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A study of phase transitions in $Cd(ClO_4)_2 \cdot 6H_2O$ by adiabatic calorimetry and infrared spectroscopy[a]

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A calorimetric study of $Cd(ClO_4)_2 \cdot 6H_2O$ from 20 to 345 K shows three phase transformations at 124.8, 238.45, and 271.62 K. Infrared spectra indicate that the low-temperature structure (below 124.8 K) contains one type of $[Cd(OH_2)_6]^{2+}$, of symmetry C_3 or C_{3v}, and two types of ClO_4^-, both strongly distorted from tetrahedral symmetry. There appears to be some disorder in this phase. The sharp transition at 124.8 K leads to major spectral changes, which indicate that hydrogen bonding is weakened, distortion of the perchlorate ions is diminished, and $[Cd(OH_2)_6]^{2+}$ symmetry is increased to D_{3d}. The more gradual phase transition at 238.45 K involves no observable infrared spectroscopic changes and may correspond to an increase in ClO_4^- disorder. The very sharp transition at 271.62 K involves only very minor changes in the infrared spectra and may involve an increased disorder of the $[Cd(OH_2)_6]^{2+}$ units.

At room temperature $Cd(ClO_4)_2 \cdot 6H_2O$ forms trigonal crystals assigned to the space group $P3m1 = C_{3v}^1$, with $a = 7.96$ Å and $b = 5.30$ Å.[1] The atomic positions were not determined, but from the resemblance to hexagonal $LiClO_4 \cdot 3H_2O$ the structure was thought to contain distorted $[Cd(OH_2)_6]^{2+}$ octahedra, hydrogen bonded to the surrounding ClO_4^- tetrahedra. The structure of $Cd(ClO_4)_2 \cdot 6H_2O$ is related to that of $LiClO_4 \cdot 3H_2O$ by the removal of every second metal ion along the c axis. In contrast with other metal perchlorate hydrates in which ions are removed at both $1/4\ c$ and $3/4\ c$, in $Cd(ClO_4)_2 \cdot 6H_2O$ all metal ions are at the same height in the unit cell.[1,2]

Below room temperature several phase transformations have been reported on the basis of studies by electron paramagnetic resonance[3–5] and proton magnetic resonance.[6] There has also been a report of a transformation from a hydrate to a pseudohydrate structure below 248 K, based on infrared spectroscopy,[7] but this observation seems to have been due to ice formation.[8]

This paper reports the results of investigations of $Cd(ClO_4)_2 \cdot 6H_2O$ by adiabatic calorimetry and by infrared spectroscopy. The purpose of calorimetric study was to determine definitively the phase transitions (and their associated thermodynamic parameters), in view of earlier contradictory reports concerning the phase transitions of $Cd(ClO_4)_2 \cdot 6H_2O$.[3–8] The infrared study has been undertaken to clarify the structural changes accompanying the phase transitions. The infrared spectra of undeuterated $Cd(ClO_4)_2 \cdot 6H_2O$ in the region of OH stretching and H–O–H bending fundamentals of the water molecules have already been reported in another connection,[8] and we are now reporting the temperature behavior of OD stretching and H–O–D bending fundamentals of isotopically dilute HDO and of the H–O–H bending fundamental of isotopically dilute

H_2O. These spectra, obtained with partly deuterated crystals, yield the most directly interpretable structural information concerning the water molecules.[9] Of the spectral features pertaining to the ClO_4^- ions, we have singled out for a detailed study the fully symmetric stretching fundamental, $\nu_1(A_1)$, which is infrared inactive under full T_d symmetry of an undistorted ClO_4^- tetrahedron. This mode becomes infrared active when the tetrahedron is distorted, and its infrared intensity may be taken as a measure of such distortion. Moreover the ν_1 band is an excellent probe of changes in the crystal environment of the perchlorate ion because it is sharp, especially compared to $\nu_3(F)$, and therefore its position can be determined accurately as a function of temperature.
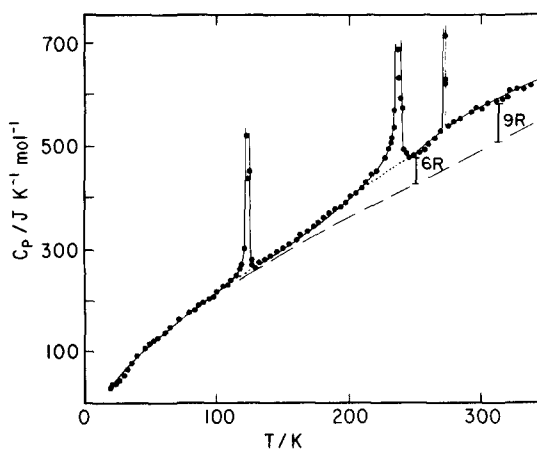

FIG. 1. The heat capacity of $Cd(ClO_4)_2 \cdot 6H_2O$ as a function of temperature. The dotted line indicates the base line heat capacity used to assess the transition enthalpies and entropies, and the dashed line represents the lattice contribution to the heat capacity assessed from the results for $LiClO_4 \cdot 3H_2O$, as described in the text.

