not surprising that theoretical calculations of Raman and infrared vibrational frequencies can be brought into agreement with observation only by the incorporation of these Pb—Pb interactions (Donaldson, Donoghue & Ross, 1974; Vigouroux et al., 1982).

Relevance to the lead-acid battery. The mean distance between the Pb atom and its twelve nearest Pb neighbours is 3·82 Å, only 0·32 Å larger than the corresponding distance in Pb metal. Since litharge and massicot have similar sub-arrays of distorted face-centred-cubic Pb atoms, the two polymorphs can be rather easily interconverted (White, Dachille & Roy, 1961; Hehner & Ritchie, 1974) by a mechanism involving relatively minor movements of the Pb atoms (Söderquist & Dickens, 1967). By a similar argument, either of the two polymorphs would be expected to be formed without difficulty by electrochemical corrosion of the positive-plate Pb-alloy grids in the lead-acid battery since the required O atoms can be intercalated between layers of Pb atoms in the metal with a minimum of structural disruption. Furthermore, as suggested by Anderson & Sterns (1959), the way is then clear for the subsequent formation of the so-called 'intermediate' oxides of lead, with composition PbO_x, where $x \approx 1·5$, by the insertion of further O atoms into the van der Waals gap in the PbO crystal structure. Studies are currently underway to elucidate the mechanism of this corrosion process during battery operation.

References

ABEL, E. W. (1973). *Lead.* In *Comprehensive Inorganic Chemistry*, pp. 105–146. Oxford: Pergamon Press.
ADAMS, D. M. & STEVENS, D. C. (1977). *J. Chem. Soc. Dalton Trans.*, pp. 1096–1103.
ANDERSON, J. S. & STERNS, M. (1959). *J. Inorg. Nucl. Chem.* 11, 272–285.
BULLOCK, K. R., TRISCHAN, G. M. & BURROW, R. G. (1983). *J. Electrochem. Soc.* 130, 1283–1289.
BYSTRÖM, A. (1943). *Ark. Kemi Mineral. Geol.* 17B, 1–6.

CAGLIOTI, G., PAOLETTI, A. & RICCI, F. P. (1958). *Nucl. Instrum.* 3, 223–228.
DAVID, W. I. F. & MATTHEWMAN, J. C. (1984). Report RAL 84064. Rutherford Appleton Laboratory, Oxfordshire.
DICKENS, B. (1965). *J. Inorg. Nucl. Chem.* 27, 1495–1501.
DONALDSON, J. D., DONOGHUE, M. T. & ROSS, S. D. (1974). *Spectrochim. Acta. Part A,* 30, 1967–1975.
GARNIER, P., CALVARIN, G. & WEIGEL, D. (1972). *J. Chim. Phys. Phys.-Chim. Biol.* pp. 1711–1718.
GRENINGER, D., KOLLONITSCH, V. & KLINE, C. H. (1975). *Lead Chemicals.* International Lead Zinc Research Organization, Inc., New York.
HEHNER, N. E. & RITCHIE, E. J. (1974). *Lead Oxides: Chemistry, Technology, Battery Manufacturing Uses, History.* Largo, Florida: Independent Battery Manufacturers Association.
HEWAT, A. W. (1979). *Acta Cryst.* A35, 248.
HEYNE, L., BEEKMANS, N. M. & DE BEER, A. (1972). *J. Electrochem. Soc.* 119, 77–84.
HILL, R. J. (1982). *Mater. Res. Bull.* 17, 769–784.
HILL, R. J. & HOWARD, C. J. (1985). *J. Appl. Cryst.* 18, 173–180.
HILL, R. J., JESSEL, A. M. & MADSEN, I. C. (1984). Proc. Lead-acid Battery Symposium, 166th Meeting of the Electrochem. Soc., New Orleans, 7–11 October.
HILL, R. J. & MADSEN, I. C. (1984). *J. Electrochem. Soc.* 131, 1486–1491.
HOWARD, C. J. (1982). *J. Appl. Cryst.* 15, 615–620.
HOWARD, C. J., BALL, C. J., DAVIS, R. L. & ELCOMBE, M. M. (1983). *Aust. J. Phys.* 36, 507–518.
JORGENSEN, J. D., VARMA, R., ROTELLA, F. J., COOK, G. & YAO, N. P. (1982). *J. Electrochem. Soc.* 129, 1678–1681.
KAY, M. I. (1961). *Acta Cryst.* 14, 80–81.
LECIEJEWICZ, J. (1961a). *Acta Cryst.* 14, 66.
LECIEJEWICZ, J. (1961b). *Acta. Cryst.* 14, 1304.
MOORE, W. J. & PAULING, L. (1941). *J. Am. Chem. Soc.* 63, 1392–1394.
PERKINS, J. (1977). *Mater. Sci. Eng.* 28, 167–199.
SAHL, K. (1970). *Lead.* In *Handbook of Geochemistry*, pp. 82A1–6. Berlin: Springer-Verlag.
SANTORO, A., D'ANTONIO, P. & CAULDER, S. M. (1983). *J. Electrochem. Soc.* 130, 1451–1459.
SÖDERQUIST, R. & DICKENS, B. (1967). *J. Phys. Chem. Solids,* 28, 823–827.
SUORTTI, P., AHTEE, M. & UNONIUS, L. (1979). *J. Appl. Cryst.* 12, 365–369.
VIGOUROUX, J. P., CALVARIN, G. & HUSSON, E. (1982). *J. Solid State Chem.* 45, 343–352.
WHITE, W. B., DACHILLE, F. & ROY, R. (1961). *J. Am. Chem. Soc.* 44, 170–174.
WILES, D. B. & YOUNG, R. A. (1981). *J. Appl. Cryst.* 14, 149–151.
YOUNG, R. A., PRINCE, E. & SPARKS, R. A. (1982). *J. Appl. Cryst.* 15, 357–359.

