Thermochemistry of Cobalt(II) Chloride Hydrates [1]

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The dehydration of cobalt(II) chloride-6-hydrate ($CoCl_2,6H_2O$) was investigated. The results can be summarized as $CoCl_2,nH_2O_{(c)} = CoCl_2,mH_2O_{(c)} + (n - m)H_2O_{(v)}$, where n is 6, 4, 2, 1; m is 4, 2, 1, and 0. The enthalpy and entropy of reaction were calculated from the behaviour of the dissociation pressures as a function of temperature. The enthalpy and entropy of formation were calculated from the thermodynamic values. Magnetic moments and spectra were determined. The probable structure of the hydrates are discussed on the basis of the chemical and physical evidence and the known structures.

COBALT(II) compounds are among those of the transition elements which change configuration from octahedral to tetrahedral during reactions. A clearer understanding of the energies and conditions which promote change can be gained from a study of reactions where there is little change in the configuration of the molecule. The hydrates of cobalt(II) chloride provide such a series of reactions. The equilibrium thermal decomposition of the cobalt(II) chloride hydrates was studied over the temperature range 292—393 K. The reactions can be written as (1)—(4) where (c) indicates the crystalline solid and (v) the vapour. The physical properties

$$CoCl_2,6H_2O_{(c)} = CoCl_2,4H_2O_{(c)} + 2H_2O_{(v)} \quad (1)$$

$$CoCl_2,4H_2O_{(c)} = CoCl_2,2H_2O_{(c)} + 2H_2O_{(v)} \quad (2)$$

$$CoCl_2,2H_2O_{(c)} = CoCl_2,1H_2O_{(c)} + H_2O_{(v)} \quad (3)$$

$$CoCl_2,1H_2O_{(c)} = CoCl_{2(c)} + H_2O_{(v)} \quad (4)$$

such as magnetic moments and the spectra indicate that these hydrates are all tetragonally distorted octahedral complexes and that anhydrous $CoCl_2$ is very close to a perfect octahedral compound. This is confirmed by X-ray studies for the 6-hydrate,[2] the 2-hydrate,[3,4] and the anhydrous $CoCl_2$.[5] The equilibrium dissociation pressures, the enthalpy and entropy of reactions (1)—(4), the heat of formation, and the lattice energies of each compound are reported here. The magnetic moments and reflection spectra are presented and a qualitative discussion of these properties is used to help interpret the data.

EXPERIMENTAL

Hydrates.—Reagent grade cobalt(II) chloride-6-hydrate was recrystallized from a concentrated solution acidified with reagent grade HCl. The other hydrates were prepared by dehydration in a vacuum system until the correct weight loss was observed. They could also be prepared by the hydration of anhydrous cobalt(II) chloride.

Analysis.—Since the end product of all dehydration steps was anhydrous $CoCl_2$, a determination of chloride ion concentration for the end product indicated whether any side reaction occurred. The chloride ion concentration was determined gravimetrically by precipitation of silver chloride from a dilute nitric acid solution. The hydrates were analysed by weight loss. The vapour formed during dehydration was found to be pure water. Sample weights varied between 0·1 and 0·5 g (Found: Co, 45·4; Cl^-, 54·6. Calc. for $CoCl_2$: Co, 45·4; Cl^-, 54·6. Found: H_2O, 11·0. Calc. for $CoCl_2,H_2O$: H_2O, 11·6. Found: H_2O, 21·0. Calc. for $CoCl_2,2H_2O$: H_2O, 20·8. Found: H_2O, 34·9. Calc. for $CoCl_2,4H_2O$: H_2O, 34·4. Found: H_2O, 44·5. Calc. for $CoCl_2,6H_2O$: H_2O, 44·2%).

Magnetic Susceptibility.—The magnetic susceptibilities were measured on a Faraday-type balance,[6] standardized against $HgCo(SCN)_4$.[7] The sample chamber can be evacuated and the sample measured under its own dissociation pressure so there is no change during measurements. The sample chamber was thermostatted and the magnetic susceptibilities measured as a function of temperature down to liquid-nitrogen temperatures (78 K). The results and some literature values are in Table 1. Agreement is satisfactory, within the expected ±3% in most cases.

