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THERMOCHEMISTRY OF THE HYDRATES OF K_2CoCl_4*

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ABSTRACT

A study of the dissociation pressure of crystalline $K_2CoCl_4 \cdot 2H_2O$. The reactions can be summed up as $K_2CoCl_4 \cdot nH_2O(c) = K_2CoCl_4 \cdot mH_2O(c) + (n-m)H_2O$ (v). Below 50 °C, $n = 2$ and 1, $m = 1$ and 0, above 50 °C, $n = 2$ and $m = 0$. Below 50 °C, the dihydrate is octahedral, the monohydrate and anhydrous compounds are tetrahedral. ΔH° and ΔS° are respectively 7.0 kcal and 14.2 e.u. for the loss of the first mole of water and 12.7 kcal and 32.0 e.u. for the loss of the last mole of water. Above 50 °C, ΔH° and ΔS° are respectively 29.8 kcal and 77.6 e.u. for the loss of both waters. The changes in structure are discussed using the spectral and magnetic properties as indications for structural changes.

INTRODUCTION

The complex halides of cobalt(II) can exist in either octahedral or tetrahedral configurations. The study of a reaction where there is a configuration change is important since it contributes to our knowledge of the conditions under which such changes occur, and to our understanding of what causes the changes in configuration. One such system in which these changes are observed is that of the potassium tetrachlorocobaltate(II) and its hydrates. This study attempts to elucidate what is occuring during the dehydration reaction. The anhydrous K_2CoCl_4 is known to exist in a tetrahedral configuration[2], and in analogy with other tetrahalocobaltate(II) compounds contains the $CoCl_4^{2-}$ ion[3]. Below 50 °C, there is a two step dehydration of the dihydrate, forming a monohydrate and an anhydrous compound. Above 50 °C, the physical evidence is consistent with phase changes, most probably in both the hydrated and anhydrous compounds, and a one step loss of both waters of hydration. This behavior could not be investigated effectively because of experimental difficulties.

The thermal decomposition of the potassium tetrachlorocobaltate(II) dihydrate was studied over the temperature range 25–60 °C. The reaction can be written as

$$K_2CoCl_4 \cdot 2H_2O(c) \rightleftharpoons K_2CoCl_4 \cdot 1H_2O(c) + H_2O(v) \qquad (1)$$

$$K_2CoCl_4 \cdot 1H_2O(c) \rightleftharpoons K_2CoCl_4(c) \qquad + H_2O(v) \qquad (2)$$

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*Taken in part from ref. 1.

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below 50 °C. Above 50 °C the evidence is unclear, although it is obvious that two moles of water are lost in one step from a dihydrate which may be an isomeric form. The symbol (c) indicates the crystalline solid and (v) indicates the vapor phase.

The equilibrium decomposition pressure, the enthalpy and entropy of reactions (1) and (2) have been determined, as well as a portion of the decomposition curve for the unknown dihydrate. The magnetic moments up to room temperature, as well as a qualitative discussion of the room temperature reflection spectra of the compounds formed in reactions (1) and (2) are also presented and are used to help in discussing the data.

EXPERIMENTAL

Preparation

Cobalt(II) chloride hexahydrate, KCl, hydrochloric acid and methanol, all reagent grade, were used in preparation of the compounds. The anhydrous K_2CoCl_4 was prepared by dissolving stoichiometric amounts of KCl and $CoCl_2$ in concentrated hydrochloric acid and evaporating the solution to dryness. The deep blue powder residue was extracted with methanol until the desired purity was reached.

The dihydrate and monohydrate were prepared by placing the anhydrous compound over wet calcium nitrate until the desired weight gain was observed. The monohydrate could also be prepared by dehydrating the dihydrate under vacuum conditions.

