

Nd₂(WO₄)₃

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Nd}-\text{O}) = 0.004$ Å; R factor = 0.025; wR factor = 0.063; data-to-parameter ratio = 27.2.

The title compound, dineodymium(III) tris[tungstate(VI)], is a member of the Eu₂(WO₄)₃ structure family and crystallizes isotypically with other rare earth tungstates and molybdates of this formula type. The structure is a derivative of the scheelite (CaWO₄) structure and can be considered as an ordered defect variant with a threefold scheelite supercell and one rare earth (*RE*) site unoccupied. The Nd³⁺ cations are coordinated by eight O atoms in form of a distorted bicapped trigonal prism. The two unique W cations are tetrahedrally surrounded by O atoms. One WO₄ tetrahedron has 2 symmetry and is relatively undistorted whereas the other tetrahedron differs considerably from an ideal geometry. This is caused by an additional remote O atom at a distance of 2.149 (4) Å. The resulting WO₄₊₁ polyhedra form W₂O₈ dimers through edge-sharing. Together with the WO₄ and NdO₈ units, the three-dimensional set-up is accomplished.

Related literature

The crystal structure determination of scheelite was reported by Dickinson (1920). For a previous investigation of the structure of Nd₂(WO₄)₃, see: Nassau *et al.* (1969). Isotypic (*RE*)₂(WO₄)₃ structures have been reported by Templeton & Zalkin (1963) for *RE* = Eu; Gärtner *et al.* (1994) for La; Rong *et al.* (2003) for Dy, Gressling & Müller-Buschbaum (1995) for Ce. For the role of the crystal structure on the thermal expansion of (*RE*)₂(WO₄)₃ compounds, see: Sumithra & Umarji (2004). For data standardization, see: Gelato & Parthé (1987).

Experimental

Crystal data

Nd ₂ (WO ₄) ₃	$b = 11.597$ (2) Å
$M_r = 1032.03$	$c = 11.516$ (2) Å
Monoclinic, $C2/c$	$\beta = 109.561$ (14)°
$a = 7.7589$ (12) Å	$V = 976.4$ (3) Å ³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 45.72$ mm⁻¹

$T = 293$ K
 $0.12 \times 0.10 \times 0.08$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	2149 independent reflections
Absorption correction: numerical (<i>HABITUS</i> ; Herrendorf, 1997)	1830 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.033$, $T_{\max} = 0.119$	$R_{\text{int}} = 0.082$
8392 measured reflections	3 standard reflections
	frequency: 120 min
	intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	79 parameters
$wR(F^2) = 0.063$	$\Delta\rho_{\text{max}} = 2.79$ e Å ⁻³
$S = 1.09$	$\Delta\rho_{\text{min}} = -5.24$ e Å ⁻³
2149 reflections	

Table 1

Selected bond lengths (Å).

Nd–O ⁴	2.387 (4)	Nd–O ²	2.497 (4)
Nd–O ²	2.391 (4)	W1–O ^{5v}	1.741 (4)
Nd–O ³	2.427 (5)	W1–O ⁴	1.771 (4)
Nd–O ⁶ⁱⁱ	2.433 (4)	W1–O ²ⁱⁱ	1.838 (4)
Nd–O ¹ⁱⁱⁱ	2.487 (4)	W1–O ⁶	1.881 (4)
Nd–O ^{5iv}	2.488 (4)	W2–O ³	1.754 (4)
Nd–O ¹	2.495 (4)	W2–O ¹	1.808 (4)

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELINA* implemented in *PLATON* (Spek, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2175).

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supporting information

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Nd₂(WO₄)₃**Matthias Weil, Berthold Stöger and Lyubomir Aleksandrov****S1. Comment**

Rare earth tungstates with formula $(RE)_2(WO_4)_3$ are interesting materials due to their negative thermal expansion behaviour (Sumithra & Umarji, 2004). Therefore detailed structural data are required for a better understanding and a quantification of these effects. For a number of $(RE)_2(WO_4)_3$ structures single-crystal data were already published: $RE =$ Eu (Templeton & Zalkin, 1963); La (Gärtner *et al.*, 1994); Dy (Rong *et al.*, 2003); Ce (Gressling & Müller-Buschbaum, 1995). Preparation and an investigation of the crystal structure and the thermal behaviour of the Nd member were also reported some time ago by Nassau *et al.* (1969), including indication of a phase transition at 1318 K. However, the structural characterization of both low- and high-temperature phases remained preliminary. Although we tried to isolate the proposed high-temperature phase of $Nd_2(WO_4)_3$ by rapid quenching of the sample from above the transition temperature, we could obtain only the low-temperature polymorph. Here we report the details of the corresponding α - $Nd_2(WO_4)_3$ structure.

