



HAL
open science

**PHASE TRANSITIONS ATTRIBUTABLE TO
DISORDER IN WATERS OF HYDRATION IN
M(ClO₄)₂.6H₂O (M=Cd, Mg, Zn)**

M. White, M. Falk

► **To cite this version:**

M. White, M. Falk. PHASE TRANSITIONS ATTRIBUTABLE TO DISORDER IN WATERS OF HYDRATION IN M(ClO₄)₂.6H₂O (M=Cd, Mg, Zn). Journal de Physique Colloques, 1987, 48 (C1), pp.C1-573-C1-578. 10.1051/jphyscol:1987178 . jpa-00226329

HAL Id: jpa-00226329

<https://hal.science/jpa-00226329>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

PHASE TRANSITIONS ATTRIBUTABLE TO DISORDER IN WATERS OF HYDRATION IN $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($M=\text{Cd}, \text{Mg}, \text{Zn}$)⁽¹⁾

M.A. WHITE and M. FALK*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

**Atlantic Research Laboratory, National Research Council of Canada, Halifax, Nova Scotia, B3H 3Z1, Canada*

RESUME: On présente les résultats d'études calorimétriques et spectroscopiques sur les transitions de phase des composés ayant la formule générale $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($M=\text{Cd}, \text{Mg}, \text{Zn}$). On discute la relation entre le désordre des eaux d'hydratation dans ces trois cristaux et leur structure.

ABSTRACT: The results of calorimetric and infrared studies of the phase transitions in compounds of the general formula $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($M=\text{Cd}, \text{Mg}, \text{Zn}$) are described. The findings with respect to the disorder of the waters of hydration are correlated with the known structural relationships among these materials.

INTRODUCTION

Salts of the general formula $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($M=\text{Cd}, \text{Mg}, \text{Zn}$) have hexagonal structures with octahedrally-coordinated $[\text{M}(\text{OH}_2)_6]^{2+}$ units surrounded by ClO_4^- ions [1]. The structures of these divalent metal perchlorate hexahydrates can be considered to be derived from that of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, in which each Li^+ is octahedrally coordinated to six water molecules such that chains of $[\text{Li}(\text{OH}_2)_3]^+$ run parallel to the c axis [2], by the removal of alternate metal ions along the c axis in order to compensate for the valency change. Since the metal ions can be "removed" at $1/4$ c or $3/4$ c, different structures, and a sort of polytypism, can result. In $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ all the metal atoms are at the same height in the unit cell, and the structure is the most ordered of the series. In $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ there is a complicated but periodic arrangement of the metal ions, such that the unit cell contains Mg ions at $1/4$ c in the corner columns and $3/4$ c in the central column. The structure of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ is the least ordered in this sense, with random shifts between the $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ structure and one shifted by $1/2$ c, as viewed along the b axis [1,3,4].

PHASE TRANSITIONS

In principle, there could be several phase transitions in $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, associated with rearrangements of the waters of hydration, disorder of the perchlorate ions, and tumbling of the $[\text{M}(\text{OH}_2)_6]^{2+}$ units. Phase transitions in salts of the general formula $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ have now been investigated by electron paramagnetic resonance [5-12], ^1H NMR [13-15], infrared [16-18] and Raman [19] spectroscopy, and adiabatic calorimetry [17,18,20,21]. The transition temperatures and enthalpy and entropy changes [17,18,21] are summarized in Table I, where "shape" refers to whether the heat capacity anomaly is abrupt or gradual.

⁽¹⁾NRCC Publication Number 26323

An assessment of the heat capacity of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, in comparison with that of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ in which no phase transformations occur [22], indicates that the intermediate transition in the Cd salt is due to disorder of the perchlorate ions, and its upper transition is due to three-dimensional disorder of the $[\text{Cd}(\text{OH}_2)_6]^{2+}$ complex [17]. In contrast, the highest-temperature transitions in the Zn and Mg salts appear to be due to perchlorate ion disorder [18]. Here we are most interested in those aspects of the phase transformations that reflect disorder in the waters of hydration.

