed some significant variations from the spectra of the solids. These were seldom large (*cf.* Tables II and III), except for salts of $[CoI_4]^{2-}$. This ion seems to be the most sensitive to its environment. Thus, $(n-Bu_4N)_2[CoI_4]$ in chloroform has a ν_2 band which is broader, more structured and centered at a very significantly higher frequency than it is in the solid compound, and even ν_3 is very noticeably affected in both contour and mean frequency. This is most likely attributable to actual solvolysis of the $[CoI_4]^{2-}$ ion rather than to mere distortion of it (although it seems surprising that $CHCl_3$ affects it more severely than does CH_3NO_2), and the addition of 0.1 mole/l. of $(n-Bu_4N)I$ to the solution dramatically alters the spectrum so that it becomes essentially the same as those of the solid compounds containing the $[CoI_4]^{2-}$ ion. A similar effect has been reported previously for $[NiX_4]^{2-}$ compounds.^{11,21}

If it is then assumed that the spectra observed for the solid compounds and their solutions in organic solvents of relatively low dielectric constant and coördinating power (with added halide salt if necessary) are the spectra of the $[CoX_4]^{2-}$

ions, then there is no doubt that the spectra observed for the solutions in concentrated aqueous HX or LiX are largely, if not entirely, those of some tetrahedral species other than $[CoX_4]^{2-}$. Most probably they are mainly the spectra of $[CoX_3H_2O]^-$ species; this supposition is in agreement with the fact that the energies of the bands in the aqueous systems are always higher than the true band energies for the $[CoX_4]^{2-}$ species, since H_2O lies to the stronger end of the spectrochemical series relative to the halide ions.

In Table VII we record the experimental results and derived parameters obtained from those spectra which are regarded as authentic for the $[CoX_4]^{2-}$ ions in the light of the above discussion. The conclusions of Buffagni and Dunn¹⁶ about the true spectrum of $[CoCl_4]^{2-}$ are in agreement with ours; their Δ value (3250 cm^{-1} , obtained in an unspecified manner) falls within our range.

Magnetic Results.—The final results of all of the new and recalculated magnetic measurements are listed in Table VI. It should first be noted that for quantitative purposes these results now supplant those reported earlier.² The earlier results were of qualitative and relative significance but because it was not then possible to make t.i.p. corrections their absolute magnitudes and all quantities calculated therefrom are superseded by the results given here.

One of the interesting and significant features of the rather extensive data in Table VI is the vari-

TABLE VI
SUMMARY OF ALL MAGNETIC MOMENTS AND θ VALUES FOR $[\text{CoX}_4]^{2-}$ COMPOUNDS IN THIS LABORATORY^a

Compound	Source and specimen no.	Corrections used		μ , B.M.	θ
		Dia.	t.i.p.		
[CoCl ₄] ²⁻					
(<i>n</i> -Bu ₄ N) ₂ [CoCl ₄]	This paper (1)	-508	700	4.72	-12
CS ₂ [CoCl ₄]Cl	This paper (1)	-135	700	4.56	-3.5
	Holm and Cotton ²	-135	700	4.50	-4
((C ₆ H ₅) ₂ MeAs) ₂ [CoCl ₄]	Holm and Cotton ²	-475	700	4.57	-1
(C ₆ H ₅ N) ₂ [CoCl ₄]	Holm and Cotton ²	-288	700	4.60	-5
[CoBr ₄] ²⁻					
(<i>n</i> -Bu ₄ N) ₂ [CoBr ₄]	This paper (1)	-548	750	4.77	-10
(C ₆ H ₅ N) ₂ [CoBr ₄]	Holm and Cotton ²	-328	750	4.68	-6
(C ₆ H ₅ N) ₂ [CoBr ₄]	Holm and Cotton ²	-254	750	4.63	0
[CoI ₄] ²⁻					
(<i>n</i> -Bu ₄ N) ₂ [CoI ₄]	This paper (1)	-612	800	4.85	-8
	This paper (2)	-612	800	4.88	-7
(Ph ₂ MeAs) ₂ [CoI ₄]	This paper (1)	-533	800	4.67	-7
	This paper (2)	-533	800	4.69	-7
	This paper (3)	-533	800	4.71	-8
(C ₆ H ₅ N) ₂ [CoI ₄]	This paper (1)	-392	800	4.79	-10
	This paper (2)	-392	800	4.74	-10
	Holm and Cotton ²	-392	800	4.79	-10

^a The experimental data from Holm and Cotton² have been used to recalculate the moments and θ values after making the indicated corrections for diamagnetism and temperature-independent paramagnetism.

