Dehydration of Potassium Tetrachlorocuprate(II) Dihydrate †

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The thermal dehydration of $K_2[CuCl_4]\cdot 2H_2O$ has been investigated by measuring the dissociation pressure as a function of composition and temperature. The enthalpy and entropy of reaction and formation have been calculated. The spectral and magnetic properties of both the hydrate and the anhydrous compound have been investigated and fitted assuming tetragonal distortion with axial elongation (D_{4h} symmetry). The crystal-field parameters used are reported. From the known structure of the dihydrate and the changes in properties, the probable structural changes to form the anhydrous compound are discussed.

PREVIOUS studies on the dehydration of transition-metal complexes[1,2] have indicated that thermodynamic values can be used to predict structural changes occurring during a reaction. The actual details must be deduced from changes in physical properties or from X-ray data, if available. A system where changes in the physical properties are observed is the thermal dehydration of potassium tetrachlorocuprate(II) dihydrate which has been studied over the temperature range 28—45 °C. The reaction occurs in one step [equation (1)] where c

$$K_2[CuCl_4]\cdot 2H_2O(c) \longrightarrow K_2[CuCl_4](c) + 2H_2O(g) \quad (1)$$

indicates the crystalline solid and g the vapour phase. It is known[3] that the copper(II) ion in the hydrate is approximately octahedral and it was considered that this would also be true in anhydrous $K_2[CuCl_4]$. Preliminary studies indicated that further investigation was merited and the results are presented here.

The highest temperature employed was determined by the dissociation pressure since it is known that at 93 °C the dihydrate dissociates into $K[CuCl_3]$, KCl, and H_2O.[4,5] The present studies were carried out below this temperature where there was no possibility of dissociation and the properties measured could safely be ascribed to the two copper compounds in equation (1). The equilibrium dissociation pressure and the enthalpy and entropy of the reaction have been determined, together with the reflection spectra and magnetic properties of the compounds. The physical properties are used in a discussion of what happens to the crystalline structure during the reaction.

EXPERIMENTAL

Preparation.—Copper(II) chloride hydrate and potassium chloride, both reagent grade, were dissolved in hot distilled water. The conditions for crystallization of the dihydrate were determined from the phase diagram of the $KCl-CuCl_2-H_2O$ system.[6] The hydrate crystals formed were a greenish blue and were kept in a desiccator over wet calcium nitrate. The anhydrous compound was prepared by drying the hydrate at 60—70 °C. It was a brownish red powder.

Analysis.—Chloride ion was determined gravimetrically, and copper ion was determined roughly by an optical emission spectrograph. The water in the hydrate was calculated from measured weight loss in a vacuum system. The vapour was trapped in a cold finger and shown by analysis to be pure water (Found: Cl^-, 49.9; Cu, 20.4. Calc. for $K_2[CuCl_4]$: Cl^-, 50.0; Cu, 22.4. Found: Cl^-, 44.4; Cu, 18.6; H_2O, 11.3. Calc. for $K_2[CuCl_4]\cdot 2H_2O$: Cl^-, 44.5; Cu, 19.9; H_2O, 11.25%).

Magnetic Susceptibility.—The magnetic susceptibility was measured with a Faraday-type balance described in the literature.[7] The balance could be evacuated and measurements were carried out under the dissociation pressure of the compound so there was no change in species. The sample chamber was thermostatted and the static magnetic susceptibility was measured as a function of temperature from room to liquid-nitrogen temperature (78 K). The balance was standardized against $Hg[Co(SCN)_4]$.[7] Previous experience indicated that the accuracy of the balance is ±2.5%.[1,2] The results are in Table 3.

Dissociation-pressure Measurements.—The equilibrium dissociation pressures were measured in an apparatus that has been described previously.[1,2] The sample chamber was submerged in a constant-temperature bath (±0.1 °C) where the temperature could be varied. The dissociation pressure was measured with a closed manometer using a cathetometer (±0.05 Torr).‡ Once an apparent equilibrium was reached (usually after 1 week) the bath temperature was varied by several degrees. The system was given time to change and was then returned to the original temperature. The return to the original pressure at the original temperature was used as evidence that equilibrium had been attained. The dissociation pressure as a function of temperature was studied at a composition such that the ratio of the two crystalline phases was *ca.* 1 : 1. The measured pressures were low enough so that the gas phase could be treated as ideal. The results are in Figures 1 and 2.