Table I. Phase transitions in $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.

M	T_{tr} / K	$\Delta H_{\text{tr}} / \text{J mol}^{-1}$	$\Delta S_{\text{tr}} / \text{J K}^{-1} \text{mol}^{-1}$	Shape	Ref
Cd	124.8+0.1	2530+12	20.3+0.1	sharp	17
	238.45+0.005	1260+90	6.1+0.4	gradual	17
	271.62+0.05	1505+15	5.54+0.06	sharp	17
Mg	107.9+0.1	800.4+0.3	7.754+0.003	sharp	21
	273.2+0.1	2132+3	8.25+0.01	gradual	21
	325.36+0.02	7120+90	21.9+0.3	gradual	21
Zn	70.1+0.2	261+1	3.70+0.01	sharp	18
	209.8+0.1	16+3	0.08+0.01	sharp	18
	290.5+0.2	2580+20	9.50+0.07	gradual	18
	349.0+0.5	7550+150	21.6+0.4	gradual	18

DISORDER IN WATERS OF HYDRATION

The OD stretching fundamental of isotopically-dilute HDO is very sensitive to the environment of the water molecules and can be used to deduce the presence of disorder. In an ordered crystal of simple structure each structurally-distinct water hydrogen gives rise to a separately-resolved OD stretching band in a spectrum with a halfwidth (i.e. full width at half maximum) of 5 cm^{-1} or less, especially at low temperatures [23,24]. Halfwidths appreciably greater than 5 cm^{-1} at 10 K indicate occurrence of some form of disorder. For example, the four OD stretching fundamentals in the spectrum of the fully ordered ice II have individual halfwidths of about 4 cm^{-1} at 100 K [25], while the halfwidth of the OD fundamental in the spectrum of the orientationally disordered ice Ih is about 20 cm^{-1} at 10 K [26], and in the positionally and orientationally disordered amorphous solid water it is about 60 cm^{-1} at 10 K [26].

Figure 1 illustrates the OD stretching fundamental of isotopically-dilute HDO in $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ at different temperatures [17,18]. The number of resolved spectral peaks and their halfwidths in the 10 K spectra allow the following deductions. In $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ there are at least four distinct types of water hydrogens, with some disorder present. In $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ there are at least 16 distinct water hydrogens (the most so far reported for any crystalline hydrate [23,24]), with some disorder present. In $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ there is an even greater amount of disorder, with a continuum of water hydrogens as indicated by the broad unresolved OD stretching band extending over a wide frequency range.

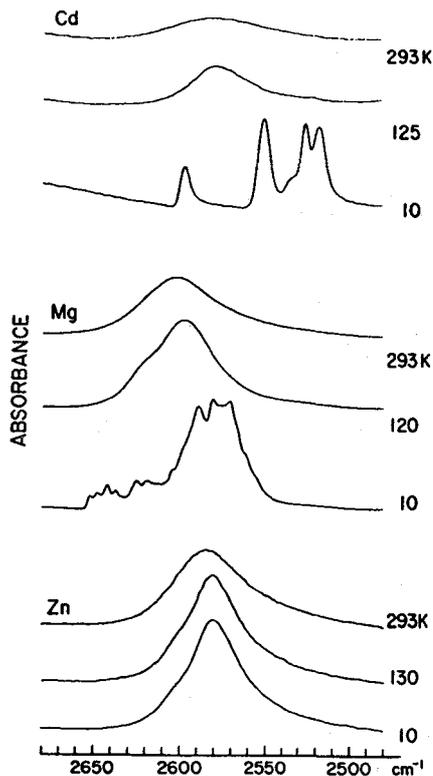


Figure 1. OD stretching frequency of isotopically dilute HDO in $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1% - 3% D) at three temperatures.