TABLE VII
SUMMARY OF ALL SPECTRAL AND MAGNETIC DATA AND DERIVED PARAMETERS FOR REGULAR TETRAHEDRAL COMPLEXES

Experimental datum or parameter	Ligand, X, in [CoX ₄]							
	I ⁻	Br ⁻	Cl ⁻	OH ⁻	N ₃ ^{-a}	-NCO ^{-a}	-NCS ^{-b}	Ph ₂ PO ^c
ν_3 , cm. ⁻¹	4,500-4,700	4,880-5,080	5,220-5,700	7,300	6,750	7,150	7,780	6,240
ν_2 , cm. ⁻¹	13,000-13,500	13,800-14,200	14,600-14,800	16,600	14,900	16,100	16,250	16,300
Δ , cm. ⁻¹	2,590-2,700	2,790-2,910	2,985-3,275	4,230	3,920	4,150	4,550	3,680
B' , cm. ⁻¹	640-690	670-720	690-730	747	658	720	691	787
β (= B'/B)	0.66-0.71	0.70-0.74	0.72-0.75	0.773	0.680	0.745	0.715	0.814
$f(\nu_2) \times 10^3$	1.11	0.710	0.721	0.581	1.49	1.37	3.44	0.647
$f(\nu_3) \times 10^3$	8.12	5.89	5.09	2.98	8.58	6.70	14.6	5.07
$R_{\text{obsd.}} = f(\nu_3)/f(\nu_2)$	7.2	8.4	7.1	5.1	5.8	4.9	4.25	7.8
$R_{\text{calcd.}} = 4\nu_3/\nu_2$	12.6	11.4	11.2	9.1	8.8	9.0	8.4	10.4
$R_{\text{obsd.}}/R_{\text{calcd.}}$	0.572	0.737	0.633	0.560	0.660	0.554	0.507	0.750
μ , B.M.	4.77 ± 0.06	4.69 ± 0.05	4.59 ± 0.05	...	4.47	4.44	4.40	4.53
λ'	140-170	145-160	130-160	...	146	145	149	147

^a Data from ref. 5. ^b Data from ref. 6. ^c Spectral data are new; magnetic moment recalculated from the data of reference 3.

ability of the magnetic moments of a given $[\text{CoX}_4]^{2-}$ species from one compound to another. While some such variability is not surprising the magnitudes are perhaps larger than might have been anticipated. They are at any rate large enough so that the range of values spanned by the $[\text{CoBr}_4]^{2-}$ ion overlaps substantially those spanned by $[\text{CoCl}_4]^{2-}$ and $[\text{CoI}_4]^{2-}$ ions. The average values together with their mean deviations for all of the compounds measured containing each of the $[\text{CoX}_4]^{2-}$ ions are recorded in Table VII. It is seen that the mean values fall quite definitely in the order $[\text{CoI}_4]^{2-} > [\text{CoBr}_4]^{2-} > [\text{CoCl}_4]^{2-}$, as would be expected from the spectrochemical series assuming no wide variations in the λ' values. Thus the main argument of the earlier paper² in which less extensive data, not corrected for t.i.p., were used, is confirmed.