Structure of Manganese(II) Iodide Tetrahydrate, MnI₂.4H₂O

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Abstract. $M_r = 380·81$, monoclinic, $P2_1/c$, $a = 6·698$ (2), $b = 7·494$ (3), $c = 9·308$ (5) Å, $\beta = 110·21$ (3)°, $V = 438·5$ (3) Å³, $Z = 2$, $D_m = 2·82$ (4), $D_x = 2·90 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 84·1 \text{ cm}^{-1}$, $F(000) = 342$, $T = 291$ K, final $R = 0·047$, for 675 unique observed reflections. Unlike

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$MnCl_2.4H_2O$ and $MnBr_2.4H_2O$ where the halogens occupy *cis* positions in the octahedral coordination of the manganese ion, $MnI_2.4H_2O$ is isostructural with $FeCl_2.4H_2O$ where the halogens occupy *trans* positions in the coordination shell.

Introduction. The tetrahydrates of manganese chloride and manganese bromide have been the subject of many experimental investigations. The chloride is perhaps one of the most extensively studied antiferromagnetic systems to date. In contrast, virtually no information exists for the chemically analogous iodide. The crystal-structure determination reported here was undertaken as a preliminary step in the thermodynamic and magnetic characterization of $MnI_2.4H_2O$. The principal question addressed in this work concerns the type of halogen coordination about the manganese ion.

Experimental. D_m by volume displacement in CCl_4. Severe deliquescence and chemical instability in air require an inert atmosphere for formation, crystal-lization, and X-ray sample preparation. Solution by direct reaction of manganese and aqueous hydrogen iodide (25%). Pink crystals of tetrahydrate obtained by evaporation at room temperature, molecular sieves as desiccant. Irregularly shaped crystal cut from a larger single crystal, mean dimension 0·15 mm, and sealed in quartz capillary. Nicolet $R3m$ diffractometer, graphite monochromator (Campana, 1981), θ–2θ scan, accurate unit-cell parameters from least-squares refinement of 12 reflections (θ range 8·21–17·84°), three standard reflections (023, $31\bar{2}$, 510) measured every 50 reflec-tions, 2% variation. Range of hkl: $0 \le h \le 7$, $0 \le k \le 8$, $-10 \le l \le 10$. 967 reflections collected ($2 \le \theta \le 25°$), 768 unique, $R_{int} = 0·04$, 93 unobserved reflections $[F < 2·5\sigma(F)]$. Empirical absorption correction carried out from azimuthal scans on 12 reflections, $\chi = 90 \pm 20°$ (Nicolet program $XEMP$). Structure solved by Patterson method, refined by full-matrix least-squares procedures, function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(F) + GF^2]$ and $G = 0·005$; non-hydrogen atoms anisotropic. Hydrogen atoms could not be detected. Manganese ion fixed to center of inversion. $R = 0·047$, $wR = 0·048$, $S = 0·88$. Scatter-ing factors for Mn, I, and O from *International Tables for X-ray Crystallography* (1968). In final cycle $(\Delta/\sigma)_{max} = 0·001$; final difference map showed residual electron density (max. $= 0·73$, min. $= 2·39$ e Å^{-3}) near iodide ion, interpreted as residual uncorrected systematic errors. Calculations carried out with *SHELXTL* package on Nicolet $R3m$ crystallographic system (Sheldrick, 1980).*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42190 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters* ($\mathring{A}^2 \times 10^2$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
Mn	0·0000	0·0000	0·0000	3·2 (1)
I(1)	0·3202 (2)	0·2826 (1)	0·0798 (1)	4·0 (1)
O(1)	0·0049 (14)	−0·0031 (16)	0·2356 (8)	7·2 (4)
O(2)	0·2515 (13)	−0·1988 (13)	0·0638 (10)	6·5 (4)

* Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Comparison of* $MnI_2.4H_2O$ *and* $FeCl_2.4H_2O$

M and X represent the metal and halogen respectively.

	$MnI_2.4H_2O$ (This work)	$FeCl_2.4H_2O$ (Verbist et al., 1972)
a	6·698 (2) Å	5·885 (3) Å
b	7·494 (3)	7·180 (6)
c	9·308 (5)	8·514 (4)
β	110·21 (3)°	111·09 (2)°
$M-X(1)$	2·921 (1) Å	2·514 (1) Å
$M-O(1)$	2·183 (8)	2·121 (1)
$M-O(2)$	2·172 (9)	2·086 (1)
$X(1)-M-O(1)$	89·8 (2)°	89·86 (2)°
$X(1)-M-O(2)$	89·8 (2)	90·24 (2)
$O(1)-M-O(2)$	88·7 (4)	88·21 (2)

Discussion. The atomic fractional coordinates with their e.s.d.'s and U_{eq} values (Hamilton, 1959) are given in Table 1. Table 2 is a comparison of the cell parameters, bond lengths, and bond angles of $MnI_2.$-$4H_2O$ and $FeCl_2.4H_2O$. The similarity in the trend of octahedral distortion suggests that the hydrogen-bond linkages in $MnI_2.4H_2O$ are similar to those of $FeCl_2.$-$4H_2O$ (Verbist, Hamilton, Koetzle & Lehmann, 1972).

The results reported here are noteworthy in the following regards: First, the trend of *cis* coordination of the halogens about manganese in $MnCl_2.4H_2O$ (El Saffar & Brown, 1970) and $MnBr_2.4H_2O$ (Sudarsanan, 1975) ends with the iodide. Second, based on the structural considerations, we expect the iodide to be closer to $FeCl_2.4H_2O$ in its magnetic properties than to either the manganese chloride or manganese bromide tetrahydrates. Comparison of the low-temperature magnetic properties of $MnI_2.4H_2O$ with $FeCl_2.4H_2O$ and the other manganese halide tetrahydrates should prove valuable in elucidating the chemical effects in magnetic behavior, as opposed to geometrical effects.

References

CAMPANA, C. F. (1981). Editor, *Nicolet P3/R3 Data Collection Manual*. Nicolet XRD Corporation, Cupertino, CA.
EL SAFFAR, Z. M. & BROWN, G. M. (1970). *Acta Cryst.* B27, 66–73.
HAMILTON, W. (1959). *Acta Cryst.* 12, 609–610.
International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

SHELDRICK, G. M. (1980). Editor, *Nicolet SHELXTL Structure Determination Manual.* Nicolet XRD Corporation Cupertino, CA.

SUDARSANAN, K. (1975). *Acta Cryst.* B31, 2720–2721.
VERBIST, J. J., HAMILTON, W. C., KOETZLE, T. F. & LEHMANN, M. S. (1972). *J. Chem. Phys.* 56, 3257–3264.