The above mentioned $(RE)_2(WO_4)_3$ compounds are isotopic with $Nd_2(WO_4)_3$ and can be considered as a derivative of the scheelite ($CaWO_4$) structure (Dickinson, 1920). The $(RE)_2(WO_4)_3$ structure is an ordered defect variant with a threefold scheelite supercell. The matrix that relates the scheelite structure with the $(RE)_2(WO_4)_3$ structure is $(110; 00\bar{1}; \bar{2}10)$ (Fig. 1). In the " $Ca_3(WO_4)_3$ " supercell structure one rare earth site is unoccupied, thus leading to the formula $(RE)_2(WO_4)_3$ and distortions of the coordination polyhedra as a consequence.

The Nd^{3+} cations are coordinated by eight oxygen atoms in form of a distorted bi-capped trigonal prism. The Nd—O distances range from 2.387 (4) to 2.497 (4), conform with the RE —O distances in the isotopic compounds. The W atoms are tetrahedrally surrounded by oxygen atoms. The W2 atom lies at Wyckoff site $4e$ with site symmetry 2 and W—O distances between 1.754 (4) and 1.808 (4) Å. The W1 atom is on a general position with similar distances between 1.741 (4) and 1.881 (4) Å. An additional O atom lies 2.149 (4) Å from W1, resulting in an overall '4 + 1' coordination for the W1 atom. These $W(1)O_{4+1}$ polyhedra share edges, thus forming $W(1)_2O_8$ dimers. Together with the $W(2)O_4$ and NdO_8 units, the three-dimensional structure is assembled (Fig. 1).

S2. Experimental

Single crystals of the title compound were obtained from the melt. Analytical grade starting materials Nd_2O_3 (Fluka, 99.9%) and WO_3 (Aldrich, 99.5%) were mixed and heated under atmospheric conditions in a platinum crucible to 1473 K. Then the furnace was slowly cooled to 1273 K during 24 h, held at that temperature for 5 h and then cooled to 1173 K during 30 h. Then the crucible was taken from the furnace and was quenched in water. Light-purple crystals of the title compound suitable for X-ray diffraction studies were broken from a large chunk by gentle crushing between two glass slides.

S3. Refinement

The highest peak is 0.76 Å from W2 and the deepest hole 0.69 Å from the same atom. Finally, structure data were standardized with the program *STRUCTURETIDY* (Gelato & Parthé, 1987).

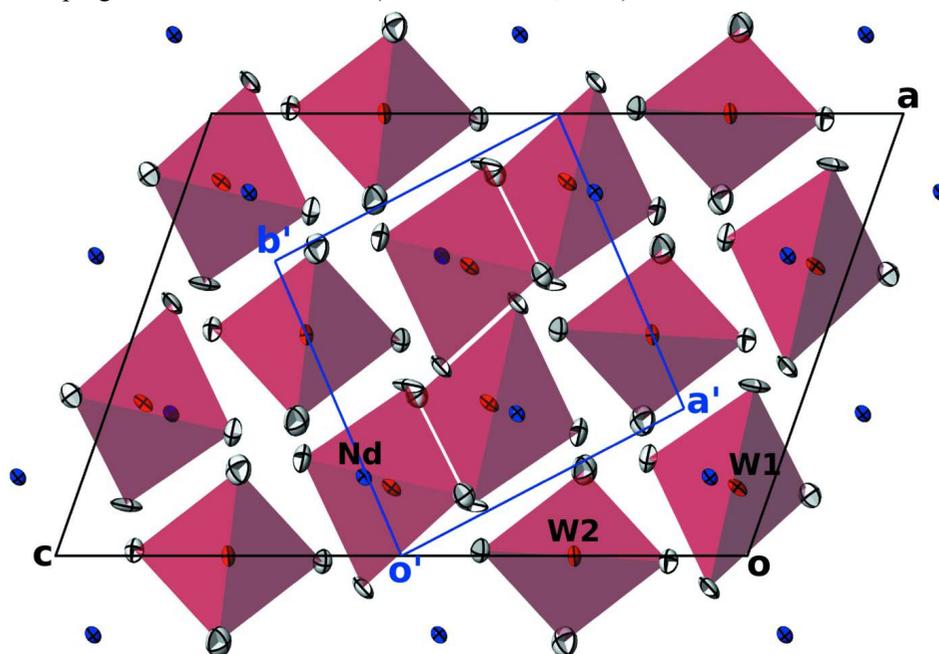


Figure 1

The crystal structure of $\text{Nd}_2(\text{WO}_4)_3$ in a projection along the b -axis, drawn with displacement ellipsoids at the 74% probability level. Nd atoms are given in blue, W atoms in red and O atoms in white. WO_4 units are given as red tetrahedra. Nd—O bonds have been omitted for clarity. The unit cell of the (distorted) scheelite substructure is indicated with blue lines.

