A triangular array of osmium atoms forms the framework of the anion with the Os(2)—Os(3) edge bridged by the SO_2 and hydride ligands and the other two edges unbridged. The structure of the anion is quite similar to that of the neutral dihydride except for the Os—Os edge bridged only by a hydride in $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SO_2)$. Removing this proton to give the anion yields an Os(1)—Os(2) distance of 2·850 (3) *vs* 3·068 (1) Å for the corresponding distance in the dihydride. The other Os—Os distances in the anion are closer to those found for the hydride–SO_2-bridged edge [2·895 (1) Å] and unbridged edge [2·848 (1) Å] of $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SO_2)$. The bridging hydride was not located, but its approximate position can be inferred from the arrangement of the carbonyl and SO_2 ligands about Os(2) and Os(3), *i.e.* *trans* to both C(5) and C(9). The bridging hydride resonance appears as a sharp singlet at δ −14·9 in the ^1H NMR spectrum of the compound in $CDCl_3$.

The N(1)—O(2) distance of 2·65 (4) Å is indicative of a hydrogen bond between the N—H group of the cation and one oxygen atom of the SO_2 ligand (Hamilton & Ibers, 1968). A weak, broad peak at 2520 cm^{-1} in the infrared spectrum of a Nujol mull of the complex was assigned to the N—H stretch and also indicated a substantial hydrogen-bonding interaction. The longer S—O(2) distance of 1·51 (3) Å compared to S—O(1) of 1·47 (3) Å is probably a manifestation of the hydrogen bond, even though this difference is less than 2σ. The identity of the species that donates a proton to the amine during the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ and SO_2 is not clear at present. Addition of tribenzylamine does alter the reaction chemistry of the $Os_3(CO)_{10}(\mu\text{-}H)_2/SO_2$ system considerably. The tribenzylammonium salt is quite stable in solution for days near 298 K, whereas $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SO_2)$ reacts under these conditions to give a number of products as indicated by NMR and IR spectra. The binding of this acidic proton by the amine thus greatly inhibits further reactions of the cluster.

The authors are grateful to D. T. Cromer and Allen C. Larson for helpful discussions. This work was carried out under the auspices of the US Department of Energy, Office of Basic Energy Sciences.

References

HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, p. 16. New York: Benjamin.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JARVINEN, G. D. & RYAN, R. R. (1984). *Organometallics*, **3**, 1434–1438.

JOHNSON, C. K. (1976). *ORTEPII. A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KUBAS, G. J. & RYAN, R. R. (1986). *Polyhedron*, **5**, 473–485.

LARSON, A. C. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 291–294. Copenhagen: Munksgaard.

LARSON, A. C. & VON DREELE, R. B. (1986). *Generalized Structure Analysis System*. Report LAUR 86-748. Los Alamos National Laboratory, USA.

RYAN, R. R. & SWANSON, B. I. (1974). *Inorg. Chem.* **13**, 1681–1684.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1988). C**44**, 1703–1707

Structures of Cadmium Magnesium Tetranitrite Dihydrate, Cadmium Calcium Tetranitrite Tetrahydrate and Cadmium Strontium Tetranitrite Tetrahydrate

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(*Received* 12 *April* 1988; *accepted* 27 *May* 1988)

