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Behavior of Ammonium Tetrachlorocobaltate(II) on Hydration

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Magnetic, spectral, and thermodynamic changes have been investigated for the formation of ammonium tetrachlorocobaltate(II) dihydrate from the anhydrous compound. In anhydrous $(NH_4)_2CoCl_4$, the magnetic moment (4.77 B.M.) and relatively large Weiss constant (22°) indicate a distorted tetrahedral structure. The spectrum was roughly fitted using the simple crystal field parameter $\Delta = 3300$ cm.$^{-1}$, in fair agreement with known tetrahedral cobalt(II) chloride compounds. The fragmented spectra are compatible with distortion, although the exact distortion could not be determined. In the hydrate $(NH_4)_2[Co(H_2O)_2Cl_4]$, the magnetic moment (5.18 B.M.) is indicative of a distorted octahedral structure. The spectrum has been fitted using the point charge model, by assuming tetragonal distortion with $\Delta = 6950$ cm.$^{-1}$ and Ds (second-order splitting parameter) $= \pm 175 \pm 25$ cm.$^{-1}$ (+ indicates axial elongation, − axial compression), ignoring Dt (fourth power splitting parameter). The reasons for choosing axial compression (two waters *trans* and closer than four planar chlorides) as the most probable structure are discussed. The dissociation pressure was investigated and indicates that both waters were lost simultaneously. The thermodynamic properties at 30° were calculated for the reaction $(NH_4)_2[Co(H_2O)_2Cl_4](s) = (NH_4)_2CoCl_4(s) + 2H_2O(g)$ from the variation of vapor pressure with temperature. This is fitted by the equation $\log p = -4140/T + 13.830$, where p is in mm. and T in °K. Gas at 1 atm. was taken as the standard state. The thermodynamic values are compatible with the postulated change of structure during hydration. The thermodynamic constants at 30° are $K_d = 3.7 \times 10^{-6}$ atm.^{2}, $\Delta H° = 38{,}090$ cal./mole, $\Delta S° = 101$ e.u., and $\Delta F° = 7530$ cal./mole.

Observations of cobalt(II) halide complexes with the general formula M_2CoCl_4 reveal that there is a change of color when the compound is hydrated.[3] Changes of color, magnetic moment, and other properties[4,5] in high spin cobalt(II) compounds can be explained by changes of configuration. There have been relatively few studies which have correlated the change in these properties with the change in structure and the energies involved in these changes. It seemed that a further study of these phenomena was justified.

Although ammonium tetrachlorocobaltate(II) has been reported,[3,6] it has not been intensively studied and has generally been described as a double salt, $2NH_4Cl \cdot CoCl_2$. The stable form under ordinary conditions is the dihydrate. The magnetic moment reported for the anhydrous compound,[7] the blue color, and other properties indicate that the compound is actually the tetrahedral complex which is more correctly represented by the formula $(NH_4)_2CoCl_4$.

When the dihydrate forms, the color changes from blue to violet and the magnetic moment and other properties change. The change in properties after the formation of the dihydate can best be explained by a change in structure from essentially a tetrahedral compound to a distorted octahedral compound.

Experimental

Preparation of Ammonium Tetrachlorocobaltate(II).—The compound can be prepared by mixing stoichiometric amounts of NH_4Cl and $CoCl_2$ hydrate in concentrated hydrochloric acid and evaporating to dryness. The light blue powder left behind is dissolved in methanol, any undissolved material being discarded. The methanol solution is evaporated to dryness, leaving the product as a blue powder. This methanol extraction can be repeated two or more times until the desired purity is obtained.

The compound can also be prepared from the red carbonatotetraamminecobalt(III) chloride[8] by dissolving this compound in concentrated hydrochloric acid and heating the solution to dryness. During this heating process, the solution turns blue, and a red precipitate is formed which must be periodically filtered. The product is a light blue powder which can be extracted by methanol in the manner described above.

Preparation of Ammonium Tetrachlorocobaltate(II) Dihydrate.—The dihydrate was formed either by allowing the anhydrous compound, prepared above, to stand in contact with air for several days until the color was violet and the weight constant, or else the anhydrous compound was placed in a closed container over water for several hours until all changes ceased.

Analysis. Anhydrous Ammonium Tetrachlorocobaltate(II).—The chloride ion concentration was determined gravimetrically by precipitation as silver chloride from a dilute nitric acid solution.[9]

Cobalt was analyzed by electrodeposition.[10] The weighed sample was dissolved in water, ammonium hydroxide and nitrate were added, and the cobalt was plated out overnight on a rotating platinum electrode using a Sargent–Slomin electrolytic analyzer.

Ammonium was analyzed by using a modified Kjeldahl method.[11] Since the nitrogen was already present in the reduced state, the weighed sample was dissolved in water, and the solution was made basic with concentrated sodium hydroxide. The ammonia was distilled off, captured in a boric acid solution, and titrated in the usual manner with standard hydrochloric acid.

