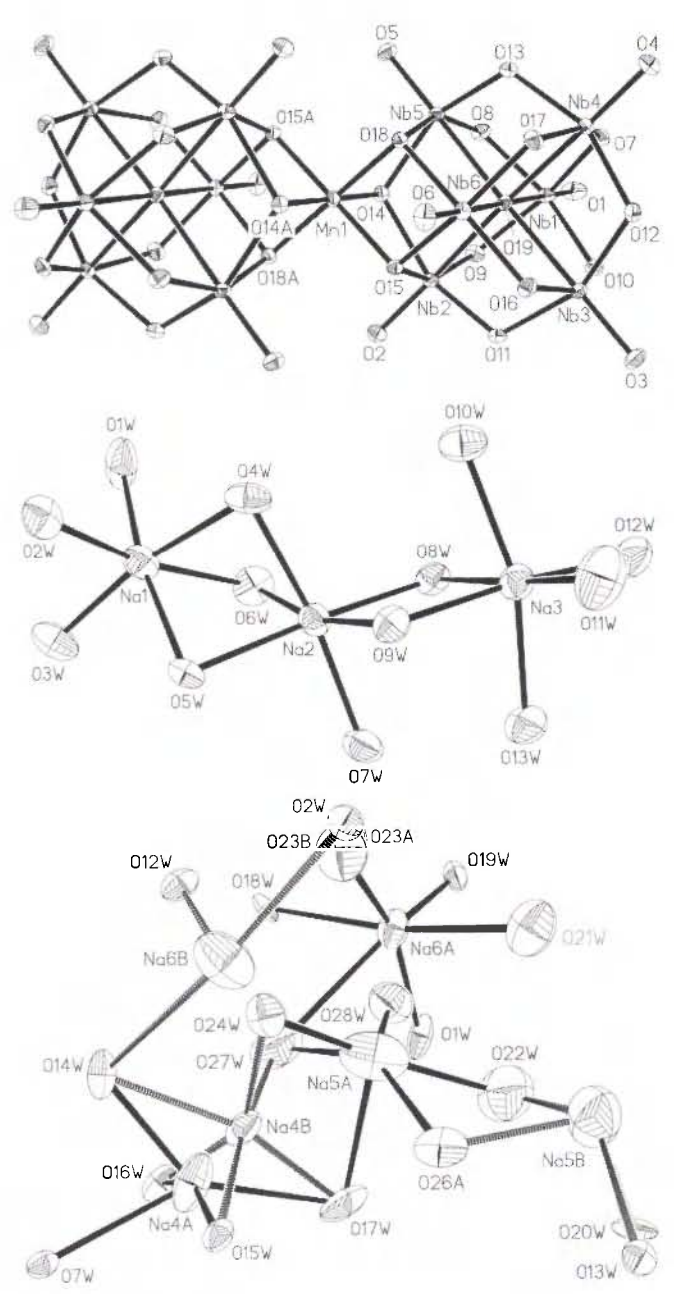
Z. Kristallogr. NCS 221 (2006) 235-237 / DOI 10.1524/ncrs.2006.0053

Re-investigation of the crystal structure of dodecasodium dodecaniobomanganate(IV) hydrate (1:52), $Na_{12}[Mn(Nb_6O_{19})_2] \cdot 52H_2O$

J.-P. Wang, P.-T. Ma and J.-Y. Niu*

Henan University, School of Chemistry and Chemical Engineering, Institute of Molecule and Crystal Engineering, Kaifeng, Henan 475001, P. R. China

Received February 26, 2006, accepted and available on-line June 14, 2006; CSD no. 409866



Abstract

$H_{114}MnNa_6Nb_{12}O_{92}$, monoclinic, $P12_1/n1$ (no. 14), a = 14.165(2) Å, b = 12.694(2) Å, c = 24.202(3) A, β = 92.500(2)°, V = 4347.7 A^3, Z = 2, $R_{gt}(F)$ = 0.030, $wR_{ref}(F^2)$ = 0.084, T = 293 K.

* Correspondence author (e-mail: jyniu@henu.edu.cn)

Source of material

The $K_7H[Nb_6O_{19}] \cdot 13H_2O$ was prepared by the literature method [1]. The crystals of $Na_{12}[Mn(Nb_6O_{19})_2] \cdot 52H_2O$ were synthesized from a solution containing $K_7H[Nb_6O_{19}] \cdot 13H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and Na_2CO_3, in hot water (50 mL) with the molar ratio 2:1:24 for half an hour at 80 °C. The mixture was cooled to room temperature and filtered. Following evaporation in ambient environment, crystals were obtained with high yield after 2 days.