Abstract. $CdMg(NO_2)_4.2H_2O$ (I), $M_r = 356·8$, monoclinic, $C2/c$, $a = 11·441$ (2), $b = 6·958$ (2), $c = 12·017$ (2) Å, $\beta = 91·70$ (2)°, $V = 956·2$ (4) Å^3, $Z = 4$, $D_x = 2·48$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 2·39$ mm^{-1}, $F(000) = 688$, $T = 296$ (1) K, final $R = 0·018$ for 933 observed unique reflections. $CaCd(NO_2)_4.4H_2O$ (II), $M_r = 408·6$, trigonal, $P3_121$ or $P3_221$, $a = 7·5003$ (6), $c = 18·413$ (3) Å, $V = 897·0$ (2) Å^3, $Z = 3$, $D_m(CCl_4/CH_3I) = 2·28$ (1), $D_x = 2·27$ Mg m^{-3}, $\mu = 2·30$ mm^{-1}, $F(000) = 600$, $T = 296$ (1) K, final $R = 0·035$ for 1327 reflections. $CdSr(NO_2)_4.4H_2O$ (III), $M_r = 456·1$, trigonal, $P3_121$ or $P3_221$, $a = 7·6379$ (7), $c = 18·707$ (4) Å, $V = 945·1$ (2) Å^3, $Z = 3$, D_m $(CCl_4/C_2H_2Br_4) = 2·37$ (1), $D_x = 2·40$ Mg m^{-3}, $\mu = 5·85$ mm^{-1}, $F(000) = 654$, $T = 295$ (1) K, final $R = 0·030$ for 1264 reflections. The structures of (II) and (III) are isomorphous. In (I), the Mg^{2+} ion is surrounded octahedrally by two water and

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four nitrite O atoms. In (II) and (III), the alkaline-earth metal ions are surrounded by four water and four nitrite O atoms. Each Cd atom in (I), (II) and (III) is surrounded by eight O atoms of four NO_2^- ions with Cd···O distances ranging from 2·313 (3) to 2·542 (2) Å. These crystals are colorless, suggesting little perturbation of NO_2^- by the Cd^{2+} ion.

Introduction. Colorations of certain post-transition-metal nitrites are explained by a spin-orbital enhancement of the triplet ← singlet transition of the NO_2^- ion (McGlynn, Azumi & Kumar, 1981). Close contacts of the metal cations with the NO_2^- ion have been studied for several nitrite salts and it was revealed that the post-transition-metal cations prefer to lie in the chelated position between two O atoms of a nitrite ion (Ohba, Matsumoto, Takazawa & Saito, 1987, and references therein). In order to confirm this trend, structures of double salts of Cd^{II} with alkaline-earth metals have been determined.

Experimental. (I): Colorless polyhedral crystals were grown from filtrate of a mixture of $CdCl_2$, $MgCl_2$ and $AgNO_2$ aqueous solutions (Cd/Mg/Ag = 1/1/4). An octahedral crystal 0·10–0·13 mm on edge was mounted on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Laue group $2/m$, systematic absences hkl, $h+k$ odd, $h0l$, h or l odd (Cc or $C2/c$); cell parameters refined by least squares for 20 2θ values ($20 < 2\theta < 30°$); intensity measurement performed to $2\theta = 55°$ (h 0→14, k −9→9, l −15→15), θ–2θ scan, scan speed 6° min^{-1} in θ. Variation of five standard reflections, $0·98 \leq \sum(|F_o|/|F_o|_{initial})/5 \leq 1·00$. 2198 reflections measured, 1685 observed reflections with $|F_o| > 3\sigma(|F_o|)$. Absorption correction with approximation of crystal shape to a sphere of diameter 0·13 mm ($\mu r = 0·16$, $0·795 < A < 0·796$). With the assumption of space group Cc, the position of Cd could be deduced from the Patterson function and those of other non-H atoms from Fourier synthesis ($R = 0·019$). However, some nitrite ions had absurd geometry. Atomic coordinates suggested that the Cd atom lies on a twofold axis parallel to **b**. A refinement adopting the alternative space group $C2/c$ succeeded. Water H atoms were located on a difference synthesis. Non-H atoms were refined anisotropically and H atoms isotropically. $\sum w||F_o| - |F_c||^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0·015|F_o|)^2$, final $R = 0·018$, $wR = 0·022$, $S = 1·02$ for 933 unique reflections ($R_{int} = 0·015$ for diffraction symmetry $2/m$). Reflections/parameter ratio 10·3, $\Delta/\sigma < 0·2$, $-0·43 \leq \Delta\rho \leq 0·28$ e $Å^{-3}$. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). *UNICS*-III program system (Sakurai & Kobayashi, 1979), FACOM M-380R computer of this university.