Spectra.—The diffuse-reflectance spectrum of the pure compounds were recorded at room temperature with a Beckman DK-1 recording spectrophotometer and reflection attachment. The spectra were measured on pure carefully powdered samples and were reproducible. The intensities measured in this way are relative. The results are in Figure 3 and Table 4.

RESULTS AND CALCULATIONS

Plots of the dissociation pressure against composition (Figure 1) are all horizontal in the three-phase region indicating that only two solid compounds, the hydrated and anhydrous forms of $K_2[CuCl_4]$, are involved in the equilibrium, as indicated in equation (1). Since this is the only reaction occurring over the temperature range studied, the dissociation pressure as a function of temperature should

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† Taken in part from a M.Sc. Thesis by T. J. N.

‡ Throughout this paper: 1 Torr = (101 325/760) Pa; 1 atm = 101 325 Pa; 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] W. Grindstaff and N. Fogel, *J.C.S. Dalton*, 1972, 1476.

[2] W. Grindstaff and N. Fogel, *Thermochim. Acta*, 1973, **6**, 299.

[3] L. Chrobak, *Z. Krist.*, 1934, **88**, 35.

[4] W. Meyerhoffer, *Z. phys. Chem.*, 1887, **3**, 336.

[5] H. Suga, M. Sorai, T. Yamanaka, and S. Seki, *Bull. Phys. Soc. Japan*, 1965, **38**, 1007.

[6] A. Chretien and R. Weil, *Bull. Soc. chim. France*, 1935, **2**, 1577.

[7] B. N. Figgis and J. Lewis in ' Modern Coordination Chemistry,' eds. J. Lewis and R. G. Wilkins, New York, 1960, p. 400.

obey equation (2) where P (in atm) is the dissociation pressure, the standard state for the gas phase is 1 atm, $\Delta H^{\ominus}$ in

$$\log P = \frac{-\Delta H^{\ominus}}{2(2.303)RT} + \frac{\Delta S^{\ominus}}{2(2.303)R} \tag{2}$$

J mol^{-1} and $\Delta S^{\ominus}$ in J K^{-1} mol^{-1} are respectively the enthalpy and entropy of reaction, R(8.314 J K^{-1} mol^{-1}) is the gas constant, and T (in K) is the absolute temperature. The number two in the denominators is the number of moles of water vaporized from the solid hydrate. The enthalpy and entropy of reaction could be determined from the temperature dependence of the dissociation pressure over the range 15—20 °C. The linearity of the plot (Figure 2) indicated that ΔC_p is relatively small and the thermodynamic parameters can be treated as constants over reasonable temperature ranges. The results extrapolated to 25 °C are in Table 1 and were calculated from equation (3) determined

$$\log P = -2\,685.24(1/T) + 6.842 \tag{3}$$

from a least-squares treatment of the data.

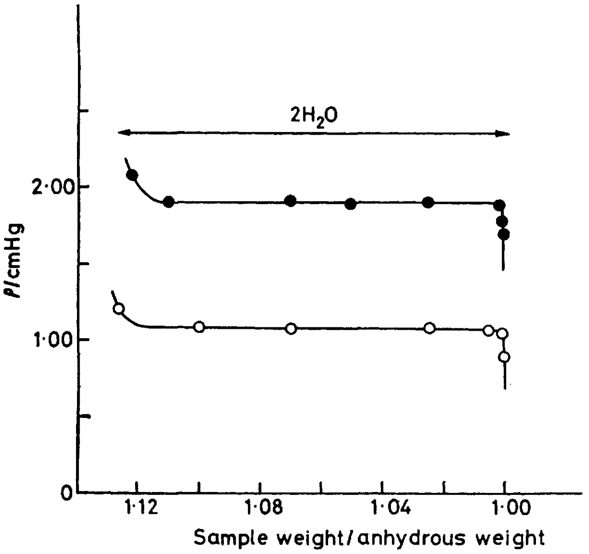

FIGURE 1 Plot of pressure against composition at 36 (○) and 45 °C (●)

