X-ray Study of $M^{II}(ClO_4)_2.6H_2O$ (M^{II} = Zn, Ni): Twinning, Disorder and Phase Transitions

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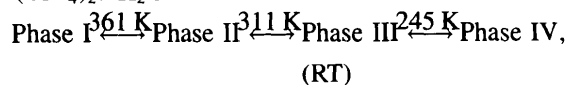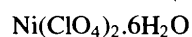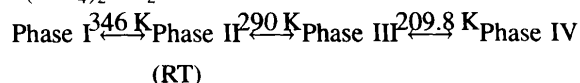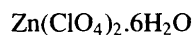
Abstract

X-ray studies of zinc and nickel perchlorate hexahydrate, $Zn(ClO_4)_2.6H_2O$ and $Ni(ClO_4)_2.6H_2O$, respectively, at different temperatures have been carried out to correlate the structural changes with phase transitions in the compounds. The crystals are pseudohexagonal ($P6_3mc$), exhibiting a three-component orthorhombic twinning ($Pmn2_1$). At high temperatures a slight deviation of the b/a ratio of the three twinned orthorhombic cells from $3^{1/2}$ results in a three-component splitting of each spot in the X-ray photograph, which on cooling to room temperature coalesce into single ones, thus restoring the original b/a ratio. The diffuse streaks disappear in the high-temperature photographs due to a decrease in the probability of error in repetition along the **b** axes of the three orthorhombic cells with temperature. A successful refinement of the heat-treated ordered $Zn(ClO_4)_2.6H_2O$ crystal verifies the continuous perchlorate–water arrangement and three-component twinning of the orthorhombic cell. Low-temperature X-ray photographs indicate no structural change.

1. Introduction

$Zn(ClO_4)_2.6H_2O$ and $Ni(ClO_4)_2.6H_2O$ belong to a series of isostructural compounds with the general formula $M^{II}(ClO_4)_2.6H_2O$, M^{II} = Mg, Mn, Fe, Co, Ni, Zn. Anomalies in the temperature variation of different physical properties in zinc and nickel perchlorate hexahydrates observed during EPR, IR, adiabatic calorimetry and magnetic susceptibility measurements (Jain & Upreti, 1978, 1980, 1982; Sartorelli, Isotani, Ochi, Samo & Piccini, 1978; White & Falk, 1986; Rachwalska & Stanek, 1978; Chaudhuri, 1974) are ascribed to phase transitions occuring in the following sequences.

$Zn(ClO_4)_2.6H_2O$

Phase I $\xrightarrow{346 K}$ Phase II $\xrightarrow{290 K}$ Phase III $\xrightarrow{209.8 K}$ Phase IV

(RT)

$Ni(ClO_4)_2.6H_2O$

Phase I $\xrightarrow{361 K}$ Phase II $\xrightarrow{311 K}$ Phase III $\xrightarrow{245 K}$ Phase IV,

(RT)

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where RT indicates room temperature (~ 300 K).

The mechanisms of phase transitions in $Zn(ClO_4)_2.6H_2O$ and $Ni(ClO_4)_2.6H_2O$ have been attributed to the structural changes at the transition points. For a proper understanding of the phenomena, knowledge of the crystal structures of the compounds at relevant temperatures, the nature of disorder in the metal-atom distribution, twinning and errors in repetition of the twin components are of fundamental importance.

X-ray studies of this series of compounds (West, 1935) and the corresponding zinc isomorph (Ghosh & Ray, 1977) at room temperature revealed that the arrangement of perchlorate tetrahedra and water octahedra were identical to that of $LiClO_4.3H_2O$ (West, 1934), with space group $P6_3mc$, $Z = 2$. The two Li atoms at $(0,0,\frac{1}{4})$ and $(0,0,\frac{3}{4})$ occupy the centers of water octahedra, which form columns along the sixfold axis (Fig. 1). With the available sites being double the number of M^{II} ions in $M^{II}(ClO_4)_2.6H_2O$, the metal atoms lie at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, respectively, in alternate rows parallel to any one of the three equivalent axial directions [100], [010] and [1$\bar{1}$0]. Consequently, the symmetry reduces to $Pmn2_1$ with an orthorhombic cell of dimensions $a = a_h$, $b = 3^{1/2}a_h$ and $c = c_h$ (subscript h refers to the hexagonal cell of the trihydrate structure). Since the **a** axis may be
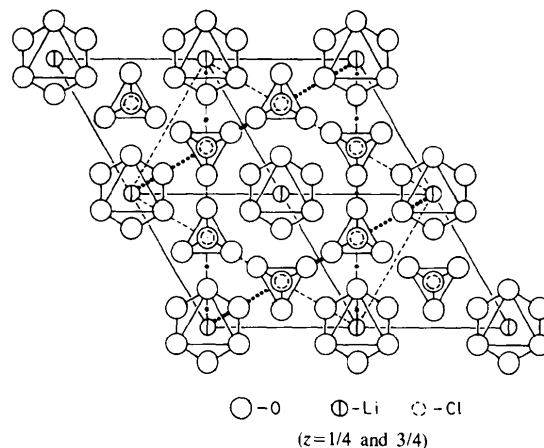

