REGULAR STRUCTURAL PAPERS

Acta Cryst. (1993). **C49**, 1875–1877

Structure of $NdMn_2O_5$

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(*Received* 15 *December* 1992; *accepted* 26 *March* 1993)

Abstract

The crystal structure of manganese neodymium oxide, $NdMn_2O_5$, has been solved from a single-crystal X-ray diffraction study. This compound is isostructural with other members of the TMn_2O_5 series where T is a rare earth. Its structure consists of Mn^{4+} octahedra $[MnO_6]$ in infinite chains parallel to the c axis linked through Mn^{3+} tetragonal pyramids $[MnO_5]$ and Nd^{3+} bicapped antiprisms $[MnO_8]$.

Comment

As part of our studies of transition-metal oxyhalides, we have prepared recently a manganese oxychloride, $Mn_8O_{10}Cl_3$, using a redox reaction between MnO_2 and $MnCl_2$ (Euzen, Léone, Palvadeau, Queignec & Rouxel, 1992) in the temperature range 573–773 K:

$$5\,MnO_2 + 3\,MnCl_2 \rightarrow Mn_8O_{10}Cl_3 + \tfrac{3}{2}Cl_2.$$

This compound has been prepared previously by direct oxidation of manganese chloride (Buisson, 1977). Mn atoms are in both 2^+ and 3^+ oxidation states in this structure; Mn^{3+} atoms occupy chloride $[MnCl_6]$ and mixed chloride–oxygen $[MnO_4Cl_2]$ octahedra, while Mn^{2+} is located in oxygen $[MnO_8]$ cubes and chloride $[MnCl_6]$ octahedra. Selective substitutions by another transition metal or halogen have been realized in this multi-site framework; $FeMn_7O_{10}Cl_3$ (Euzen, Palvadeau, Queignec & Rouxel, 1991) and $Mn_{7.5}O_{10}Br_3$ (Euzen, Léone, Mansot, Bonneau, Queignec & Palvadeau, 1992) have been published recently.

Substitutions by rare earths were tried in order to follow the magnetic behaviour and to induce optical properties. In fact, it has not been possible to obtain rare-earth oxyhalides in this way, only TMn_2O_5 oxides (T = rare earth) were formed. Compounds with similar formulae have been prepared previously (Quezel-Ambrunaz, Bertaut & Buisson, 1964) by the decomposition at 1273 K of a mixture of manganese and rare-earth nitrates. The magnetic properties of some phases have been investigated (Buisson, 1973). Crystalline or magnetic structure determinations were solved in several cases (Quezel-Ambrunaz, Bertaut & Buisson, 1964; Abrahams & Bernstein, 1967; Gardner, Wilkinson, Forsyth & Wanklyn, 1988). Neodymium was not considered. The new method of preparation introduced in the present work yields single crystals of good quality, allowing a precise structural determination. $NdMn_2O_5$ was prepared by the reaction of MnO_2 and $NdCl_3$ in silica tubes, sealed under vacuum at 1123 K, for a week:

$$5\,MnO_2 + 2\,NdCl_3 \rightarrow 2\,NdMn_2O_5 + MnCl_2 + 2\,Cl_2.$$

Mn(1) is in an octahedral environment with very slightly different Mn—O distances (Table 2). Angular distortions from orthogonal Mn—O bonds are more pronounced [O(2)—Mn(1)—O(2) < 80°]. The octahedra form infinite chains by edge sharing running along the c axis (Fig. 1). These chains are linked by the other coordination polyhedra.

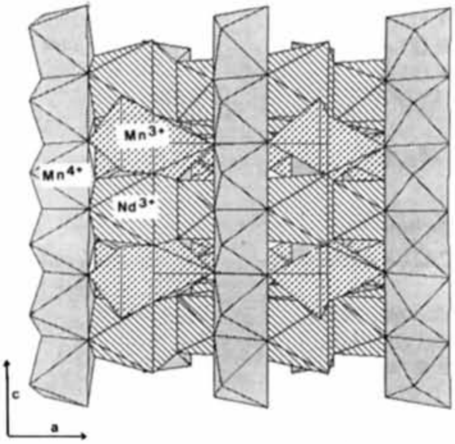

Fig. 1. Structure of $NdMn_2O_5$ viewed down the b axis.

Mn(2) is located in a distorted-tetragonal pyramid with very significantly different bond lengths. Four O atoms are in a square plane with an average Mn—O distance of 1.90 Å; the apical atom is at a distance of 2.05 Å. This fact appears to be quite general for tetragonal pyramidal configurations. A sixth O atom is at a distance of 3.07 Å, too far away to belong to the Mn coordination shell.

The Nd atoms have height-first neighbours at an average distance of 2.43 Å. They form an approximately bicapped square antiprism. This coordination has been found previously for several rare-earth ions.