Analysis

The chloride ion was determined gravimetrically by precipitation of silver chloride from dilute nitric acid solutions. The water concentration was determined by weight loss during dehydration under vacuum conditions. The vapor was trapped in a cold finger and shown by analysis to be pure water. The end product of all reactions was the anhydrous K_2CoCl_4 since nothing else was vaporized but water, so the chloride analysis was also a check that no side reactions had occured. Cl^-: theor., 50.80; found, 50.95 ±0.20%. Hydrates: $K_2CoCl_4 \cdot 1H_2O$, water: theor., 6.07; found, 6.2 ±0.2; $K_2CoCl_4 \cdot 2H_2O$, water: theor., 11.44; found, 11.3 ±0.2%.

Magnetic susceptibility

The magnetic susceptibilities were measured with a Faraday type balance[4]. The sample chamber can be evacuated and the measurements carried out under the vapor pressure of the compound so there is no change in species during measurements. The sample chamber was thermostated and the magnetic susceptibilities measured as a function of temperature from room temperature to liquid nitrogen temperature (78 °K). The balance was standardized against $HgCo(SCN)_4$[5]. Previous use had shown accuracy to be ±2.5%[6]. The results are in Table 2 (see Results and Discussion).

Pressure measurements

The equilibrium dissociation pressures were measured in an apparatus that has been described in the literature[6]. The apparatus was completely submerged in a constant temperature water bath (±0.1 °C) where the temperature could be varied at will. The dissociation pressure was measured with a closed manometer using a cathetometer (±0.05 mm Hg).

Once an apparent equilibrium was reached (usually after several days), the bath temperature was varied several degrees, both above and below the original temperature. The system was given time to adjust and then returned to the original temperature. The return to the original pressure at the initial temperature was taken as evidence that equilibrium had been reached.

The curves of dissociation pressure versus composition are all relatively flat (Fig. 1) in the three phase region. The enthalpy and entropy of reaction were determined from the variation of dissociation pressure as a function of temperature at a composition such that the ratio of the two crystalline phases was approximately unity. The standard states were one atmosphere for the gas and the crystalline form for the solids. The dissociation pressures were low enough so that the gas phase could be treated as ideal.

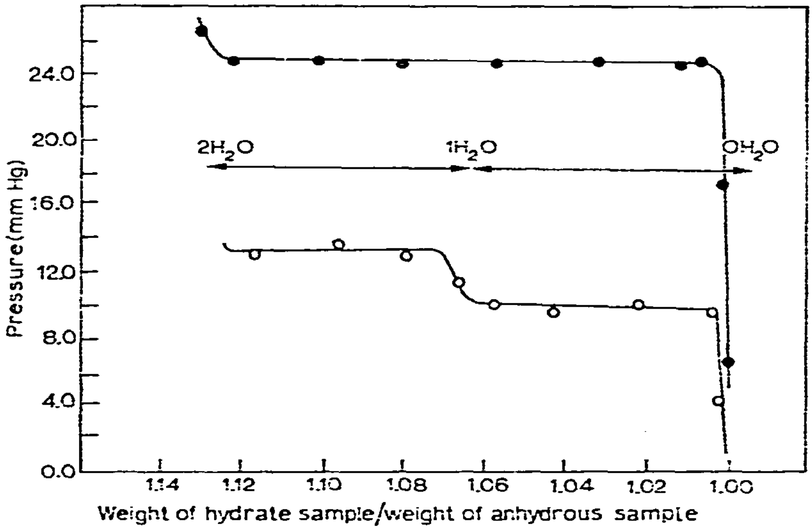

Fig. 1. Dissociation pressures of K_2CoCl_4 hydrates as a function of composition. ○, temperature 40 °C; ●, temperature 54.5 °C.

Spectra

The diffuse reflection spectrum of each of the pure compounds was measured at room temperature with a Beckman DK-1 recording spectrophotometer equipped with a reflection attachment. The spectra were measured on pure, carefully powdered samples mounted in a well on a glass slide. The spectra were reproducible. The standard, magnesium oxide, was mounted in the same way. Absolute intensities were not measured, although relative intensities were obvious. The spectra are not presented here, but a short discussion will be used in the interpretation of the data.