Table 1. *Positional parameters* (× 10^4, × 10^5 *for* Cd, × 10^3 *for* H) *and equivalent isotropic temperature factors* (*Hamilton,* 1959)

	x	y	z	B/B_{eq}(Å^2 × 10)
Compound (I)				
Cd	0	1472 (3)	25000	17
Mg	2500	2500	0	15
N(1)	−94 (2)	−2755 (3)	796 (2)	26
O(11)	769 (2)	−2346 (3)	1401 (2)	26
O(12)	−984 (2)	−1732 (3)	987 (2)	21
N(2)	1786 (2)	3105 (3)	2285 (2)	23
O(21)	1227 (2)	2678 (3)	3128 (2)	27
O(22)	1539 (2)	2016 (2)	1467 (1)	20
O(*w*)	2874 (2)	322 (2)	5015 (2)	21
H(*w*1)	314 (3)	84 (5)	451 (3)	48
H(*w*2)	325 (3)	94 (5)	558 (5)	39
Compound (II)				
Cd	−3799 (6)	0	−33333	20
Ca	0	−4876 (2)	−1667	18
N(1)	−3005 (7)	−3058 (7)	−2294 (3)	30
O(11)	−3395 (5)	−1879 (6)	−2682 (2)	31
O(12)	−1234 (6)	−2773 (6)	−2391 (2)	28
N(2)	2530 (6)	2838 (7)	−2314 (2)	29
O(21)	2860 (6)	1663 (6)	−2729 (2)	31
O(22)	789 (5)	2654 (5)	−2398 (2)	27
O(*w*1)	−2528 (6)	−5240 (6)	−788 (2)	34
O(*w*2)	−3088 (6)	−7514 (6)	−2247 (2)	32
Compound (III)				
Cd	3535 (7)	0	33333	20
Sr	0	4872 (1)	1667	19
N(1)	2993 (8)	3054 (9)	2337 (3)	33
O(11)	3368 (6)	1902 (7)	2711 (2)	34
O(12)	1253 (7)	2732 (7)	2429 (2)	31
N(2)	−2500 (8)	−2778 (9)	2334 (3)	32
O(21)	−2841 (7)	−1661 (8)	2722 (2)	33
O(22)	−792 (7)	−2567 (7)	2417 (2)	31
O(*w*1)	2612 (8)	5300 (7)	736 (3)	41
O(*w*2)	3271 (7)	7669 (7)	2229 (3)	37

(II): Pale-yellow prisms grown from filtrate of a mixture of $CdCl_2$, $CaCl_2$ and $AgNO_2$ aqueous solutions (Cd/Ca/Ag = 1/1/4). A spherically ground crystal of diameter 0·40 (1) mm, Laue group $3ml$, systematic absences $00l$ with $l \neq 3n$ ($P3_121$ or $P3_221$); intensity measurement performed to $2\theta = 55°$ (h −9→9, k −9 →9, l 0→23). Variation of five standard reflections, $1·00 \leq \sum(|F_o|/|F_o|_{initial})/5 \leq 1·03$. 4240 reflections measured, 4013 observed, 1327 unique ($R_{int} = 0·010$ for 'diffraction symmetry' 321 where the anomalous-dispersion effect was taken into account). Absorption correction ($\mu r = 0·46$, $0·510 < A < 0·518$). The structural data of (III) were available before the crystal structure determination of (II). The lattice constants, Laue group and systematic absences showed that (II) and (III) are isomorphous. Least-squares refinement of the structure was performed by utilizing the atomic coordinates of (III). No water H atoms located on difference synthesis. Final $R = 0·035$, $wR = 0·052$, $S = 3·10$ for 1327 unique reflections including Bijvoet pairs. The absolute structure was determined to be $P3_221$ by the anomalous-dispersion technique. The enantiomeric structure was rejected by larger R factors, $R = 0·039$ and $wR = 0·057$. Reflection/parameter ratio 14·4, $\Delta/\sigma < 0·2$, $-1·98 \leq \Delta\rho \leq 1·01$ e $Å^{-3}$.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Compound (I)