Structure du Pentabromure et Disulfure de Trinéodyme, Nd₃Br₅S₂

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Abstract. $M_r = 896 \cdot 36$, orthorhombic, *Pnma*, $a = 7 \cdot 186$ (1), $b = 22 \cdot 39$ (1), $c = 6 \cdot 814$ (4) Å, $V = 1096$ (1) Å³, $Z = 4$, $D_m(293$ K$) = 5 \cdot 39$ (4), $D_x = 5 \cdot 43$ g cm⁻³, λ(Mo $K\alpha$) $= 0 \cdot 71069$ Å, $\mu = 337$ cm⁻¹, $F(000) = 1548$, $T = 293$ K, $R = 0 \cdot 044$ for 1372 independent observed reflections. This structure is built up of [Nd₄S] tetrahedra. These tetrahedra are linked in ribbons which are parallel to the *a* axis and surrounded by Br atoms. The Nd atoms found in the middle of the ribbon are bonded to four S and four Br atoms, while those at the edge are surrounded by two S and five Br atoms.

Introduction. Le composé Nd₃Br₅S₂ a été mis en évidence, comme le composé Nd₄Br₆S₃ (Rysanek, Mazurier, Laruelle & Dagron, 1980), au cours de la cristallisation de NdBrS au sein d'un bain fondu de NdBr₃ vers 950 K par Dagron & Thévet (1980).

Partie expérimentale. Les cristaux s'altèrent facilement à l'air et nous avons dû placer le monocristal dans un capillaire scellé pour mesurer les intensités des réflexions. Le cristal utilisé se présente sous la forme d'une aiguille transparente mauve de dimensions 30 × 30 × 260 μm. Les corrections d'absorption n'ont pas été faites car l'absorption du cristal, dans les deux directions de faible épaisseur, est du même ordre de grandeur que celle produite par le tube de verre protecteur. D_m mesurée par la méthode de la balance hydrostatique en atmosphère inerte. 15 réflexions utilisées pour affiner les paramètres de la maille ($5,7 \leq \theta \leq 11,8°$). 2039 réflexions indépendantes enregistrées à la température ambiante (293 K) à l'aide d'un diffractomètre automatique à quatre cercles Syntex, $\sin\theta/\lambda_{max} = 0,758$ Å⁻¹ ($10 \geq h \geq 0$, $33 \geq k \geq 0$, $10 \geq l \geq 0$). Balayage ω–2θ (2θ variant de $2\theta_1 - 0,7°$ à $2\theta_2 + 0,7°$, θ_1 et θ_2 étant respectivement les angles de diffraction correspondant aux longueurs d'onde $K\alpha_1$ et $K\alpha_2$ du molybdène), réflexions de contrôle: 207 et 026 vérifiées toutes les cinquante

mesures, valeur de l'écart-type relatif sur l'instabilité $\sigma_i = 0,025$. Intensités corrigées des facteurs de Lorentz et de polarisation. Résolution de la structure par la méthode d'addition symbolique suivant le programme de *LSAM* de Germain & Woolfson (1968) (268 valeurs de E supérieures à 1,5 retenues).

Parmi 16 solutions possibles, celle dont les figures de mérite sont les plus élevées, donne une série de Fourier où on peut identifier deux atomes lourds qui sont les atomes de néodyme. Un atome de brome, puis un de soufre et finalement deux atomes de brome ont été trouvés à partir de la densité électronique calculée avec les phases déterminées par les deux premiers atomes. Affinements réalisés à l'aide du programme *ORXFLS* de Busing (1971), facteurs de structure calculés à partir des facteurs de diffusion donnés par *International Tables for X-ray Crystallography* (1974).

Indice résiduel $R = 0,059$ pour les 1706 réflexions* telles que $I > \sigma(I)$, l'écart-type $\sigma(I)$ sur la mesure de l'intensité I est déduit de l'écart-type σ_c sur le taux de comptage et de l'écart-type relatif σ_i sur la variation des réflexions de référence par la relation: $\sigma(I) = (\sigma_c^2 + \sigma_i^2 I^2)^{1/2}$. $wR = 0,042$ avec $w = 1/\sigma^2(F)$, $S = 2,27$; $(\Delta/\sigma)_{max} = 0,018$. Correction de l'extinction secondaire faite à l'aide du programme de Becker & Coppens (1975) (cristal mosaïque): la distribution angulaire est gaussienne, valeur moyenne 66″. Fluctuations de la densité électronique sur la dernière carte de Fourier des différences varient de 1,9 à −1,6 e Å⁻³.

Discussion. Le Tableau 1 donne les valeurs des coordonnées atomiques et des facteurs d'agitation thermique équivalents isotropes des atomes.