Fig. 1. Four unit cells of the lithium perchlorate trihydrate structure projected along **c**. The three orientations of the orthorhombic cell are shown by three different dotted lines.

$\bigcirc$–O $\oplus$–Li $\bigcirc$–Cl
($z = 1/4$ and $3/4$)

aligned, with equal probablity, along the three equivalent directions, as mentioned earlier, these crystals grow as three-component twins (Fig. 1) and exhibit an apparently hexagonal unit cell with $a = 2a_h$ and $c = c_h$. The reflections revealing this doubling have contributions from the metal atoms only and are observed as diffuse streaks in the X-ray photographs of $Zn(ClO_4)_2.6H_2O$. This diffuse nature is due to one-dimensional disorder involving errors in repetition along the respective orthorhombic **b** axes of the three twin components (Ghosh & Ray, 1977). The perchlorate–water arrangement with its hexagonal symmetry is continuous throughout the bulk of the crystal; discontinuity occurs only in the M^{II}-atom distribution at the twin boundaries.

The present paper reports the X-ray investigation of zinc and nickel perchlorate hexahydrates at various temperatures and their structural correlation with the proposed mechanism of phase transitions in the compounds.

2. Experimental

2.1. Preparation of crystals and preliminary observations

Zinc and nickel perchlorates were prepared by adding perchloric acid to excess of the corresponding carbonates. Hexahydrate crystals were grown from the filtered solution kept in a desiccator. Needle-shaped colorless single crystals of $Zn(ClO_4)_2.6H_2O$ [pale green in the case of $Ni(ClO_4)_2.6H_2O$], suitable for X-ray studies, were obtained by recrystallization from water. Due to their highly hygroscopic nature, the crystals had to be encased immediately in thin-walled glass capillaries.

Oscillation and Weissenberg photographs of $Zn(ClO_4)_2.6H_2O$ and $Ni(ClO_4)_2.6H_2O$ could be indexed on hexagonal cells with $a = 15.43$, $c = 5.22$ and $a = 15.46$, $c = 5.17$ Å, respectively. The **c**-axis odd-layer Weissenberg photograph of the zinc compound at room temperature (~ 300 K) showed, in addition to the usual sharp spots, diffuse streaks forming a network of hexagons (Figs. 2 and 3). A corresponding photograph of the nickel compound also revealed similar streaks, an observation not reported earlier. In this case, however, the streaks were of comparatively smaller extension, indicating a lower probability of error in repetition.

2.2. X-ray studies of high-temperature phases of $Zn(ClO_4)_2.6H_2O$ and $Ni(ClO_4)_2.6H_2O$

A steady stream of hot air with controlled variable temperature was used to maintain the crystal in the desired phases. The **c**-axis oscillation photographs of $Zn(ClO_4)_2.6H_2O$ at 365 K and $Ni(ClO_4)_2.6H_2O$ at 380 K (~ 20 K above the respective temperatures of transition into Phase I in both cases) showed the following features: (i) no change in **c**-axial length; (ii) the disappearance of streaks along the layer lines; (iii) splitting

of spots into two or three components lying along the odd-layer lines.

