that the vacancy in RX^+ arises from a non-bonding electron with RI or RBr but from a bonding electron with RCl.[20] Also, there may be substantial resonance for $R'\ X\vdots X\ R''^{+}$, *viz.* similar X and dissimilar R, but in general rather less for $R\ X'\vdots\ X''\ R^+$. It has been estimated that the bond dissociation energies are $D(RBr\vdots BrR^+) = 20$ kcal./mole and $D(RI\vdots IR^+) \cong 16$ kcal./mole.[21]

Rare gas–water mixtures were examined because of the well known hydration of gaseous ions observed in ion mobility measurements.[22] The present results suggest that XeH_2O^+ formation would require a triple collision.

When the experiments with methanol were performed, it was intended to investigate the possibility of locked-in ion-permanent dipole interaction since the cross sections are much too large to be accounted for in terms of a freely rotating dipole.[21] We have recently learned that the CHO^+ and CH_3O^+ ions also contribute importantly to $CH_3OH_2^+$ formation.[23] The appearance potentials in Table III can only demonstrate the involvement of the ion of lowest appearance potential,[24] CH_3OH^+. Consequently it is impossible to analyze the data of Table VI. If the Q *vs.* $E_e^{-1/2}$ dependence applied to each contributing reaction, it would also describe their linear combination. In fact, it does not. If the ion-permanent dipole force law applies, *i.e.*

$$V = -e\mu r^{-2}\cos\theta$$

there are two limiting cases. If the dipole is rotating freely, the contribution to reaction cross section is averaged out and there remains the ion-induced dipole contribution. If the dipole "locks in" on the ion with $\theta = 0°$, then

$$QE_e = \sigma \ln (E_e/E_i)$$

where σ represents collected constants and E_i is the initial (thermal) ion energy. The applicability of this equation cannot be tested adequately, but qualitatively it can account for the very large measured cross section obtained from equation 1.

Acknowledgment.—We are indebted to Professor J. L. Magee and Dr. John V. Dugan, Jr., for helpful discussions.

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[20] R. S. Mulliken, *ibid.*, **47**, 413 (1935).

[21] J. Dugan, Ph.D. dissertation, University of Notre Dame, 1961.

[22] J. R. Munsen and A. M. Tyndall, *Proc. Roy. Soc.* (*London*), **172A**, 28 (1939).

[23] P. Wilmenius and E. Lindholm, *Arkiv för Fysik*, in press. We are indebted to Professor Lindholm for the opportunity to examine this unpublished work.

[24] Most of the published reaction cross sections are unreliable because of possible involvement of primary ions other then the one reported, *viz.* that reacting primary ion of lowest appearance potential. When only one primary ion is involved, the calculated cross section will be constant over a range of ionizing voltage.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION, CHINA LAKE, CALIFORNIA]

Halide Complexes of Cobalt(II) in Acetone Solution[1]

BY DWIGHT A. FINE

RECEIVED AUGUST 17, 1961

Chloride, bromide and iodide complexes of cobalt(II) in acetone solution have been studied spectrophotometrically. Complexes having 2, 3 and 4 coördinated halides have been detected, and the absorption spectra of the individual complexes have been determined. The spectra of the dihalo and trihalo complexes were determined by the mole ratio method; the spectra obtained in concentrated halide solutions are identical with the known spectra of the tetrahalo complexes. Approximate values of equilibrium constants for the different species have been obtained. The absorption spectra indicate that all of the species are tetrahedral in structure.

Introduction

Previous investigations of cobalt(II) halide systems in organic solvents have indicated the possible presence of complexes having from one to four coördinated halides.[2–5] Characterization of the individual complexes is of interest; knowledge of the nature of these species and of their absorption spectra would be an aid in interpreting spectral measurements of aqueous solutions, solid media and ionic melts. The spectra would also be of interest to ligand field theory.

Katzin and Gebert[4] made an extensive study of cobaltous chloride in organic solvents, using the method of continuous variations. Their results indicated the presence of species having chloride to cobalt ratios of 2, 3, and 4. The peaks observed in the spectra of the solutions were assigned to the different species, but the complete spectra of the individual species were not elucidated. The subsequent development of more powerful experimental tools and methods, and of the ligand field theory, has made a more rapid and conclusive investigation possible. The present investigation makes use of the Cary recording spectrophotometer, and the mole ratio method for the determination of complexes. The investigation was confined to a single solvent, acetone.