Sample weights varied between 0.100 and 0.300 g. *Anal.* Calcd.: Co, 24.9; NH_3, 14.4; Cl^-, 59.88. Found: Co, 24.0 ± 0.4; NH_3, 14.4–15; Cl^-, 59.90 ± 0.08.

Hydrate.—The hydrate, prepared in the manner described above, was analyzed by studying the dissociation pressure as a

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[1] Alfred P. Sloan Foundation Fellow.

[2] Taken in part from a thesis for the degree of Master of Science in Chemistry.

[3] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, The Clarendon Press, Oxford, England, 1950, p. 1390.

[4] (a) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5464 (1950); (b) *ibid.*, **75**, 2831 (1953).

[5] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

[6] F. W. J. Clendinnen, *ibid.*, **121**, 802 (1922).

[7] E. F. Herroun, *Proc. Phys. Soc.* (London), **46**, 872 (1934).

[8] J. Jorgensen, *Z. anorg. Chem.*, **2**, 281 (1892).

[9] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, p. 303.

[10] N. H. Furman, Ed., "Scott's Standard Methods of Chemical Analysis," 5th Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 315.

[11] Reference 9, p. 538.

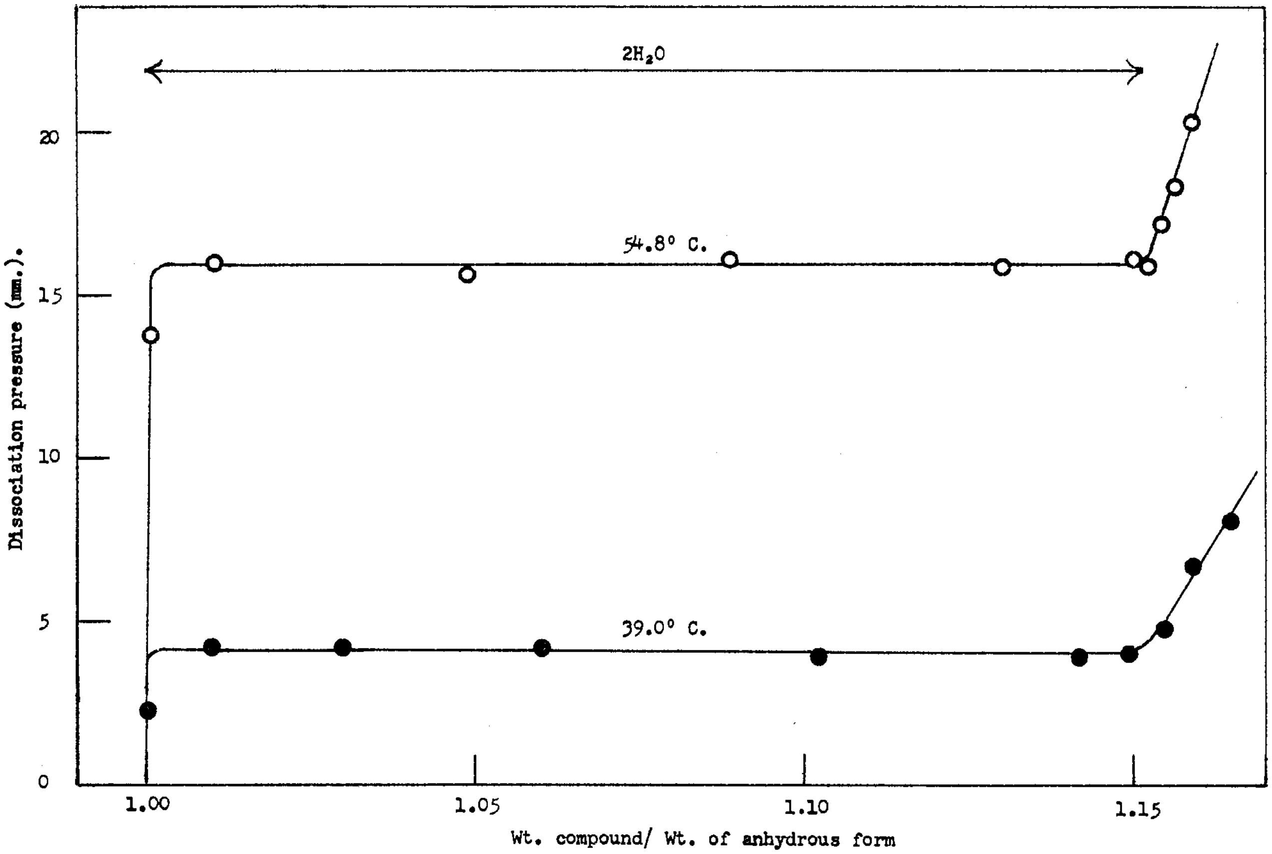

Fig. 1.—Dissociation pressure *vs.* composition.

function of the weight of the sample using the apparatus described by Fogel and Christian.[12] The loss of weight from the sample during dehydration was 13.0 ± 0.2%; the theoretical value for the loss of two moles of water per mole of compound is 13.2%.