In considering possible reasons for the variability in the magnetic moments it is important to note that Table III shows a general relationship between the moments and the Δ values for solid compounds of a given $[\text{CoX}_4]^{2-}$ species.²² The

relationship is not perfect but appears valid within experimental errors. For instance, the $[\text{CoCl}_4]^{2-}$ salts having moments of 4.53-4.60 B.M. have Δ values of 3200-3275 cm.⁻¹, while the one with the significantly higher moment of 4.72 B.M. has a significantly lower Δ value of 2985 cm.⁻¹. It would appear that the data of Table III warrant the following statement: There is, within the limits of experimental uncertainty, a correlation between the μ and Δ values and sufficient constancy of the λ' values to indicate that the variations in the magnetic moments are caused mainly by small variations in the ligand field strengths from one compound to another.

The cause of the small variations in ligand field strength is most likely to be variations in the amount of compression of the $[\text{CoX}_4]^{2-}$ ions in crystals with different cations. Distortions alone would have no first order effect on the Δ or μ values although they might be partially or wholly responsible for the θ values and their variability,

(22) Relationship meaning in the sense of the well-known^{21,23} equation $\mu_{\text{obs}} = 3.89(1 - 4\lambda'/\Delta)$.

as has been suggested by Figgis.¹³ Recently Stephens and Drickamer¹⁷ have completed a study of the effects of pressure on the spectra of the Cs₂-CoX₄ salts. They find that both ν_2 and ν_3 are significantly sensitive to pressure. The Δ_p/Δ_0 ratio varied from 1.0 to as much as ~ 1.15 for the [CoCl₄]²⁻ and [CoBr₄]²⁻ compounds at ~ 75 kbar. and 1.25 for the [CoI₄]²⁻ compound at ~ 50 kbar. Similarly, Weakliem²³ has found that Δ for Co(II) substituted for the metal ion of the host lattice varies from 3300 cm.⁻¹ in CdS to 3750 cm.⁻¹ in ZnS.

Spin-Orbit Coupling Constants.—One of the most interesting results of the coordinated spectral and magnetic study reported here and in several preceding papers^{5,6} are the λ' values, that is, the effective values of the spin-orbit coupling constants for the Co(II) ion in the complexes. It was pointed out by Owen²⁴ that λ' values in complexes appear generally to be lower than the λ values in the free ions, and Owen²⁴ and Dunn²⁵ have discussed possible reasons for this. Both orbital overlap resulting in delocalization of the d electrons and interpenetration of metal and ligand charge clouds resulting in increased screening of the d electrons, which in turn increases their mean orbital radii, have been suggested. These are probably best considered as alternative descriptions of the same physical process.

As shown in the bottom row of Table VII λ' values in all of the tetrahedral Co(II) complexes which have been studied are 60 to 90% of the free ion value (178 cm.⁻¹); the average λ' is $\sim 0.83\lambda$. Although the uncertainties are sufficient to obscure small variations of λ' with ligand field strength or B' values, the data in Table VII do not reveal any marked correlation of λ' values with other electronic structure parameters.

Since the β values and the λ'/λ ratios are all thought to be related to the degree of orbital overlap in the metal-ligand bonding, it might be supposed that plotting one of these against another would yield a straight line. However, this was not found to be so; instead, the scatter seemed random. In view of the facts that for the λ' values the uncertainties in each of the values are about equal to the whole range covered and for the β 's the uncertainties are perhaps equal to about half of the entire range covered, the lack of any good straight-line relationship is without significance.

The Average Ligand Field Approximation.—It is reasonable to suppose that when a complex contains several kinds of ligands which do not differ sufficiently to produce distinct splittings of the spectral bands, it will be possible to treat the complex as though it contained identical ligands whose properties will be numerical averages of those of the actual ligands. The availability of reliable Δ , B' and μ values for the [CoX₄]²⁻ species, the [Co(Ph₃PO)₄]²⁺ ion and the several [Co(Ph₃PO)₂-X₂] complexes makes it possible to test the idea in the realm of tetrahedral Co(II) complexes.

(23) H. A. Weakliem, R.C.A. Laboratories, to be published.

(24) J. Owen, *Proc. Roy. Soc. (London)*, **A227**, 183 (1955); *Discussions Faraday Soc.*, **19**, 127 (1955).