Experimental

Apparatus.—All absorption spectra were measured on a Cary Recording Spectrophotometer Model 14, Serial 244. Matched quartz cells of 1 cm. or 5 cm. path length were employed. It was not possible to maintain constant ionic strength in acetone solution; concentrations were therefore kept as dilute as possible in order to minimize changes in activity coefficients and also to minimize danger of deviation from Beer's Law. The use of the 5 cm. cells was found convenient for this purpose.

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[1] Presented in part at the American Chemical Society meeting in Chicago, September, 1961.

[2] Y. Wormser, *Bull. Soc. chim. France*, 395 (1948).

[3] M. C. Barbinok, *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **12**, 636 (1948).

[4] L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5464 (1950).

[5] S. A. Shchukarev and O. A. Lobaneva, *Doklady Akad. Nauk S.S.S.R.*, **105**, 741 (1955).

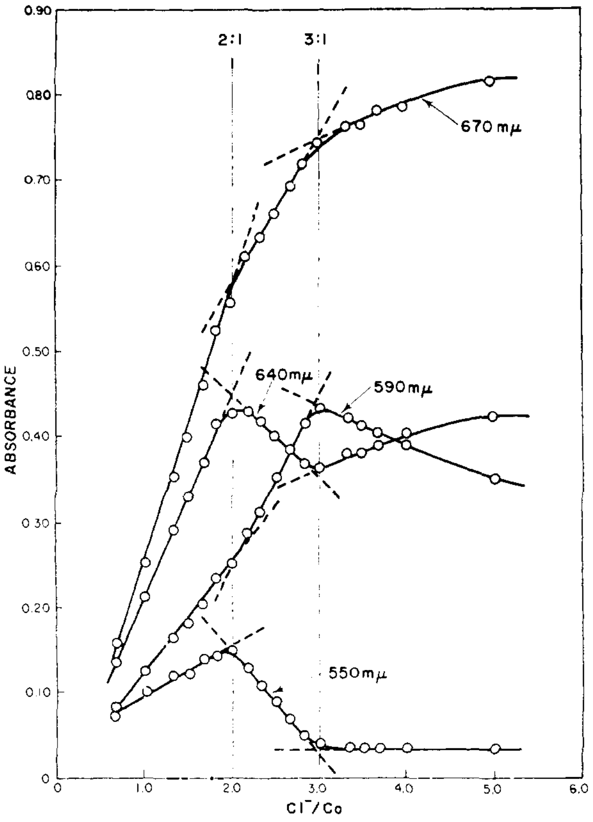

Fig. 1.—Examples of mole ratio plots for solutions of $Co(ClO_4)_2$ + LiCl in acetone.

Solutions for spectrophotometric measurement were prepared in 25 cc. volumetric flasks. Stock solutions of cobaltous perchlorate or halide in acetone were mixed with stock solutions of alkali halide in acetone and the resulting solution was diluted to the mark with acetone. The reference cell was filled with pure acetone.

Reagents.—Cobaltous perchlorate was G. F. Smith Co. $Co(ClO_4)_2 \cdot 6H_2O$. Cobaltous chloride was Merck Reagent $CoCl_2 \cdot 6H_2O$.

Lithium chloride was recrystallized C.P. J. T. Baker Analyzed Reagent. Lithium bromide was recrystallized Mallinckrodt N. F. VIII. Sodium iodide was recrystallized Baker and Adamson reagent.

Analytical.—Cobalt in solution was determined by converting the cobalt to the thiocyanate complex in *ca.* 50% acetone solution and determining the $Co(SCN)_4^=$ spectrophotometrically. The maximum at 622 mμ was used for analysis. A calibration curve of absorbance at 622 mμ *vs.* cobalt concentration was prepared, using standards from stock cobaltous perchlorate solutions which had been analyzed by titration with standard KCN[6] and also using standards prepared by weighing out recrystallized C.P. J. T. Baker Analyzed $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The thiocyanate complex in acetone showed good obedience to Beer's Law, with the molar extinction coefficient at 622 mμ equal to 1830. The method, suggested by Sandell,[7] was found to be more rapid and convenient and to give much better reproducibility than the usual spectrophotometric method involving extraction of $Co(SCN)_4^=$ with amyl alcohol; the absence of appreciable quantities of nickel from the solutions eliminated the disadvantages of the acetone method.

Chloride, bromide and iodide in solution were determined by titration with standard silver nitrate, using the methods of Mohr and Fajans.