The cobalt in both the anhydrous and hydrated forms was shown to be divalent by the standard thiocyanate test for a cobaltous ion,[13] the magnetic moments, and the spectra. All chemicals used were reagent grade.

Spectra.—The infrared spectra were recorded by a Perkin-Elmer double beam recording infrared spectrophotometer, Model 21. In both the infrared and visible, studies were made using potassium bromide disks.

The reflectance spectra were measured on several different machines. For preliminary studies a Beckman DU spectrophotometer fitted with a reflectance attachment was used,[14] and for later studies two different Cary recording spectrophotometers with automatic reflectance attachments were used. The spectra were measured against a calcium fluoride[15] or magnesium oxide[14] standard. The wave lengths for individual peaks are reported in Tables III and IV, the wave length being reported in both wave numbers and mμ. No attempt has been made to determine the molar absorptivity constants, but only the relative intensity is reported.

Magnetic Susceptibility.—The magnetic susceptibility was measured with a Curie–Chevenaux type balance where the temperature was controlled.[16] The sample was suspended by a quartz spring and the magnetic force determined from the spring deflection. The balance was calibrated by using small platinum rods and was found to be accurate to within 2% (±0.05 B.M.).

The magnetic susceptibilities of the solid crystalline samples of the anhydrous and hydrated compounds have been measured over the temperature range of 77 to 300°K.

Dissociation Pressures.—The dissociation pressures were determined by methods described in the literature[12] where the sample was weighed into a sample tube connected to a manometer, and the tube was placed in a constant temperature bath (±0.2°). After evacuation the sample was brought to temperature and the pressure was measured by the manometer. The tube could then be removed and weighed to determine weight changes. When a constant pressure region was reached the temperature could be varied so the pressure could be studied as a function of temperature. The consistency of the vapor pressure was checked by introducing excess water vapor and allowing the system to equilibrate. The measured pressures were the same (within experimental error) as those measured by removing successive increments of water vapor. The phase diagrams constructed from these studies are in Fig. 1.

Results

Magnetic Moments.—The magnetic data are tabulated in Table I. It has been customary to determine μ_{eff} (in Bohr magnetons) from the equation

$$\mu_{\text{eff}} = 2.84(\chi_M T)^{1/2} \qquad (1)$$

where T is the absolute temperature in °K. and χ_M is the molar magnetic susceptibility after correction for the diamagnetic susceptibilities of the ions. This approach neglects the Weiss constant (θ) and the

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[12] N. Fogel and S. D. Christian, *J. Am. Chem. Soc.*, **80**, 5356 (1958).

[13] C. H. Sorum, "Introduction to Semi-micro Qualitative Analysis," 3rd Ed., Prentice Hall Inc., Englewood Cliffs, N. J., 1960, p. 123 ff.

[14] We are indebted to Dr. K. Schug of the Chemistry Department of the Illinois Institute of Technology for the preliminary measurements and for the additional details of the visible and near-ultraviolet spectra.

[15] We are indebted to Dr. D. S. McClure, formerly of the R.C.A. laboratories, for the reflectance spectra in the near-infrared and visible to approximately 20,000 cm.$^{-1}$.

[16] Some early measurements were made on a Curie–Chevenaux balance of the type described by P. Selwood, "Magnetochemistry," 1st Ed., Interscience Publishers, Inc., New York, N. Y., 1943, p. 11, where the temperature could not be controlled. This was constructed by Mr. John Blair, formerly of this department. We are indebted to Mr. W. H. Brumage for his assistance in making the measurements reported in Table I.

Table I

Observed Magnetic Susceptibilities (in Units of 10^{-3} c.g.s.-e.m.u. per Mole) of $(NH_4)_2CoCl_4$ and $(NH_4)_2CoCl_4 \cdot 2H_2O$

$(NH_4)_2CoCl_4$		$(NH_4)_2CoCl_4 \cdot 2H_2O$	
T, °K.	χ_M, uncor.[a]	T, °K.	λ_M, uncor.[a]
84	27.2	78	34.2
125	18.9	98	28.3
191	13.3	109	25.8
225	11.7	118	24.4
276	9.65	166	18.2
297	9.05	209	15.0
		231	13.7
		295	10.9
μ_{eff} = 4.77 B.M.		μ_{eff} = 5.18 B.M.	
θ = 22°K.		θ = 21°K.	
TIP = 500×10^{-6} c.g.s. unit		TIP = 220×10^{-6} c.g.s. unit	

[a] Correction for diamagnetism = 1.2×10^{-4} c.g.s. unit, used for both compounds.