Experimental details

All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were not located.

Discussion

Polyoxometalates are a significant class of inorganic compounds, which exhibit an enormous structural variety combined with fascinating properties [2-3]. Their chemistry is mainly dominated by those of W, Mo and V. The polyoxoanions can be formed simply by acidification of solution of their oxoanions at ambient conditions. Nevertheless, polyoxoniobates chemistry dominated by the formation of the Linqvist-type precursors anion $[Nb_6O_{19}]^{8-}$ are difficult to realize in similar chemical environment. The isopolyniobate precursor can be obtained from basic solution [4]. The formation and structure of the analogous compound sodium 12-niobomanganate(1V), $Na_{12}MnNb_{12}O_{38} \cdot 50H_2O$, have been reported [5-6]. Recently, two novel Keggin type heteropolyniobates, $[TNb_{12}O_{40}]^{10-}$ (T = Si or Ge) and $[H_4Si_4Nb_{16}O_{56}]^{14-}$ were prepared by hydrothermal method [7], and, subsequently, heteropolyniobates related to research with respect to Keggin type were reported [8,9].

Except for twelve sodium ions acting as counter cations, the crystal structure of the title compound is composed of a dimeric polyoxoanion $[Mn(Nb_6O_{19})_2]^{12-}$ and fifty-two crystal water molecules. The polyoxoanion $[Mn(Nb_6O_{19})_2]^{12-}$ consists of two Linqvist-type $[Nb_6O_{19}]^{8-}$ moieties linked by a Mn^{IV} atom, resulting in a sandwich-type structure with idealized D_{3d} symmetry (figure, top). The symmetrical $[Nb_6O_{19}]^{8-}$ subunit is fused together with six edge-shared NbO_6 octahedra, in which the oxygen atoms can be divided into three groups: O_t (terminal oxygen and just connecting to one Nb atom), O_b (bridging oxygen and connecting edge-shared NbO_6 octahedra) and O_c (oxygen atom connecting the six NbO_6 octahedra in the center of cage). Relevant Nb—O bonds can be classified in three categories: (1) Nb—O_t, varied from 1.767(3) Å to 1.779(3) Å; (2) Nb—O_b, being in the range of 1.910(3) Å – 2.111(3) Å; (3) Nb—O_c, 2.366(3) Å – 2.430(3) Å with the mean bond distance of 2.391 Å. It can be noted that the bond distances of Nb—O14, Nb—O15 and Nb—O18 are longer than other Nb—O_b bonds, because O14, O15 and O18 are coordinated to manganese center. Bond-valence sum [10] calculations demonstrate the oxidation state of manganese atom is +4, which

is consistent with the previous literature [6]. The manganese atom is bound to two $[Nb_6O_{19}]^{8-}$ moieties via six bridging oxygen atoms from the two moieties. The MnO_6 group is a distorted octahedron with Mn—O bond lengths in the range of 1.902(3) Å – 1.908(3) Å, corresponding to their mean value 1.905 Å, which is obviously longer than the mean Mn—O bond distance (1.87 Å) for the sodium dodecaniobomanganate(IV) $Na_{12}MnNb_{12}O_{38} \cdot 50H_2O$ [6]. The results may be due to the bad quality of crystal data (R_F = 11.6 %) in reported literature [6]. While the bond angles in the MnO_6 group are 83.9(1)° – 96.1(1)°, the O14-Mn-O14′ axis is just along the threefold axis of polyoxoanion. Beside the polyoxoanion, twelve sodium cations and fifty-two water molecules were found in one half of the unit cell (figure, middle and bottom). Six of the sodium cations are disordered, joined together via different water molecules and adopt five- and six-coordinations (figure, bottom). Moreover, the sodium atom Na6B has a distance of 2.79(1) Å to the O12 oxygen atom of the polyoxoanion. At the same time, it is linked with the water molecule O12W, which is also connected to the other sodium atom Na3. One water molecule (O25W) has no bonds with sodium ions.

Table 1. Data collection and handling.