RESULTS AND DISCUSSION

The dissociation pressure is displayed as a function of composition in Fig. 1, and as a function of temperature in Fig. 2. The data indicate that below 50 °C only

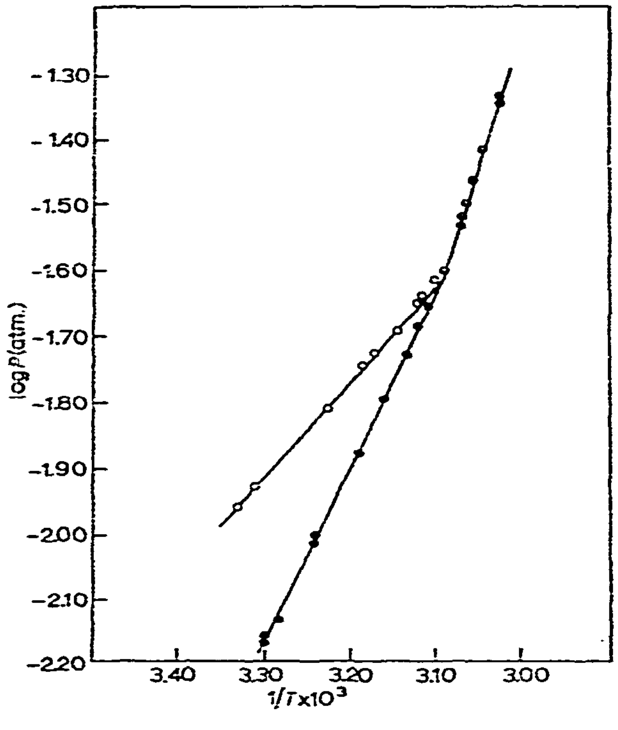

Fig. 2. Logarithm of the dissociation pressure as a function of temperature.
○, $K_2CoCl_4 \cdot 2H_2O(c) \rightleftharpoons K_2CoCl_4 \cdot 1H_2O(c) + H_2O(v)$;
●, $K_2CoCl_4 \cdot 1H_2O(c) \rightleftharpoons K_2CoCl_4(c) + H_2O(v)$;
⊖, $K_2CoCl_4 \cdot 2H_2O(c) \rightleftharpoons K_2CoCl_4(c) + H_2O(v)$.

the dihydrate, monohydrate and anhydrous potassium tetrachlorcobaltate(II) are formed under the experimental conditions. Since each species could be formed as a pure compound, each could be studied separately. Conditions were maintained so there was no change in composition during the studies. Under these conditions reactions (1) and (2) can be summarized

$$K_2CoCl_4 \cdot nH_2O(c) \rightleftharpoons K_2CoCl_4 \cdot mH_2O(c) + (n-m)H_2O(v) \qquad (3)$$

The dissociation pressures were found to follow the equation

$$\log P = \frac{-\Delta H^\circ}{(n-m)2.303\,RT} + \frac{\Delta S^\circ}{(n-m)2.303\,R} \qquad (4)$$

where P is the dissociation pressure in atmospheres, ΔH° is the standard enthalpy of reaction in calories mole^{-1}, ΔS° is the standard entropy of reaction in entropy units mole^{-1}, n and m are respectively the number of water molecules in the reactant and product. In this case $(n-m)$ is equal to one. The enthalpy and entropy of reaction can be calculated from the best fit of the logarithm of the dissociation pressure as an inverse function of temperature. The linearity of these plots is indicated in Fig. 2 for temperature changes of approximately 30°. The linearity of the plots indicate ΔC_p is relatively small and that the enthalpy and entropy could be treated as constants over reasonable temperature changes. The results are in Table 1, with the mean temperature for each series. The extrapolation necessary to calculate the values at 25 °C was small.