Dissociation-pressure Measurements.—The equilibrium dissociation pressures were measured in an apparatus pre-

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[1] Taken in part from W. K. Grindstaff, Thesis, Oklahoma, 1966.

[2] J. Mizuno, *J. Phys. Soc. Japan*, 1960, **15**, 1412.

[3] B. K. Vainshtein, *Doklady Akad. Nauk S.S.S.R.*, 1949, **68**, 301.

[4] B. Morosin and E. J. Graeber, *Acta Cryst.*, 1963, **16**, 1176.

[5] H. Grime and J. A. Santos, *Z. Krist.*, 1934, **88**, 136.

[6] C. R. Quade, W. H. Brummage, and C. C. Lin, *J. Chem. Phys.*, 1962, **37**, 1368.

[7] B. N. Figgis and J. Lewis, 'The Magnetochemistry of Complex Compounds,' in J. Lewis and R. G. Wilkins, 'Modern Co-ordination Chemistry,' Interscience Publishers Inc., New York, 1960, p. 400.

viously described.[8,9] The limit of dissociation-pressure

standard, magnesium oxide, was measured in the same way.

The data indicate that only the species in equations (1)—(4) were formed under the experimental conditions. Although a 1·5-[10] and a 3-hydrate[11] have been reported, no evidence for these compounds has been found in this research. Since each species was formed as a pure compound, each could be studied separately. Conditions were maintained so there was no change during measurements.

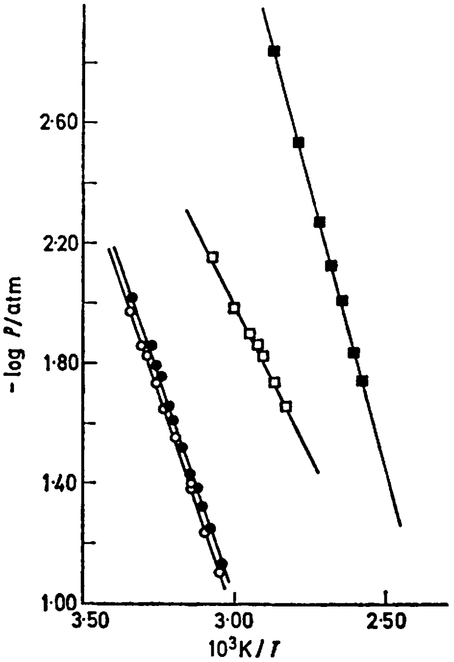

FIGURE 4 Dependence of the dissociation pressure on temperature for $CoCl_2,6H_2O$ (○), $CoCl_2,4H_2O$ (●), $CoCl_2,2H_2O$ (□), and $CoCl_2,H_2O$ (■)

Under these conditions, reactions (1)—(4) can be summarized as (5). The dissociation pressures follow

$$\mathrm{CoCl_2,}n\mathrm{H_2O_{(c)}} \longrightarrow \mathrm{CoCl_2,}m\mathrm{H_2O_{(c)}} + (n - m)\mathrm{H_2O_{(v)}} \quad (5)$$

the equation

$$\log P = -\Delta H^\circ/(n - m)2{\cdot}303RT + \Delta S^\circ/(n - m)2{\cdot}303R \quad (6)$$

where P/atm is the pressure, ΔH°/J mol^{-1} K^1 is the enthalpy of reaction, ΔS°/cal mol^{-1} K^{-1} is the entropy, n is the number of water molecules in the reactant, m is the number in the product, and the remaining symbols are standard. The enthalpy and entropy of reaction were calculated from the temperature dependence of the dissociation pressures (Figure 4) over a range of 30—40 K. The linearity indicates ΔC_p is relatively small and the thermodynamic parameters could be treated as constants over reasonable temperature changes. The results at 25 °C are in Table 3 with the mean temperature.