dineodymium(III) tris[tungstate(VI)]

Crystal data

$\text{Nd}_2(\text{WO}_4)_3$
 $M_r = 1032.03$
 Monoclinic, $C2/c$
 Hall symbol: $-C\ 2yc$
 $a = 7.7589\ (12)\ \text{\AA}$
 $b = 11.597\ (2)\ \text{\AA}$
 $c = 11.516\ (2)\ \text{\AA}$
 $\beta = 109.561\ (14)^\circ$
 $V = 976.4\ (3)\ \text{\AA}^3$
 $Z = 4$

$F(000) = 1752$
 $D_x = 7.021\ \text{Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$
 Cell parameters from 25 reflections
 $\theta = 10.5\text{--}16.9^\circ$
 $\mu = 45.72\ \text{mm}^{-1}$
 $T = 293\ \text{K}$
 Block, light-purple
 $0.12 \times 0.10 \times 0.08\ \text{mm}$

Data collection

Enraf–Nonius CAD-4
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 $\omega/2\theta$ scans
 Absorption correction: numerical
 (*HABITUS*; Herrendorf, 1997)

$T_{\min} = 0.033$, $T_{\max} = 0.119$
 8392 measured reflections
 2149 independent reflections
 1830 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.082$
 $\theta_{\max} = 35.0^\circ$, $\theta_{\min} = 3.3^\circ$
 $h = -12 \rightarrow 12$

$k = -18 \rightarrow 18$
 $l = -18 \rightarrow 18$

3 standard reflections every 120 min
 intensity decay: none

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.063$
 $S = 1.09$
 2149 reflections
 79 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 $w = 1/[\sigma^2(F_o^2) + (0.0271P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.79 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -5.24 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00516 (13)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Nd	0.17830 (3)	0.12676 (2)	0.59450 (2)	0.00552 (7)
W1	0.15461 (2)	0.355585 (18)	0.048983 (19)	0.00616 (7)
W2	0.0000	0.11826 (3)	0.2500	0.00700 (7)
O1	0.0124 (5)	0.0407 (4)	0.3888 (4)	0.0087 (6)
O2	0.0717 (5)	0.3000 (4)	0.4608 (4)	0.0103 (7)
O3	0.1944 (5)	0.2058 (4)	0.2795 (4)	0.0138 (8)
O4	0.2205 (6)	0.4270 (4)	0.1932 (4)	0.0127 (7)
O5	0.3630 (5)	0.0366 (4)	0.0596 (4)	0.0104 (7)
O6	0.3846 (5)	0.2870 (4)	0.0765 (4)	0.0115 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nd	0.00501 (10)	0.00694 (12)	0.00528 (12)	-0.00035 (7)	0.00262 (8)	0.00007 (8)
W1	0.00522 (9)	0.00682 (10)	0.00802 (10)	-0.00014 (6)	0.00430 (6)	0.00015 (6)
W2	0.00763 (11)	0.01014 (13)	0.00401 (12)	0.000	0.00297 (8)	0.000
O1	0.0106 (15)	0.0089 (16)	0.0069 (15)	-0.0007 (12)	0.0032 (12)	0.0005 (12)
O2	0.0089 (14)	0.0138 (18)	0.0111 (17)	0.0023 (13)	0.0074 (12)	0.0020 (14)
O3	0.0163 (17)	0.0133 (19)	0.0120 (18)	-0.0018 (14)	0.0050 (14)	-0.0037 (15)
O4	0.0142 (15)	0.0180 (19)	0.0057 (15)	0.0012 (15)	0.0031 (12)	-0.0004 (14)
O5	0.0110 (15)	0.0111 (17)	0.0102 (17)	-0.0023 (13)	0.0048 (13)	0.0025 (14)
O6	0.0035 (13)	0.0133 (18)	0.0178 (19)	-0.0002 (12)	0.0036 (13)	-0.0059 (15)

Geometric parameters (Å, °)