Crystal:	brown block, size 0.16 × 0.18 × 0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	18.19 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS IV, ω/φ
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	22101, 7657
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6873
$N(param)_{refined}$:	583
Programs:	SHELXS-97 [11], SHELXL-97 [12]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)	4e		0.11127(3)	0.18891(3)	0.18698(2)	0.0226(2)	0.0160(2)	0.0231(2)	−0.0019(1)	−0.0061(2)	−0.0009(1)
Nb(2)	4e		0.11626(2)	−0.02610(3)	0.10781(2)	0.0167(2)	0.0162(2)	0.0210(2)	0.0010(1)	−0.0003(1)	0.0009(1)
Nb(3)	4e		−0.01359(3)	−0.02466(3)	0.21846(2)	0.0239(2)	0.0183(2)	0.0178(2)	−0.0002(1)	0.0004(1)	0.0024(1)
Nb(4)	4e		−0.12439(3)	0.19534(3)	0.17599(2)	0.0228(2)	0.0201(2)	0.0202(2)	0.0047(1)	0.0015(1)	−0.0024(1)
Nb(5)	4e		0.00104(2)	0.20736(3)	0.06275(1)	0.0216(2)	0.0144(2)	0.0189(2)	−0.0002(1)	−0.0010(1)	0.0015(1)
Nb(6)	4e		−0.13082(2)	−0.01797(3)	0.09611(1)	0.0166(2)	0.0199(2)	0.0192(2)	−0.0025(1)	0.0011(1)	−0.0009(1)
Mn(1)	2a		0	0	0	0.0189(4)	0.0175(4)	0.0159(4)	−0.0004(3)	0.0015(3)	−0.0012(3)
O(1)	4e		0.2008(2)	0.2652(2)	0.2218(1)	0.041(2)	0.023(2)	0.048(2)	−0.006(1)	−0.021(2)	−0.002(2)
O(2)	4e		0.2051(2)	−0.1093(2)	0.0821(1)	0.026(2)	0.030(2)	0.033(2)	0.007(1)	0.003(1)	−0.001(1)
O(3)	4e		−0.0182(2)	−0.1093(3)	0.2766(1)	0.040(2)	0.034(2)	0.026(2)	−0.001(1)	0.003(1)	0.011(1)
O(4)	4e		−0.2118(2)	0.2795(3)	0.2024(1)	0.038(2)	0.034(2)	0.034(2)	0.014(2)	0.007(1)	−0.004(1)
O(5)	4e		0.0059(2)	0.2939(2)	0.0055(1)	0.040(2)	0.024(2)	0.027(2)	0.000(1)	−0.000(1)	0.006(1)
O(6)	4e		−0.2205(2)	−0.0937(3)	0.0622(1)	0.027(2)	0.038(2)	0.031(2)	−0.011(1)	0.001(1)	−0.005(1)
O(7)	4e		−0.0056(2)	0.2597(2)	0.2060(1)	0.032(2)	0.020(2)	0.025(2)	0.004(1)	−0.003(1)	−0.005(1)
O(8)	4e		0.0992(2)	0.2604(2)	0.1128(1)	0.028(2)	0.020(2)	0.027(2)	−0.007(1)	−0.003(1)	0.002(1)
O(9)	4e		0.1885(2)	0.0820(2)	0.1460(1)	0.017(1)	0.024(2)	0.030(2)	−0.001(1)	−0.003(1)	−0.001(1)
O(10)	4e		0.0876(2)	0.0755(2)	0.2411(1)	0.030(2)	0.023(2)	0.021(1)	0.000(1)	−0.006(1)	0.000(1)
O(11)	4e		0.0826(2)	−0.0991(2)	0.1731(1)	0.024(1)	0.019(1)	0.024(1)	0.004(1)	−0.001(1)	0.004(1)