From the enthalpy and entropy of reaction combined with the literature values for the entropy and enthalpy of formation of anhydrous crystalline cobalt(II) chloride,[12] the heat and entropy of formation of each crystalline hydrate was calculated and are reported in Table 4 with comparative values from the literature. The lattice energy of each of the compounds has been calculated by use of a Born–Haber cycle as in equation (7) where $\Delta H^\circ_{f,m}$ is defined, S is the sublimation energy,

$$\Delta H^\circ_{f,m} = S + D + 2E + I_1 + I_2 + U + m\Delta H_f^\circ(\mathrm{H_2O_{(v)}}) \quad (7)$$

E is the electronegativity of the Cl, I_n is the ionization energy of the appropriate electron of Co, and U is the lattice energy, all in kJ mol^{-1}. The results are in Table 5.

The magnetic moments, corrected for diamagnetism and temperature-independent paramagnetism (t.i.p.) are in Table 1. The Weiss constant (θ) and t.i.p. were calculated by the method of Quade *et al.*[6] Values from the literature are included for comparison. The magnetic moments are all in the range expected for octahedral or distorted octahedral structures indicating the retention of the co-ordination number six through the dehydration reactions. The spectra confirm the retention of the co-ordination number. None of the spectra have the higher intensity or the distinctive peak between 600 and 700 nm characteristic of the tetrahedral cobalt(II) structure.

The thermodynamic data are compared with the ice–vapour equilibrium. Equations (8) and (9) for the enthalpy and entropy of reaction can be written,

$$\Delta H^\circ_{\mathrm{reax}} = [\Delta H^\circ_{f,m(\mathrm{c})} - \Delta H^\circ_{f,n(\mathrm{c})}] + (n - m)\Delta H^\circ_{f,\mathrm{H_2O(v)}} \quad (8)$$

$$\Delta S^\circ_{\mathrm{reax}} = [S^\circ_{f,m(\mathrm{c})} - S^\circ_{f,n(\mathrm{c})}] + (n - m)S^\circ_{f,\mathrm{H_2O(v)}} \quad (9)$$

where ΔH°_f and S°_f represent the enthalpy and entropy of formation of the appropriate hydrate and n and m have been defined before. Equations (8) and (9) indicate that $(n - m)$ moles of water are vaporized, and if these moles of water are in an ice-like environment, this corresponds to the vaporization of that number of moles of ice. The values for the vaporization of ice at 25 °C are, ΔH (sublimation) = 51·9 kJ mol^{-1}, ΔS (sublimation) = 149·4 J mol^{-1} K^{-1}, calculated by standard methods from the literature.[12,13] From these values a heat and entropy of reaction were calculated and are compared with the experimental values in Table 3.

That this comparison is valid can be shown in another way. The enthalpy and entropy of formation of ice at 25 °C are respectively 293·7 kJ mol^{-1} and 44·4 J mol^{-1} K^{-1}. In an ice-like lattice, this is the contribution of water to the heat and entropy of formation of the compound. The loss of $(n - m)$ moles of water should lead to a difference of $(n - m)$ times the enthalpy or entropy of

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[10] N. V. Sidgewick, 'Chemical Elements and Their Compounds,' vol. II, The Clarendon Press, Oxford, 1950, p. 1376.

[11] L. I. Katzin and J. R. Ferraro, *J. Amer. Chem. Soc.*, 1952, **74**, 2752.

[12] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, 49th edn., Chemical Rubber Co., Cleveland, Ohio, 1968, Section D.