N(1)–O(11)	1·242 (3)	Cd···O(11)–N(1)	101·1 (2)
N(1)–O(12)	1·269 (3)	Cd···O(12)–N(1)	94·5 (2)
O(11)–N(1)–O(12)	113·2 (2)	Cd···O(21)–N(2)	103·4 (2)
N(2)–O(21)	1·250 (3)	Cd···O(22)–N(2)	93·9 (1)
N(2)–O(22)	1·266 (3)	Mg^{i}···O(12)	2·140 (2)
O(21)–N(2)–O(22)	112·3 (2)	Mg···O(22)	2·132 (2)
Cd···O(11)	2·366 (2)	Mg^{i}···O(12)–N(1)	113·7 (2)
Cd···O(12)	2·482 (2)	Mg···O(22)–N(2)	116·0 (2)
Cd···O(21)	2·362 (2)	Mg···O(w^{ii})	2·010 (2)
Cd···O(22)	2·542 (2)	O(11)···H($w1^{iii}$)	2·11 (4)
		N(1)–O(11)···H($w1^{iii}$)	92 (1)
		O(21)···H($w2^{iv}$)	1·91 (4)
		N(2)–O(21)···H($w2^{iv}$)	113 (1)

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

Compound (II)

N(1)–O(11)	1·279 (8)	Ca···O(12)	2·565 (5)
N(1)–O(12)	1·248 (7)	Ca^{i}···O(22)	2·587 (4)
O(11)–N(1)–O(12)	113·2 (5)	Ca···O(12)–N(1)	120·0 (4)
N(2)–O(21)	1·281 (7)	Ca^{i}···O(22)–N(2)	117·1 (3)
N(2)–O(22)	1·252 (6)	Ca···O($w1$)	2·402 (4)
O(21)–N(2)–O(22)	113·6 (4)	Ca···O($w2$)	2·416 (3)
Cd···O(11)	2·313 (3)	O(11)···O($w1^{ii}$)	2·810 (6)
Cd···O(12)	2·532 (4)	O(12)···O($w1^{iii}$)	2·813 (7)
Cd···O(21)	2·381 (4)	N(1)–O(11)···O($w1^{ii}$)	113·3 (3)
Cd···O(22)	2·439 (4)	N(1)–O(12)···O($w1^{iii}$)	171·9 (4)
Cd···O(11)–N(1)	102·6 (3)	N(2)···O($w2^{iv}$)	2·939 (7)
Cd···O(12)–N(1)	92·1 (3)	O(21)···O($w2^{v}$)	2·920 (6)
Cd···O(21)–N(2)	98·1 (3)	O(22)···O($w2^{vi}$)	2·860 (6)
Cd···O(22)–N(2)	96·1 (3)	O(21)–N(2)···O($w2^{iv}$)	158·5 (3)
		O(22)–N(2)···O($w2^{iv}$)	87·1 (3)
		N(2)–O(21)···O($w2^{v}$)	102·2 (3)
		N(2)–O(22)···O($w2^{vi}$)	166·9 (4)

Symmetry code: (i) $x, 1+y, z$; (ii) $-1-x, -x+y, -\frac{1}{3}-z$; (iii) $-x, -x+y, -\frac{1}{3}-z$; (iv) $-x, 1-x+y, -\frac{1}{3}-z$; (v) $1+x, 1+y, z$; (vi) $x, 1+y, z$

Compound (III)

N(1)–O(11)	1·264 (9)	Sr···O (12)	2·680 (6)
N(1)–O(12)	1·237 (9)	Sr^{i}···O(22)	2·710 (6)
O(11)–N(1)–O(12)	112·3 (5)	Sr···O(12)–N(1)	118·7 (4)
N(2)–O(21)	1·243 (9)	Sr^{i}···O(22)–N(2)	116·2 (4)
N(2)–O(22)	1·242 (9)	Sr···O($w1$)	2·543 (6)
O(21)–N(2)–O(22)	113·9 (6)	Sr···O($w2$)	2·564 (4)
Cd···O(11)	2·329 (4)	O(11)···O($w1^{ii}$)	2·827 (8)
Cd···O(12)	2·501 (5)	O(12)···O($w1^{iii}$)	2·952 (9)
Cd···O(21)	2·403 (4)	N(1)–O(11)···O($w1^{ii}$)	114·2 (4)
Cd···O(22)	2·415 (4)	N(1)–O(12)···O($w1^{iii}$)	170·4 (5)
Cd···O(11)–N(1)	102·3 (4)	N(2)···O($w2^{iv}$)	3·003 (9)
Cd···O(12)–N(1)	94·6 (4)	O(21)···O($w2^{v}$)	2·900 (8)
Cd···O(21)–N(2)	97·7 (5)	O(22)···O($w2^{vi}$)	3·038 (8)
Cd···O(22)–N(2)	97·2 (4)	O(21)–N(2)···O($w2^{iv}$)	155·1 (5)
		O(22)–N(2)···O($w2^{iv}$)	90·3 (5)
		N(2)–O(21)···O($w2^{v}$)	103·9 (4)
		N(2)–O(22)···O($w2^{vi}$)	165·7 (5)