O(12)	4e		−0.1112(2)	0.0822(2)	0.2324(1)	0.028(2)	0.028(2)	0.020(1)	0.003(1)	0.003(1)	0.000(1)
O(13)	4e		−0.0990(2)	0.2658(2)	0.1036(1)	0.027(2)	0.021(2)	0.024(2)	0.006(1)	−0.001(1)	0.000(1)
O(14)	4e		0.0893(2)	0.0816(2)	0.0426(1)	0.018(1)	0.019(1)	0.019(1)	−0.003(1)	0.002(1)	0.001(1)
O(15)	4e		−0.0062(2)	−0.0818(2)	0.0659(1)	0.021(1)	0.016(1)	0.019(1)	−0.002(1)	0.002(1)	0.001(1)
O(16)	4e		−0.1074(2)	−0.0930(2)	0.1642(1)	0.025(2)	0.022(2)	0.024(1)	−0.005(1)	0.002(1)	0.003(1)
O(17)	4e		−0.2015(2)	0.0943(2)	0.1282(1)	0.018(1)	0.028(2)	0.027(2)	0.002(1)	0.003(1)	−0.002(1)
O(18)	4e		−0.0904(2)	0.0871(2)	0.0340(1)	0.020(1)	0.019(1)	0.018(1)	0.001(1)	0.001(1)	−0.001(1)
O(19)	4e		−0.0063(2)	0.0859(2)	0.1400(1)	0.020(1)	0.017(1)	0.017(1)	−0.001(1)	−0.002(1)	0.000(1)
Na(1)	4e		0.2017(2)	0.5664(2)	0.13869(9)	0.062(1)	0.041(1)	0.046(1)	−0.004(1)	−0.001(1)	0.000(1)
Na(2)	4e		0.0719(2)	0.5636(2)	0.24362(8)	0.045(1)	0.038(1)	0.044(1)	−0.0046(9)	0.0030(9)	0.0005(9)
Na(3)	4e		0.0124(1)	0.4565(2)	0.37126(9)	0.038(1)	0.054(1)	0.050(1)	−0.000(1)	0.0037(9)	0.003(1)
O(1W)	4e		0.2217(4)	0.4154(4)	0.0815(2)	0.111(4)	0.057(3)	0.108(4)	−0.043(3)	0.060(4)	−0.028(3)
O(2W)	4e		0.3673(3)	0.6122(4)	0.1487(2)	0.072(3)	0.066(3)	0.039(2)	0.002(2)	−0.005(2)	0.004(2)
O(3W)	4e		0.1690(4)	0.6788(3)	0.0608(2)	0.091(3)	0.045(2)	0.067(3)	−0.002(2)	−0.030(3)	0.005(2)
O(4W)	4e		0.2235(3)	0.4781(3)	0.2319(2)	0.045(2)	0.031(2)	0.071(3)	0.003(2)	−0.016(2)	−0.007(2)
O(5W)	4e		0.1581(2)	0.7043(2)	0.2022(1)	0.042(2)	0.024(2)	0.043(2)	0.000(1)	−0.010(2)	0.003(1)
O(6W)	4e		0.0406(3)	0.4952(4)	0.1506(2)	0.065(3)	0.072(3)	0.055(3)	−0.003(2)	−0.009(2)	−0.010(2)
O(7W)	4e		−0.0595(3)	0.6751(3)	0.2575(2)	0.050(2)	0.040(2)	0.086(3)	0.001(2)	0.004(2)	0.010(2)
O(8W)	4e		−0.0319(3)	0.4272(3)	0.2759(2)	0.048(2)	0.037(2)	0.047(2)	−0.005(2)	0.003(2)	−0.015(2)
O(9W)	4e		0.1174(2)	0.5914(3)	0.3385(2)	0.028(2)	0.050(2)	0.048(2)	−0.001(2)	−0.002(2)	0.000(2)
O(10W)	4e		0.1403(3)	0.3352(3)	0.3502(2)	0.046(2)	0.054(3)	0.076(3)	0.006(2)	−0.010(2)	−0.009(2)
O(11W)	4e		0.0774(4)	0.4882(5)	0.4644(2)	0.082(4)	0.131(5)	0.067(3)	−0.016(3)	0.004(3)	−0.015(3)
O(12W)	4e		−0.1039(3)	0.3379(4)	0.4035(2)	0.060(3)	0.063(3)	0.095(4)	−0.007(2)	0.032(3)	−0.003(3)