Nd—O4 ⁱ	2.387 (4)	W1—O5 ^v	1.741 (4)
Nd—O2 ⁱ	2.391 (4)	W1—O4	1.771 (4)
Nd—O3 ⁱ	2.427 (5)	W1—O2 ^{vi}	1.838 (4)
Nd—O6 ⁱⁱ	2.433 (4)	W1—O6	1.881 (4)
Nd—O1 ⁱⁱⁱ	2.487 (4)	W1—O6 ^v	2.149 (4)
Nd—O5 ^{iv}	2.488 (4)	W2—O3	1.754 (4)
Nd—O1	2.495 (4)	W2—O3 ^{vi}	1.754 (4)
Nd—O2	2.497 (4)	W2—O1 ^{vi}	1.808 (4)
Nd—Nd ⁱ	3.9708 (7)	W2—O1	1.808 (4)
O4 ⁱ —Nd—O2 ⁱ	110.36 (14)	O5 ^v —W1—O4	105.4 (2)
O4 ⁱ —Nd—O3 ⁱ	70.63 (16)	O5 ^v —W1—O2 ^{vi}	111.35 (18)
O2 ⁱ —Nd—O3 ⁱ	70.79 (14)	O4—W1—O2 ^{vi}	101.06 (18)
O4 ⁱ —Nd—O6 ⁱⁱ	99.92 (14)	O5 ^v —W1—O6	105.45 (19)
O2 ⁱ —Nd—O6 ⁱⁱ	130.65 (14)	O4—W1—O6	94.60 (19)
O3 ⁱ —Nd—O6 ⁱⁱ	84.51 (15)	O2 ^{vi} —W1—O6	134.0 (2)
O4 ⁱ —Nd—O1 ⁱⁱⁱ	73.56 (14)	O5 ^v —W1—O6 ^v	96.3 (2)
O2 ⁱ —Nd—O1 ⁱⁱⁱ	148.71 (14)	O4—W1—O6 ^v	157.2 (2)
O3 ⁱ —Nd—O1 ⁱⁱⁱ	135.38 (14)	O2 ^{vi} —W1—O6 ^v	76.80 (16)
O6 ⁱⁱ —Nd—O1 ⁱⁱⁱ	76.29 (14)	O6—W1—O6 ^v	72.57 (17)
O4 ⁱ —Nd—O5 ^{iv}	87.53 (15)	O3—W2—O3 ^{vi}	109.3 (3)
O2 ⁱ —Nd—O5 ^{iv}	70.42 (14)	O3—W2—O1 ^{vi}	104.30 (18)
O3 ⁱ —Nd—O5 ^{iv}	124.37 (14)	O3 ^{vi} —W2—O1 ^{vi}	109.20 (19)
O6 ⁱⁱ —Nd—O5 ^{iv}	150.80 (14)	O3—W2—O1	109.20 (19)
O1 ⁱⁱⁱ —Nd—O5 ^{iv}	78.93 (13)	O3 ^{vi} —W2—O1	104.30 (18)
O4 ⁱ —Nd—O1	139.13 (15)	O1 ^{vi} —W2—O1	120.3 (3)
O2 ⁱ —Nd—O1	95.50 (13)	W2—O1—Nd ⁱⁱⁱ	126.85 (18)
O3 ⁱ —Nd—O1	149.90 (14)	W2—O1—Nd	119.87 (19)
O6 ⁱⁱ —Nd—O1	84.99 (14)	Nd ⁱⁱⁱ —O1—Nd	111.72 (15)
O1 ⁱⁱⁱ —Nd—O1	68.28 (15)	W1 ^{vi} —O2—Nd ⁱ	134.6 (2)
O5 ^{iv} —Nd—O1	71.57 (13)	W1 ^{vi} —O2—Nd	115.63 (18)
O4 ⁱ —Nd—O2	140.26 (15)	Nd ⁱ —O2—Nd	108.61 (14)
O2 ⁱ —Nd—O2	71.39 (14)	W2—O3—Nd ⁱ	136.9 (2)
O3 ⁱ —Nd—O2	73.11 (15)	W1—O4—Nd ⁱ	137.0 (3)
O6 ⁱⁱ —Nd—O2	60.61 (13)	W1 ^v —O5—Nd ^{vii}	138.8 (2)
O1 ⁱⁱⁱ —Nd—O2	126.35 (12)	W1—O6—W1 ^v	107.43 (17)
O5 ^{iv} —Nd—O2	127.07 (13)	W1—O6—Nd ^{viii}	130.5 (2)
O1—Nd—O2	77.15 (13)	W1 ^v —O6—Nd ^{viii}	106.94 (16)

Symmetry codes: (i) $-x+1/2, -y+1/2, -z+1$; (ii) $x-1/2, -y+1/2, z+1/2$; (iii) $-x, -y, -z+1$; (iv) $x, -y, z+1/2$; (v) $-x+1/2, -y+1/2, -z$; (vi) $-x, y, -z+1/2$; (vii) $x, -y, z-1/2$; (viii) $x+1/2, -y+1/2, z-1/2$.