EXPERIMENTAL

Cd(ClO$_4$)$_2$ · 6H$_2$O was prepared by the aqueous reaction of stoichiometric quantities of perchloric acid and cadmium carbonate. The product was twice recrystallized from water to remove small traces of HClO$_4$, and for the infrared measurements the crystals were further recrystallized from an H$_2$O/D$_2$O solution of the desired H/D ratio.

The heat capacity of 29.179 g of Cd(ClO$_4$)$_2$ · 6H$_2$O was measured from 20 to 345 K in an adiabatic calorimeter that was fitted with a calibrated platinum resistance thermometer.[10] The measurements were carried out by the heat pulse method, and temperature equilibrium was attained within ~ 15 min of each heat pulse throughout the temperature range of the experiment.

For the infrared experiments, fluorocarbon mulls were prepared under a flow of dry nitrogen and then sandwiched between calcium fluoride or silver chloride windows. The mulls were kept overnight at 0.01 Torr within the cryostat prior to low-temperature spectroscopy. This procedure yielded spectra which appeared to correspond to the pure hexahydrate. Spectra were obtained with a Fourier-trans-form infrared spectrometer (Bomem DA3.02) fitted with a closed-cycle helium refrigerator (Displex model 202, Air Products and Chemicals Co.). The variable-temperature spectral runs were made in the heating mode. The spectral range examined was 4000–500 cm^{-1}, the low wave number cutoff being due to the transparency limit of the AgCl windows.

RESULTS

The phase diagram of Cd(ClO$_4$)$_2$ · 6H$_2$O

The experimental molar heat capacities of Cd(ClO$_4$)$_2$ · 6H$_2$O are illustrated in Fig. 1 and given in Table I. (As there were no sample history effects, the values in the table are given in order of increasing temperature).

From Fig. 1 it is immediately apparent that there are three phase transformations in Cd(ClO$_4$)$_2$ · 6H$_2$O between 20 and 345 K. The temperatures of the transitions were determined from the maxima in C_p, and the transition enthalpies and entropies were calculated as the areas under the C_p vs T and C_p/T vs T curves, respectively, in excess of that due to the "baseline" heat capacity (shown as a dotted line in Fig.

TABLE I. The experimental values of the heat capacity of Cd(ClO$_4$)$_2$ · 6H$_2$O.

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
19.99	27.08	125.32	1009	197.09	387.2	266.09	515.6
22.05	34.56	125.78	451.0	198.69	389.3	266.15	521.6
24.42	35.54	126.50	278.8	200.87	402.3	267.57	521.3
27.50	40.78	128.12	269.7	201.35	404.4	270.01	529.8
30.36	51.23	128.89	264.6	201.77	402.0	271.53	1314
33.18	63.10	130.49	270.4	206.21	409.5	271.58	3177
36.33	74.68	132.76	277.4	206.38	407.4	271.72	1647
41.03	90.70	133.47	275.5	210.13	417.5	271.89	1121
46.31	105.8	135.93	279.3	212.71	429.3	272.19	785.6
50.72	115.1	136.20	279.4	214.21	428.3	272.49	711.8
54.17	121.5	140.71	287.2	218.39	444.1	272.83	628.6
57.19	124.6	144.10	291.2	222.09	450.4	273.17	620.1
60.67	134.8	145.10	295.2	226.89	476.5	275.14	537.3
65.46	147.0	148.86	302.0	227.36	476.9	276.46	540.3
72.38	164.7	149.36	304.0	229.58	492.7	279.37	547.1
80.03	179.3	149.42	299.9	231.81	505.4	281.95	549.6
83.69	182.6	151.60	302.2	232.76	515.7	284.57	549.0
86.91	192.5	153.58	308.6	234.94	536.8	286.87	553.6
88.38	192.6	156.70	317.0	234.96	566.7	287.87	556.3
91.33	197.9	157.66	314.7	238.30	686.0	288.48	558.1
94.56	203.7	159.19	315.6	238.62	685.8	288.88	559.5
99.05	212.8	160.56	317.6	238.93	629.6	293.76	562.8
100.44	215.8	161.74	316.0	239.24	587.3	297.61	573.0
106.13	229.9	164.40	328.3	241.09	572.9	301.42	570.8
107.52	230.1	165.18	325.4	242.10	490.5	302.79	579.3
110.93	239.1	166.50	329.9	242.83	487.4	305.65	578.6
114.62	246.4	167.40	330.9	243.37	482.4	309.01	580.9
115.02	249.8	168.38	338.8	243.90	484.5	309.05	580.7
116.01	252.3	169.76	337.1	245.74	477.4	312.76	585.8
116.73	252.6	173.96	342.9	246.26	477.1	315.16	585.3
118.21	263.2	175.55	350.9	248.77	479.2	316.68	584.9
119.47	272.6	178.08	352.6	249.79	481.4	319.91	588.7
121.68	302.5	179.04	357.8	252.16	487.1	321.18	605.6
123.58	434.0	182.13	359.3	254.51	488.7	326.78	603.9
123.68	519.2	182.22	360.7	256.65	494.5	327.21	608.0
124.09	908.3	186.10	370.0	257.47	489.3	333.17	607.3
124.51	1311	188.99	373.2	259.95	501.3	333.92	615.8
124.76	2150	190.06	376.3	262.15	509.9	339.08	615.0
125.02	1596	193.60	380.7	263.44	507.8	344.95	636.1

TABLE II. The phase transitions in $Cd(ClO_4)_2 \cdot 6H_2O$.