temperature-independent paramagnetism[17] (TIP), so the alternative approach is to plot $1/\chi_M$ *vs.* T, after correcting for the TIP, and in this way determine the Weiss constant. Since the TIP term is difficult to calculate, except for cases of pure cubic symmetry, the constant was evaluated in the following way. Where the evidence indicated that the compound was a tetrahedral Co(II) case, the TIP for the $^4A_2$ ground state could be estimated from the expression

$$\text{TIP} = \frac{8kN\beta^2}{\Delta} = \frac{2.09k}{\Delta} \qquad (2)$$

where k is the delocalization factor, which in this case was taken to be 0.8,[18,19] and Δ is the crystal field parameter, which was calculated to be 3300 cm.$^{-1}$ from the spectra. These values give the value of TIP as 500×10^{-6} c.g.s. unit. This probably is not accurate, but gives an estimate which can be used in magnetic moment calculation, since this term is small. In the octahedral case, the ground state is a $^4T_{1g}$ and the calculation is difficult because both the ground state and the first excited level ($^4T_{1g}$ and $^4T_{2g}$) are split; therefore no attempts was made to approximate a value for the hydrate (the octahedral compound), but the value was determined experimentally by the following procedure. Quade, Brumage, and Lin[20] have plotted χ_M against $1/(T + \theta)$, replotting with varying values of θ until the best straight line was obtained. In this type of plot both the Weiss constant (θ) and the TIP are automatically obtained, the TIP appearing as the intercept. If this procedure is followed, μ_{eff} = 5.22 B.M. for the hydrated complex, compared to 5.20 B.M. obtained by plotting $1/\chi_M$ *vs.* T. For the anhydrous compound the results are somewhat ambiguous since the data can be fitted (to within experimental error) with widely varying values of θ. Even with the highest θ, μ_{eff} is about 4.79 B.M., which is compatible with the values from the other methods discussed before. It is for this reason that no attempt was made to determine TIP for the anhydrous compound experimentally.

The value of 4.77 B.M. calculated for the anhydrous compound lies between the corresponding values of 4.70 B.M. for Cs_3CoCl_5 and 4.80 B.M. for $(C_9H_8N)_2CoCl_4$. Both compounds are known to contain the tetrahedral $CoCl_4^{-2}$ ion,[21] and the stoichiometry of the anhydrous compound is in agreement with a four-coordinate ion.

The magnetic moment of a tetrahedral cobalt(II) complex will be related to the crystal field parameter (Δ) by the equation[22]

$$\mu = 3.89(1 - 4\lambda/\Delta) \qquad (3)$$

where μ = the magnetic moment in Bohr magnetons corrected for TIP, λ = the spin-orbit coupling constant, and Δ has its usual meaning. If the spin-orbit coupling constant is calculated using 4.77 B.M. for μ and 3300 cm.$^{-1}$ for Δ, the value found is -174 cm.$^{-1}$. This is below the value found for the free ion (-177 cm.$^{-1}$), but well above those observed for tetrahedral Co(II) ions in crystals (approximately -150 cm.$^{-1}$).[23] If possible errors in measurements are considered, the value may be as low as -154 cm.$^{-1}$; however, this seems unlikely. The high value here may be indicative of distortion, which splits the $^4T_{2g}$ and $^4T_{1g}$ states. With a strong distortion, the splitting of the $^4T_{2g}$(F) may be so large that eq. 3 is no longer applicable.

If χ_M for the anhydrous complex is corrected for diamagnetism and TIP, and then $1/\chi_M$ *vs.* T is plotted, the Weiss constant (θ) has a value of $-22 \pm 2°$. This value is large compared to the values observed for most tetrahedral complexes of cobalt(II). Figgis has shown that the Weiss constant may be due to distortion as well as antiferromagnetism, and indicates that this is probably true for the tetrahedral cobalt(II) ion. An attempt was made to fit the magnetic moments of the anhydrous complex by assuming that only the axial symmetry was disturbed (the tetragonal case). While the observed values at each temperature could be calculated to within 3%, the split in the $^4T_2$ term was of the order of 2000 cm.$^{-1}$. There was also a systematic drift in the error which suggested that other types of distortion were present.

The value of 5.20 to 5.22 B.M. observed for the hydrated compound is larger than any possible magnetic moment for a tetrahedral tetrahalocobalt(II) complex (5.01 B.M. for CoI_4^{-2}), but is in the range expected for octahedral complexes.[5] The large change in the magnetic moment indicates an extensive rearrangement of the electronic structure and a different ground state than was observed in the anhydrous

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[17] P. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers Inc., New York, N. Y., 1956, p. 80.

[18] B. N. Figgis, *Trans. Faraday Soc.*, 1553 (1960).

[19] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 131.