(25) T. M. Dunn, *J. Chem. Soc.*, 623 (1959).

TABLE VIII

COMPARISON OF OBSERVED AND CALCULATED AVERAGE LIGAND FIELDS IN [Co(Ph₃PO)₂X₂] COMPLEXES

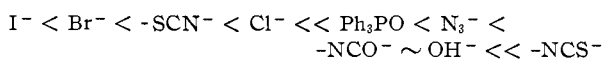
X	Observed values ^a			Calculated values ^c		
	Δ	B'	μ	Δ	B'	μ
Cl	3270	760	4.58 ^b	3405	749	4.56
Br	3180	754	4.63 ^b	3265	741	4.61
-NCS	4030	725	4.46	4115	739	4.47

^a See ref. 6 for these figures. ^b These moments are slightly lower than those in ref. 6 because they are corrected *exactly* for the t.i.p. rather than approximately using a value of 500×10^{-6} c.g.s. units. ^c All of these values are calculated by averaging those found in Table VII for the [CoX₄]²⁻ and [Co(C₆H₅)₃PO₄]²⁺ species.

As shown by the figures in Table VIII the approximation works fairly well for these complexes.

General Conclusions.—Using the data in Table VII and some data from previous papers in this series^{6,26} the following general conclusions can be stated.

(1) The order of Δ values calculated from the observed ν_2 and ν_3 bands of both simple and mixed tetrahedral Co(II) complexes leads to the following spectrochemical series of the ligands which have been used



This order is consistent with previous inferences^{3,26} from relative values of magnetic moments of tetrahedral Co(II) complexes and also with the generally accepted order of ligands in the spectrochemical series,²⁷ as derived from spectra of complexes of many other metal ions. The position of the OH⁻ ion is perhaps further to the strong end in the above series than in the one given by Dunn,²⁷ but there is not enough overlap in the region concerned to afford a sure comparison.

(2) The ratio of the intensities of the ν_3 and ν_2 bands in all complexes examined is significantly below the theoretical value obtained by Ballhausen and Liehr^{10,28} for a rigorously tetrahedral complex assuming single electron excitation to be dominant. Probably one or both of these restrictions are not closely enough satisfied in the complexes we have studied.

(3) The B' values for all complexes are of the order of 65 to 80% of the free ion values, which suggests that there is appreciable orbital overlap. The order of the β values for the complexes of the several ligands studied is $I^- \sim N_3^- < -NCS^- \sim Br^- \sim Cl^- \sim -NCO^- < OH^- < Ph_3PO$, but the accuracy of the β values is too low to establish this nephelauxetic series with very much certainty.

(4) The λ' values for all complexes are in the range 130–170 cm.⁻¹ compared to the free ion value of 178 cm.⁻¹. These results also suggest to us that there is significant orbital overlap.

(5) No definite relationship was found between the β and λ'/λ values because the experimental uncertainties are comparable to the ranges spanned by these quantities in the complexes studied.

(26) F. A. Cotton, O. D. Faut, D. M. L. Goodgame and R. H. Holm *J. Am. Chem. Soc.*, **83**, 1780 (1961).

(27) See, for example, T. M. Dunn in "Modern Coördination Chemistry," J. Lewis and R. G. Wilkins, Editors, Interscience Publishers, Inc., New York, N. Y., 1960, pp. 266.

(28) Eq. (17) of ref. (10) contains a typographical error and should read $f(\nu_3)/f(\nu_2) = 4\nu_3/\nu_2$.

(6) Magnetic moments and Δ values of a particular complex anion, $[\text{CoX}_4]^{2-}$ vary, somewhat (usually $\sim 4\%$, occasionally as much as 10%) from one compound to another due, presumably, to variations in compression forces in the crystal lattices.

(7) Solvent effects on the spectra of $[\text{CoX}_4]^{2-}$ species are often significant. True spectra can usually be obtained in nonaqueous solutions by adding excess X^- ion, but in aqueous solutions, even saturated with HX or LiX , full conversion of Co(II) to $[\text{CoX}_4]^{2-}$ species does not seem to occur.

