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Synthesis and crystal structure of anhydrous Na[MnO₄]

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Abstract: There are numerous reports in the literature about the amount of hydrate water in sodium permanganate, which is said to be between one half and three water molecules per Na[MnO₄]. Because no structural descriptions of the hydrate and the anhydrous compound can be found yet, this work reports the synthesis of anhydrous Na[MnO₄] via the Muthmann method and its crystal structure. Na[MnO₄] crystallizes as dark purple needles in the monoclinic space group $P2_1/n$ with $a = 572.98(5)$, $b = 842.59(7)$, $c = 715.47(6)$ pm, $\beta = 92.374(3)^\circ$ and $Z = 4$. As such and with its isotype to Ag[MnO₄], Na[MnO₄] completes the series of anhydrous alkali-metal permanganates, comprising Li[MnO₄] (orthorhombic, $Cmcm$, Cr[VO₄] type) and the isostructural heavier congeners A[MnO₄] ($A = K, Rb, Cs$; orthorhombic, $Pnma$, Ba[SO₄] type).

Keywords: crystal structures; permanganates; sodium.

Dedicated to: Professor Hanskarl Müller-Buschbaum on the occasion of his 85th birthday.

1 Introduction

Several permanganates of sodium have been reported in the literature [1–3], but all of them seem to contain water of hydration in varying amounts, ranging from Na[MnO₄] · 1/2 H₂O to Na[MnO₄] · 3 H₂O. Neither of these publications offers a detailed crystal structure of the reported products, however. The work reported shows a successful way to synthesize anhydrous Na[MnO₄] and its crystal structure determination, which clearly reveals the isotype to Ag[MnO₄] [4–6], exhibiting a sevenfold coordinated Na⁺

cation carrying seven independent, vertex-grafted, isolated [MnO₄][−] anions.

2 Results and discussion

We were successful in synthesizing anhydrous Na[MnO₄], as opposed to the various hydrated products mentioned in the literature [1–3]. The thin, dark purple needles of Na[MnO₄] adopt the monoclinic space group $P2_1/n$ (no. 14) with $a = 572.98(5)$, $b = 842.59(7)$, $c = 715.47(6)$ pm and $\beta = 92.374(3)^\circ$ for four formula units per unit cell (Table 1). In the crystal structure of Na[MnO₄] (Table 2), the unique Na⁺ cations reside in a sevenfold oxygen coordination, resulting in a distorted pentagonal bipyramid (Fig. 1) as coordination sphere with $d(\text{Na–O}) = 235\text{–}277$ pm (Table 3). These [NaO₇]^{13−} polyhedra are connected to strands via two O2 atoms, which become further linked to adjacent strands through shared O3···O3 and O4···O4 edges. Because of the helical nature of a singular chain, these strands join together with other strands of this kind to form the achiral $^3\{[\text{Na}(\text{O}1)_{1/1}(\text{O}2)_{2/2}(\text{O}3)_{2/2}(\text{O}4)_{2/2}]^{7−}\}$ framework (Fig. 2), thereby generating the missing space group symmetry elements of a glide plane (n) perpendicular to the screw axis (2₁) and thus the inversion center. The O1 atom, which contributes only once to a [NaO₇]^{13−} polyhedron, points into channels running along [010], filled by the Mn⁷⁺ cations thereby forming isolated [MnO₄][−] tetrahedra (Fig. 3) with $d(\text{Mn–O}) = 159\text{–}162$ pm. In isotypic Ag[MnO₄], the Mn–O distances within the permanganate units are slightly longer and range between 160 and 164 pm, while its lattice parameters ($a = 562.3(4)$, $b = 834.9(5)$, $c = 714.0(5)$ pm, $\beta = 92.44(5)^\circ$ [6]) are smaller as compared to Na[MnO₄]. This causes markedly shorter Ag–O distances (230–267 pm) in a more narrow interval than for the Na–O distances in Na[MnO₄], where only six of them range from 235 to 259 pm, while the seventh one (Na–O2') is 277 pm long. In this particular case, the stronger covalently bonded Ag⁺ cation ($\Delta EN(\text{Ag}/\text{O}) = 1.5$ vs. $\Delta EN(\text{Na}/\text{O}) = 2.5$) [11], which is considered larger ($r_i = 115$ pm for $CN = 6$) [12] than Na⁺ ($r_i = 102$ pm for $CN = 6$) [12], does not only lead to a shrinking of the unit cell in comparison to Na[MnO₄], but seems to compensate this marginally by expanding the [MnO₄][−] tetrahedron.