Symmetry code: (i) $x, -1+y, z$; (ii) $1-x, -x+y, \frac{1}{3}-z$; (iii) $-x, -x+y, \frac{1}{3}-z$; (iv) $-x, -1-x+y, \frac{1}{3}-z$; (v) $-1+x, -1+y, z$; (vi) $x, -1+y, z$

(III): Pale-yellow prisms grown from filtrate of a mixture of $CdCl_2$, $SrCl_2$ and $AgNO_2$ aqueous solutions (Cd/Sr/Ag = 1/1/4). Spherically ground crystal of diameter 0·45 (1) mm, Laue group $\bar{3}ml$, systematic absences $00l$ with $l \neq 3n$; intensity measurement performed to $2\theta = 55°$ (h −9→9, k −9→9, l 0→24). Variation of five standard reflections, $1{\cdot}00 \leq \sum(|F_o|/|F_o|_{\rm initial})/5 \leq 1{\cdot}02$. 4383 reflections measured, 3705 observed, 1264 unique ($R_{\rm int} = 0{\cdot}017$). Absorption correction ($\mu r = 1{\cdot}32$, $0{\cdot}162 < A < 0{\cdot}183$). The Laue group and systematic absences showed that the space group is $P3_121$ or $P3_221$. D_m and V suggested that the chemical formula is $CdSr(NO_2)_4.4H_2O$ with $Z = 3$ and that the Cd and Sr atoms lie on the twofold axis. Structure solved by Patterson and Fourier methods. The absolute structure was determined to be $P3_121$. Water H atoms could not be located on difference synthesis. Final $R = 0{\cdot}030$, $wR = 0{\cdot}039$, $S = 1{\cdot}90$ for 1264 unique reflections.* The enantiomeric structure, $P3_221$, gave larger R factors, $R = 0{\cdot}066$ and $wR = 0{\cdot}089$. Reflection/parameter ratio 13·7, $\Delta/\sigma < 0{\cdot}3$, $-2{\cdot}04 \leq \Delta\rho \leq 0{\cdot}83$ e Å^{-3}.

An attempt to determine the structure of barium cadmium tetranitrite failed owing to the disorder of the nitrite ions: $BaCd(NO_2)_4$, pale-yellow prisms, tetragonal, $P4_12_12(?)$, $a = 12{\cdot}2341$ (7), $c = 23{\cdot}022$ (2) Å, $V = 3445{\cdot}8$ (3) Å^3, $Z = 16$, D_m ($C_2H_2Br_4/CH_2I_2$) = 3·30 (1), $D_x = 3{\cdot}35$ Mg m^{-3}, μ(Mo $K\alpha$) = 7·04 mm^{-1}, $T = 297$ (1) K. The unit cell consists of 2 × 2 × 4

* Lists of structure factors and anisotropic thermal parameters for (I), (II) and (III) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51084 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