[20] C. R. Quade, W. H. Brumage, and C. C. Lin, *J. Chem. Phys.*, **37**, 1368 (1962); W. H. Brumage, C. R. Quade, and C. C. Lin, *Phys. Rev.*, **131**, 949 (1963).

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

[22] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers Inc., New York, N. Y., 1960, p. 427.

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

TABLE II

SPECTRUM OF ANHYDROUS $(NH_4)_2CoCl_4$

Band	Center of band mμ	Center of band cm.$^{-1}$	Centers of individual peaks, cm.$^{-1}$	Description
1[a]	7190	1,390	1,390	Sharp
2[a,b]	3280	3,050	2,800 3,250 sh[c]	Broad band with apparently 2 peaks, not clearly defined, of medium strength
3[a,b]	1667	6,000	4,250 w 4,500 w 5,300 m 6,600 s	Broad and jagged. Same intensity as 2 and 4 in reflection spectra, lower in KBr
4[a,b]	656	15,250	14,451 15,038 15,504 15,873 16,207 sh	Very broad, all approx. same intensity. Intensity medium to high, approx. same as band 2
5[a,b]	542	18,422	18,182 sh 18,762	Both weak, observed on slope of band 4
6[b]	450	22,222	22,222 w	
7[b]	410	24,390	24,390	On side of band 9
8[b]	220	45,454	31,250 sh 45,454 s	A strong intense band, broad

[a] Spectra from KBr pellet. [b] Spectra taken by reflection method. [c] sh, shoulder; w, weak intensity; m, medium intensity; s, strong intensity. All of these intensities are relative.

compound. The magnetic moments are lower than the maximum observed for octahedral configurations, and lower than the theoretical maximum. This may be indicative of distortion in the hydrate.

Spectra. Anhydrous Salt.—The spectra of the anhydrous salt are reported in Table II. The magnetic moments for the anhydrous salt are most easily interpreted on the assumption that this compound is essentially a tetrahedral cobalt(II) complex, and the spectra agree with this assumption. Some of the bands have been identified and a partial assignment has been made. The first band, at 1390 cm.$^{-1}$, is due to the N–H bending frequency.[24] No bands were observed at lower wave numbers to the limit of the spectrophotometer (approximately 650 cm.$^{-1}$). The absence of any bands in the region is evidence that the nitrogen is present as the ammonium ion, and not as an ammine complex, since in ammine complexes an N–H rocking frequency would be expected between 900 and 700 wave numbers.[25] The next band, observed at about 3200 cm.$^{-1}$, is a fairly broad band. The N–H stretching frequency is observed in this portion of the spectrum as well as the first electronic transition ($^4A_2(F) \rightarrow {}^4T_2(F)$). A careful examination of the spectra of the KBr pellet indicates the presence of a shoulder at approximately 3300 cm.$^{-1}$ which is absent in the hydrate. Although this shoulder appears at the expected wave length for the first electronic transition, it may also be due to an asymmetric transition in the tetrahedral ammonium ion, especially if distortion occurs in the crystal. The spectrum of carefully dried ammonium chloride shows the same type of shoulder at the same wave length, so assignment here is very uncertain. The rest of the band is clearly due to the N–H stretching frequency. The shoulder could not be clearly resolved in the reflection spectra. A third band is observed at 6000 cm.$^{-1}$, with about four peaks and fairly broad. From the weighted center of this band, the crystal field parameter Δ (= $10Dq$) was calculated to be 3300 ± 200 cm.$^{-1}$, in fair agreement with other reported values for the tetrahedral $CoCl_4^{-2}$ ion.[26–28] The relative intensity of the third band assigned to the $^4A_2(F) \rightarrow {}^4T_1(F)$ is surprisingly high in the reflection spectra, and this is probably due to distortion. In the spectra from the KBr pellet this band is low compared to the second and fourth band, as would be expected from a two-electron transition. The fourth band, at approximately 15,250 cm.$^{-1}$, is assigned to the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition. The broadness of this band can be partially ascribed to distortion and partly to transitions to the $^2T_1(G)$ and $^2A_1(G)$ as well as the possibility of transitions to higher excited levels. The fourth band shows some similarity to the band observed in the reflection spectra of Cs_2CoCl_4,[3b] which is known to be tetrahedral. The spectrum from the KBr pellet shows more details in this band, and the details show much the same structure as similar bands observed for tetrahedral Co(II) compounds dissolved in solid ZnO, ZnS, and CdS crystals.[29] The series of weak bands between 18,422 and 31,250 cm.$^{-1}$ is probably due to transitions to various components of such states as ^2G, ^2H, and ^2D. No attempts were made to identify these bands any further since distortion would preclude any accurate calculation. The last band, at 45,454 cm.$^{-1}$, is most probably due to a change-transfer process. The intensity is high and

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(24) A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. IX, W. West, Ed., "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, p. 247 ff.

(25) D. B. Powell and N. Shepard, *J. Chem. Soc.*, 3108 (1956).