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Table 1: Crystallographic data for Na[MnO₄] and numbers pertinent to data collection and structure refinement.^a

Formula	Na[MnO ₄]
Molecular mass M_r	141.93
Crystal system	monoclinic
Space group	$P2_1/n$ (no.14)
Formula units, Z	4
Lattice constants a , pm	572.98(5)
b , pm	842.59(7)
c , pm	715.47(6)
β , deg	92.374(3)
Calculated density D_x , g cm ⁻³	2.732
Molar volume V_m , cm ³ mol ⁻¹	51.97(2)
Electron sum, $F(000)/e$	272
Diffractometer; radiation	IPDS-I (STOE); MoK α
Wavelength λ , pm	$\lambda = 71.07c$
Index range, $\pm h, \pm k, \pm l$	10, 12, 8
θ range, deg	2.8–28.3
Absorption coefficient μ , mm ⁻¹	3.79
Number of refined parameters	56
Refined extinction coefficient, g	0.130(12)
Data corrections	Background, polarization and Lorentz factors; numerical absorption correction; program HABITUS [7]
Collected vs. unique reflections	4941, 1280
R_{int}, R_σ	0.049, 0.043
Structure solution and refinement	Program package SHELXS/L-97 [8, 9]
Scattering factors	International tables, Vol. C [10]
R_1 , reflections with $ F_o > 4 \sigma(F_o)$	0.066; 879
$R_1; wR_2$ for all reflections	0.045; 0.122
Goodness of fit (GooF)	1.032
Residual electron densities ($\rho/e \cdot 10^{-6}$ pm ³), min; max	-0.60; 0.93

^aFurther details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, <https://www.fiz-karlsruhe.de/en/leistungen/kristallographie/kristallstrukturdepot/order-form-request-for-deposited-data.html>) on quoting the deposition number CSD-431105.

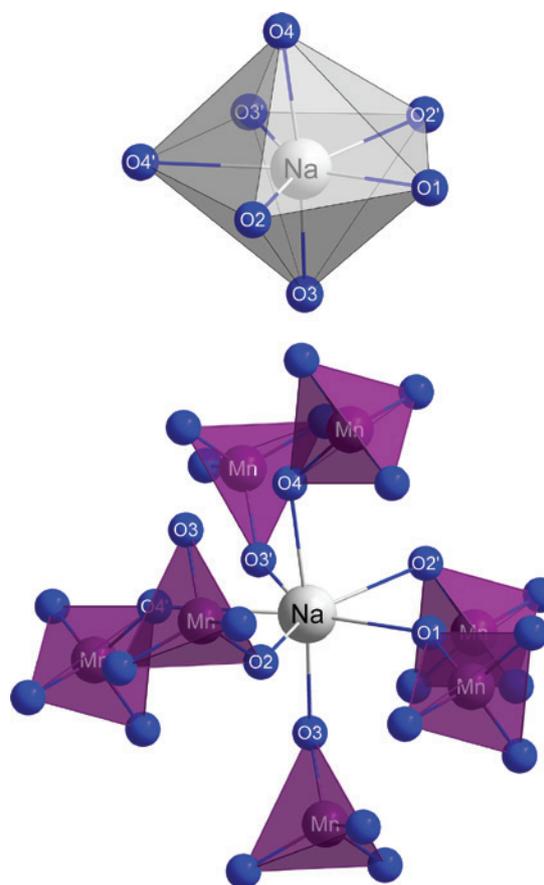
3 Conclusions

Anhydrous Na[MnO₄] with its sevenfold coordinated sodium cations crystallizes in the monoclinic space group $P2_1/n$ and thus isotypically with Ag[MnO₄] [6]. It fits well into the series of the anhydrous alkali-metal permanganates, which starts with Li[MnO₄] [13] crystallizing in the orthorhombic space group $Cmcm$ with the Cr[VO₄]-type structure and displaying a sixfold coordination of oxygen around the Li⁺ cations. The permanganates A[MnO₄] of the heavier homologues potassium, rubidium and cesium [14–16] all crystallize in the orthorhombic space group $Pnma$ with the very flexible and adaptive baryte-type

Table 2: Fractional atomic coordinates and equivalent isotropic displacement parameters (U_{eq} , pm²) for Na[MnO₄].