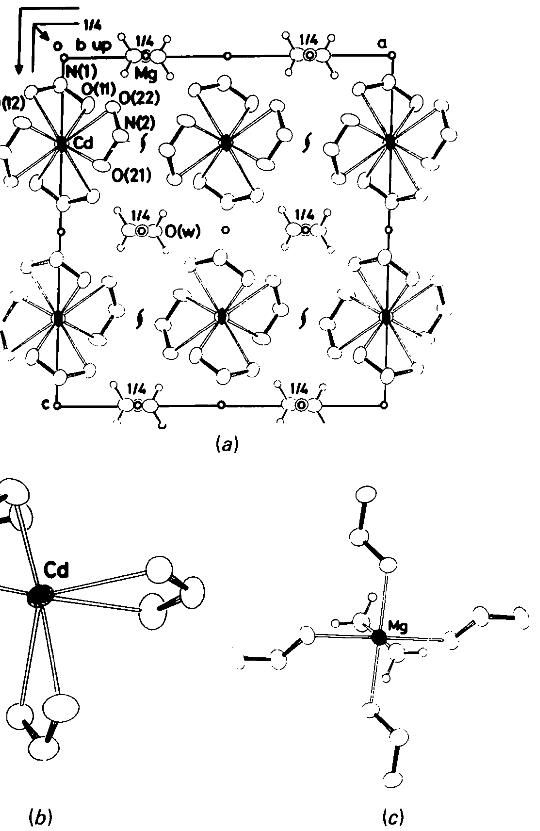

Fig. 1. (*a*) Projection of the crystal structure of (I) along **b** and environment of (*b*) the Cd^{2+} and (*c*) the Mg^{2+} ions.

pseudo-subcells in which the Ba^{2+} ions lie at the corners and a Cd^{2+} ion at the center ($R = 0{\cdot}22$ for 1133 unique reflections).

Discussion. Final atomic coordinates and interatomic distances and bond angles are presented in Tables 1 and 2. The crystal structure of (I) is shown in Fig. 1. The Cd^{2+} ion lies on the twofold axis and the Mg^{2+} ion lies at the center of symmetry. The Cd^{2+} ion is coordinated to eight O atoms of the four nitrite ions arranged tetrahedrally. The complex anion, $[Cd(O_2N)_4]^{2-}$, is also observed in (II), (III) and $Cd(NO_2)_2.2KNO_2$ (Ohba, Matsumoto, Takazawa & Saito, 1987). The Mg^{2+} ion is surrounded octahedrally by two water molecules and four nitrite O atoms. The Cd^{2+} and Ca^{2+} ions in (II) (Fig. 2) lie on the twofold axes perpendicular to **c**. The Ca^{2+} ion is surrounded by four water and four nitrite O atoms. The crystal structure of (III) is isomorphous with (II). This is because the ionic radius of Sr^{2+} is nearly equal to that of Ca^{2+}.

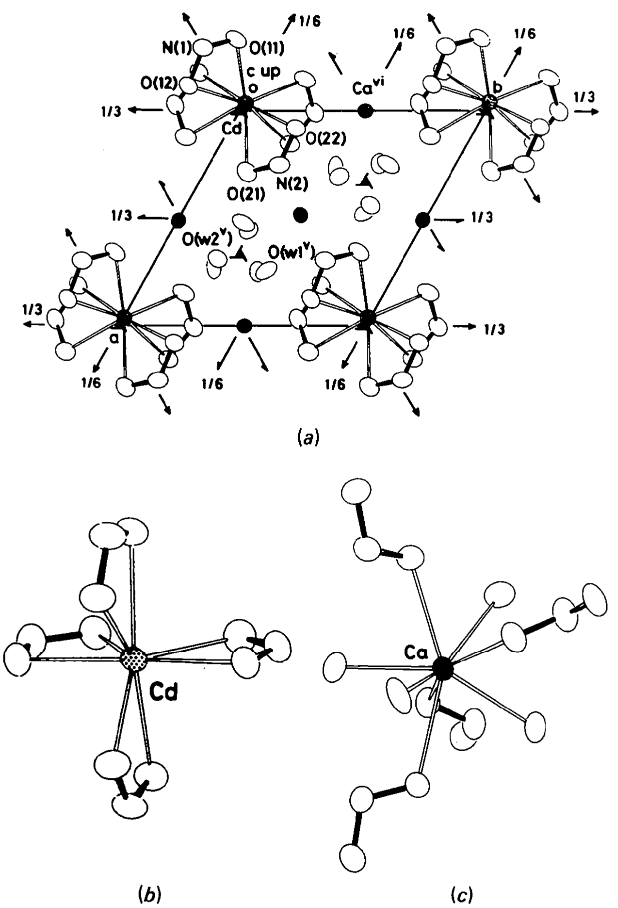

Fig. 2. (*a*) Projection of the crystal structure of (II) along **c** and environment of (*b*) the Cd^{2+} and (*c*) the Ca^{2+} ions. The symmetry code is given in Table 2.