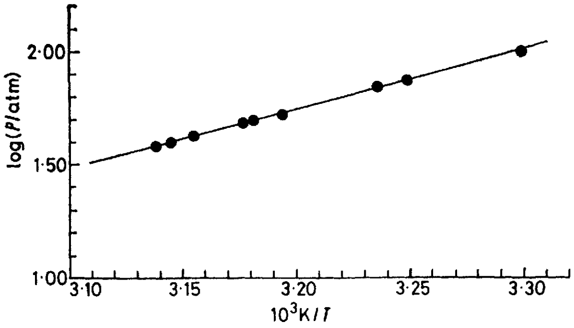

FIGURE 2 Plot of the logarithm of pressure against reciprocal temperature

TABLE 1

Thermodynamic values for the reaction $K_2[CuCl_4]\cdot 2H_2O(c) \longrightarrow K_2[CuCl_4](c) + 2H_2O(g)$

Parameter	Expt.	Calc.	
		a	b
$\Delta H^{\ominus}$(reaction)/kJ mol^{-1}	102.8 ± 1.7	103.8	110.4
$\Delta S^{\ominus}$(reaction)/J K^{-1} mol^{-1}	261.7 ± 1.3	298.8	298.4

[a] From the sublimation of ice. [b] See text.

The values for the enthalpy and entropy of formation can be calculated from the enthalpy and entropy of reaction and literature data.[5,8] The results are in Table 2. These values can be compared to the solid–vapour equilibrium in ice and other hydrate systems. The enthalpy and entropy of the dehydration reaction can be written as in (4) and (5)

$$\Delta H^{\ominus}\text{ (reaction)} = \Delta H_f^{\ominus}(K_2[CuCl_4]\cdot 2H_2O,\ c) - \Delta H_f^{\ominus}(K_2[CuCl_4],\ c) + \Delta H_f^{\ominus}(H_2O,\ g) \tag{4}$$

$$\Delta S^{\ominus}\text{(reaction)} = S_f^{\ominus}(K_2[CuCl_4]\cdot 2H_2O,\ c) - S_f^{\ominus}(K_2[CuCl_4],\ c) + S_f^{\ominus}(H_2O,\ g) \tag{5}$$

where $\Delta H_f^{\ominus}$ and $S_f^{\ominus}$ represent the enthalpy of formation and entropy of the compounds. For the ice system, at 25 °C, $\Delta H^{\ominus}$(subl.) = 51.9 kJ mol^{-1} and $\Delta S^{\ominus}$(subl.) = 149.4 J K^{-1} mol^{-1}.[9] For hydrate systems it has been observed [1,2] that for many reactions $\Delta(\Delta H_f^{\ominus})$ = 293.7 kJ mol^{-1} and $\Delta(\Delta S_f^{\ominus})$ = 44.4 J K^{-1} mol^{-1} which gives $\Delta H^{\ominus}$(reaction) = 55.2x kJ mol^{-1} and $\Delta S^{\ominus}$ (reaction) = 150.4x J K^{-1} mol^{-1} in good agreement with what is observed for the ice–water vapour equilibrium (x = 2 for this system). The differences in the enthalpies and entropies of formation were calculated from the data and are in Table 2 for comparison with values calculated from the equations above. The experimental enthalpy and entropy of reaction, as well as the differences in the enthalpy and entropy of formation of the hydrate and the anhydrous compound, are lower than the calculated values. Calculated values fit best when few structural changes occur during a reaction.[1,2]

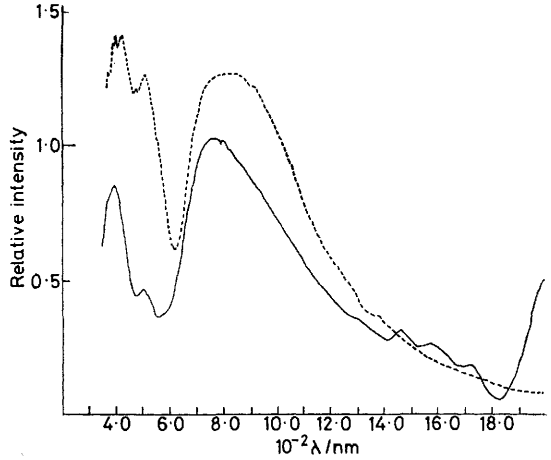

FIGURE 3 Spectra of $K_2[CuCl_4]\cdot 2H_2O$ (——) and $K_2[CuCl_4]$ (— — —)