Results

Chloride Complexes: Application of Mole Ratio Method.—This method was introduced by Yoe and Jones[8] and extended by Meyer and Ayres to multicomponent systems.[9] In several ways, the method possesses distinct advantages over the method of continuous variations, which has been the method most often employed in previous investigations of cobalt(II) halide complexes.

A series of solutions of cobaltous perchlorate + lithium chloride in acetone was prepared, with cobalt concentration held constant at 3.75×10^{-4} mole/l. Chloride concentrations were such as to yield chloride to cobalt mole ratios of 1, 2, 3, 4 and 5, plus at least three ratios intermediate between successive integral values. Addition of chloride to the pale pink cobaltous perchlorate solutions turned the color of the solutions to blue. Two distinct shades of blue were observed: an indigo blue when the chloride to cobalt ratio was less than or equal to 2, and an ultramarine blue when the chloride to cobalt ratio was greater than 2. The visible spectra were measured on the Cary and the absorbances at selected wave lengths were plotted against the mole ratios. Plots were made for wave lengths at 10 mμ intervals between 550 and 720 mμ and also for wave lengths of the principal maxima (575, 590, 674, 688 mμ) and minima (594, 616 mμ). Some typical plots are shown in Fig. 1. It is seen that changes in slope occur at mole ratios of 2 and 3, indicating the presence of dichloro and trichloro complexes, $CoCl_2$ and $CoCl_3^-$. The curves rise or fall asymptotically beyond a mole ratio of 3. The curves were extrapolated to the mole ratios of 2 and 3, and the values of the absorbances at these points were taken as the absorbances of the pure complexes. Molar extinction coefficients were calculated from these absorbances.

Chloride Complexes: Production of $CoCl_4^=$. Interpretation of the results of experiments on the cobalt(II) chloride system is greatly aided by the fact that the spectrum of the tetrachloro complex $CoCl_4^=$ is now known. The spectrum has been determined by measurements of the spectra of a number of tetrachlorocobaltate salts, in the solid state and in solvents such as nitromethane and nitrobenzene.[10-13] Such a spectrum was not observed in the measurements of the acetone solutions which were used in the work described in the preceding section. There were hints, however, that the spectrum might be starting to appear at the higher chloride to cobalt ratios. Experiments were therefore done involving further addition of chloride.

When the chloride to cobalt ratio became about 8:1, a spectrum was produced which looked similar to the $CoCl_4^=$ spectrum. The spectrum gradually became constant upon further addition of chloride;

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[6] R. S. Young, "Industrial Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 75–77.

[7] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishing Co., New York, N. Y., 1944, pp. 200–205.

[8] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 11 (1944).

[9] A. S. Meyer and G. H. Ayres, *J. Am. Chem. Soc.*, **79**, 49 (1957).

[10] H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 359 (1935).

[11] L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **75**, 2830 (1953).

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[13] F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