These double salts, $CdM(NO_2)_4.xH_2O$ (M = Mg, Ca or Sr), provide information about the relative strength of the attractive interaction between the cation and nitrite ions. Fig. 3 shows the arrangement of metal cations and water molecules lying nearly on a nitrite plane. The chelated position between the two O atoms of NO_2^- is occupied by the Cd^{2+} ion independent of M^{2+}. It suggests that the attraction of the nitrite ion is stronger for Cd^{2+} than for alkaline-earth-metal cations. The M^{2+} cations are close to one of the nitrite O atoms with $M{\cdots}O{-}N$ angle 113·7 (2) to 120·0 (4)°. This is because the O atoms have sp^2 hybridization and the metal cation approaches one of the lone-pair lobes (Ohba, Kikkawa & Saito, 1985). It is difficult to describe the color of the small crystals because there is a very slight difference between colorless and pale

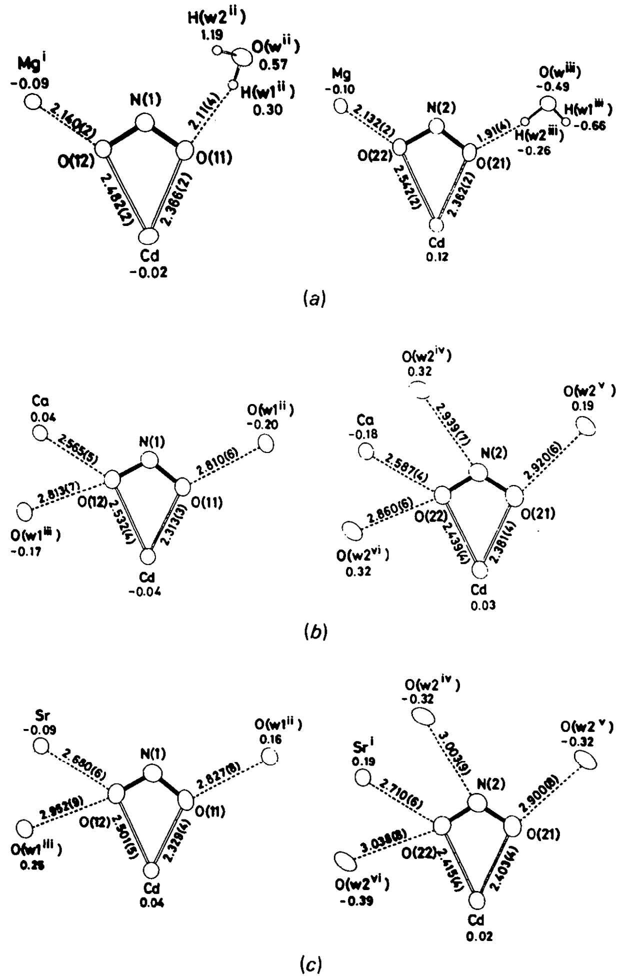

Fig. 3. Arrangement of metal cations and water molecules around the NO_2^- ions in (*a*) (I), (*b*) (II) and (*c*) (III) with distances from the NO_2 plane less than 0·5 Å, which are indicated by numbers near the atom labels (e.s.d.'s ~0·005 Å). The symmetry code is given in Table 2. Distances in Å.

yellow. The cadmium nitrite salts can be said to be colorless, in contrast with the bright-yellow color of $Pb(NO_2)_2.H_2O$ and $Hg_2(NO_2)_2$ crystals. The present study confirmed that the perturbation of the NO_2^- by the Cd^{2+} ion is too small to give coloration.