The reflection spectra are in Figure 3 and peak positions are in Table 4. The hydrate has a relatively sharp peak at 750 nm and a long trailing edge toward longer wavelengths, with some evidence for shoulders. The hydrate also has some peaks in the near i.r. that can be ascribed to overtones of water. The electronic spectra of both the hydrate and anhydrous compounds were fitted by assuming that the

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[8] S. A. Schukarev, I. V. Vasilkova, and G. M. Barvinok, *Vestnik Leningrad Univ.* (*Fiz. Khim.*), 1965, **20**, 145.

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

major distortion was of tetragonal symmetry (D_{4h}) with elongation along the Z axis. The ground state will then have ${}^2B_{1g}$ symmetry. The g factors for the dihydrate [10,11] indicate that this assumption is correct. The magnetic moments and spectra are consistent with axial elongation for both compounds.

TABLE 2

Thermodynamic values for $K_2[CuCl_4]\cdot 2H_2O$(c) and $K_2[CuCl_4]$(c) at 25 °C

	$K_2[CuCl_4]\cdot 2H_2O$	$K_2[CuCl_4]$
$\Delta H_f^\ominus$/kJ mol^{-1}	$-1\,673.2 \pm 20$	$-1\,087.6 \pm 10$
$\Delta S_f^\ominus$/J K^{-1} mol^{-1}	355.3 ± 4	239.9 ± 3
$\Delta H_f^\ominus(K_2[CuCl_4]) - \Delta H_f^\ominus(K_2[CuCl_4]\cdot 2H_2O)$	586.0 (calc. 587.4 kJ mol^{-1})	
$S_f^\ominus(K_2[CuCl_4]) - S_f^\ominus(K_2[CuCl_4]\cdot 2H_2O)$	-115.4 (calc. -88.8 J K^{-1} mol^{-1})	
U(expt.)/kJ mol^{-1}	$-4\,269.0 \pm 40.0$	$-4\,166.6 \pm 40.0$
U(calc.)/kJ mol^{-1}	$-2\,938.5$ {$[CuCl_4(OH_2)_2]^{2-}$, g},	$-1\,353.5$ * ($K_2[CuCl_4]\cdot 2H_2O$, c)
U(total)/kJ mol^{-1}	$-4\,292.0$	

* Calculated using the extended Kaputsinskii equation with a thermochemical radius of 3.98 Å for the $[CuCl_4(OH_2)_2]^{2-}$ ion and 1.33 Å for K^+.

TABLE 3

Magnetic parameters of $K_2[CuCl_4]\cdot 2H_2O$ and $K_2[CuCl_4]$

μ/B.M.	1.97 ± 0.05	1.87 ± 0.05
	1.95 [13]	1.85 [14]
	1.91 [a]	1.88 [b]
Weiss constant (θ/°)	2.5 ± 3	27 ± 3
	8.0 [13]	
	-1.2 [15]	
10^{-6} t.i.p. (c.g.s. units)	58.0 ± 30	57.0 ± 30
(calc.)	60.5 [c]	52.6 [c]
g	2.27 ± 0.05 [d]	2.16 ± 0.05 [d]
	2.17 ($g_\parallel$ 2.38, $g_\perp$ 2.06) [10,11]	
(calc.)	2.22 ($g_\parallel$ 2.43, $g_\perp$ 2.10) [e]	2.17($g_\parallel$ 2.35, $g_\perp$ 2.08) [e]

[a] Calculated from equations (9) and (10) using $\Delta_2 = 9\,800\ k$, $\Delta_3 = 12\,250\ k$, and $\lambda = -660\ k$ and averaging the results. [b] Calculated from equations (9) and (10) using $\Delta_2 = 10\,900\ k$, $\Delta_3 = 12\,500\ k$, and $\lambda = -634\ k$ and averaging the results. [c] From equations (2) and (3) using the Δ_2 and Δ_3 in (*a*) and (*b*) above; $k = \lambda_{obs.}/\lambda_{free\ ion} = 0.795$ for the hydrate and 0.763 for $K_2[CuCl_4]$. The results given are average values. [d] Calculated from the experimental magnetic moments. [e] From equations (15) and (16) using the data in the notes above.