(26) C. K. Ballhousen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

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(28) D. A. Fine, *J. Am. Chem. Soc.*, **84**, 1139 (1962).

(29) H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).

TABLE III

SPECTRUM OF THE DIHYDRATE $(NH_4)_2CoCl_4 \cdot 2H_2O$

	Center of band		Centers of individual peaks, cm.$^{-1}$		Calculated values Dq = 695 cm.$^{-1}$	
Band	mμ	cm.$^{-1}$		Description	Ds = 175 cm.$^{-1}$	Ds = −200 cm.$^{-1}$
1[a]	7153	1,398	1,398	Sharp, fairly intense		
2[a]	6231	1,605	1,605	Sharp, weaker than 1		
3[a,b]	3571	2,800	2,700 sh,[c] m	Broad band with one sharp peak		
			2,800 sh, m			
			3,000 s			
			3,100 sh, m			
4[b]	1818	5,500	4,900 sh	Broad band. Possible to separate the individual peaks. Fairly intense	5,031	4,760
			5,250 sh		5,133	5,044
			5,600		6,158	5,844
			6,100		6,268	6,128
5[b]	1282	7,800	7,800	Broad band of very low intensity		
6[b]	635	15,750	12,000 sh	Broad band of low intensity compared to bands 4 and 7. Starts at 11,000 cm.$^{-1}$ and runs into band 7	12,083	11,710
			13,500 ctr. of broad plateau		13,210	12,794
			15,250			
			15,800			
7[b]	540	18,520	16,949 sh	Broad fairly intense band	17,893	17,670
			18,248		18,418	18,270
			19,084		19,020	18,754
			19,802 sh		19,545	19,354
8[b]	220	45,454	45,454	Very intense band, like band 8, Table II		

[a] Spectra taken from KBr pellet. [b] Spectra taken by reflection method. [c] sh, shoulder; s, strong intensity; m, medium intensity. The intensities described here are relative.

the energy involved is large. This last band may also mask some weak bands due to transitions to higher excited levels.

The badly fragmented spectra seem to indicate that there is probably rhombic distortion.

Hydrated Salt.—The spectra of the hydrate are reported in Table III. The KBr pellet spectra were not as revealing in the hydrate as in the anhydrous compound. At higher wave numbers than 3000 cm.$^{-1}$ the absorbancy was so great that no details could be distinguished, and all bands at higher wave numbers were determined from the reflection spectra. The first band, at 1398 cm.$^{-1}$, can be ascribed to the N–H bending frequency. No bands were observed below 1400 cm.$^{-1}$ to the limit of the spectrophotometer, confirming that nitrogen is present as the NH_4^+ ion in the hydrate. The second band, at 1600 cm.$^{-1}$, is due to the O–H bending frequency,[24] while the third band, at 2800 cm.$^{-1}$, is most probably due to a combination of the O–H and N–H stretching frequencies. Most of the details of this band were determined from the KBr pellet spectrum. The band at 5500 cm.$^{-1}$ is assigned to the first electronic transition within the d shell. If this band were to be assigned to the second transition in the tetrahedral case, then the shifting of the bands observed at 3300 and 6000 cm.$^{-1}$ in the anhydrous compound to a lower value in the hydrate would have to be interpreted to mean that the addition of two waters lowered the strength of the crystalline field, contrary to much experimental evidence.[30] If the dihydrate is considered to be an octahedral compound, the band at 5500 cm.$^{-1}$ can be assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and the crystal field parameter (Δ) will have a value of 6950 cm.$^{-1}$. Two other bands would be expected, ν_2 at 12,510 cm.$^{-1}$ and ν_3 at 18,670 cm.$^{-1}$.[31]

A broad flat band starting at 11,000 cm.$^{-1}$ extends with various peaks (see Table III) to about 16,000 cm.$^{-1}$, where it merges into the next band (no. 7), which is badly split, but has an approximate center at 18,520 cm.$^{-1}$, in agreement with the value calculated for the third transition in the d shell. The band at 11,000 cm.$^{-1}$ is in good agreement with the calculated value for the second electronic transition, and the relative intensity is low compared to the other two electronic transitions, as would be expected from a two-electron transition. The second electronic transition (band 6) contains transitions to higher excited states which broaden the band. The last clearly observed band (no. 8) is observed at 45,454 cm.$^{-1}$, and from the intensity and position is most probably a charge-transfer band. It probably masks some transitions to the higher excited states. It should be pointed out that band 8 is at the same wave length in both compounds, which supports the contention that it is a charge-transfer band.

The major features of the spectrum are in agreement with an octahedral configuration, however the extra peaks and shoulders are indicative of distortion. The simplest type of distortion expected in an octahedral compound with two water molecules and four chloride

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(30) L. E. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960.