References

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98, 102, 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

MCGLYNN, S. P., AZUMI, T. & KUMAR, D. (1981). *Chem. Rev.* **81**, 475–489.

OHBA, S., KIKKAWA, T. & SAITO, Y. (1985). *Acta Cryst.* C**41**, 10–13.

OHBA, S., MATSUMOTO, F., TAKAZAWA, H. & SAITO, Y. (1987). *Acta Cryst.* C**43**, 191–194.

SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.

Acta Cryst. (1988). C**44**, 1707–1709

Electron Difference Density in Potassium Zinc Fluoride Perovskite

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(*Received* 12 *February* 1988; *accepted* 27 *May* 1988)

Abstract. $KZnF_3$, $M_r = 161{\cdot}47$, cubic, $Pm3m$, $a = 4{\cdot}056\,(1)$ Å, $V = 66{\cdot}72\,(3)$ Å^3, $Z = 1$, $D_x = 4{\cdot}018$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10{\cdot}81$ mm^{-1}, $F(000) = 76$, $T = 298$ K, final $R = 0{\cdot}009$, $wR = 0{\cdot}008$ for 101 unique reflections. The difference density near the Zn atom is not isotropic. The largest peak of 0·38 e Å^{-3} is 0·61 Å from the Zn atom on the Zn—F bond axis. The greatest depletion of −0·56 e Å^{-3} is at the mid point between K atoms. The signs of atomic charges based on the independent atom model (IAM) are consistent with atomic electronegativities but their magnitudes are less than the formal values. The difference density based on the ionic model closely resembles that based on the IAM. The effective charges based on the ionic model are also markedly less than the formal values.

Introduction. Compounds with the formula KMF_3, where M is a divalent metal, have been studied because of their magnetic structure (Hirakawa, Hirakawa & Hashimoto, 1960; Scatturin, Corliss, Elliott & Hastings, 1961). The series provides examples of displacive structural phase transitions (Rousseau, 1979). Recently, interest in $KZnF_3$ has focused on heat-capacity analysis (Burriel, Bartolomé, González, Navarro & Ridou, 1987), in view of its structural stability down to 4 K.

Difference density maps have been obtained for the isomorphic Mn, Fe, Co and Ni structures as well as the Jahn–Teller distorted Cu compound, in connection with studies of spin states of $3d$ electrons (Tanaka, Konishi & Marumo, 1979; Kijima, Tanaka & Marumo, 1981, 1983; Miyata, Tanaka & Marumo, 1983). The focal point of those studies was the redistribution of $3d$ electrons associated with transition metals with incomplete $3d$ subshells. However, there were other significant features in the maps, notably near the F nucleus, but also at the point midway between the K nuclei, which are outside the normal bond radii for all the atoms in the structures. The nature of these features changed markedly through the series Mn, Fe, Co and Ni, the changes also being related to cell size (Spadaccini, 1988). There was strong correlation between the features associated with the transition-metal $3d$ electrons and those elsewhere in the structure. The main problem in explaining those features that correlated was to differentiate cause from effect. That is, did the repopulation of the $3d$ subshell induce polarization at other locations in the structure, or was the correlation because all were produced by the same crystal field?

In order to help resolve this question we have studied the $KZnF_3$ structure. The electron difference density in the Zn compound provides a reference standard for comparison with the transition-metal perovskites studied previously. Because the Zn atom has a filled $3d$ subshell, it is intrinsically less polarizable than that of transition metals with incomplete $3d$ subshells.

Experimental. Crystals of $KZnF_3$ were grown by slow diffusion of 0·6 M KF into 0·2 M $Zn(NO_3)_2$ through a fine capillary over a period of weeks (chemicals suggested by Palmer, 1962). They were washed several times with water and dried. The crystals were found to exhibit a mixture of mainly {100} and {111} faces, the largest being 0·25 × 0·25 × 0·25 mm in size.

The crystal selected for data collection was a deformed octahedron with seven {111} faces and a (211) face (the latter being the area of attachment to

0108-2701/88/101707-03$03.00