Atom	x/a	y/b	z/c	U_{eq} , pm ²
Na	0.2518(3)	0.0364(2)	0.1593(2)	385(4)
Mn	0.25709(9)	0.18805(6)	0.65959(7)	267(2)
O1	0.2511(6)	0.0616(4)	0.4932(4)	440(7)
O2	0.9932(6)	0.2235(4)	0.7159(4)	414(6)
O3	0.8802(6)	0.1504(3)	0.0917(4)	393(6)
O4	0.4049(6)	0.1171(4)	0.8381(4)	400(6)

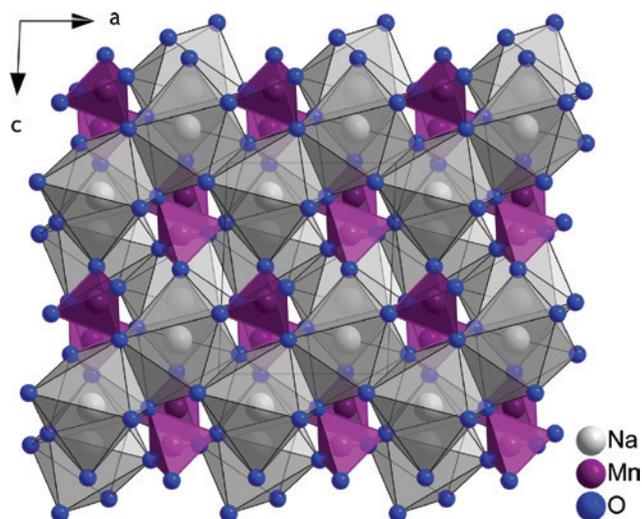
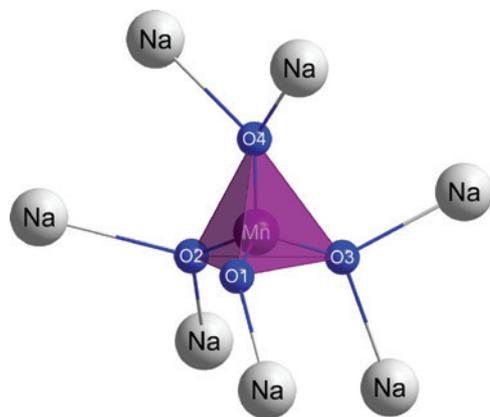
All atoms occupy the general Wyckoff sites $4e$.

**Fig. 1:** Coordination sphere of the [NaO₇]¹³⁻ polyhedron in Na[MnO₄] (top) and its connectivity to seven vertex-grafted [MnO₄]³⁻ tetrahedra (bottom).

structure of Ba[SO₄] allowing for an 8- to 12-fold coordination of the A⁺ cations (A = K, Rb, Cs) by oxygen atoms. As opposed to what can be found in the literature, where sodium permanganate occurs with from one half up to three water molecules per formula unit, the sodium permanganate now prepared via the Muthmann method crystallizes anhydrously just like the structurally prototypic Ag[MnO₄], even though the samples are synthesized from aqueous solution.

Table 3: Motifs of mutual adjunction, selected interatomic distances (d , pm) and bond angles (\angle , deg) in Na[MnO₄].

	O1	O2	O3	O4
Na	1/1 239.8(4)	2/2 247.5(3) 276.9(4)	2/2 236.7(3) 248.2(3)	2/2 235.5(3) 258.4(3)
Mn	1/1 159.7(3) -O2: 108.6(2) -O3: 109.5(2)	1/1 160.9(3) -O3: 110.2(2) -O4: 109.7(2)	1/1 161.7(3) -O4: 109.1(2)	1/1 161.8(3) -O1: 109.7(2)

**Fig. 2:** View at the crystal structure of Na[MnO₄] along [010]. The fusion of the [NaO₇]¹³⁻ polyhedra forms channels along the b axis, in which the isolated [MnO₄]⁻ tetrahedra reside.**Fig. 3:** The isolated permanganate anion [MnO₄]⁻ in Na[MnO₄] shown as a tetrahedron with its immediate Na⁺ surrounding.

4 Experimental section

Na[MnO₄] was synthesized by adding 100 mmol Na₂[SO₄] dissolved in 50 mL demineralized water to a solution

of 100 mmol Ba[MnO₄]₂ in 50 mL demineralized water, obtained through the Muthmann method described elsewhere in detail [17, 18]. After the complete metathesis and the removal of the precipitated Ba[SO₄] from the deep purple solution, needle-shaped single crystals, a few millimeters in length, of anhydrous Na[MnO₄] with the same color grew by fast isothermal evaporation in a P₂O₅-filled, evacuated desiccator. We were successful in synthesizing a single-phase product, from which we selected thin, needle-shaped, dark purple crystals for single-crystal X-ray diffraction.

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