(31) The value 14,500 cm.$^{-1}$ was used in calculating ν_3 rather than the measured difference between the atomic ^4F and ^4P levels (15,400 cm.$^{-1}$) for reasons discussed in ref. 23 and 19.

ions is the two waters *trans* and either closer (axial compression) or farther (axial elongation) than the four chlorides. Tetragonal distortion (axial compression) of this type is observed in $CoCl_2 \cdot 2H_2O$,[32] which involves the same central ion and coordinating groups. The reflection spectrum of $CoCl_2 \cdot 2H_2O$ from 15,000 to 20,000 cm.$^{-1}$ [26] is similar to that observed for the dihydrate, which provides some support for the model.

From the point charge model the tetragonal field will split the $^4T_{1g}(F)$ into a $^4A_{2g}$ at $-6Dq - 4Ds$ and a ^4E_g at $-2Dq + 4Dqs + Ds$. The $^4T_{2g}(F)$ will split into a $^4B_{2g}$ at $+2Dq$ and a ^4E_g at $6Dq - 4Dqs + Ds$. The $^4A_{2g}$ is not split by the tetragonal field. The $^4T_{1g}(P)$ splits into a $^4A_{2g}$ at $-2Ds$, and a ^4E_g at $+Ds$, from the undistorted level. In these calculations Dq is the octahedral field splitting parameter (*i.e.*, $\Delta = 10Dq$), Ds is the second-power splitting parameter for the tetragonal field, and Dqs is the interaction parameter, defined as $[(Dq)^2 + (Ds)^2 + DqDs/2]^{1/2}$.[33] Since the data are not sufficient to determine Dt, the fourth-power splitting parameter for the tetragonal field has been neglected in these calculations. In many cases it has been observed that this factor is small compared to Ds.[34,35] To test the assumption of tetragonal distortion, calculated results for $Dq = 695$, $Ds = 175$ (axial elongation), and $Ds = -200$ cm.$^{-1}$ (axial compression) are compared to the observed values in Table III. These values were chosen for minimum error and a variation ±25 cm.$^{-1}$ should be allowed. Reasonable agreement is observed, which partially justifies the neglect of Dt.

Since both cases are in reasonable agreement with the observed spectrum, no decision as to the correct structure can be made from the optical spectrum, nor could the spectroscopic data alone rule out the possibility of distortions of lower symmetry (such as rhombic). However in view of the results of the study of many cobalt compounds which have been found to have tetragonal distortions, it seems to be a reasonable assumption, and the spectroscopic evidence is compatible with a tetragonal structure.

Dissociation Pressure.—The results of the pressure *vs.* composition determinations are shown in Fig. 1 for runs made at 39 and 53.2°. The pressure due to all vapors (in mm.) is plotted against the ratio of sample weight to the weight of the complex after the loss of all the vapor. The vapors were condensed and found to be pure water.

The results of three separate determinations of dissociation pressure as a function of temperature (from 15 to 60°) were fitted by the method of least squares, and were found to follow the expression

$$\log P = -4140/T + 13.830 \qquad (4)$$

where P is the dissociation pressure (in mm.) and T is the absolute temperature (°K.) to within the experimental error (±0.1 mm.).

An examination of Fig. 1 shows that both waters are released in a single dissociation step. From the width of the plateau, the change in molecular weight due to the reaction can be calculated. A line drawn on the plot of Fig. 1 indicates the plateau width expected for the loss to two water molecules.

From eq. 4, the value of K_d (dissociation constant), $\Delta H°$, $\Delta F°$, and $\Delta S°$ have been calculated for the dissociation process at 30°, assuming the equilibrium reaction to be

$$(NH_4)_2CoCl_4 \cdot 2H_2O(s) = (NH_4)_2CoCl_4(s) + 2H_2O(g) \qquad (5)$$

The values are given in Table IV, using gas at 1 atm. as the standard state for the water and the solid crystal as the standard state for both the anhydrous and hydrated forms of the compound.

TABLE IV

THERMODYNAMIC CONSTANTS FOR THE REACTION AT 30°

$(NH_4)_2[Co(H_2O)_2Cl_4](s) = (NH_4)_2CoCl_4(s) + 2H_2O(g)$

K_d (dissociation constant), atm.^{2}	3.74×10^{-6}
$\Delta H°$, cal./mole	38,088
$\Delta F°$, cal./mole	7,525
$\Delta S°$, e.u./mole	100.9

Discussion

The magnetic moments and the major features of the spectrum indicate that the anhydrous compound is essentially tetrahedral with a $^4A_2$ ground state. However, the high value of the spin–orbit coupling constant (λ) calculated from the magnetic moment (assuming a regular tetrahedral configuration) and the Weiss constant (θ) are suggestive of distortion. Although the high value for the Weiss constant could arise from antiferromagnetism, plots of $1/\chi_M$ *vs.* T are linear over the temperature range from room temperature to 84°K., whereas if antiferromagnetism were important some curvature would be expected. Most tetrahedral salts of cobalt(II) where antiferromagnetism of the same type might be expected have values of 4 to 10° for their Weiss constants. The suggestion that the large values for the spin–orbital coupling constant and the Weiss constant arise from distortion is reinforced by the spectral data.