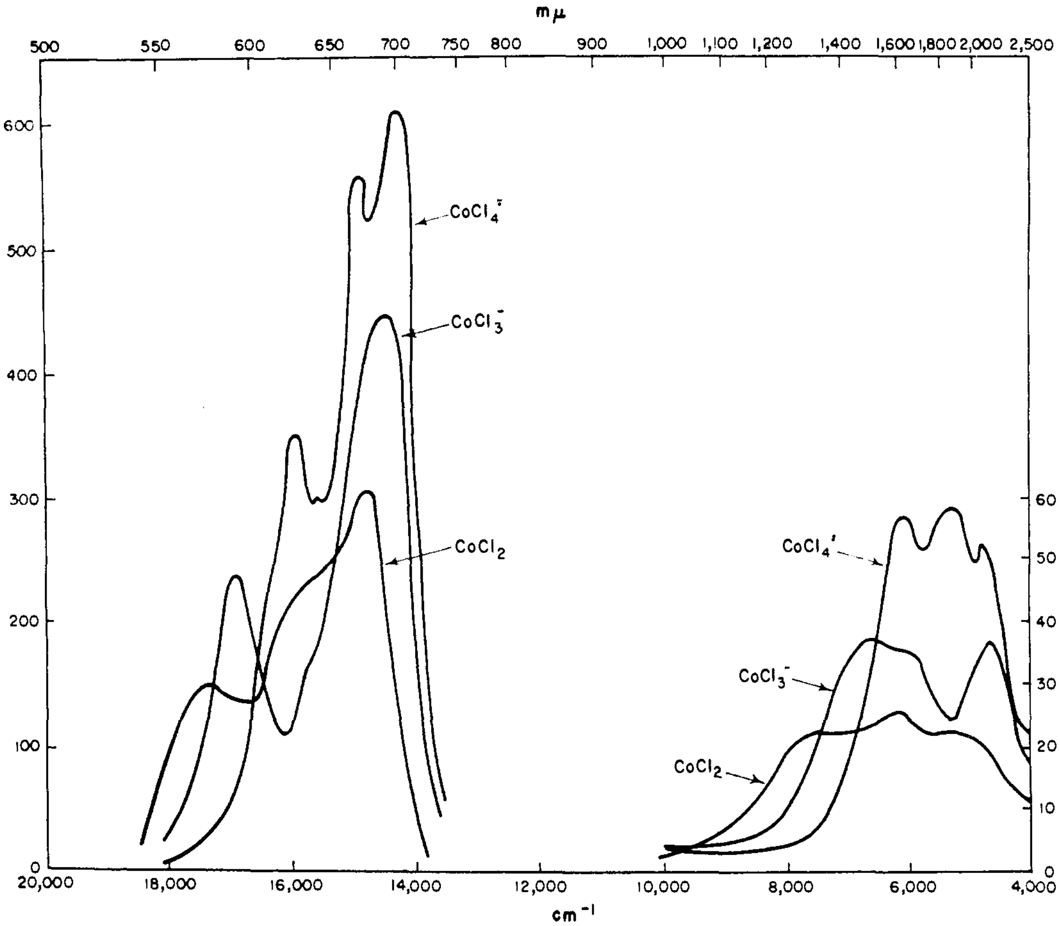

Fig. 2.—Absorption spectra of chloride complexes of cobalt(II) in acetone solution.

addition of chloride beyond a chloride to cobalt ratio of about 100:1 produced no further changes. The constant spectrum was unmistakably that of $CoCl_4^=$; the spectrum was quite similar to the spectra observed for the tetrachlorocobaltate salts.

The mole ratio method had failed to indicate the presence of $CoCl_4^=$. This was due to the fact that this complex is largely dissociated at the stoichiometric chloride to cobalt ratio of 4:1. The cobalt(II) chloride system in acetone serves to illustrate both the usefulness and limitations of the mole ratio method; the method is successful for two of the three complexes but fails in the case of the third because the formation constant of the latter is too small.

Bromide and Iodide Complexes.—Experiments similar to those described for chloride solutions were performed on solutions of $Co(ClO_4)_2$ and $CoBr_2$ with added LiBr, and on solutions of $Co(ClO_4)_2$ and CoI_2 with added NaI. In the case of the bromide solutions, the results were completely analogous to those obtained for the chloride solutions: dibromo and tribromo complexes were found by the mole ratio method, and a spectrum known to be that of a tetrabromo complex[12,13] was observed in concentrated bromide solutions. Solutions of the dibromo complex are light blue, and solutions of the higher complexes are blue-green. The experiments on iodide solutions yielded similar results, except that the triiodo complex was appreciably dissociated at the stoichiometric mole ratio and required an iodide to cobalt ratio between 6 and 10 for complete formation. Solutions of the diiodo complex are emerald green, and solutions of the higher complexes are olive green.

Spectra.—The visible absorption spectra of the complexes are shown in Figs. 2–4. The principal absorption maxima are listed in Table I, along with the corresponding molar extinction coefficients. The spectra of the dihalo and trihalo complexes were determined graphically by the mole ratio method. The spectra of the tetrahalo complexes were determined from measurements of concentrated halide solutions of cobaltous perchlorate and of anhydrous cobaltous chloride, bromide and iodide, in acetone.

The maxima in the spectra of the chloride complexes occur within 5 mμ of the maxima assigned to these three complexes by Katzin and Gebert.[4] The spectra obtained for the bromide complexes are similar in shape to the spectra obtained by Shchukarev and Lobaneva.[5] These authors, however, assigned the "$CoBr_3^-$" spectrum to a tetrabromo species, and the "$CoBr_4^=$" spectrum to a hexabromo species. It seems unlikely that any complexes higher than the tetrabromo are present.[12]

The iodide complexes, unlike the bromide and chloride complexes, show electron-transfer bands in the near ultraviolet. These bands occur be-