[13] National Bureau of Standards, Circular 500, Washington, D.C., 1952.

formation of ice from the two adjacent hydrates, as in equations (10) and (11). These differences in the

$$\Delta H^\circ_{f,m(c)} - \Delta H^\circ_{f,n(c)} = (n - m)293{\cdot}7 \text{ kJ mol}^{-1} \qquad (10)$$

$$-[S^\circ_{f,m(c)} - S^\circ_{f,n(c)}] = (n - m)44{\cdot}4 \text{ J mol}^{-1}\text{ K}^{-1} \qquad (11)$$

enthalpy and entropy of formation are compared with the observed values in Table 4. The loss of the first four water molecules is in good agreement with the values calculated. For the remaining hydrates, the agreement with the enthalpy values are fair (±20·92 kJ mol^{-1}) but the entropy values show a greater divergence. To test the idea further, the enthalpy of formation differences of over 200 hydrates in the literature were examined,[12,13] and the average difference found was 301·7 kJ mol^{-1}. The average entropy difference has already been reported as 39·3 J mol^{-1} K^{-1},[14] in reasonable agreement with expectations. These values are not unexpected since much of these values are due to the formation of the water molecule, but it is interesting that it is so consistent over so large a number of hydrates. Fluctuations in enthalpy, with a few exceptions, were *ca.* ±12·6 kJ mol^{-1}. With many of the higher hydrates (*i.e.*, four waters or above) the average difference was *ca.* 297 kJ mol^{-1}, close to the ice value. For the higher hydrates at 25 °C equations (8) and (9) can be transformed to (8a) and (8b) which for one mole are close to

$$\Delta H^\circ_{\text{reax}} = -(n - m)[55{\cdot}2] \text{ kJ} \qquad (8a)$$

$$\Delta S^\circ_{\text{reax}} = (n = m)150{\cdot}4 \text{ J mol}^{-1}\text{ K}^{-1} \qquad (9a)$$

the values for the vaporization of ice (see Table 3).

TABLE 3

Thermodynamic constants for the deaquation $CoCl_2,nH_2O_{(c)} = CoCl_2,mH_2O_{(c)} + (n - m)H_2O_{(v)}$

			ΔH°/kJ mol^{-1}			ΔS°/J mol^{-1} K^{-1}		
n	*m*	Mean temp./K	Obs.	Calc.[a]	Calc.[b]	Obs.	Calc.[a]	Calc.[b]
6	4	311	112·1 ± 2·1	103·8	110·4	299·2 ± 4·2	294·6	298·7
4	2	314	112·1 ± 2·1	103·8	110·4	297·9 ± 4·2	294·6	298·7
2	1	339	38·1 ± 0·8	51·9	55·2	75·3 ± 0·8	147·3	149·4
1	0	368	75·3 ± 1·7	51·9	55·2	161·9 ± 2·9	147·3	149·4

[a] Calculated from the vaporization of ice at 25 °C. [b] Calculated from equations (8a) and (9a).

TABLE 4

Standard enthalpy and entropy of formation of the hydrates

	ΔH°_f/kJ mol^{-1}		$\Delta H^\circ_{f,m} - \Delta H^\circ_{f,n}$		S°_f/J mol^{-1} K^{-1}	$-[S^\circ_{f,m} - S^\circ_{s,n}]$/J mol^{-1} K^{-1}	
Compound	Found	Lit.[a]	Found	Calc.[b]	Found	Found	Calc.[b]
$CoCl_2$	—	−325·5			106·2[a]		
$CoCl_2,1H_2O$	−642·7	—	317·1	293·7	133·5	27·3	44·4
$CoCl_2,2H_2O$	−922·6	−932·6	279·9	293·7	246·8	71·3	44·4
$CoCl_2,4H_2O$	−1518·4	−1536·4	595·8	587·4	327·2	80·4	88·7
$CoCl_2,6H_2O$	−2114·2	−2129·2	595·8	587·4	406·3	79·1	88·7

[a] Ref. 13. The standard values for anhydrous $CoCl_2$ were used as initial values. [b] Calculated by using equations (10) and (11).