TABLE 1

ENTHALPY AND ENTROPY OF REACTION FOR THE REACTION $K_2CoCl_4\cdot nH_2O(c) \rightleftarrows K_2CoCl_4\cdot mH_2O(c)+(n-m)H_2O(v)$

n	*m*	*Mean temp. (°K)*	ΔH° *(kcal mole^{-1})*			ΔS° *(e.u. mole^{-1})*		
			Expt.	*Calc.*[a]	*Calc.*[b]	*Expt.*	*Calc.*[a]	*Calc.*[b]
2	1	308	6.96±0.1	13.2	12.4	14.2±0.1	35.7	35.2
1	0	310	12.7 ±0.2	13.2	12.4	32.0±0.2	35.7	35.2
2[c]	0[c]	325	29.8 ±0.3	26.4	24.8	77.6±0.4	71.4	70.4

[a] Using averaged values observed for $(\Delta H^\circ_{T,m}-\Delta H^\circ_{T,a})$ and $(S^\circ_{T,m}-S^\circ_{T,a})$ in eqns (5) and (6). [b] Calculated using values from the vaporization of ice at 25 °C. See Discussion. [c] These are probably isomeric forms of the dihydrate and anhydrous compounds stable above 50 °C, but the ratio of KCl to $CoCl_2$ is still 2/1.

The magnetic moments corrected for diamagnetism and temperature independent paramagnetism are in Table 2. The Weiss constant (θ) and the temperature independent paramagnetism were calculated from the best fit to a straight line of $\chi_{\text{corrected}}$ versus $(T+\theta)^{-1}$ (Ref. 4). The magnetic moment for the dihydrate is higher than any of the others and is in the range observed for distorted octahedral complexes of Co(II). The magnetic moments of the monohydrate and anhydrous compounds are in the range expected for tetrahedral tetrahalo complexes[8] and are close to the

TABLE 2

MAGNETIC MOMENTS OF THE CRYSTALLINE HYDRATES AND ANHYDROUS K_2CoCl_4[a]

Compounds	*Magnetic moments (Bohr magnetons)*	*Weiss constant (θ in °K)*	*Temperature independant magnetism × 10⁶ (c.g.s. units)*
K_2CoCl_4	4.85	15	400
$K_2CoCl_4\cdot 1H_2O$	4.87	10	250
$K_2CoCi_4\cdot 2H_2O$	5.22	10	300

[a] None of these are the forms that are present above 50 °C.

values observed for $(NH_4)_2CoCl_4$[9] which has been shown to be tetrahedral. The magnetic moments are high for symmetrical tetrahedral complexes and are probably indicative of distortion. This is confirmed by the high values for the Weiss constant. Figgis[10] has shown that the Weiss constant can be due to distortion of the molecule. The values here are higher than those reported for other tetrahalo complexes of cobalt(II) indicating considerable distortion.

These conclusions are supported by the diffuse reflection spectra of the compounds. The spectrum of the dihydrate is similar (but not identical) to that of the cobalt(II) chloride dihydrate with bands centered around 6–7, 16 and 19–20 kK. An attempt to fit the spectrum using first order crystal-field theory, assuming tetragonal distortion but no spin–orbit coupling, leads to a *Dq* value of 845, *Ds* and *Dt* values of −220 and 110 k respectively. These values imply an axially compressed tetragonal distortion such as is found in cobalt(II) chloride dihydrate[11]. The spectra of the monohydrate and anhydrous K_2CoCl_4 are similar with two bands centered around 6 and 16.5 kK. The band at 16.5 kK shows the high intensity and structure observed in compounds known to contain the tetrahedral $CoCl_4^{2-}$ ion. These spectra were fitted with crystal-field theory, assuming a symmetrical undistorted tetrahedral $CoCl_4^{2-}$ ion and ignoring spin–orbit coupling, with a *Dq* of 335 ±20 k, in the range expected for these types of complexes.