T_{trans}/K	$\Delta H_{trans}/J\ mol^{-1}$	$\Delta S_{trans}/J\ K^{-1}\ mol^{-1}$
124.8 ± 0.1	2530 ± 10	20.3 ± 0.1
238.45 ± 0.05	1260 ± 90	6.1 ± 0.4
271.62 ± 0.05	1505 ± 15	5.54 ± 0.06

1). The phase transition parameters are summarized in Table II.

Phase transitions in $Cd(ClO_4)_2 \cdot 6H_2O$ have previously been detected by EPR of Mn^{2+} doped in $Cd(ClO_4)_2 \cdot 6H_2O$ at 115.5 and 272 K,[3] and at 115.5, 259, and 272 K,[4] and at 116, 259, 272, and 363 K[5]; by ^{1}H NMR at 110 and 266–274 K[6]; by an earlier infrared investigation at 248 K.[7] The last result has been ascribed to the crystallization of water in the hygroscopic sample.[8]

Although the calorimetric results do not coincide with those of earlier EPR and NMR experiments, the present results are favored for several reasons: the measurements are carried out on a thermally equilibrated sample; the thermometer used has been calibrated to ± 0.005 K; calorimetery probes the macroscopic state of the specimen and therefore cannot miss phase transitions to which microscopic probes may be insensitive. In addition, the temperatures of two of the three transitions are corroborated by the infrared results.

Infrared spectrum: Water vibrations

Spectrum at 10 K

Figure 2 presents the H–O–D bending absorption of isotopically dilute HDO in $Cd(ClO_4)_2 \cdot 6H_2O$. At 10 K the absorption in this region consists of a quartet of incompletely resolved bands at 1459, 1443, 1431, and 1425 cm^{-1}. The quartet clearly corresponds to four distinct hydrogens in the low-temperature structure, but the rather large half-widths (about 30 cm^{-1} for the 1443 cm^{-1} peak; about 15 cm^{-1} for the other three; half-widths are defined throughout as full width at half-height) may signal the occurrence of some structural disorder involving the hydrogens.

Figure 3 shows the OD stretching region of the spectrum of isotopically dilute HDO. At 10 K this spectrum is also a quartet of bands at 2597, 2550, 2525, and 2517 cm^{-1}, consistent with four distinct hydrogens in the low-temperature structure. We will number these hydrogens H^1 to H^4 in the order of decreasing OD stretching frequencies, presumably corresponding to increasing strength of hydrogen bonding. The intensities of the quartet are consistent with equal abundance for the four hydrogens and hence the water spectrum points to the probable occurrence of two types of water molecules occupying asymmetric sites in the structure.[9] An additional weak absorption band at about 2533 cm^{-1}, appears to be a genuine feature of the spectrum and indicates some disorder in which the H_2O molecules have alternative orientations. The relatively large half-widths of the main
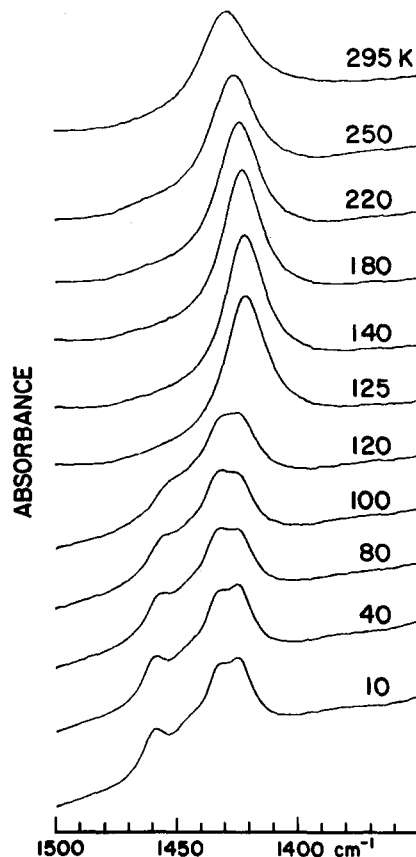

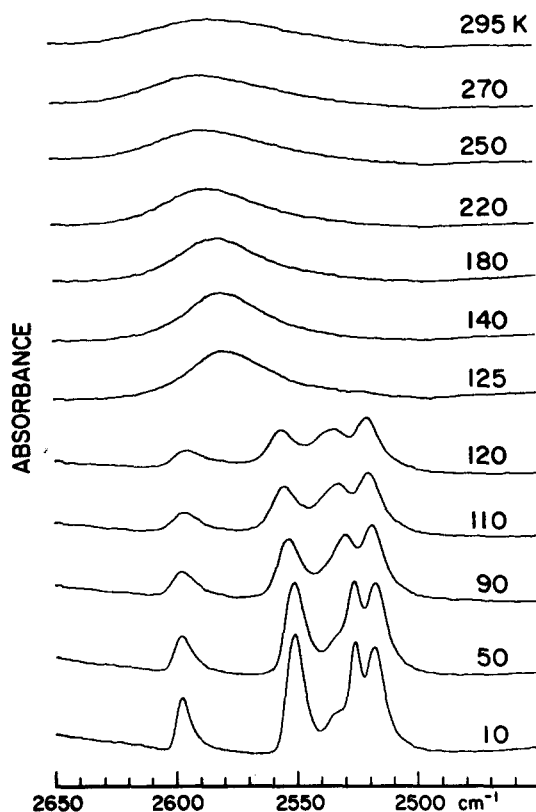FIG. 2. H–O–D bending fundamental of isotopically dilute HDO in $Cd(ClO_4)_2 \cdot 6H_2O$ (5% D) at different temperatures.