TABLE 5

Lattice energies/kJ mol^{-1} of the crystalline hydrates of $CoCl_2$

Compound	U_{obs}	U_{lit}	U_{calc}	Crystal field stab. energy	U_{total}
$CoCl_2$	−2666·5[a]	−2598·3[17] −2707·0[17]	−2574·4[b]	−46·9	−2621·3
$CoCl_2,1H_2O$	−2741·8	—	−2843·4	−56·1	−2899·5
$CoCl_2,2H_2O$	−2779·8	—	−2843·4	−56·1	−2899·5
$CoCl_2,4H_2O$	−2892·0	—	−2797·4	−60·7	−2858·1
$CoCl_2,6H_2O$	−3004·1	—	−2797·4	−60·7	−2858·1[c]

[a] Calculated from literature values by use of equation (7). [b] Calculated by use of Kapustinskii's extended equation, r_{Co-Cl} = 2·47 Å. [c] This neglects the hydrogen bonds for the external two waters. If we assume the value for each water is 41·8 kJ mol^{-1} (10 kcal mol^{-1}), this is 2941·8 kJ mol^{-1}.

For $CoCl_2,6H_2O$ and $CoCl_2,4H_2O$: r_{Co-Cl} = 2·43 Å; r_{Co-H_2O} = 2·12 Å (add 0·3 Å to this value to get to centre of dipole); μ_{H_2O} (total) = 3·0 D, μ_{H_2O} (induced) = 1·15 D. These are values for the $CoCl_2,6H_2O$ from ref. 3.

For $CoCl_2,2H_2O$ and $CoCl_2,1H_2O$: r_{Co-Cl} = 2·46 Å; r_{Co-H_2O} = 2·04 Å (add 0·3 Å to this value to get to centre of dipole); μ_{H_2O} (total) = 3·2 D, μ_{H_2O} (induced) = 1·35 D. These distances are for $CoCl_2,2H_2O$ from ref. 4.

Note: *U* calculated this way is for a temperature of 0 K.

This is consistent with relatively weak bonding in hydrates, and a relatively unchanged environment during reaction. In a constant environment, bonding would remain approximately the same and only the values associated with the water molecule itself would be lost.

The calculated heat and entropy of reaction are in good agreement with the experimental values. This can be correlated with the known structure of the hydrates. In the 6-hydrate[3] two waters are external to the $Co(H_2O)_4Cl_2$ inner co-ordination sphere

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[14] W. M. Latimer, ' Oxidation Potentials,' 2nd edn., Prentice-Hall, Inc., Englewood Cliffs, N.J., 1952, pp. 359 *et seq.*

and are hydrogen-bonded, with distances close to that found in ice (O–O distance = 2·69 Å in hydrate, 2·76 Å in ice[15]). The loss of the first two water molecules leaves the lattice structure relatively the same. The spectra of the 6- and 4-hydrate are similar (Figure 2) and the low values of the magnetic moment are consistent with tetragonal distortion, as indicated by the spectra. The loss of the second pair of water molecules is at the same energy as the loss of the first pair, although the second pair must be from the inner co-ordination sphere. Both the entropy and enthalpy compare closely with the vaporization of two moles of ice. The probable structure change is that with the loss of the first two waters, the $Co(H_2O)_4Cl_2$ molecular units come closer together without altering the structure of the unit cell. The loss of the next two waters can be understood if the chloride ions of the two adjacent $Co(H_2O)_4Cl_2$ units replace the water molecule in the next unit. This produces the square of chloride ions around each cobalt(II) ion, and links all the central metal ions into a polymeric structure along the *b*-axis with the chloride ions acting as the linking ion. The unit cell is unchanged.

The spectra of the 6- and 4-hydrates reflect an axially compressed octahedron, while the spectra of the 2-hydrate is consistent with an axially elongated octahedron expected from a $Co(H_2O)_2Cl_4$ unit. The magnetic moments are all reasonably close and compatible with tetragonal distortion of this type.

The loss of water from the 2-hydrate takes much less energy than the vaporization of a mole of ice. This can be explained by realizing that in the 2-hydrate water molecules in adjacent units are in line with each other and so distant that there is probably no interaction. The water molecules are hydrogen-bonded to the chloride ions of an adjacent $Co(H_2O)_2Cl_4$ unit. The O–O distance is 4·50 Å, longer than the distance in ice.[4]

To form the 1-hydrate, a water molecule must be lost from an inner co-ordination sphere. The molecular unit formed may resemble the final product of dehydration (anhydrous $CoCl_2$), it may resemble the 2-hydrate, or it may be completely different. The spectrum and magnetic moments are close to those of the 2-hydrate and indicate a distorted octahedron as the most likely structure. A chloride ion can displace a water molecule in the inner co-ordination sphere, creating a molecular unit with five chloride ions and one water molecule, with an approximately C_{4v} symmetry, or one molecule of water can be left (of the pair in the dihydrate) to bond two adjacent Co^{II} ions forming a $Co–H_2O–Co$ unit that links adjacent polymeric chains.

