

Rubidium sodotricadmate,  $\text{Rb}[\text{NaCd}_3\text{O}_4]$ 

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## Key indicators

Single-crystal X-ray study

 $T = 293\text{ K}$ Mean  $\sigma(\text{O}—\text{O}) = 0.002\text{ Å}$ 

Disorder in main residue

 $R$  factor = 0.041 $wR$  factor = 0.098

Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

$\text{Rb}[\text{NaCd}_3\text{O}_4]$  presents, to the best of our knowledge, the first example of a  $4d$  transition metal oxide in this  $A[(\text{MO})_4]$  structure type. The structure consists of a three-dimensional network of edge- and corner-linked distorted tetrahedral  $[\text{MO}_4]$  entities, with  $M = \text{Na}^+$  and  $\text{Cd}^{2+}$  in a 1:3 ratio sharing a common site set on Wyckoff position  $8h$  in space group  $I4/m$ . The large cavities are occupied by  $A = \text{Rb}^+$  in an almost cubic coordination ( $4/m$  symmetry), giving rise to one-dimensional chains of face-sharing  $[\text{RbO}_8]$  polyhedra along  $[001]$ .

## Comment

$\text{Rb}[\text{NaCd}_3\text{O}_4]$ , (I), is isotypic with  $\text{Rb}[\text{LiMn}_3\text{O}_4]$ , (II), and  $\text{Rb}[\text{LiZn}_3\text{O}_4]$ , (III) (Hoppe *et al.*, 1988). The structure consists of edge- and corner-sharing distorted tetrahedral  $[\text{MO}_4]$  units [ $M = \text{Na}^+$  and  $\text{Cd}^{2+}$  in (I), and  $\text{Li}^+$  and  $\text{Mn}^{2+}$  or  $\text{Zn}^{2+}$  in (II) and (III)], forming a three-dimensional network (Fig. 1). These cation pairs differ in charge and share a common crystallographic site,  $8h$ . The differences in their effective ionic radii according to Shannon (1976) are  $0.21\text{ Å}$  for (I),  $0.07\text{ Å}$  for (II) and  $0.00\text{ Å}$  for (III). The mean interatomic distance  $M—\text{O}$  of  $2.20\text{ Å}$  in (I) is in agreement with the weighted average value of  $2.21\text{ Å}$  calculated from  $\frac{3}{4}(\text{Cd}—\text{O}) + \frac{1}{4}(\text{Na}—\text{O})$ . Distortion of these  $[\text{MO}_4]$  units occurs as a consequence of the three-dimensional connectivity. The  $\text{O}—M—\text{O}$  angles in (I) differ from the ideal value of  $109.5^\circ$  by  $-16^\circ$  [ $93.5(2)^\circ$ ] for a common edge and by  $10^\circ$  [ $119.4(3)^\circ$ ],  $5^\circ$  [ $114.5(4)^\circ$ ] and  $-1^\circ$  [ $108.5(5)^\circ$ ] for the linkages *via* apices. In comparison with (II)

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Dedicated to Professor Josef Hahn on the occasion of his 65th birthday.

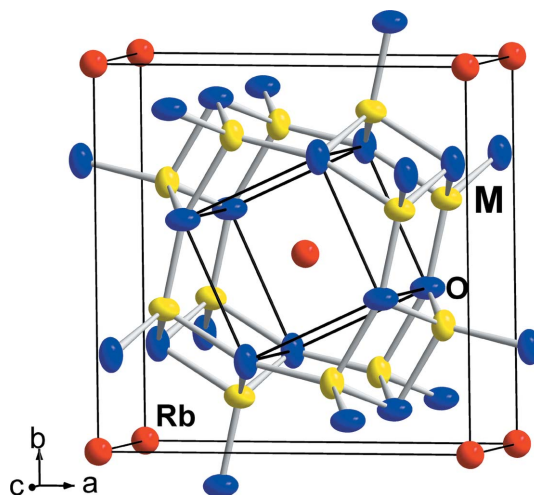


Figure 1

A perspective view of the crystal structure of  $\text{Rb}[\text{NaCd}_3\text{O}_4]$ , showing the atom-labelling scheme and 75% probability displacement ellipsoids. The cubic cavity centred by Rb is indicated by bold lines.