FIG. 3. OD stretching fundamental of isotopically dilute HDO in $Cd(ClO_4)_2 \cdot 6H_2O$ (1% D) at different temperatures.
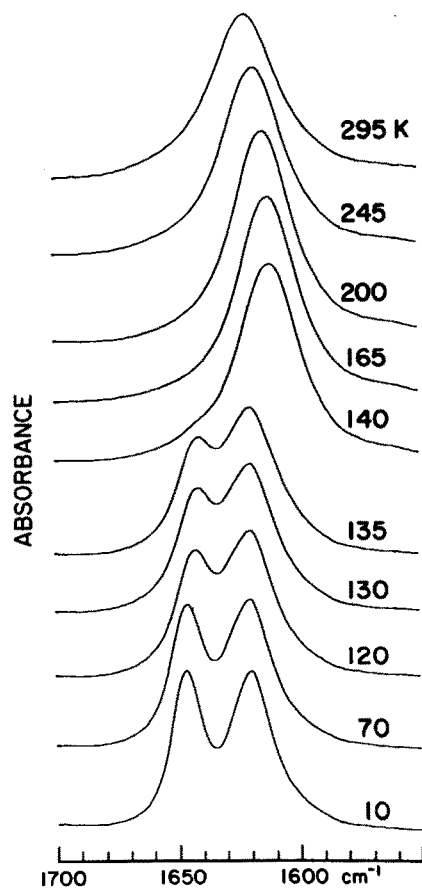
FIG. 4. H–O–H bending fundamental of isotopically dilute H$_2$O in Cd(ClO$_4$)$_2$ · 6H$_2$O (70% D) at different temperatures.
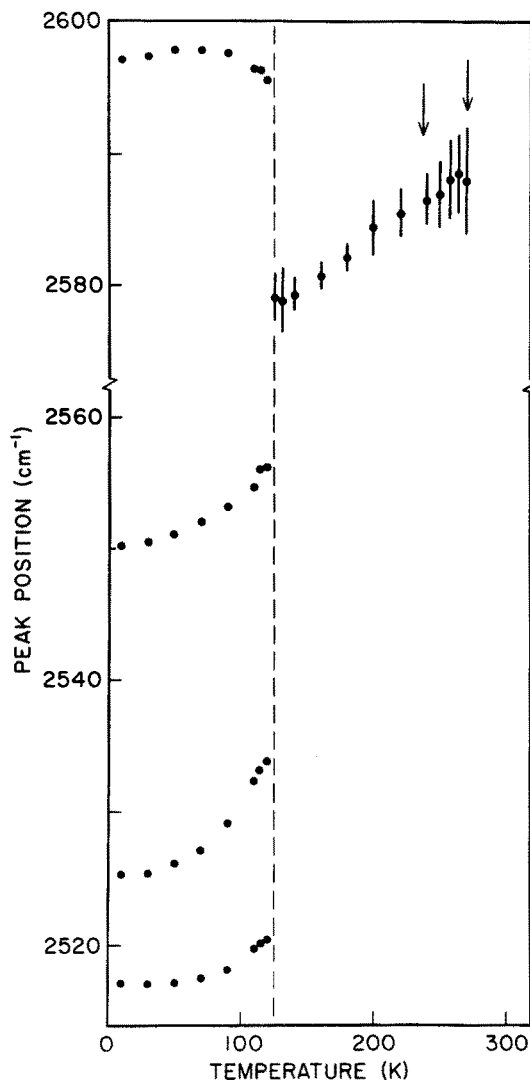

FIG. 5. Positions of the band maxima of OD stretching vs temperature. Broken lines denote transitions detected calorimetrically and spectroscopically; arrows denote transitions not detected spectroscopically.

quartet (about 10 cm^{-1}; by contrast those observed for the corresponding OD stretching bands of HDO in LiClO$_4$ · 3H$_2$O are about 3 cm^{-1} at 108 K[11]), also consistent with the occurrence of disorder.