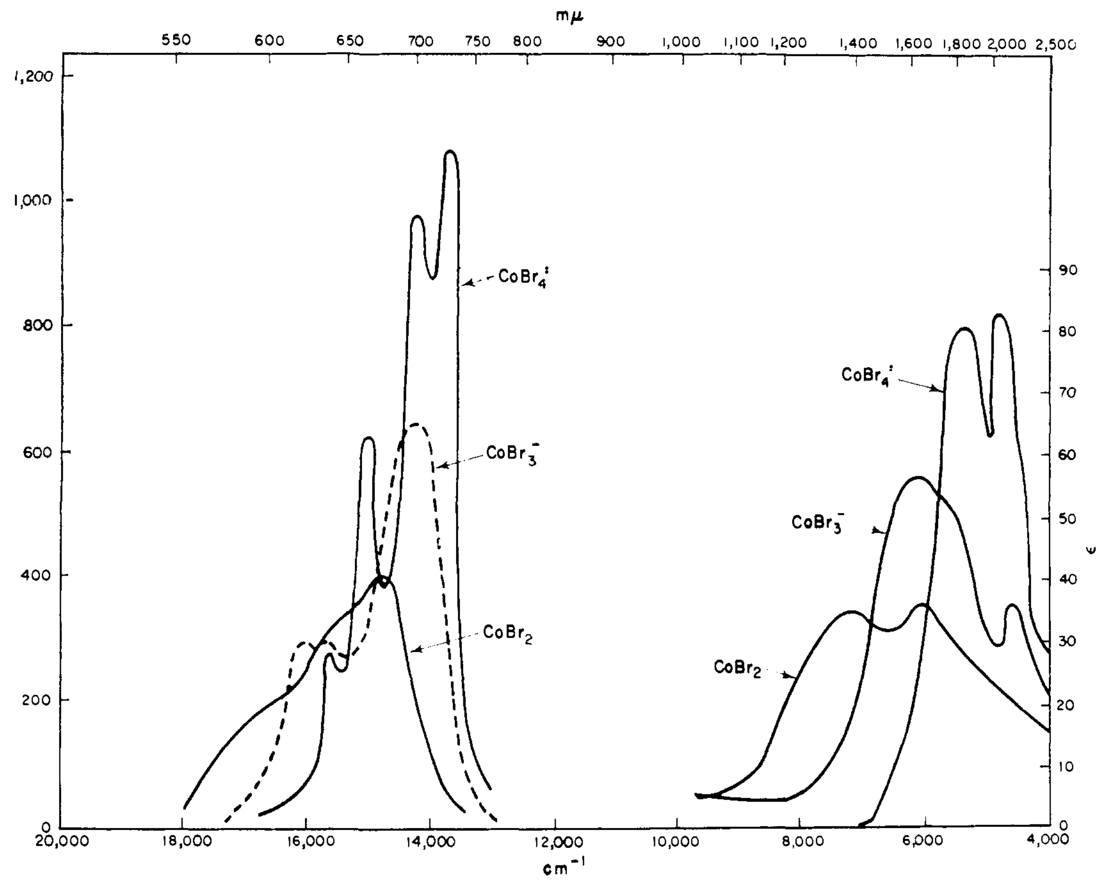

Fig. 3.—Absorption spectra of bromide complexes of cobalt(II) in acetone solution.

tween 370 and 400 mμ and have extinction coefficients as high as 4000.

Solutions in which the cobalt was almost entirely in the form of a single complex, as indicated by the visible absorption spectrum, were examined in the infrared region. The solutions were prepared by addition of lithium or sodium halide to anhydrous cobaltous halide in acetone. Solutions of tetraethyl ammonium salts of the tetrahalo cobaltate ions were also examined; solutions of these salts in acetone consisted mainly of the trichloro complexes, and addition of halide produced the tetrahalo complexes. The reference cell contained a solution identical in composition with the sample solution, except for the absence of the cobalt salt. The complexes showed very broad absorption bands, starting at about 1 μ and extending past 2.5 μ. The infrared spectra obtained are shown in Figs. 2–4, along with the visible spectra, and the principal maxima are listed in Table I. The bands show similarities to the visible bands, although they are only about one tenth as intense.