As the temperature is increased, at the lowest-temperature transition in the Cd salt ($T_{tr} = 124.8$ K) the OD stretching absorption broadens drastically into a single band. In the spectrum of the Zn salt the very broad band occurring at low temperatures remains essentially unchanged at the lowest transition ($T_{tr} = 70.1$ K). The OD stretching absorption is insensitive to higher-temperature transitions in $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ [17], and changes only slightly near the 290.5 K transition in $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. In $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, the OD stretching doublet broadens as the temperature is increased, until it becomes a singlet at the transition at 273.2 K. Analogous spectral changes are also observed in the region of the H-O-H bending fundamental of isotopically-isolated H_2O in the infrared spectra of these compounds [17,18].

These findings are interpreted as follows. At 10 K each of the salts has some disorder that involves water. The amount of disorder increases in the order $\text{Cd} < \text{Mg} < \text{Zn}$. At temperatures that correspond to the lowest-temperature phase transition in the Cd and Mg salts there occur increases in the disorder to the point of it becoming comparable with that of the Zn salt. These results also can be understood in terms of the thermodynamics of the phase transformations and the known structures of these compounds: the entropy change associated with the

lowest-temperature phase transition follows the same ranking as the overall structural order with respect to the position of the metal ions, and the water ordering at low temperatures, namely $Cd > Mg > Zn$.

CONCLUSIONS AND FURTHER REMARKS

The salts of the general formula $M(ClO_4)_2 \cdot 6H_2O$ ($M=Cd, Mg, Zn$) show considerable disorder in the waters of hydration, and a direct relationship between the disorder in the waters and polytypism in the structure. In particular, the Zn salt, which has the least ordered structure in terms of the periodicity of the metal atoms, has a very great number of different environments for water protons at 10 K. $Mg(ClO_4)_2 \cdot 6H_2O$, which has a complex but periodic structure shows an exceptionally large number of distinct water protons at 10 K. In addition, the large range of OD stretching frequencies indicates a very wide variation of hydrogen-bond strengths, some of which are unusually low. $Cd(ClO_4)_2 \cdot 6H_2O$, which has the most regular structure of the series with regard to the placement of the metal atoms, shows several distinct water protons at 10 K, but fewer than the Mg and Zn salts. The Cd salt also contains a wide range of hydrogen-bond strengths, but, on the average, these are considerably stronger than in the Zn and Mg compounds.

These materials therefore offer a wide range of environments in which one can locate waters of hydration, to study, for example, the effects of local environment on hydrogen-bond strength. Although the room temperature structures have been reported, low-temperature structures have not been determined, and such investigations of $M(ClO_4)_2 \cdot 6H_2O$ would make a valuable contribution to this field.

ACKNOWLEDGEMENTS

We gratefully acknowledge the experimental assistance of P. Seto, K. Nightingale, A. Weaver, R. Clifton and M. Van Oort, and grants in support of this research (to MAW) from the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

1. C.D. West, Z. Kristallogr. Sect. A 91 (1935) 480-493.
2. A. Sequeira, I. Bernal, I.D. Brown and R. Faggiani, Acta Crystallogr. Sect. B 31 (1975) 1735-1739.
3. M. Ghosh and S. Ray, Ind. J. Phys. 48 (1974) 1149-1152.
4. M. Ghosh and S. Ray, Z. Kristallogr. 145 (1977) S146-154.
5. R. Dayal, PhD Thesis, IIT Kanpur, 1976.
6. R. Dayal, D. Ramachandra Rao and P. Venkateswarlu, Can. J. Phys. 56 (1978) 1175-1181.
7. A.K. Jain and G.C. Upreti, Solid State Commun. 28 (1978) 571-574.
8. R. Dayal, D. Ramachandra Rao and P. Venkateswarlu, J. Chem. Phys. 70 (1979) 2487-2490.
9. R. Dayal, Ind. J. Phys. A 53 (1979) 514-519.
10. A.K. Jain and G.C. Upreti, Phys. Status Solidi A 58 (1980) 155-163.
11. A.K. Jain and G.C. Upreti, J. Phys. Chem. Solids 43 (1982) 563-569.
12. A.K. Jain and G.C. Upreti, J. Phys. Chem. Solids 44 (1983) 549-557.
13. B. Borzecka, S.F. Sagnowski and S. Hodorowicz, Phys. Status Solidi A 64 (1981) 557-564.
14. I. Svare and B.O. Fimland, J. Chem. Phys. 74 (1981) 5977-5980.
15. I. Svare, B.O. Fimland, K. Ottes, J.A. Janik, J.M. Janik, E. Mikuli and A. Migdal-Mikuli, Physica B 106 (1981) 195-199.
16. M. Falk, P. Seto and M.A. White, J. Chem. Phys. 81 (1984) 3752-3753.
17. M.A. White and M. Falk, J. Chem. Phys. 83 (1985) 2467-2474.