and (III), all angles decrease, with larger differences of the ionic radii for a given pair  $M^+/M^{2+}$ , apart from the largest O—M—O angle, which increases along the series. The average O—M—O angle is approximately  $108^\circ$  for this structure type.

The three-dimensional framework of connected  $[MO_4]$  units displays rather low densities in the case of these compounds. An overview of the framework density for silicates and aluminosilicates was given by Liebau (1985), and a reduction of approximately seven tetrahedral units per  $1000 \text{ \AA}^3$  relative to quartz marks the onset of clathrasil and zeolite types of structures. Since the structure of ZnO (Sawada *et al.*, 1996) is known, we can use the given definition to obtain the framework densities  $d_f(\text{ZnO})$  and  $d_f(\text{III})$  of 42.0 and 34.7 tetrahedral units per  $1000 \text{ \AA}^3$ , respectively. This qualitatively marks the onset of open framework types of structure. Due to the increasing M—O distances, compounds (II) and (I) have even lower  $d_f$  values, of 32.8 and 27.0 tetrahedral units per  $1000 \text{ \AA}^3$ , respectively.

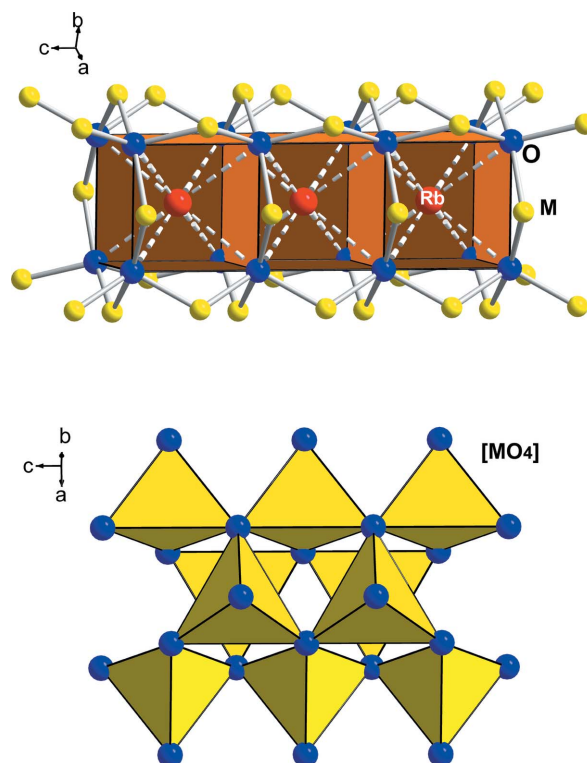
As in aluminosilicates, the framework has a negative charge, which has to be compensated for by a cation, in the case of (I) by  $\text{Rb}^+$ . The two cavities present in this structure type of linked tetrahedra are face- and edge-sharing along  $[001]$ . The cubic cage (Fig. 2, top), with an average edge length of  $3.62 \text{ \AA}$  in (I), is occupied by  $\text{Rb}^+$  and is approximately  $0.21 \text{ \AA}$  larger than in (II), again highlighting the differences in the sizes of the respective  $[MO_4]$  entities.

The deviations from an ideal cubic  $[\text{RbO}_8]$  coordination are relatively small in terms of the expected angles, and all distances are equal to  $3.137(8) \text{ \AA}$  within standard deviations. Due to the larger ionic radius of  $\text{Rb}^+$  compared with  $\text{Cd}^{2+}$  and  $\text{Na}^+$ , the sixfold coordination of O resembles a drastically distorted octahedron, consisting of four M and two Rb atoms. The latter atoms are in a *cis*-arrangement, with an Rb—O—Rb angle of  $72.1(2)^\circ$ . The *trans* constituents display M—O—Rb angles of  $155.9(4)^\circ$  and M—O—M angles of  $161.5(5)^\circ$ .