TABLE 4

Spectral parameters (cm^{-1}) for $K_2[CuCl_4]\cdot 2H_2O$ and $K_2[CuCl_4]$

	$K_2[CuCl_4]\cdot 2H_2O$			$K_2[CuCl_4]$		
		Calc.			Calc.	
Parameter	Expt.	*a*	*b*	Expt.	*a*	*b*
${}^2E_g$ (3)	12 500	12 250	12 327	13 000	12 820	12 728
	12 000		11 789	11 834		12 189
${}^2B_{2g}$ (2)	9 800	9 800	9 807	10 990	10 990	10 850
${}^2A_{1g}$ (1)	13 100	13 108	13 475	7 435	7 407	7 416
${}^2B_{1g}$	0	0	0	0	0	0
Dq		980.0	980.5		1 099.0	1095.8
Ds		2 221.4	2 144.4		1 319.6	1 252.4
Dt		842.9	751.5		425.7	494.2
λ		0.0	-660.0		0.0	-634.0

[a] From equations (6)—(8). [b] With the program that diagonalizes the spin–orbit coupling matrix.

Three transitions are expected for the crystal-field spectra in D_{4h} symmetry. The energy of the transitions in axial elongation is given by equations (6)—(8). In the known

$$\Delta_1 = {}^2A_{1g} \longleftarrow {}^2B_{1g} = 4Ds + 5Dt \qquad (6)$$

$$\Delta_2 = {}^2B_{2g} \longleftarrow {}^2B_{1g} = 10Dq \qquad (7)$$

$$\Delta_3 = {}^2E_g \longleftarrow {}^1B_{1g} = 10Dq + 3Ds - 5Dt \qquad (8)$$

symmetry of the hydrate (D_{2h}), the Δ_3 transition is split, the ${}^2E_g$ energy level forming two energy levels ${}^2B_{2g}$ and ${}^2B_{3g}$. In the higher symmetry (D_{4h}) spin-orbit coupling will also split the Δ_3 transition. In most spectra these split transitions overlap. In the case of the hydrate, two close transitions were observed as shoulders on the main transition. For purposes of calculation, the centre of the two shoulders assigned to the split Δ_3 band is assumed to be the energy of transition to the ${}^2E_g$ (Δ_3) energy level.

In considering assignments for the spectrum of $K_2[CuCl_4]\cdot 2H_2O$, approximate values for Δ_2 and Δ_3 could be calculated from equations (15) and (16) and the g values in the literature.[10,11] The nearest shoulders were then assigned to these transitions. The known structural asymmetry and the sharpness of the peak at 13 100 cm^{-1} (750 nm) lead to an assignment of this peak to the singly degenerate ${}^2A_{1g}$ (Δ_1) transition. This treats the hydrate as a square-planar complex. It will be observed in Table 4 that Dq for the hydrate is lower than for the anhydrous compound, but the distortion parameters (Ds and Dt) are very large. If the correct symmetry is used the Dq value is increased above that for the anhydrous compound while the distortion parameters remain relatively high. The lower magnetic moment and broader peak for the anhydrous compound are consistent with a higher symmetry and assignment of the transitions on the basis of D_{4h} symmetry with the energy of transition following the number order in equations (6)—(8), Δ_1 being of lowest energy and Δ_3 of highest. The splitting diagrams for the two cases are found in Figure 6. The effect of spin–orbit coupling was calculated using a program that diagonalized the spin matrix. The best values from all the calculations are in Table 4.

The magnetic properties can be calculated from the spectral data using a first-order approach which assumes the

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[10] H. Abe, K. Ono, I. Hayashi, J. Shimoda, and K. Iwanaga, *J. Phys. Soc. Japan*, 1954, **9**, 814.