In the first-layer Weissenberg photographs of $Zn(ClO_4)_2.6H_2O$ at 365 K all spots were elongated along the ω direction. In a couple of them two/three distinct sharp regions in the elongated spots were observed. The corresponding photographs of the Ni isomorph at 380 K contained three distinct sharp regions of intensities along the direction of elongation (Fig. 4), thus supplementing the three-component orthorhombic twin hypothesis. A similar photograph of the intermediate phase II (311–361 K) in the Ni crystal, obtained at 323 K, showed an extension of spots along the ω direction with localization of intensity at one end. This indicated that the changes in the Ni structure probably started at ~ 311 K, where a small change in entropy in contrast to a large change at ~ 361 K was observed by Rachwalska & Stanek (1978). The overall hexagonal symmetry of the room-temperature structure of zinc and nickel crystals was, however, preserved.
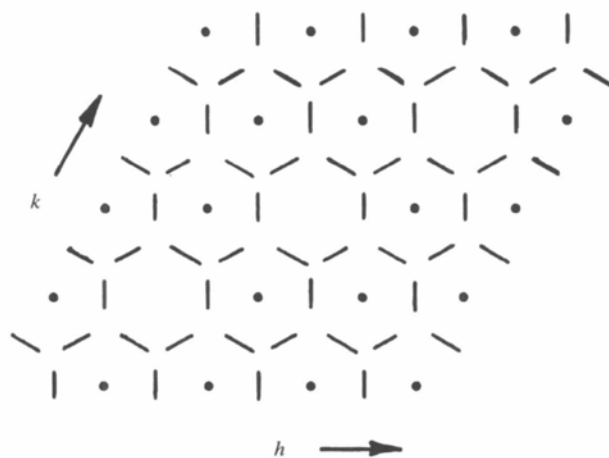

Fig. 2. A schematic drawing of the first-layer reciprocal lattice rotated about the c axis at room temperature.
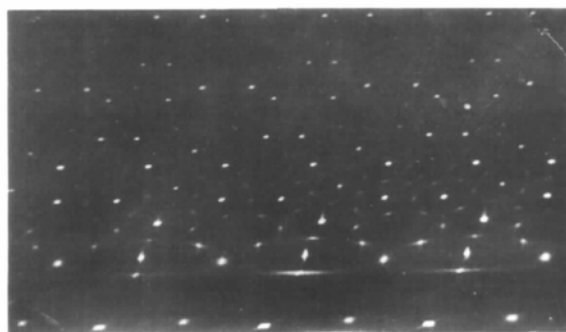

Fig. 3. First-layer Weissenberg photograph at room temperature rotated about the c axis.

From the high-temperature X-ray studies of both the Zn and Ni isomorphs the following changes in the crystal structures can be envisaged. Firstly, since all the spots, whether sharp or diffuse at room temperature, had similar appearances in the high-temperature photograph, it may be concluded that the error in repetition in the metal-atom distribution in each orthorhombic component of the crystal has disappeared at high temperature. Secondly, the extension of spots along the ω direction in the first-layer Weissenberg photograph at high temperature may be considered as arising out of unresolved individual spots due to three orthorhombic twin components, apart from the increased thermal vibration of the atoms. Since ω is functionally related to the cylindrical coordinate ξ of the reciprocal space, the three unresolved spots contained in an extended spot differ slightly in their d values. At room temperature, when the perchlorate–water arrangement maintained a strictly hexagonal symmetry, each of the three orthorhombic cells had the ratio $b/a = 3^{1/2}$ and consequently each sharp spot on the Weissenberg photograph was actually the superposition of three reflections from the respective orthorhombic components, with three different sets of hkl having the same d value. However, after a high-temperature transition, the said hexagonal symmetry breaks down and the b/a ratio deviates slightly from its original value of $3^{1/2}$. Consequently, the reflections from three orthorhombic components, which used to register previously as a single spot, are now drawn out. Thus, in the high-temperature phase the crystal loses its unusual twinning characteristics and becomes just an ordinary twin with three distinct components.

2.3. X-ray studies of room-temperature phases of $Zn(ClO_4)_2.6H_2O$ and $Ni(ClO_4)_2.6H_2O$ after heat treatment

On slow cooling the crystals to room temperature the identity periods were found to be unchanged. Elongation of Weissenberg spots, observed at high temperature, disappeared. The overall hexagonal symmetry of the crystal
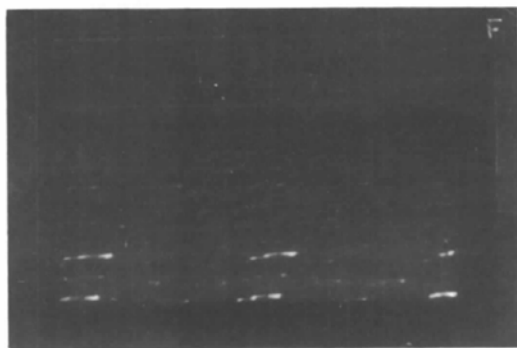

Fig. 4. First-layer Weissenberg photograph at high temperature rotated about the c axis.

was retained. These facts confirmed the reversible nature of the transition. However, an interesting observation was that the diffuse spots were converted into sharp ones, indicating ordered structures of the crystals after recycling.