The physical data are consistent with a change structure from a distorted octahedral to tetrahedral structure with the loss of the first molecule of water, and a retention of the tetrahedral structure with the loss of the last molecule of water. The data for the monohydrate are not sufficient to indicate if the water molecule is in the first coordination sphere, forming a $Co(H_2O)Cl_3^-$ ion, or in the outer sphere so a $CoCl_4^{2-}$ ion is formed. The spectrum however does not show the shift to higher wavenumbers expected if the water molecule were in the first coordination sphere. The magnetic moments for both monohydrate and anhydrous forms are the same within experimental error, but the Weiss constant indicates some difference in distortion. The data are more compatible with a $CoCl_4^{2-}$ ion in both molecules.

The thermodynamic data are best interpreted by comparison with the solid–vapor equilibrium in water and other hydrate systems. The heat and enthalpy of the dehydration reaction (eqn (3)) can be written

$$\Delta H^\circ(\text{reaction}) = [\Delta H^\circ_{f,m} - \Delta H^\circ_{f,n}](\text{c}) + (n-m)\Delta H^\circ_{f,H_2O}(\text{v}) \qquad (5)$$

and

$$\Delta S^\circ(\text{reaction}) = [S^\circ_{f,m} - S^\circ_{f,n}](\text{c}) + (n-m)S^\circ_{f,H_2O}(\text{v}) \qquad (6)$$

where ΔH°_f and S°_f represent the enthalpy and entropy of formation of the respective compounds with *m* and *n* moles of water and pure water from their standard states. The enthalpy and entropy of reaction can be compared to the enthalpy and entropy of sublimation of ice at 25 °C, where ΔH(sublimation) = 12.4 kcal mole^{-1}, ΔS (sublimation) = 35.2 e.u. mole^{-1}, and these are compared to the enthalpy and entropy of the dehydration reaction in Table 1.

In a previous paper[11] it was observed that an average value for the dehydration reaction in many hydrates is $\Delta H(\text{reaction}) = 13.2$ kcal mole^{-1} and $\Delta S(\text{reaction}) = 35.7$ e.u. mole^{-1} while $\Delta H^{\circ}_{f,m} - \Delta H^{\circ}_{f,n} = 72$ kcal mole^{-1} and $-(S^{\circ}_{f,m} - S^{\circ}_{f,n}) = 9.4$ e.u. mole^{-1}, all in good agreement with what is seen for the ice–vapor reaction. The difference in the enthalpy and entropy of formation of adjacent hydrates is easily calculated using the experimental values of the dehydration reaction in eqns (5) and (6) as well as the known value for the formation of water. The results are recorded in Table 3, along with the estimated enthalpy and entropy of formation of the hydrates and the anhydrous compound from the elements in their standard states.

TABLE 3

ENTHALPY AND ENTROPY OF FORMATION OF THE CRYSTALLINE COMPOUNDS

Compound	ΔH°_f (*kcal mole*$^{-1}$)	$(\Delta H^{\circ}_{f,m} - \Delta H^{\circ}_{f,n})^c$		S°_f (*e.u. mole*$^{-1}$)	$-(S^{\circ}_{f,m} - S^{\circ}_{f,n})^c$	
		Exp.	*Calc.*		*Exp.*	*Calc.*
K_2CoCl_4[a]	−291.6			66.6		
		70.5	72.0		13.1	9.4
$K_2CoCl_4 \cdot 1H_2O$[a]	−356.4			79.7		
		64.8	72.0		30.9	9.4
$K_2CoCl_4 \cdot 2H_2O$[a]	−426.9			110.6		
$(KCl)_2CoCl_2$[b]						
		145.4	144.0		12.6	18.8
$(KCl)_2CoCl_2 \cdot 2H_2O$[b]						

[a] The compounds stable below 50 °C. [b] The compounds stable above 50 °C. The ratio of 2KCl to 1CoCl$_2$ may indicate isomeric forms or different compounds where one or the other may be in excess. [c] Calculated from eqns (5) and (6) using ΔH° of reaction and ΔH°_f of formation of H_2O.