The OD stretching bands span a wide wave number range of 2597–2517 cm^{-1}, pointing to a wide variety of hydrogen-bond strengths. The hydrogen bond involving H[1] is almost as weak as those in the very weakly hydrogen-bonded perchlorate salt hydrates such as LiClO$_4$ · 3H$_2$O (OD stretching at 2619 cm^{-1} at 108 K) or NaClO$_4$ · H$_2$O (OD stretching at 2641 and 2611 cm^{-1} at 108 K).[11] On the other hand, the hydrogen bond involving H[4] is almost as strong as the average in liquid water (center of OD stretching band at 2502 cm^{-1} at 298 K).[12]

Spectra of isotopically dilute H$_2$O molecules are shown in Fig. 4 in the region of H–O–H bending fundamental. At 10 K the absorption in this region is a doublet at 1645 and 1620 cm^{-1}, confirming that the low-temperature structure contains two distinct types of water molecules, which we will designate H$_2$O(A) and H$_2$O(B). H$_2$O(A), with its bending vibration some 25 cm^{-1} above that of H$_2$O(B), must be more strongly hydrogen bonded.[13] The half-widths of the doublet components are 20–25 cm^{-1}, much larger than is typical for crystalline hydrates at low temperatures,[11] which again confirms the occurrence of some structural disorder.

Spectrum between 10 and 120 K

With increasing temperature between 10 and 120 K only gradual and relatively minor spectral changes are observed, corresponding to gradual changes in the structure: ν(OD^1) moves to *lower* frequency, while ν(OD^2), ν(OD^3), and ν(OD^4) move to *higher* frequency (Fig. 5). This indicates that hydrogens 2, 3, and 4 participate in linear or nearly linear hydrogen bonds, which undergo a general weakening with increased temperature, while hydrogen 1 probably participates in a highly bent, perhaps bifurcated hydrogen bond. Such bonds tend to be strengthened with increasing temperature.[14]

The frequency of the bending mode of H$_2$O(B) is almost unaffected by temperature increase in this range (Fig. 6), while that of H$_2$O(A) decreases rapidly with increasing temperature, indicating that its hydrogen bond is, on the average, weakened. Considering the values of the four OD stretching frequencies and their temperature behavior, it appears likely that H[1] is associated with H$_2$O(B). There is no way at present to assign the other three protons definitively.
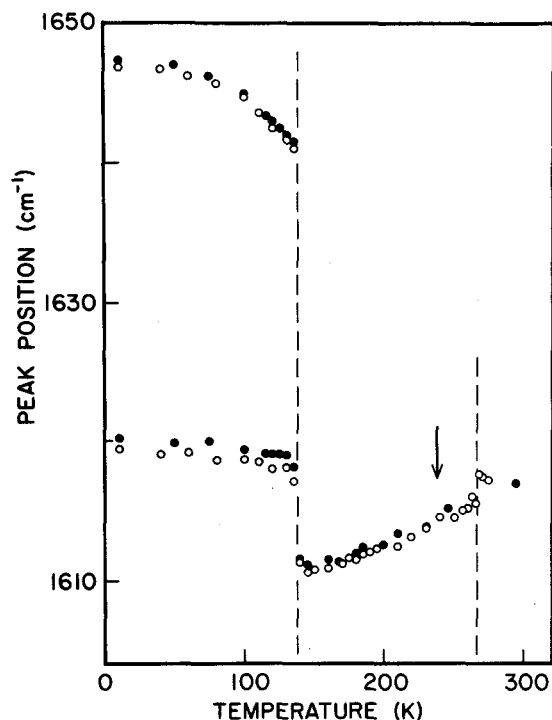
FIG. 6. Positions of the band maxima of H–O–H bending vs temperature. Open and full circles denote two series of experiments. Broken lines and arrow as in Fig. 5.

Spectral changes at 125 K

At about 125 K the spectrum of $Cd(ClO_4)_2 \cdot 6H_2O$ undergoes a sharp transformation: (1) the H–O–D bending quartet becomes a singlet at 1421 cm^{-1} (Fig. 2); (2) the OD stretching quartet becomes a singlet at 2580 cm^{-1} (Fig. 3); (3) the H–O–H bending doublet becomes a singlet at 1611 cm^{-1} (Fig. 4). The temperature of this transformation is a function of D content, occurring at about 140 K in the fully deuterated samples and at temperatures between 125 and 140 K in the partially deuterated samples. The spectral changes indicate a transition to a higher-temperature structure in which all water molecules are effectively equivalent and occupy symmetric sites, so that all hydrogen atoms are also spectroscopically equivalent. The large half-widths (37 cm^{-1} for OD stretch, 18 cm^{-1} for H–O–D bend, and 28 cm^{-1} for H–O–H bend) indicate static or dynamic disorder.

The OD stretching singlet is shifted about 30 cm^{-1} upward from the mean of the low-temperature quartet, while the H–O–D and H–O–H bending singlets are shifted about 20 cm^{-1} downward from the mean of the low-temperature quartet and doublet, respectively. All these changes indicate a general *weakening* of the hydrogen bonding in the higher-temperature structure.

Spectrum between 125 and 293 K

With further increases of temperature the frequency of the H–O–D bending fundamental shifts gradually to *higher* values, but its very large half-width remains nearly constant until room temperature (Fig. 2). This is consistent with the band width being largely due to structural disorder. The H–

O–H bending fundamental behaves similarly (Fig. 4). The OD stretching fundamental broadens somewhat more with increasing temperature (Fig. 3). No changes were observed in any of the spectral parameters near 238.45 K, the temperature of the third calorimetrically determined phase transition. On the other hand, a small shift in the frequency of the HOH bending (Fig. 6) and HOD bending fundamentals near 270 K appears to correspond to the observed phase transition at 271.62 K.