2.4. Structure analysis of the heat-treated crystal of $Zn(ClO_4)_2.6H_2O$

To study the effect of cycling through the high-temperature transition point on the structure and nature of twinning, X-ray analysis of the heat-treated ordered $Zn(ClO_4)_2.6H_2O$ was undertaken. Intensity data for 2116 reflections were collected (CAD-4 diffractometer, monochromatized Mo $K\alpha$ radiation, ω–2θ scan) and processed applying an Lp correction. A hexagonal cell with $a = 15.5919$ (4), $c = 5.3033$ (3) Å was established. However, a search for systematic absences revealed the following observations.

(i) $h_e k_e l_o$, $h_o k_o l_o$ and $h_o k_e l_o$ all present;

(ii) $h_e k_o l_e$, $h_o k_o l_e$ and $h_o k_e l_e$ all absent;

(iii) $h_e k_e l_o$ present except $h_e h_e l_o$;

(iv) $h_e k_e l_e$ present;

subscripts e and o indicating even and odd, respectively. These observations did not lead to any hexagonal or trigonal space group and West's postulation of a continuous $LiClO_4.3H_2O$-like perchlorate–water arrangement with a discontinuity in bivalent metal-ion distribution was indicated.

However, since the present experimental data was capable of providing accurate values of coordinates, bond lengths $etc.$, for the continuous part of the structure, the analysis was continued, but, of necessity, in two stages.

In the first stage 115 unique reflections (594 measured) of $h_e k_e l$ (both l_e and l_o) type, having contributions from both the metal and perchlorate–water arrangements, were re-indexed using a smaller $LiClO_4.3H_2O$-like unit cell with $a' = a/2 = 7.7959$ and $c' = c = 5.3033$ Å. Patterson and iterative Fourier syntheses ($SHELXS86$; Sheldrick, 1985) revealed the structure with $\frac{1}{2}$Zn at $(0,0,\frac{1}{4})$ and $(0,0,\frac{3}{4})$. Anisotropic refinement ($SHELXL93$; Sheldrick, 1993) of the non-H atoms (a single H atom located from the difference map was treated isotropically) converged to $R_1 = 0.038$ and $wR_2 = 0.107$. The refined atomic coordinates, bond distances and angles are given in Tables 1–4.* The results of the structure analysis confirmed the continuity of the perchlorate–water arrangement in the crystal and its isostructurality with $LiClO_4.3H_2O$ (Chomnilpan,

Table 1. *Experimental details*

Crystal data

Chemical formula	$H_{12}Cl_2O_{14}Zn$
Chemical formula weight	372.37
Cell setting	Hexagonal
Space group	$P6_3mc$
a (Å)	7.7959 (4)
c (Å)	5.3033 (3)
V (Å^3)	279.13 (3)
Z	1
D_x (Mg m^{-3})	2.215
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	25
θ range (°)	10–15
μ (mm^{-1})	2.751
Temperature (K)	293 (2)
Crystal form	Prism
Crystal size (mm)	$0.30 \times 0.25 \times 0.20$
Crystal color	Colorless

Data collection

Diffractometer	Enraf–Nonius CAD-4
Data collection method	ω–2θ scans
Absorption correction	None
No. of measured reflections	594
No. of independent reflections	115
No. of observed reflections	114
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0387
θ_{max} (°)	24.90
Range of h, k, l	$-9 \rightarrow h \rightarrow 8$
	$0 \rightarrow k \rightarrow 9$
	$0 \rightarrow l \rightarrow 6$
No. of standard reflections	3
Frequency of standard reflections	Every 100 reflections
Intensity decay (%)	None

Refinement

Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0380
$wR(F^2)$	0.1071
S	1.211
No. of reflections used in refinement	115
No. of parameters used	26
H-atom treatment	H atoms refined isotropically
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0759P)^2 + 0.16P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.567
$\Delta\rho_{max}$ (e Å^{-3})	0.299
$\Delta\rho_{min}$ (e Å^{-3})	-0.730
Extinction method	*SHELXL*93 (Sheldrick, 1993)
Extinction coefficient	0.09 (4)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)
Absolute configuration	Flack (1983)