18. M.A. White and M. Falk, J. Chem. Phys. 84 (1986) 3484-3490.
19. J.M. Janik, A. Migdal-Mikuli, E. Mikuli and T. Stanek, Acta Phys. Polonica A 59 (1981) 599-602.
20. E. Mikuli, A. Migdal-Mikuli, M. Rachwalska and T. Stanek, Physica B 104 (1981) 326-330.
21. M.A. White, J. Chem. Thermodyn. 16 (1984) 885-890.
22. M.A. White and K. Nightingale, J. Phys. Chem. Solids 46 (1985) 321-324.
23. M. Falk and O. Knop in "Water - A Comprehensive Treatise", Vol. 2, F. Franks, Ed., Plenum Press, New York, 1973, pp 55-113.
24. B. Berglund, J. Lindgren and J. Tegenfeldt, J. Mol. Struct. 43 (1978) 169-177.
25. J.E. Bertie and E. Whalley, J. Chem. Phys. 40 (1974) 1646-1659.
26. T.C. Sivakumar, D. Schuh, M.G. Sceats and S.A. Rice, Chem. Phys. Lett. 48 (1977) 212-218.

COMMENTS

W.F. KUHS

The Mg-compound shows 16 distinct OD (H_2O) stretch bonds. The number of crystallographically distinct hydrogen atoms correspondingly is at least 16, which would mean a rather large unit cell and or a rather low symmetry. Are there any crystallographic data available for this compound ?

Answer :

The only crystallographic study of $Mg(ClO_4)_2 \cdot 6H_2O$ of which I am aware is C.D. West, Z. Kristallogr. A 91, 480 (1935). This was a room-temperature structure, and certainly much more precise experiments should be carried out at room-temperature and also at lower temperatures. I should caution you that although it is very easy to get good crystals at room temperature (just by dissolving $Mg(ClO_4)_2$ in water and allowing the solvent to evaporate), the phase transition ($T_{tr} = 107.9$ K) which takes the salt into the phase with the large number of distinct water H's is very first-order. By the way, from the H-O-H bending fundamental of $Mg(ClO_4)_2 \cdot 6H_2O$ at $T = 10$ K, we think that the lowest-temperature phase contains at least 8 crystallographically-distinct water molecules, each with crystallographically-distinct hydrogens.

T. MATSUO

The zinc compound seems to have a residual entropy. Could you determine its magnitude ?

Answer :

Unfortunately, we do not have sufficient data to make this calculation. To do so would require further information about the vapor-phase, as well as further thermodynamic information both above and below the temperature range of our experiments. Although tempting, it would not be prudent to compare, say, ΔS (20 K 360 K) for each of the salts, in order to look for residual entropy, since the degrees of freedom of the high-temperature phase of each depends on the metal : Cd, Mg or Zr. That said, I will agree that the Zn compound seems to have residual entropy particularly in light of the OD stretching results in the infrared spectroscopy experiments.

E. OFFENBACHER

Can you form these octahedra with other ions such as Cr for example ?

Answer :

To my knowledge, Cd, Mg and Zn are the only divalent metals that form these structures. Others appear to prefer tetrahedral coordination, rather than the octahedral coordination seen here.