Acta Crystallographica Section C
ISSN 0108-2701 ©1993

As assumed by Bertaut, Buisson, Durif, Mareschal, Montmory & Quezel-Ambrunaz (1965) and Abrahams & Bernstein (1967), and in agreement with various well known structures, Mn(1) (MnO_6 octahedra) is certainly present in the Mn^{4+} oxidation state and Mn(2) (MnO_5 pyramids) is in the d^4 configuration (Mn^{3+}).

The shortest metal–metal distance previously noticed in this family was Mn(1)—Mn(1) = 2.87 Å in $DyMn_2O_5$. In $NdMn_2O_5$, an Mn(1)—Mn(1) distance of 2.750 (2) Å is observed, significantly shorter than in the dysprosium compound. The implications of this will probably be important for the magnetic and electrical properties. With the controversies concerning magnetic structures, susceptibilities and other physical properties, we think that important work still has to be performed.

Experimental

Crystal data

Mn_2NdO_5
$M_r = 334$
Orthorhombic
Pbam
$a = 7.471$ (1) Å
$b = 8.588$ (2) Å
$c = 5.684$ (1) Å
$V = 364.7$ (1) Å^3
$Z = 4$
$D_x = 6.1$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2$-$35°$
$\mu = 20.5455$ mm^{-1}
$T = 293$ K
Needle
0.2 × 0.03 × 0.02 mm
Black

Data collection

Nonius CAD-4 diffractometer
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.955$, $T_{max} = 1.213$
1086 measured reflections
617 independent reflections

938 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.028$
$\theta_{max} = 35°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity variation: 0.7%

Refinement

Refinement on F
Final $R = 0.020$
$wR = 0.021$
$S = 1.6124$
444 reflections
45 parameters
$w = 1/\{1 + [(F-31)/21]^2\}$
$\Delta\rho_{min} = -1.080$ e Å^{-3} at (0.3320,0.4570,0.4160)
$\Delta\rho_{max} = -1.237$ e Å^{-3} at (0.0596,0.3176,0.4994)

Extinction correction: *DIFABS*
Extinction coefficient: 3.46×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

	x	y	z	B_{eq}
Nd	0.14247 (6)	0.17269 (6)	0.0	0.670 (6)
Mn(1)	0.0	0.5	0.2581 (2)	0.61 (2)
Mn(2)	0.4103 (2)	0.3518 (2)	0.5	0.66 (2)
O(1)	0.0	0.0	0.276 (1)	0.79 (9)
O(2)	0.1562 (9)	0.4490 (6)	0.0	0.9 (1)
O(3)	0.1536 (8)	0.4360 (7)	0.5	0.78 (9)
O(4)	0.4023	0.2063 (4)	0.2500 (7)	0.79 (7)

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *in various coordination polyhedra and metal–metal distances* (Å)

Mn^{4+} octahedron			
Mn(1)—O(2)	1.925 (4) ×2	Mn(1)—O(3)	1.874 (4) ×2
Mn(1)—O(4)	1.916 (4) ×2		
Mn^{3+} tetragonal pyramid			
Mn(2)—O(1)	1.921 (4) ×2	Mn(2)—O(3)	2.050 (6)
Mn(2)—O(4)	1.894 (4) ×2		
Nd^{3+} bicapped prism			
Nd—O(1)	2.407 (4) ×2	Nd—O(2)	2.375 (8)
Nd—O(2)	2.440 (7)	Nd—O(4)	2.423 (3) ×2
Nd—O(4)	2.514 (4) ×2		
Metal-metal distances			
Nd—Mn(1)	3.3447 (7)	Nd—Mn(2)	3.3362 (6)
Mn(1)—Mn(1)	2.750 (2)	Mn(1)—Mn(2)	3.386 (1)
Mn(2)—Mn(2)	2.878 (2)	Mn(1)—Mn(2)	3.593 (1)
Nd—Nd	3.6510 (7)		
Mn^{4+} octahedron			
O(2)—Mn(1)—O(3)	97.0 (2)	O(2)—Mn(1)—O(4)	87.8 (2)
O(2)—Mn(1)—O(2)	80.7 (2)	O(3)—Mn(1)—O(3)	85.6 (2)
O(3)—Mn(1)—O(4)	88.9 (2)		
Mn^{3+} tetragonal pyramid			
O(1)—Mn(2)—O(1)	83.1 (2)	O(1)—Mn(2)—O(3)	95.3 (2)
O(1)—Mn(2)—O(4)	87.2 (2)	O(3)—Mn(2)—O(4)	101.7 (2)
O(4)—Mn(2)—O(4)	97.3 (2)		
Nd^{3+} bicapped prism			
O(1)—Nd—O(1)	81.3 (2)	O(1)—Nd—O(2)	77.7 (1)
O(1)—Nd—O(4)	92.6 (1)	O(2)—Nd—O(2)	139.5 (2)
O(2)—Nd—O(4)	66.4 (1)	O(4)—Nd—O(4)	68.8 (1)

A Jeol JM-35C electron microscope equipped with a Tractor TN 5500 micro Z system was used for X-ray microanalysis (energy-dispersive spectroscopy) of both microcrystalline powder and single crystals. The X-ray powder-diffraction pattern is in agreement with previous results. Chemical analyses were confirmed by structural determination.