Computer programs

Data collection	*CAD*-4 software (Enraf–Nonius, 1989)
Cell refinement	*CAD*-4 software (Enraf–Nonius, 1989)
Data reduction	*CAD*-4 software (Enraf–Nonius, 1989)
Structure solution	*SHELXS*86 (Sheldrick, 1990)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn	0.0	0.0	1/4	0.036 (1)
Cl	1/3	2/3	0.0062 (12)	0.038 (1)
O1	1/3	2/3	0.2796 (26)	0.064 (4)
O2	0.4320 (4)	0.5680 (4)	-0.0869 (16)	0.064 (3)
OW	0.1242 (4)	0.8758 (4)	0.5044 (21)	0.054 (2)

Table 3. *Selected geometric parameters (Å, °)*

Zn—OW^i	2.123 (7)	Cl—O2	1.421 (5)
Zn—OW^{ii}	2.152 (7)	OW—H	0.92 (9)
Cl—O1	1.450 (15)		
OW^i—Zn—OW^{iii}	86.3 (4)	OW^{ii}—Zn—OW^{iv}	84.9 (3)
OW^i—Zn—OW^{ii}	179.0 (5)	O2^{iv}—Cl—O2	108.5 (2)
OW^{iii}—Zn—OW^{ii}	94.4 (1)	O2—Cl—O1	110.3 (5)

Symmetry codes: (i) $-x, 1 - y, z - \frac{1}{2}$; (ii) $x, y - 1, z$; (iii) $y - 1, -1 - x + y, z - \frac{1}{2}$; (iv) $1 - y, 1 + x - y, z$.

Table 4. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	$D\cdots A$	D—H$\cdots A$
OW—H$\cdots$O1^i	3.065 (8)	125 (5)
OW^{ii}—H$\cdots$O2^{iii}	3.050 (4)	145 (7)

Symmetry codes: (i) $-y, x - y, z$; (ii) $x - y, 1 - y, \frac{1}{2} + z$; (iii) $-y, x - y, z$.

bond lengths [1.450 (15) and 1.421 (5) Å] define the perchlorate ion distortion. Water molecules with OW atoms lying on mirror planes are hydrogen-bonded to O1 and O2 [OW—H$\cdots$O1 3.065 (8), OW—H$\cdots$O2 3.050 (4) Å]. Similar hydrogen bonding is reported in LiClO$_4$.3H$_2$O (Chomnilpan, Liminga & Tellgren, 1977).

In the second stage of structure solution the metal-atom distribution in the unit cell, responsible for the lowering of the symmetry to $Pmn2_1$, and three-component twinning were considered. Reflections having only a metal contribution were selected and re-indexed in terms of the LiClO$_4$.3H$_2$O-type hexagonal cell. The number of reflections with h fractional (odd multiples of 1/2), k fractional and both h and k fractional were 140, 141 and 141, respectively. The orthorhombic indices for
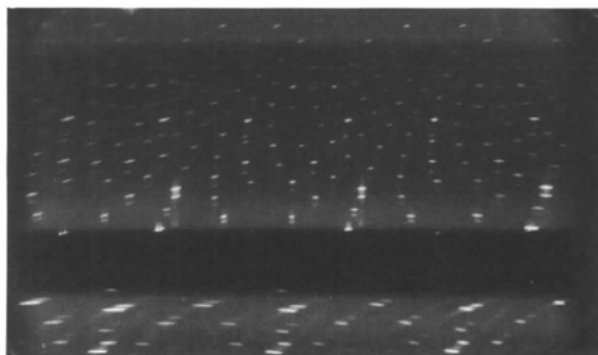

Fig. 5. First-layer Weissenberg photograph of the heat-treated crystal rotated about the c axis.

Liminga & Tellgren, 1977), except $\frac{1}{2}$Zn lying on the sixfold axis occupied $(0,0,\frac{1}{4})$ or $(0,0,\frac{3}{4})$. An *ORTEP*II (Johnson, 1976) view of the molecule with atom-numbering scheme is given in Fig. 6. The Cl and O1 atoms of the ClO$_4^-$ ions are located on a threefold axis and the two crystallographically different Cl—O

these three groups of reflections were derived using the matrices

$$\begin{pmatrix} 0 & 1 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Since for the space group $Pmn2_1$ the origin is taken on the 2_1 axis which lies half-way between the two 6_3 axes in its supergroup $P6_3mc$, the Zn atom was placed at $(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$ and its symmetry-equivalent position $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$. Isotropic refinement for the above three sets of data converged to $R_1 = 0.070, 0.071$ and 0.070, respectively. Thus, the distribution of metal atoms resulting in three orthorhombic twin components of the crystal, in spite of a continuous perchlorate–water arrangement, was verified. Repetition of similar analysis with the Ni isomorph was considered unnecessary.