[11] K. Ono and M. Ohtsuka, *J. Phys. Soc. Japan*, 1958, **13**, 206.

ground state is a pure state (*i.e.* $d_{x^2-y^2}$). This leads to equations (9)—(11) for the magnetic moments, parallel and

$$\mu_{\parallel} = 3[1 - (4k_{\parallel}\lambda/\Delta_2)] \tag{9}$$

$$\mu_{\perp} = 3[1 - (k_{\perp}\lambda/\Delta_3)] \tag{10}$$

$$\mu_{\text{av.}} = [(\mu_{\parallel}^2 + 2\mu_{|}^2)/3]^{\frac{1}{2}} \tag{11}$$

perpendicular to the *z* axis. The temperature-independent paramagnetism (t.i.p.), parallel and perpendicular, is given by equations (12)—(14). The *g* factors in this symmetry are

$$(\text{t.i.p.})_{\parallel} = 8N\beta^2k_{\parallel}^2/\Delta_2 \tag{12}$$

$$(\text{t.i.p.})_{\perp} = 2N\beta^2k_{\perp}^2/\Delta_3 \tag{13}$$

$$(\text{t.i.p.})_{\text{av.}} = [(\text{t.i.p.})_{\parallel} + 2(\text{t.i.p.})_{\perp}]/3 \tag{14}$$

given by (15)—(17). In these equations $k_{\parallel}$ and $k_{\perp}$ are the orbital reduction factors and λ is the spin–orbit constant

$$g_{\parallel} = 2[1 - (4k_{\parallel}\lambda/\Delta_2)] \tag{15}$$

$$g_{\perp} = 2[1 - (k_{\perp}\lambda/\Delta_3)] \tag{16}$$

$$g_{\text{av.}} = [(g_{\parallel}^2 + 2g_{\perp}^2)/3]^{\frac{1}{2}} \tag{17}$$

for the free Cu^{2+} ion ($-830\,k$).[12] The experimental data were fitted using the standard equation (18) where χ is the magnetic susceptibility (in c.g.s. units), *C* is the Curie constant, *T* the absolute temperature, and θ the Weiss constant. The observed and calculated magnetic properties are in Table 3. The magnetic data are in good agreement with those reported by Ray and Sen [13] for the dihydrate and by Ghatnagar *et al.*[14] for the anhydrous compound. Ray and Sen report a Weiss constant (θ) of 8; ours is *ca.* 2. A study at low temperatures gave a Weiss constant of -1.2.[15] This value is also consistent with our data, but gives a higher t.i.p. than was thought probable. Considering the extrapolations involved however, this would be well within the experimental error. The magnetic moments are affected slightly if the Weiss constant is varied between -1 and 8. The magnetic and spectral data are in reasonable agreement with each other. The experimental magnetic moments are higher than calculated using the *g* values, but ferromagnetic interactions [15] were not considered in these calculations.

$$\chi = \frac{C}{T + \theta} + \text{t.i.p.} \tag{18}$$

DISCUSSION

The thermodynamic data indicate that the anhydrous compound has considerably more ordering than would be expected from just the removal of two water molecules. The entropy lost by the removal of two waters, with no change in structure, would be expected to be -88.8 J K^{-1} mol^{-1}, but the experimental value is -115.4 J K^{-1} mol^{-1}. This large decrease in entropy is consistent with considerable ordering in the crystal structure. The value of the enthalpy is close to the expected value. A similar situation has been observed when a chloride ion replaces a water molecule in a molecular structure.[1,2] This suggests that the molecular structure becomes more symmetrical, and is consistent with the spectral and magnetic changes observed on forming the anhydrous compound.