Above 50 °C there is a clear indication of change in the system. The enthalpy and entropy of the dehydration reaction where both waters are lost in one step are not the sum of the reactions below 50 °C, where the reaction occurs in two steps. It is possible that a completely new set of compounds are formed and that we are dealing with a different dehydration reaction. The amount of water lost is consistent with a change from a dihydrate to an anhydrous compound. We were unable to study the situation at these temperatures because of experimental conditions, but it is clear from the analysis of the product that the ratio of KCl to $CoCl_2$ remains two to one. There is some evidence that there may be an isomeric form of K_2CoCl_4 above the transition temperature[12] and also some indication that the hydrate may have some other form, or even that a completely different compound is stable at higher temperatures[13,14]. Since so little is known, only the enthalpy and entropy values for a dehydration reaction of the type

$$M \cdot 2H_2O(c) \rightleftharpoons M(c) + 2H_2O(v) \tag{7}$$

(M is a compound where the ratio of KCl to $CoCl_2$ present in the mixture is 2 to 1) is calculated from the variation of pressure with temperature. The results are presented in Table 1 and have been calculated from eqn (4). The differences in the enthalpy and entropy of formation of the solids can be calculated from eqns (5) and (6) and the results are presented in Table 3, although no attempt was made to estimate the enthalpy and entropy of formation of the compounds involved.

The enthalpy of formation of the compound K_2CoCl_4 at room temperature (Table 3) was estimated from a Born–Haber cycle where the energy of formation of the $CoCl_4{}^{2-}$ ion (called ΔH(complex)) was estimated from data for Cs_2CoCl_4 and Rb_2CoCl_4 as 602.4 kcal mole^{-1}. The lattice energy for the formation of K_2CoCl_4 was then calculated using the extended Kaputsinskii equation with a thermochemical radius of 3.14 Å for the $CoCl_4^{2-}$ ion[15]. The equation used is

$$\Delta H_f^\circ = \Sigma S + 2D + \Sigma I + 4E_a + \Delta H(\text{complex}) + \Delta H_L \tag{8}$$

where ΣS is the sublimation energy of Co and 2K, D the dissociation energy of Cl_2, ΣI the appropriate ionization energies for Co and K, E_a the electronegativity of Cl, ΔH(complex) and ΔH_L the lattice energy are discussed above. Equation (8) was then used to calculate the heat of formation (ΔH_f°) of K_2CoCl_4. The entropy of formation (S_f°) was estimated from Latimer's[17] rules.

CONCLUSIONS

At temperatures below 50 °C the dehydration of the dihydrate takes place in two distinct steps, with one molecule of water lost in each step. The dihydrate is a tetragonally distorted octahedral complex with the probable formula $K_2[Co(H_2O)_2Cl_4]$. The physical properties are consistent with an axially compressed octahedron. The structural change to a distorted tetrahedron occurs with the loss of the first molecule of water. The remaining water molecule probably moves out of the inner coordination sphere. This produces considerable ordening in the lattice as can be seen from the entropy change (Table 3). The loss of the molecule of water from the monohydrate has enthalpy and entropy values close to what is observed for the average change, which seems to involve small change in the structure of the molecule[12].

Above 50°C there are clearly some phase changes in the system, probably involving both the reactant and product species. The entropy changes are consistent with some ordering of the crystal structure.

It is interesting that the change from an octahedral to tetrahedral configuration takes so little energy, only 7 kcal mole^{-1}. Some of the energy change is due to the electronic rearrangement of the ground state. The change from a $^4T_{1g}$ to a $^4A_{2g}$ ground state is only about 3 kcal mole^{-1} from unsophisticated crystal-field type calculations ignoring distortion. It should be observed that the structural change from a distorted octahedral to tetrahedral configuration in $Co(py)_2Cl_2$ (py = pyridine) is approximately 3 kcal mole^{-1} [17]. In this reaction the ligands are not removed from the lattice.

A distorted octahedral configuration seems the preferred structure for the cobalt(II) ion at room temperatures. Further investigation of the system KCl, $CoCl_2$

and H_2O are necessary for the elucidation of what occurs during these reactions at higher temperatures.

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