Infrared spectrum: Perchlorate Ions

In the 10 K spectrum the band due to the $v_1(A_1)$ fundamental of ClO_4^- is observed as a small, incompletely resolved doublet centered at about 922 cm^{-1}. Its two components occur at about 920 and 930 cm^{-1}, the former being of appreciably higher intensity (Fig. 7). The total integrated intensity of the doublet is roughly 1/1000 of that of the band due to the degenerate stretching fundamental of ClO_4^-, $v_3(F)$, which is observed as a complex absorption extending from 1045 to 1180 cm^{-1}. The nonzero intensity of the v_1 mode attests to the distortion of ClO_4^- from ideal T_d symmetry, while the doubling implies the occurrence of two distinct perchlorate ions in the 10 K structure. The low frequency of this mode (its position in the infrared spectra of other hydrated and anhydrous perchlorate salts extends from 928 to 938 cm^{-1} [15]) is consistent with relatively strong hydrogen bonding.
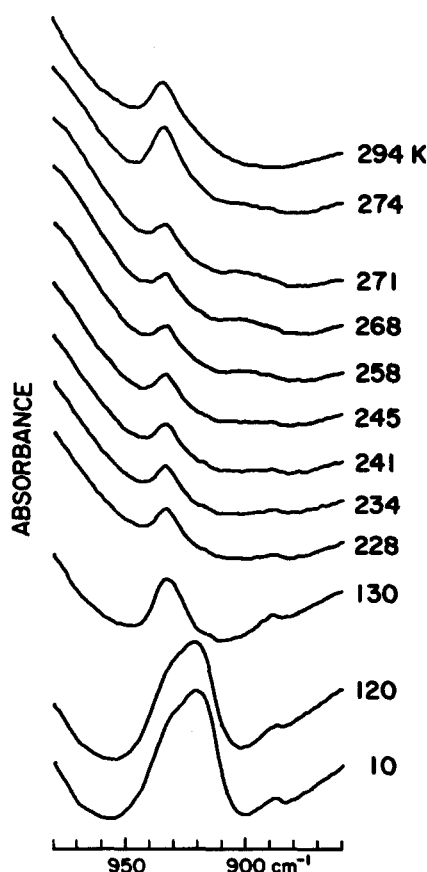

FIG. 7. ClO_4^- fully symmetric stretching fundamental, v_1, in $Cd(ClO_4)_2 \cdot 6H_2O$ at different temperatures.
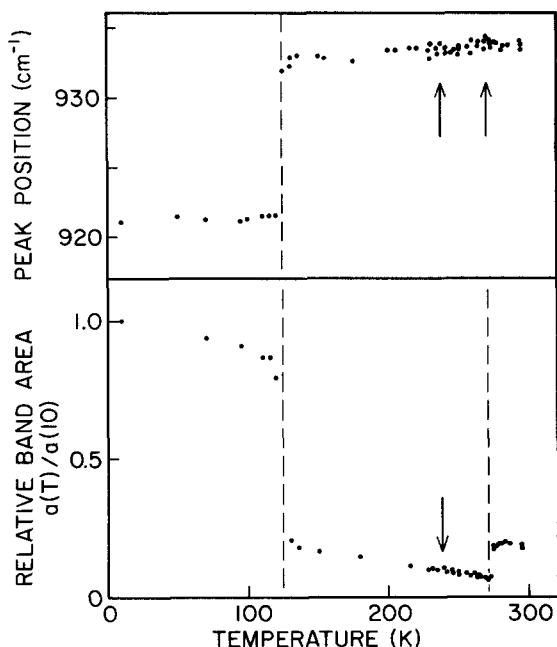
FIG. 8. A plot of peak position and relative band area (band area divided by the band area at 10 K) for the ν_1 fundamental of the perchlorate ion. Broken lines and arrows as in Fig. 5.

TABLE III. Some possible configurations of an $M(OH_2)_6$ complex.[a]

	Site symmetry		Sets of equivalent atoms[b]	
M^d	O	H	O	H
T_d	C_{2v}	C_s	(6)	(12)
T_h	C_{2v}	C_s	(6)	(12)
T	C_2	C_1	(6)	(12)
$D_{3d}^{(a)}$	C_s	C_1	(6)	(12)
$D_{3d}^{(b)}$	C_s	C_s	(6)	2(6)
D_{2h}	C_{2v}	C_s	3(2)	3(4)
S_6	C_1	C_1	(6)	2(6)
$C_{3v}^{(a)}$	C_s	C_1	2(3)	2(6)
$C_{3v}^{(b)}$	C_s	C_s	2(3)	4(3)
C_3	C_1	C_1	2(3)	4(3)
C_2	C_2, C_1	C_1	2(2) + 2(1)	2(2) + 4(2)
$C_s^{(c)}$	C_1	C_1	(2) + 4(1)	6(2)
C_1	C_1	C_1	6(1)	12(1)

[a] The unlikely configurations in which the six oxygen atoms are coplanar, D_{6h}, C_{6v}, and C_6, have been omitted.

[b] Symbol (n) denotes one set of n equivalent atoms; $m(n)$ denotes m distinct sets of n equivalent atoms in each set.