The second cavity (Fig. 2, bottom) is of an octahedral shape, with two opposite triangular faces being shared with tetrahedral units. Although the O—(cavity centre) distances of approximately  $2.94 \text{ \AA}$  are within the range of common Rb—O distances, this site cannot be occupied by a cation, because the resulting cation—M distances would be too short. Therefore, this channel remains empty.

## Experimental

$\text{Rb}[\text{NaCd}_3\text{O}_4]$  was obtained as a by-product from the reaction of  $\text{Rb}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3$ , V and  $\text{CdO}$  (molar ratio 6:1:1:1) in a silver crucible, which was loaded and sealed under an argon atmosphere. For safety reasons, this container was enclosed under a vacuum within a silica ampoule. The reaction mixture was heated directly to  $523 \text{ K}$  and then heated at a rate of  $20 \text{ K h}^{-1}$  to  $973 \text{ K}$ . After 40 h, the sample was cooled to  $673 \text{ K}$  ( $1.5 \text{ K h}^{-1}$ ) and then to  $523 \text{ K}$  ( $2 \text{ K h}^{-1}$ ); the furnace was then switched off. At lower temperatures alkali metal cadmate(s) are formed, *e.g.*  $\text{Rb}_6\text{CdO}_4$ ,  $\text{Rb}_2\text{CdO}_2$  or  $\text{Rb}_2\text{Cd}_2\text{O}_3$  (Baier *et al.* 1987). These intermediate products react with the vanadium metal in a redox reaction (Möller, 2005), yielding oxovanadate(s) and cadmium metal. Here, this process was not complete and we obtained



**Figure 2**

The two different one-dimensional linked cavities created by the three-dimensional connectivity of the tetrahedral  $[MO_4]$  units, with M = Na or Cd denoted by yellow and O by blue. Illustrated at the top are the Rb (red) centred cavities, and at the bottom the empty cavities.

$\text{Rb}[\text{NaCd}_3\text{O}_4]$ , a rather alkali metal-poor compound. The main product was a yellowish, almost colourless, poorly crystallized powder of as yet unknown composition. Small quantities of orange-red single crystals of irregular shape, which were selected under a microscope in an argon-filled dry box and mounted in glass capillaries, were identified as  $\text{Rb}[\text{NaCd}_3\text{O}_4]$ . The composition of these crystals was determined by single-crystal X-ray diffraction techniques and checked by energy-dispersive X-ray experiments, providing the confirmation that Rb, Na and Cd are the only metals present in this compound.

## Crystal data

$\text{Rb}[\text{NaCd}_3\text{O}_4]$

$M_r = 509.69$

Tetragonal,  $I4/m$

$a = 8.957(2) \text{ \AA}$

$c = 3.694(1) \text{ \AA}$

$V = 296.4(2) \text{ \AA}^3$

$Z = 2$

$D_x = 5.712 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\mu = 18.82 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Irregular block, orange-red  
 $0.27 \times 0.15 \times 0.10 \text{ mm}$

## Data collection

Stoe IPDS-I diffractometer

$\varphi$  scans

Absorption correction: numerical

[*X-RED32* (Stoe & Cie, 2001), after optimizing the crystal shape using *X-SHAPE* (Stoe & Cie, 1999)]

$T_{\min} = 0.026$ ,  $T_{\max} = 0.145$

1250 measured reflections

203 independent reflections

192 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\max} = 27.8^\circ$

## Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$\Delta\rho_{\max} = 2.03 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.098$	$\Delta\rho_{\min} = -1.87 \text{ e } \text{\AA}^{-3}$
$S = 1.21$	Extinction correction: <i>SHELXL97</i>
203 reflections	(Sheldrick, 1997)
16 parameters	Extinction coefficient: 0.012 (2)
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 3.5767P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ). $M = \text{Na}$  and  $\text{Cd}$ .