The complexity of the details of the spectral band structure is consistent with a distortion of a low symmetry type such as rhombic, although it is possible that the spin–orbit splitting and distortion splitting are of equal magnitude, which could produce the complex spectra. The spectral behavior and the magnetic moment are both consistent with distortion in the anhydrous compound.

For the hydrate, the magnetic and spectral data indicate an essentially octahedral configuration, and the detailed structure of the spectral bands is consistent with a distortion of the tetragonal type, although some minor trigonal or rhombic components may be present. Tetragonal distortion has been observed in $CoCl_2 \cdot 2H_2O$[32] and $(Co(H_2O)_6)Cl_2$,[36] and these compounds

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have been used as models for the hydrate. If tetragonal distortion is assumed as the main distortion in the hydrate, the question arises whether the two waters are closer to the central ion than the four chlorides (axial compression) or further (axial elongation). Neither spectral nor magnetic data offer sufficient evidence to draw any conclusions, although axial compression fits the spectral data slightly better. A study of the X-ray data for some cobalt(II) and copper(II) halides, hydrated and unhydrated,[32,37] simple and complex, indicates that in all these cases the water molecule is closer to the central ion than is the halide. The cobalt–chloride distance would be expected to be smaller in the tetrahedral configuration than in octahedral configurations involving the same ions.[38] The compound Cs_2CoCl_4 has a tetrahedral structure, and the measured distance between the cobalt and chloride ions (2.22 to 2.25 Å.)[39] was greater than any of the metal–water distances in the above compounds with octahedral configuration (although somewhat distorted).

An increase in the metal–halide distances in transformations from a tetrahedral to an octahedral configuration could explain why the crystal field parameter for the hydrate (Δ) is smaller than the value calculated from the averaged field approximation. The averaged field approximation is

$$\Delta_{\text{oct}} = {}^2/_3\Delta_{\text{oct Cl}^-} + {}^1/_3\Delta_{\text{oct H}_2\text{O}} \qquad (6)$$

The $\Delta_{\text{oct H}_2\text{O}}$ is known (9300 cm.$^{-1}$) from experimental data,[30] but $\Delta_{\text{oct Cl}^-}$ is estimated from the relationship $\Delta_{\text{oct}} = {}^9/_4\Delta_{\text{tetra}}$. This relationship assumes that the distance in the tetrahedral and octahedral structures is the same, but an increase in distance would produce a decrease in the calculated Δ_{oct}. The experimental value for the hydrate crystal field parameter is 6950 cm.$^{-1}$, compared to 8050 cm.$^{-1}$ calculated from (6) assuming $\Delta_{\text{tetra}} = 3300$ cm.$^{-1}$ as an average for the $CoCl_4^{-2}$.[26-28]

The energy necessary to remove two moles of water from the solid state (in the hydrate) to the vapor state and to form the anhydrous crystal is 38.1 kcal./mole of compound. Because there are so little thermodynamic data available for comparison, it may be of interest to look at the energy necessary to take two moles of water from the solid state (ice) to the vapor state. This value is approximately 23.4 kcal. for two moles at 30°, and therefore the bonding of each water molecule in the complex halide is about 7 kcal./mole stronger than the bonding of the water molecules in ice. This fairly strong bond would be compatible with the assumption that the water is in the first coordination sphere in the hydrate.

The entropy change of 101 e.u. for the reaction is relatively high. The entropy change involved in taking two moles of water from the ice phase (a tetrahedral configuration) to the gas phase (at 30°) is 77 e.u. For comparative purposes, the entropy for taking two moles of water from the solid to the gaseous phase in the $ZnBr_2 \cdot 2H_2O$ system (at 30°) is about 47.3 e.u.[40] The structure of both the anhydrous and hydrated forms of zinc(II) bromide is octahedral.[37] It would seem that most of the entropy change here is due to the change in phase of the water molecules (approximately 69 e.u. from liquid water to vapor at 30°), and there is probably a decrease from the entropy observed for water due to an ordering of the crystal. The relatively large value observed for the complex cobalt chloride indicates that the anhydrous crystal structure is more disordered than the hydrated compound. This picture is compatible with the postulation of a distorted tetrahedral compound changing to a more symmetrical tetragonal compound on hydration.

The changes in the chemical and physical properties are consistent with the assumption that in ammonium tetrachlorocobaltate(II), the anhydrous compound is a distorted tetrahedron, which changes to a more regular tetragonal structure on hydration. The two waters in the hydrate are in the inner coordination sphere, most probably *trans* to each other and closer to the central cobalt ion than are the four chloride ions.

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