In the last structure the symmetry of the unit cell is preserved, and the ordering is greater, so the entropy difference should be greater than for the 4-hydrate or the other structure suggested above. The loss of the last water molecule should have a much higher enthalpy change than the loss of the previous waters since it is bonded to two central metal ions. Experimentally the value is approximately doubled from the 2-hydrate. The entropy of loss of the last water should be approximately normal (as is observed) since a chloride ion can replace the water as a linking unit and the structure would be that of anhydrous $CoCl_2$. The property changes are therefore more consistent with this structure than with the others discussed above.

The major entropy loss in the hydrates is in the change from the 2- to the 1-hydrate (Tables 3 and 4). The ligand-field parameters are similar for the last two hydrates (Table 2). This again indicates that the central ion in the 1-hydrate has approximately the same environment as in the 2-hydrate.

The most likely structure being used for the 1-hydrate, the anhydrous structure (hexagonal close-packed D^5_{3d}—$R\bar{3}m$) is formed by moving the polymeric chloride-linked chains that were in the centre of the face of the 2-hydrate, and are unchanged in position in the 1-hydrate, by half a cell length to the centre of the cell and reducing the dimensions of the unit cell so that the chloride ions move into the position occupied by the water molecules. This establishes an octahedron of chloride ions around each central metal ion.

Since the lattice energy was determined experimentally it seemed logical to see if a reasonable value could be calculated from a simple electrostatic model by considering only the interactions in the molecular unit. The experimental distances for the 6- and 2-hydrates were used, with the centre of the water dipole assumed to be 0·3 Å behind the actual oxygen-atom distances. The values used for the water dipole were 3·0 and 3·2 D respectively for the 6- and 2-hydrate, following Haseda.[16] The attractions considered were those between the central ion, the chloride ions, and the water-dipole interaction with both these ions. The repulsion terms were those of each species for itself and the repulsion of the ligand electrons for those of the central ion in the form $6B/r^9$. B Was evaluated by differentiation with respect to r. The energy of formation of the induced water dipole was assumed to be half the energy of stabilization of the induced dipole. The final term considered was the crystal-field stabilization energy (c.f.s.e.). The results are in Table 5 and were reasonable for the hydrates (2—6%), but the value for anhydrous $CoCl_2$ was so low that Kapustinskii's extended equation[17] was used for this compound. The agreement is interesting, but probably fortuitous because of the simplicity of the model.

Conclusions.—It seems that in the hydrates the differences in enthalpy and entropy of formation ($\Delta H^\circ_{f,m(c)} - \Delta H^\circ_{f,n(c)}$ and $S^\circ_{f,m(c)} - S^\circ_{f,n(c)}$) can be used to indicate when unusual changes occur in the structure. This will be reflected in the enthalpy and entropy of reaction. When the value is close to that found for the vaporization of ice, it appears that only small structural

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[15] A. F. Wells, 'Structural Inorganic Chemistry,' 3rd edn., The Clarendon Press, Oxford, 1962, p. 566.

[16] T. Haseda, *J. Phys. Soc. Japan*, 1960, **15**, 483.

[17] M. F. C. Ladd and W. H. Lee, 'Lattice Energies and Related Topics,' in 'Progress in Solid State Chemistry,' vol. 1, ed. H. Reiss, The MacMillan Co., New York, 1964, p. 37.

changes occur. It also seems that the substitution of a chloride ion for a water molecule leaves the structure

The formation of anhydrous $CoCl_2$ is thus merely the exchange of a linking water molecule by a linking chloride