Rb—O <sup>i</sup>	3.137 (8)	M—O <sup>iii</sup>	2.196 (5)
M—O	2.123 (9)	M—O <sup>iv</sup>	2.294 (9)
M—O <sup>ii</sup>	2.196 (5)		
O <sup>i</sup> —Rb—O <sup>v</sup>	180.0 (2)	M—O—M <sup>viii</sup>	103.2 (3)
O <sup>i</sup> —Rb—O <sup>vi</sup>	69.7 (1)	M <sup>viii</sup> —O—M <sup>ix</sup>	114.5 (4)
O <sup>v</sup> —Rb—O <sup>vi</sup>	110.3 (1)	M—O—M <sup>x</sup>	161.5 (5)
O <sup>i</sup> —Rb—O <sup>vii</sup>	72.1 (2)	M <sup>viii</sup> —O—M <sup>x</sup>	86.5 (2)
O <sup>v</sup> —Rb—O <sup>vii</sup>	107.9 (2)	M—O—M <sup>x</sup>	161.5 (5)
O—M—O <sup>ii</sup>	119.4 (3)	M—O—Rb <sup>xi</sup>	83.8 (2)
O—M—O <sup>iii</sup>	119.4 (3)	M <sup>viii</sup> —O—Rb <sup>xi</sup>	155.9 (4)
O <sup>ii</sup> —M—O <sup>iii</sup>	114.5 (4)	M <sup>ix</sup> —O—Rb <sup>xi</sup>	85.5 (1)
O—M—O <sup>iv</sup>	108.5 (5)	M <sup>x</sup> —O—Rb <sup>xi</sup>	81.2 (2)
O <sup>ii</sup> —M—O <sup>iv</sup>	93.5 (2)	Rb <sup>xi</sup> —O—Rb <sup>xii</sup>	72.1 (2)
O <sup>iii</sup> —M—O <sup>iv</sup>	93.5 (2)		

Symmetry codes: (i)  $-y + \frac{1}{2}, x - \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $y + \frac{1}{2}, -x + \frac{3}{2}, -z + \frac{1}{2}$ ; (iii)  $y + \frac{1}{2}, -x + \frac{3}{2}, -z - \frac{1}{2}$ ; (iv)  $-y + 1, x, z$ ; (v)  $y - \frac{1}{2}, -x + \frac{1}{2}, -z - \frac{1}{2}$ ; (vi)  $x - \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$ ; (vii)  $-y + \frac{1}{2}, x - \frac{1}{2}, z - \frac{1}{2}$ ; (viii)  $-y + \frac{3}{2}, x - \frac{1}{2}, z + \frac{1}{2}$ ; (ix)  $-y + \frac{3}{2}, x - \frac{1}{2}, z - \frac{1}{2}$ ; (x)  $y, -x + 1, -z$ ; (xi)  $x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$ ; (xii)  $x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$ .

The highest peak was observed 0.38  $\text{\AA}$  from Rb and the deepest hole 0.87  $\text{\AA}$  from the  $M$  site. The site-occupancy factors for  $M = \text{Na}$  and  $\text{Cd}$  were constrained to 0.25 and 0.75, respectively. Furthermore, the constraint of equal atomic coordinates and atomic displacement parameters was applied for these two statistically disordered atoms.

Data collection: *IPDS* (Stoe & Cie, 1997); cell refinement: *IPDS*; data reduction: *X-RED32* (Stoe & Cie, 2001); program used to solve structure: *SHELXS97* (Sheldrick, 1997); program used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *CIF-Editor* (Wieczorrek, 1999).

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