(8) Co(OH)_2 dissolves in concentrated alkali metal hydroxide to form, at least partly, one or more tetrahedral species. It is believed that these are $[\text{Co(OH)}_3(\text{H}_2\text{O})]^-$, $[\text{Co(OH)}_4]^{2-}$ or both.

(9) The intensities of the ν_2 and ν_3 bands in all tetrahedral Co(II) complexes studied to date appear to be $\sim 10^2$ times as great as the band intensities in octahedral Co(II) complexes. This ratio is comparable to those found for Ni(II) ²¹ and

Mn(II) ²⁹ and in agreement with previously reported observations, notably those of Gill and Nyholm,¹¹ Ballhausen and Jørgensen⁸ and Bufagni and Dunn.¹⁶

(10) The Δ values for $[\text{CoX}_4]^{2-}$ complexes are 80–85% of those in the corresponding $[\text{NiX}_4]^{2-}$ complexes.²¹ Whereas the $[\text{NiI}_4]^{2-}$ and $[\text{Ni-Br}_4]^{2-}$ complexes had Δ values which were equal within experimental error, the Δ value for $[\text{Co-Br}_4]^{2-}$ is 5–10% greater than that for $[\text{CoI}_4]^{2-}$.

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(29) D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 3735 (1961); F. A. Cotton, D. M. L. Goodgame, M. Goodgame, *J. Am. Chem. Soc.*, in press.

[CONTRIBUTION NO. 1023 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA]

A Polarographic Study of Mixed-ligand Complex Formation; Complexes of Copper and Cadmium with Oxalate Ion and Ethylenediamine

BY WARD B. SCHAAP AND DONALD L. McMASTERS¹

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The polarographic method for the study of mixed-ligand complexes is discussed and then applied to the determination of the formation constants of the mixed-ligand complexes of copper(II) and cadmium(II) in the presence of both oxalate ion (ox) and ethylenediamine (en). Results for the one mixed complex of copper, $[\text{Cu(en)(ox)}]$, agree well with results based on other physical measurements. The constants for the three possible mixed complexes of cadmium are $\log K_{11} = 7.9$ for $[\text{Cd(en)(ox)}]$, $\log K_{12} = 8.8$ for $[\text{Cd(en)(ox)}_2]^{-2}$ and $\log K_{21} = 11.5$ for $[\text{Cd(en)}_2(\text{ox})]$. The effects of the relative charges of the unsaturated complex and the incoming ligand on the stepwise formation constants are those predicted by charge neutralization and entropy considerations when a second ligand adds to either copper or cadmium; abnormal effects accompany the addition of a third ligand to cadmium.

Introduction

An increasing number of studies of mixed-ligand complex formation has appeared during the past decade. Mixed-ligand complexes are those in which more than one kind of ligand, other than the solvent molecule, are present in the innermost coordination sphere of the central metal ion and can be represented by the general formula $[\text{MX}_i\text{Y}_j\text{Z}_k \dots]$. Most of the previous studies have made use of spectrophotometric measurements,^{2–12} some have involved potentiometric measurements using metal–metal ion or oxidation–reduction elec-

trodes,^{2,3,13,14} while others made use of data obtained from $p\text{H}$ titration curves.^{3,15–19}

The formation constants evaluated in the above studies, as well as purely statistical considerations, indicate that mixed-ligand complex formation is a general and common phenomenon whenever two or more ligands are present in solution and that actually mixed complexes should be preferred over simple complexes whenever the concentrations of the ligands involved are such that the products of the formation constants for the simple complexes and the concentrations of the ligands, raised to the appropriate power, are approximately equal, *i.e.*, $K_{\text{MX}_i}[\text{X}]^i = K_{\text{MY}_j}[\text{Y}]^j = K_{\text{MZ}_k}[\text{Z}]^k \dots$

Although the polarographic method has been widely used in the study of single-ligand systems, no general discussion of the application of the method to the study of mixed-ligand complexes

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