[c] There are several additional configurations of symmetry C_s.

[d] Symmetry symbols marked (a) designate variants in which the pairs of hydrogens on each H_2O are related by a mirror plane. Those marked (b) denote variants in which such pairs of hydrogens are on a mirror plane and thus are not related by symmetry.

From 10 to 120 K the ν_1 doublet undergoes only a very slight and gradual change, but near 125 K an abrupt spectral change occurs, clearly corresponding to the calorimetrically detected phase transition at 124.8 K. The ν_1 band becomes a much smaller singlet at 931 cm^{-1}. The simple band shape implies the occurrence of only one distinct perchlorate anion above 125 K, while the decrease of intensity, by a factor of about 3, indicates a much decreased distortion of the ClO_4^- tetrahedron. The increased frequency is consistent with an average weakening of hydrogen bonding to perchlorate ions.

Between 125 and 271 K the ν_1 band undergoes only a gradual diminution of intensity with almost no change of band position (Fig. 8). Specifically, no changes are observed near 238.45 K, the temperature of the second calorimetrically determined transition. At about 272 K the intensity of the ν_1 peak abruptly increases, corresponding closely to the third calorimetrically observed phase transition, at 271.62 K. This indicates an increase in the effective distortion of the ClO_4^- tetrahedron.

DISCUSSION

At temperatures below 124.8 K, the infrared spectra indicate the occurrence of two types of water molecules and four distinct types of hydrogen. It follows from Table III that the site symmetry of $[Cd(OH_2)_6]^{2+}$ must be either C_3 (illustrated in Fig. 9) or C_{3v} with both hydrogens on each water molecule lying on mirror planes. The latter configuration, designated C_{3v} (b) in Table III, seems much less likely. The four distinct hydrogens participate in hydrogen bonds of widely differing strength. There are also two distinct types of ClO_4^- ions, both strongly (but unequally) distorted from tetrahedral symmetry, probably to C_3 or C_{3v}.

There is a sharp transition at 124.8 K, concurrent with profound changes in the infrared spectra of both the water and perchlorate species. This structural transition, which leads to one type of H_2O and one type of H, could correspond to a rotation of the water molecules about the Cd–O bond plus a small translation, which together result in the appearance of new elements of symmetry for $[Cd(OH_2)_6]^{2+}$: three twofold axes at right angles to the threefold axis (causing the two sets of H_2O to become equivalent), three dihedral mirror planes (causing the pairs of hydrogens on each H_2O to become equivalent), and the resultant center of symmetry. Four site symmetries for the $[Cd(OH_2)_6]^{2+}$ ion are consistent with one O and one H: T_d, T_h, T, and D_{3d} (cf. Table III). The first three require a cubic space group and are unlikely. The fourth possibility, D_{3d} (Fig. 9) is compatible with three trigonal space groups $(P\bar{3}1m = D_{3d}^1$, $P\bar{3}m1 = D_{3d}^3$, and $R\bar{3}m = D_{3d}^5)$, but is incompatible with the space group $(P3m1 = C_{3v}^1)$ proposed by West for Cd(ClO₄)₂·6H₂O at room temperature.[1] The matter is open and redetermination of the room temperature structure, as well as determination of the lower temperature structures, would be useful. The change in disorder of the water molecules at the 124.8 K transition is also substantiated by the calorimetric results. If the total entropy change was associated with each of the six waters of hydration going from a low-temperature ordered structure to one in which the waters can experience relatively rapid 180° flips (as shown by NMR[6], one would expect a transition entropy of 6R ln 2(= 34.6 J K^{-1} mol^{-1}). From our infrared results we know that some disorder of the waters exists already in the low temperature phase, and indeed the observed transition entropy (20.3 J K^{-1} mol^{-1}) falls short of 34.6 J K^{-1} mol^{-1}. Another feature of the structure
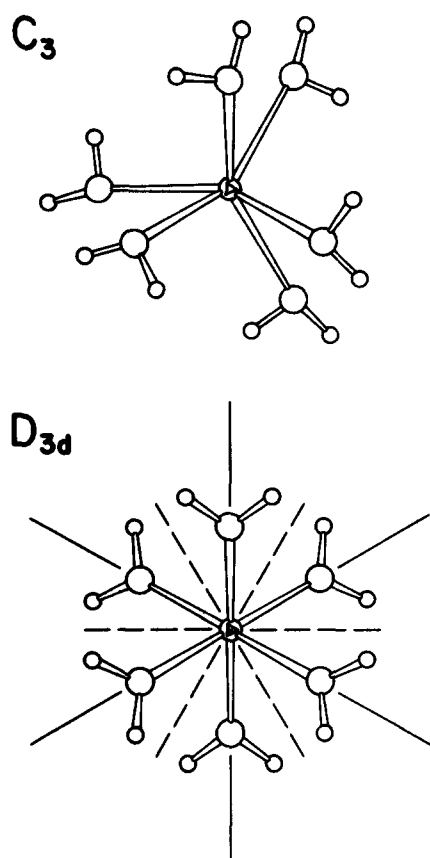
FIG. 9. Two possible configurations of the $[Cd(OH_2)_6]^{2+}$ complex, showing elements of symmetry. Triangle: threefold axis; broken line: twofold axis; full line: mirror plane; dot: center of symmetry.

from 124.8 to 238.45 K is the much weaker average hydrogen bonding and the diminished distortion of the ClO_4^- ions, compared with the lowest-temperature structure.