TABLE I

SPECTRA OF HALIDE COMPLEXES OF COBALT(II) IN ACETONE

	λmax, visible			λmax, infrared		
Species	mμ	Cm.$^{-1}$	$\epsilon_{max.}$	μ	Cm.$^{-1}$	$\epsilon_{max.}$
CoCl$_2$	575	17,400	150	1.33	7500	23
	~630(sh)	15,900	225	1.61	6200	26
	674	14,800	306	1.96	5100	23
CoCl$_3^-$	590	17,000	237	1.51	6600	38
	~630(sh)	15,900	150	~1.61(sh)	6200	37
	688	14,500	455	2.17	4600	38
CoCl$_4^=$	~610(sh)	16,400	248	1.64	6100	57
	625	16,000	353	1.89	5300	59
	~640(sh)	15,600	287	2.08	4800	52
	667	15,000	557			
	697	14,400	612			
CoBr$_2$	~590(sh)	17,000	171	1.39	7200	36
	~640(sh)	15,600	314	1.64	6100	37
	670	14,900	403			
CoBr$_3^-$	618	16,200	284	1.61	6200	57
	634	15,800	302	~1.96(sh)	5100	52
	700	14,300	655	2.17	4600	36
CoBr$_4^=$	639	15,600	287	1.85	5400	81
	664	15,100	630	2.04	4900	83
	697	14,400	989			
	723	13,800	1090			
CoI$_2$	~620(sh)	16,100	215	1.41	7100	57
	~690(broad)	14,500	393	1.67	6000	53
	~740(sh)	13,500	295			
CoI$_3^-$	398	25,100	2690	1.69	5900	92
	~665(sh)	15,000	380	~1.89(sh)	5300	82
	~695(sh)	14,400	530			
	744	13,400	920			
CoI$_4^=$	390	25,600	4010	2.00	5000	154
	~670(sh)	14,900	245			
	694	14,400	522			
	722	13,800	710			
	~750(sh)	13,300	877			
	777	12,900	1120			

Equilibrium Constants.—It was thought desirable to obtain some indication as to the values of the equilibrium constants between the various halide complexes in acetone solution. The spectral data obtained as described in the preceding sections were utilized for this purpose. If the extinction coefficients of two complexes are known,

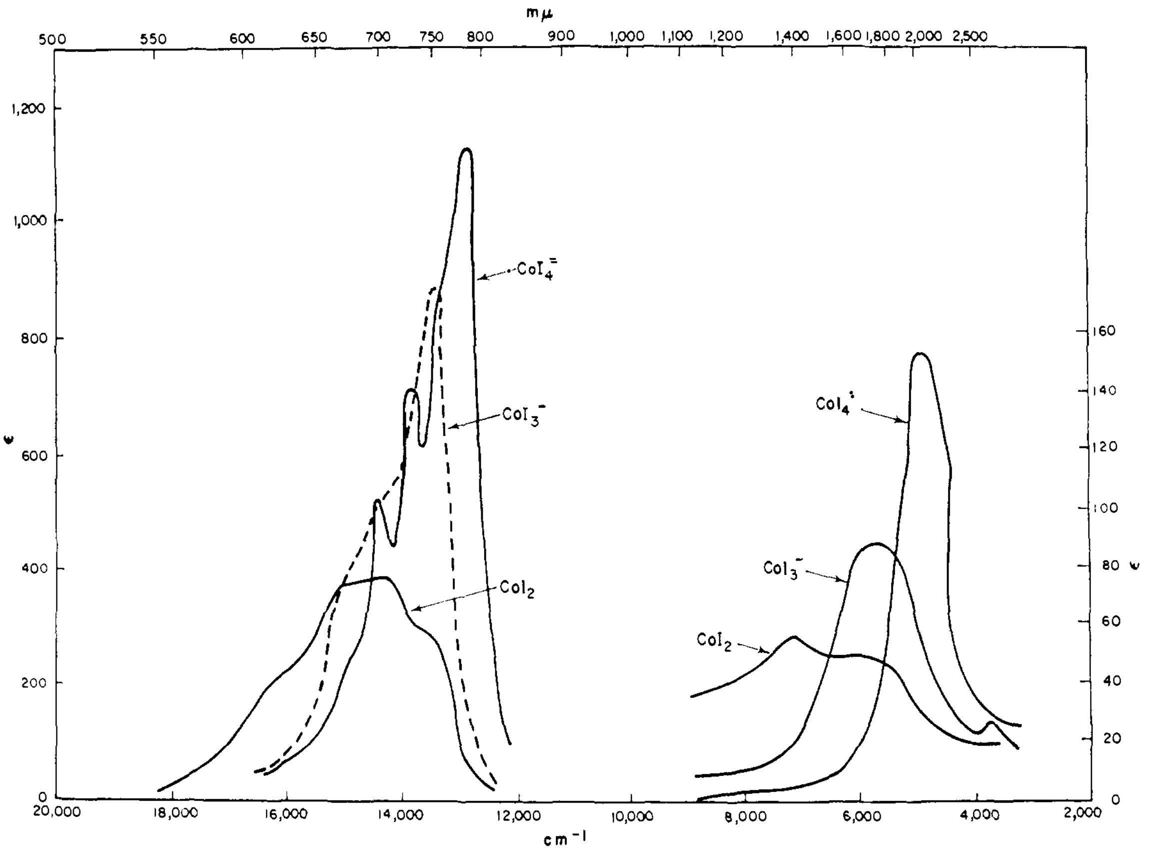

Fig. 4.—Absorption spectra of iodide complexes of cobalt(II) in acetone solution.