Lorentz-polarization corrections were applied using *DIFABS*. All calculations were performed using the *SDP-Plus* program (Frenz, 1985).

It is noteworthy that the cell parameters are significantly different from those of Bertaut, Buisson, Durif, Mareschal, Montmory & Quezel-Ambrunaz (1965): $a = 7.54$, $b = 8.63$, $c = 5.70$ Å. Systematic absences ($h0l$ with $h = 2n + 1$, $0kl$ with $k = 2n + 1$) are consistent with two possible space groups, *Pbam* (centrosymmetric) and *Pba*2 (non-centrosymmetric). The structure was solved in the centrosymmetric space group *Pbam*. The Mn and Nd atoms were determined from a Patterson map and the remaining O atoms were located in successive difference Fourier syntheses. The effects of anomalous dispersion were included in F_c (Cromer & Ibers, 1974).

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71226 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1038]

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Acta Cryst. (1993). C**49**, 1877–1879

Structure of $Tl_2Mo_2P_2O_{11}$

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(*Received* 22 *December* 1992; *accepted* 29 *April* 1993)

Abstract

Dimolybdenum dithallium diphosphate, $Tl_2Mo_2P_2O_{11}$, is isotypic with $K_2Mo_2P_2O_{11}$. Its framework is built from the original $Mo_2P_2O_{15}$ unit, formed by one Mo_2O_{11} group sharing four of its corners with two PO_4 tetrahedra, leading to $[Mo_2P_2O_{13}]_\infty$ chains running along **c**. The $[Mo_2P_2O_{11}]_\infty$ framework forms two different intersecting tunnels running along **c** and ⟨110⟩, where the Tl^+ ions are located.

Comment

The synthesis and structure determination of the title compound were undertaken in order to test the possible replacement of potassium by thallium in the phase $K_2Mo_2P_2O_{11}$ (Gueho, Borel, Grandin, Leclaire & Raveau, 1993). The crystals of the new phase $Tl_2Mo_2P_2O_{11}$ were synthesized from the nominal composition $Tl_2Mo_2P_2O_{11}$ heated at 1123 K for one day in an evacuated silica ampoule and cooled at 2 K h^{-1} to 923 K. Finally, the sample was quenched to room temperature and brown crystals were extracted. The phosphate $Tl_2Mo_2P_2O_{11}$ is isotypic with $K_2Mo_2P_2O_{11}$, *i.e.* its framework is built from $Mo_2P_2O_{15}$ units, formed by one Mo_2O_{11} group sharing four of its corners with two PO_4 tetrahedra along **c**, leading to $[Mo_2P_2O_{13}]_\infty$ chains running along **c**. Laterally in the (001) plane, the $[Mo_2P_2O_{13}]_\infty$ columns share the corners of their polyhedra leading to the three-dimensional framework $[Mo_2P_2O_{11}]_\infty$. This framework forms two different intersecting tunnels running along **c** and ⟨110⟩. Like the potassium cations in $K_2Mo_2P_2O_{11}$, the Tl cations are distributed over three kinds of sites. The Tl(1) cations are located on the symmetry centre and exhibit eightfold coordination with Tl—O distances ranging from 2.73 (1) to 2.90 (1) Å; they are strongly linked to the surrounding O atoms, in agreement with the value of their thermal factors (close to 1.60 Å^2). The Tl(2) cations located in the [001] tunnels are characterized by ninefold coordination with large Tl—O distances ranging from 2.80 (1) to 3.34 (1) Å. The Tl(3) cations

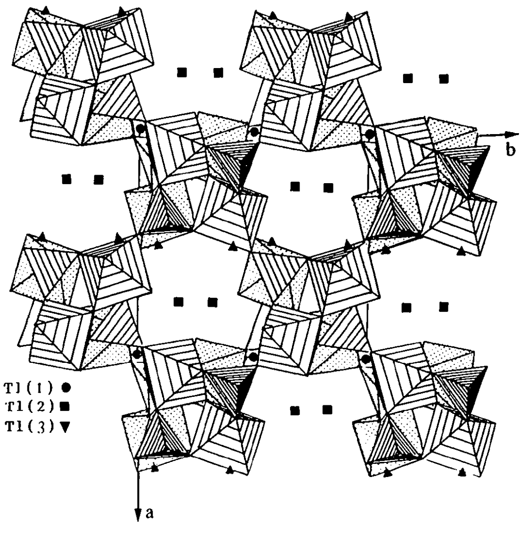

Fig. 1. Projection of $Tl_2Mo_2P_2O_{11}$ along [001].