The phase transition at 238.45 K is gradual in the calormetric experiment, and involves no observable change in the infrared spectra of either the waters or the perchlorate ions. EPR studies[3,5] have shown that the axial crystal field parameter also is insensitive to this transition, which indicates that there is probably no change in the symmetry at the Cd^{2+} site. The EPR resonance lines also were found to be much narrower than one might expect for an order–disorder transition involving the $[Cd(OH_2)_6]^{2+}$ ions.[5] It therefore seems unlikely that either further disorder of the waters of hydration or disorder of the $[Cd(OH_2)_6]^{2+}$ ions can account for the transition at 238.45 K in $Cd(ClO_4)_2 \cdot 6H_2O$, and although the evidence for an increase in perchlorate disorder as the cause of this transition is not direct, we favor this explanation. The heat capacity around this transition has a gradual component, indicative of an order–disorder transition, yet the infrared results show that the water molecules are not greatly perturbed at this transition. Because the hydrogen bonding is already weak, an increased disorder in the perchlorate ions may be reconcilable with an absence of change in the infrared spectra of the H_2O and and ClO_4^-. In addition,

perchlorate ions are well known to be disordered in many structures at room temperature and below; perchlorate disorder would be particularly favored in a system such as this with weak, and possibly bifurcated, hydrogen bonds.

The very sharp transition at 271.62 K is observed both calorimetrically and in the infrared spectrum of the ClO_4^- ion, which indicates an increased ClO_4^- distortion from tetrahedral symmetry. The infrared spectra of the water molecules are almost unchanged by this transition, which we could again take as an indication of a lack of change in the water configurations. However, this transition is prominent in the EPR study of $Mn^{2+}:Cd(ClO_4)_2 \cdot 6H_2O^{3-5}$ and the discontinuity in the axial crystal field parameter at the transition is indicative of a change in the $[Cd(OH_2)_6]^{2+}$ ions. If this transition is due to increased disorder in the $[Cd(OH_2)_6]^{2+}$ units, it is somewhat surprising that the calormetric experiments show it to be sharp. However, comparisons with $LiClO_4 \cdot 3H_2O$ give further support for three-dimensional disorder in $[Cd(OH_2)_6]^{2+}$ as the source of this transition, as described below.

$LiClO_4 \cdot 3H_2O$ has a very similar structure to $Cd(ClO_4)_2 \cdot 6H_2O$; the major diference is that the lithium salt has twice as many metal ions so that there are chains of $Li(OH_2)_{3+x}^+$ parallel to the c axis, rather than the discrete $[Cd(OH_2)_6]^{2+}$ ions of the cadmium salt. The structure $LiClO_4 \cdot 3H_2O$ has been studied by x-ray and neutron diffraction,[16] and found to be ordered at room temperature. In addition, infrared studies of the waters of hydration have shown only smooth evolution of the spectra as a function of temperature,[17,18] and a calorimetric study of $LiClO_4 \cdot 3H_2O$ showed no phase transitions between 17 and 343 K.[19] However, the half-widths of water and perchlorate fundamentals for the room-temperature structure of $Cd(ClO_4)_2 \cdot 6H_2O$ [OD stretching of HDO: 60 cm^{-1}; HOD bending; 25 cm^{-1}; $\nu_1(ClO_4^-)$: ~12 cm^{-1}] are much larger than for $LiClO_4 \cdot 3H_2O$ [OD stretch of HDO: 7 cm^{-1}; HOD bend: 12 cm^{-1}; $\nu_1(ClO_4^-)$: ~6 cm^{-1}], which argues for the occurence of disorder in the room-temperature structure of $Cd(ClO_4)_2 \cdot 6H_2O$. It therefore seems reasonable to use the $LiClO_4 \cdot 3H_2O$ heat capacity results to assess the excess heat capacity in $Cd(ClO_4)_2 \cdot 6H_2O$ due to its additional degrees of freedom. Using the assumption that $\theta_D(T)$ values for the lattice contributions to the heat capacities of the two salts will have parallel temperature dependences, and assuming that $Cd(ClO_4)_2 \cdot 6H_2O$ has no additional degrees of freedom below 100 K, the heat capacity "expected" for $Cd(ClO_4)_2 \cdot 6H_2O$ without disorder contributions is given by the dashed line in Fig. 1. This figure shows that the additional degrees of freedom commence with the transition at 124.8 K, and increase gradually until just above the transition at 271.62 K. The excess heat capacity is ~$6R$ just above the 238.45 K transition, and increases to ~$9R$ at the 271.62 K transition. These values are in good agreement with what one might expect for the excitation of three-dimensional torsional oscillations in two species (two ClO_4^-) and three species (two ClO_4^- and one $[Cd(OH_2)_6]^{2+}$) respectively, in agreement with the discussion above concerning the sources of the two higher-temperature phase transitions in $Cd(ClO_4)_2 \cdot 6H_2O$.

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