2.5. X-ray studies of low-temperature phases of $Zn(ClO_4)_2.6H_2O$ and $Ni(ClO_4)_2.6H_2O$

Low-temperature X-ray diffraction studies of the heat-treated ordered $Zn(ClO_4)_2.6H_2O$ and $Ni(ClO_4)_2.6H_2O$ were undertaken to detect any possible structural change related to the reported phase transition. A similar study on the ordered $Fe(ClO_4)_2.6H_2O$ isomorph indicating phase transitions was reported by Ghosh & Ray (1981). In the present work the low temperatures were attained by flowing cool nitrogen gas over the sample crystals. An accurate temperature was ascertained by placing a thermocouple near the crystal.
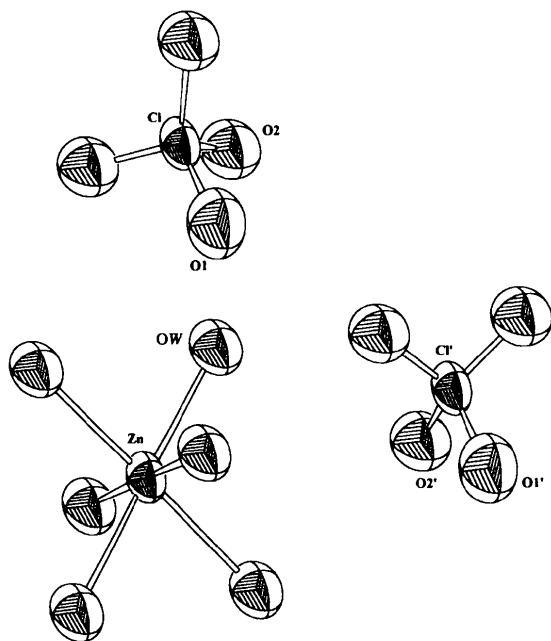

Fig. 6. An *ORTEPII* (Johnson, 1976) view (50% probability level) of the molecule.

Oscillation and Weissenberg photographs of the zinc isomorph were recorded at $\sim$273 and $\sim$203 K (reported transition points 290 and 209.8 K, respectively) and the corresponding photographs of the nickel isomorph were obtained at 223 K (reported transiton point 245 K). Repeated experiments with both crystals failed to detect any phase transition, suggesting that possible changes in the structures at the reported transition temperatures were very subtle, involving no change in symmetry or in the perchlorate–water continuity. The IR study of the zinc isomorph (White & Falk, 1986) also did not reveal any drastic change at low temperature.

3. Conclusions

Contrary to the proposed mechanism of high-temperature phase transitions in $Zn(ClO_4)_2.6H_2O$ and $Ni(ClO_4)_2.6H_2O$, involving perchlorate–water disorder (Rachwalska & Stanek, 1978; White & Falk, 1986) the present single crystal structure analysis of the heat-treated zinc crystal at ambient temperature showed no unusually high thermal parameters of any atom, indicating the absence of any disorder in the perchlorate tetrahedra or the water octahedra. The inadequacy of the symmetry-lowering hypothesis (Jain & Upreti, 1982; Chaudhuri, 1974) associated with the high-/low-temperature phase transition in the compounds was evident from the unchanged overall hexagonal nature of the crystals exhibited in the X-ray photographs throughout the range of temperature (365–203 K for the zinc compound and 380–223 K for nickel). With an increase in temperature the probability of error in repetition along the **b** axis of the three orthorhombic cells decreased and finally the streaking vanished completely above the respective transition point. Thus, in the ordered state the metal atoms are either at $(0,0,\frac{1}{4})$ or $(0,0,\frac{3}{4})$. The three-component twinning of the compounds at high temperature was a consequence of a slight deviation of the b/a ratio from $3^{1/2}$ for the orthorhombic cells. On cooling the crystals to room temperature the b/a ratio regained its original value and the ordering of the metal atoms was preserved.

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