measurement of the spectrum of a mixture of the two complexes permits calculation of the composition of the mixture. If f_1 is the fraction of cobalt present as species 1, ϵ_1 and ϵ_2 are the extinction coefficients of species 1 and 2, and $\epsilon_{\text{obsd.}}$ is the measured extinction coefficient, then

$$f_1\epsilon_1 + (1 - f_1)\epsilon_2 = \epsilon_{\text{obsd.}}$$

Since the total cobalt and halide concentrations in solution are known, the concentration of each species and the free halide concentration may then be calculated. This permits the calculation of an equilibrium quotient. (The values thus derived will hence forth be referred to as "quotients" rather than "constants," since concentrations rather than activities were employed in the calculations.)

For calculation of the equilibrium quotient between Co^{++} and CoX_2, the spectra obtained for halide to cobalt ratios between 0 and 2 were used; it was assumed that only Co^{++} and CoX_2 were present. Similarly, the spectra obtained for mole ratios between 2 and 3 were used to calculate the quotient between CoX_2 and CoX_3^-, and only these two species were assumed to be present. For calculation of the quotient between CoX_3^- and $CoX_4^=$, additional data were taken, with cobalt concentration held constant at two different values between 10^{-5} and 10^{-4} mole/l. In chloride solution, the mole ratio of halide to cobalt ranged from 4 to 22, in bromide solution from 40 to 300 and in iodide solution from 150 to 800. All spectra were measured at room temperature, 26°.

The calculated quotients are shown in Table II. The parentheses designate concentrations in mole/l. In each case, the composition of the mixture was calculated from extinction coefficients at five or more different wave lengths. Spectra for at least four different mole ratios were utilized and the results averaged. In the case of the quotients for the trichloro and tribromo complexes, it was not possible to determine an accurate value of the free halide concentration, which was very small. The order of magnitude of the quotients was estimated by assuming the free halide concentration to be less than 1% of the total halide concentration.

TABLE II

EQUILIBRIUM QUOTIENTS FOR HALIDE COMPLEXES OF COBALT(II) IN ACETONE SOLUTION, CALCULATED FROM ABSORPTION SPECTRA TAKEN AT 26°

Quotient	X = Chloride	X = Bromide	X = Iodide
$\frac{(CoX_2)}{(Co^{++})(X^-)^2}$	3×10^9	2×10^9	$\geq 10^9$
$\frac{(CoX_3^-)}{(CoX_2)(X^-)}$	$>10^5$	$>10^5$	2.2×10^4
$\frac{(CoX_4^=)}{(CoX_3^-)(X^-)}$	5.4×10^2	42	16

Discussion

The tetrahalo complexes are known to be tetrahedral in structure.[11-14] It seems most likely that the dihalo and trihalo complexes are also tetrahedral, with the remaining sites on the tetrahedron occupied by acetone molecules to give complexes

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

of the type $Coac_2X_2$ and $CoacX_3^-$. The same structures were postulated by Katzin and Gebert.[4] The apparent stepwise formation of the complexes with increasing halide concentration, yielding a final complex which is tetrahedral, would indicate a tetrahedral structure for all three of the halide complexes. Conversely, when salts of the tetrahalo cobaltate ions, such as $(NEt_4)_2CoX_4$, are dissolved in acetone, the spectrum produced is that of a mixture of CoX_3^- and a small fraction of $CoX_4^=$, indicating formation of CoX_3^- by loss of a halide from tetrahedral $CoX_4^=$, with no apparent change in configuration. Also, there is no evidence for stereoisomers of any of the complexes. A monomeric structure for the lower complexes is indicated by the obedience of their spectra to Beer's Law and by their formation through loss of halides from the tetrahalo complexes, which are known to be monomers.