Much of this becomes understandable if the structure of the dihydrate as shown in Figures 4 and 5 is considered. The molecular symmetry is D_{2h} with the two waters ***trans*** to each other and perpendicular to the plane formed by the four chloride ions. The chloride ions make up a rhomb, with one long axis and one short axis. There are two molecules per unit cell, one at the corner (0,0,0), the other in the centre of the unit cell ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$). The long axis of the molecule at the corner is rotated 90° from the long axis of the molecule in the centre of the unit cell. There are therefore alternate layers where the long axis shifts direction from one layer to the next. The *Z* axis (from e.s.r. data) falls on the long chloride axis of the

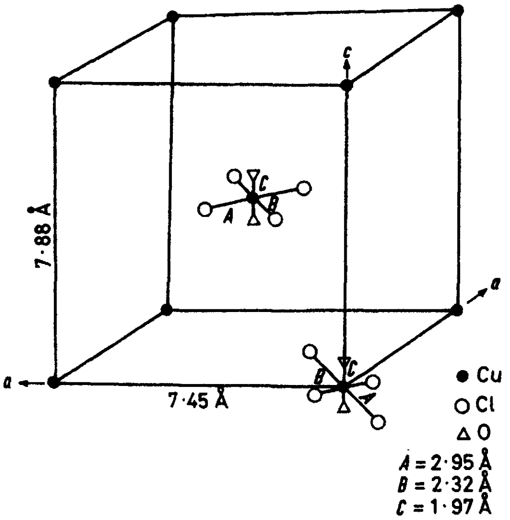

FIGURE 4 Unit cell for $K_2[CuCl_4]\cdot 2H_2O$

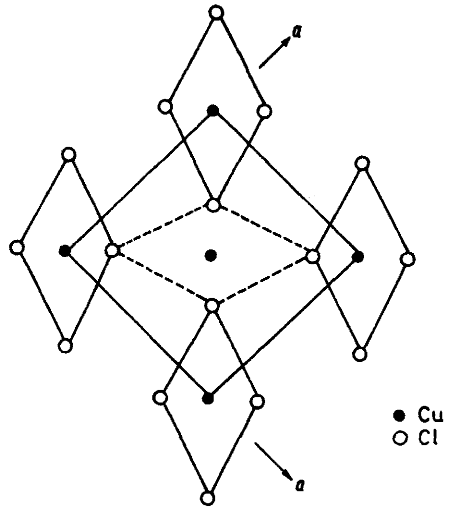

FIGURE 5 Looking down the *c* axis at the base plane of $K_2[CuCl_4]\cdot 2H_2O$. Broken lines indicate molecules in the centre of the unit cell, half a unit up the *c* axis. The Cl^- ions are directly above the Cl^- ions of the unit in the base plane. Water molecules are directly above the Cu^{2+} ions and are not shown here

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[12] F. E. Mabbs and D. J. Machin, 'Magnetism and Transition Metal Complexes,' Chapman and Hall, London, 1973.

[13] P. Ray and D. N. Sen, *J. Indian Chem. Soc.*, 1948, **25**, 473.

[14] S. S. Ghatnagar, H. Lessheim, and M. L. Khanna, *J. Indian Chem. Soc.*, 1937, **14**, 445.

[15] A. Miedema, H. Van Kempen, and W. J. Huiskamp, *Physica*, 1963, **29**, 1266.

rhomb. The long-axis chloride ion of one layer is above the chloride ion on the short axis of the molecule in the other layers. This produces an unstable situation which is stabilized by hydrogen bonds formed by the water molecules.

Both water molecules in the hydrated compound are in the same environment, so it is not surprising that they are both removed in the same step. This removes the stabilizing force and the simplest apparent move is for alternate layers to shift until, in the anhydrous compound, the chloride ions are approximately over the central copper(II) ion in the molecular units in the alternate layers. The move is symmetrical so there is an approximate octahedron of chloride ions surrounding each central copper ion. The most likely symmetry is C_{2v}, a subgroup of D_{2h}, so there is no sharp change of symmetry movement. Another factor is retained: the rhomb axis remains at 90° in alternate layers as before. It is to be noted that there would be an averaged *g* value in e.s.r. data along one plane for the anhydrous compound if this structure is correct, just as there is in the *g* values for the dihydrate.[10,11]

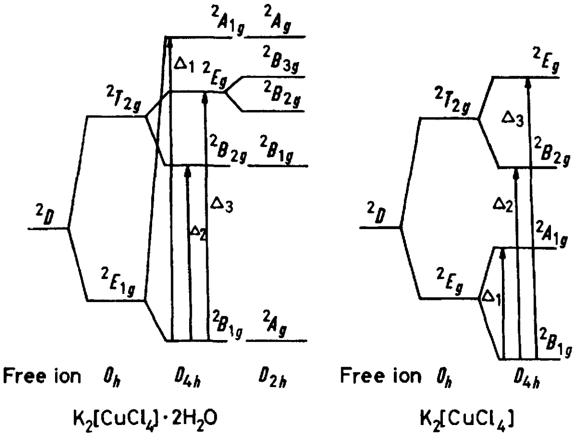

FIGURE 6 Splitting diagrams for copper(II) compounds

The analysis of the spectral and magnetic data indicates that the distortion parameters (*Ds* and *Dt*) are smaller in anhydrous $K_2[CuCl_4]$ than in the dihydrate $K_2[CuCl_4]\cdot 2H_2O$ (Table 4). The lower magnetic moment is consistent with the $^2B_{2g}$ level being higher in the anhydrous compound than in the hydrate. This indicates a more symmetrical compound in the sense that one axis is not sharply different from the other two in the anhydrous compound, as it is in the hydrate. There are probably some changes in the lattice parameters when the anhydrous compound is formed, bringing the chloride ions closer to the central ion. The centre of the band of $K_2[CuCl_4]$, at *ca.* 12 500 cm^{-1}, indicates that the angle between *trans*-chloride ions is *ca.* 160°,[16] far from the tetrahedral angle and reasonably close to the octahedral angle of 180°.

Shrinkage of the lattice parameters in the anhydrous compound is also indicated, although not proven, by the calculation of $\Delta H^\ominus$ of formation using a Born–Haber approach for both compounds. The lattice energy (*U*) for the hydrate was calculated in two parts. Assuming that the ions come together from the gas phase to the same positions and distances as in the crystal, an enthalpy of formation can be calculated for the $[CuCl_4(OH_2)_2]^{2-}$ (g) ion. The extended Kaputsinskii equation can be used to estimate the energy released when the two potassium ions and the diaquatetrachlorocuprate(II) ion form the crystalline solid.[17] A thermochemical radius of 3.98 Å was necessary for the $[CuCl_4(OH_2)_2]^{2-}$ ion to reproduce the experimental lattice energy, using the sum of the two calculated energies, the enthalpy of formation of the gaseous ion, and the lattice energy calculated from the Kaputsinskii equation. The results are in Table 2, together with the experimental values for comparison.

The attempt to calculate values for the anhydrous compound using the same parameters as for the hydrate were unsuccessful. Lattice and molecular parameters had to be shortened. Since any calculations would be guesswork, the results are not included here except to remark that the shortening of the molecular parameters is consistent with the relatively high *Dq* and the much smaller distortion parameters for the anhydrous compound. It implies that the chloride ions are closer in general in $K_2[CuCl_4]$, in a more regular octahedron, and that this compensates for the much stronger influence of the water molecules that have been removed from the lattice. It was necessary to use indirect evidence since no structural analysis for $K_2[CuCl_4]$ could be found, and no crystals large enough to study could be crystallized.

The most consistent picture that appears from the interpretation of the data is that in going from the dihydrate to the anhydrous compound alternate layers in the crystal shift so that the chloride ion of the molecule in the shifted layer now moves into a position vacated by the water molecules. The central copper(II) ion now becomes part of a chain linking all the central metal ions in a linear polymer. The chloride ions all move closer to the central metal ion to compensate for the loss of the water molecules, and the resulting structure, although having a lower symmetry, has a much more symmetrical charge distribution. This is consistent with the thermodynamic parameters, since a linear chain and a more symmetrically charged molecule will produce considerable ordering in the system, but leave the bonds approximately the same strength, so that only the enthalpy of the water molecules is lost to the crystal. This also fits the crystal-field and magnetic parameters. The result is a reasonable picture of what happens in the crystal during the dehydration of $K_2[CuCl_4]\cdot 2H_2O$.

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[16] R. D. Willett, J. A. Haugen, J. Lebsack, and J. Morrey, *Inorg. Chem.*, 1974, **13**, 2510.

[17] S. J. Ashcroft and C. T. Mortimer, 'Thermochemistry of Transition Metal Complexes,' Academic Press, New York, 1970, p. 296.