The spectra of the dihalo and trihalo complexes provide additional evidence for a tetrahedral structure. The extinction coefficients of the visible absorption bands are comparable to those of the tetrahalo complexes and are much higher than the coefficients observed for d-d transitions of octahedral cobalt(II) complexes.[14] Such comparatively high extinction coefficients have also been observed for tetracoördinate complexes of Mn(II), Cu(II) and Ni(II), including a number of tetrahedral Ni(II) and Co(II) complexes of the type ML_2X_2 and MLX_3^-.[15-17] Measurements of the crystal spectra of tetrahedral cobalt(II) complexes, including complexes of the type $CoPy_2X_2$, have yielded results similar to those obtained for the dihalo complexes in acetone solution.[18]

The positions of the absorption bands are compatible with those observed for Co(II) in ligand fields of tetrahedral symmetry. The visible absorption is ascribable to the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition, the infrared absorption to the $^4A_2(F) \rightarrow {}^4T_1(F)$ transition.[14,19] Tetrahedral dihalo and trihalo complexes would have fields of C_{2v} and C_{3v} symmetry, respectively; this decrease in symmetry from the T_d symmetry of the tetrahalo complexes would be expected to produce splittings of the bands. The spectra of the trichloro and tribromo complexes show the strongest possibility of symmetry-induced splitting. It is interesting, however, that the visible bands of the tetrahalo complexes show more components than do the corresponding bands of the dihalo and trihalo complexes. The infrared bands show the expected splitting for the dihalo and trihalo complexes. The bands of the tetrahalo complexes also show some splitting, the splitting being greatest for the tetrachloro and least for the tetraiodo species. Ferguson's measurements[18] have indicated that the infrared band of crystalline Cs_3CoCl_5 shows the same splitting.

It is seen from Figs. 2–4 that the effect of successive coördinations of halide is to shift the visible and infrared bands to lower energies and to increase the molar extinction coefficients. The spectra of corresponding complexes of the different halides clearly indicate crystal field strengths in the order $I^- < Br^- < Cl^-$, in agreement with the spectrochemical series.[19] The values obtained for the equilibrium constants indicate stabilities in the usual order $I^- < Br^- < Cl^-$.

Because the infrared bands are quite broad, it is difficult to assign definite wavenumbers to them. However, the spectrum of the tetrachloro complex indicates that the wavenumber is definitely less than the 6300 cm.$^{-1}$ reported by Dreisch and Trommer for aqueous solutions[20] and utilized in previous ligand field calculations.[14,19] The center of the band occurs at approximately 5600 cm.$^{-1}$; this yields a value of 310 for the ligand field parameter Dq, compared to 350 for the older value. Recently, Buffagni and Dunn have reported a maximum at 5850 cm.$^{-1}$, which yields a Dq of 325.[21] The infrared spectra obtained here for $CoBr_4^=$ and $CoI_4^=$ indicate band centers at about 5100 and 4900 cm.$^{-1}$, respectively, yielding Dq values of 280 and 270; previously reported bands at 5300 and 5000 cm.$^{-1}$ correspond to Dq's of 290 and 280.[19] Recent spectral measurements of tetrahalocobaltate salts by Cotton, Goodgame and Goodgame[13] have yielded average Dq's of 313, 285 and 265 for chloride, bromide and iodide.

An estimate of Δ ($= 10\,Dq$) for acetone may be obtained from the positions of the bands. According to ligand field theory for d^7 in a tetrahedral environment, the energy ν_2 of the infrared band is given by $\nu_2 = {}^9/_5\,\Delta$, and the energy ν_3 of the visible band is given by $\nu_3 = {}^6/_5\,\Delta + \text{const.}$[14] If Δ for $Coac_2X_2$ is taken to be $^1/_2\,\Delta_{X^-} + {}^1/_2\,\Delta_{ac}$, and Δ for $CoacX_3^-$ to be $^3/_4\,\Delta_{X^-} + {}^1/_4\,\Delta_{ac}$, then Δ_{ac} may be calculated from the frequencies of the bands and from the values of Δ_{X^-} previously obtained from the $CoX_4^=$ spectra. This concept of "averaged environment" has been shown empirically to be valid for numerous complexes.[13,22] Estimation of the wave number of the center of gravity of each band and computation of Δ_{ac} from these wave numbers yields an average value of $(4.3 \pm 0.4) \times 10^3$. This corresponds to a Δ of about 9700 for an octahedral field of acetone molecules, a value intermediate between that of water (9000) and ammonia (10,500).[14] This is reasonable from the spectrochemical series.

Acknowledgment.—I wish to thank Professor F. A. Cotton for communication of some of his results prior to publication.

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