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(13W)	4e		–0.1026(3)	0.5981(4)	0.3659(2)	0.035(2)	0.066(3)	0.088(3)	0.007(2)	0.009(2)	0.006(2)
Na(4A)	4e	0.50	–0.1584(9)	0.6069(6)	0.1669(4)	0.21(1)	0.071(5)	0.126(7)	–0.036(6)	0.076(7)	–0.007(5)
Na(4B)	4e	0.50	–0.2184(7)	0.6001(5)	0.1321(3)	0.162(7)	0.069(4)	0.055(4)	0.046(4)	–0.004(4)	–0.012(3)
Na(5A)	4e	0.50	–0.3477(8)	0.517(1)	0.0833(5)	0.151(9)	0.25(1)	0.143(9)	0.018(9)	0.033(7)	0.084(9)
Na(5B)	4e	0.50	–0.427(1)	0.250(1)	0.0629(5)	0.241(9)	0.177(8)	0.156(7)	–0.007(8)	–0.016(7)	–0.012(7)
Na(6A)	4e	0.50	–0.3575(5)	0.6658(5)	–0.0543(3)	0.101(5)	0.071(4)	0.096(5)	–0.019(3)	0.023(4)	–0.009(3)
Na(6B)	4e	0.50	–0.430(1)	0.677(1)	0.1656(5)	0.163(8)	0.198(9)	0.134(7)	–0.038(7)	–0.015(6)	0.052(7)
O(14W)	4e		–0.2342(4)	0.7545(4)	0.1893(2)	0.105(4)	0.068(3)	0.059(3)	–0.048(3)	0.035(3)	–0.011(2)
O(15W)	4e		–0.2163(3)	0.4957(3)	0.2300(2)	0.040(2)	0.050(2)	0.102(4)	0.001(2)	0.008(2)	–0.020(2)
O(16W)	4e		–0.0471(4)	0.6976(4)	0.1134(2)	0.122(5)	0.049(3)	0.099(4)	0.012(3)	0.040(4)	0.010(3)
O(17W)	4e		–0.1647(6)	0.4662(5)	0.0917(4)	0.184(8)	0.056(4)	0.182(8)	0.041(4)	–0.005(6)	0.026(4)
O(18W)	4e		–0.2864(2)	0.8453(3)	–0.0433(1)	0.028(2)	0.085(3)	0.028(2)	–0.020(2)	–0.002(1)	–0.002(2)
O(19W)	4e		–0.3755(4)	0.6872(4)	–0.1534(2)	0.103(4)	0.057(3)	0.103(4)	–0.004(3)	–0.053(3)	–0.009(3)
O(20W)	4e		–0.2883(3)	0.1572(4)	0.0172(2)	0.046(2)	0.114(4)	0.033(2)	0.037(2)	0.008(2)	0.024(2)
O(21W)	4e		–0.4561(8)	0.4982(7)	–0.0646(4)	0.23(1)	0.152(8)	0.137(7)	0.003(8)	0.041(7)	–0.010(6)
O(22W)	4e		–0.325(1)	0.388(1)	0.0076(5)	0.30(2)	0.21(1)	0.17(1)	0.06(1)	–0.03(1)	–0.054(9)
O(23A)	4e	0.50	–0.453(2)	0.736(2)	–0.012(1)	0.21(2)	0.16(2)	0.23(3)	–0.08(2)	0.10(2)	–0.08(2)
O(23B)	4e	0.25	–0.482(4)	0.722(5)	0.017(2)	0.19(2)	0.18(2)	0.19(2)	–0.01(1)	0.01(1)	–0.01(1)
O(24W)	4e		–0.386(1)	0.614(1)	0.1500(4)	0.108(9)	0.103(9)	0.044(6)	–0.010(7)	0.007(6)	0.006(6)
O(25W)	4e	0.50	–0.0616(9)	0.5041(8)	0.0077(6)	0.13(1)	0.046(6)	0.15(1)	–0.008(6)	0.020(9)	0.018(7)
O(26A)	4e	0.50	–0.364(2)	0.354(3)	0.1367(9)	0.07(1)	0.13(2)	0.06(1)	0.04(1)	0.05(1)	0.01(1)
O(26B)	4e	0.50	–0.369(2)	0.360(3)	0.1378(9)	0.06(1)	0.15(3)	0.07(1)	0.02(1)	–0.029(9)	–0.00(1)
O(27W)	4e	0.50	–0.2263(8)	0.6764(8)	0.0426(4)	0.261(8)	0.140(6)	0.163(7)	0.072(6)	–0.019(6)	0.005(6)
O(28W)	4e	0.25	–0.331(2)	0.584(2)	0.004(1)	0.12(1)	0.12(1)	0.12(1)	–0.009(9)	–0.005(9)	0.019(9)

Acknowledgments. This work was supported by the Specialized Research Fund for the Doctoral Program of Higher Education (grant no. 20040475001), Henan Innovation Project for University Prominent Research Talents, the Foundation of Educational Department of Henan Province (grant no. 0524480020) and the Natural Science Foundation of Henan Province. The authors thank Dr. G. Zahn (editorial office of the journal) for help in crystallographic topics and the analysis of the disordered cationic fragment.

References

1. Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W.: Oxygen-17 nuclear magnetic resonance spectroscopy of polyoxometalates. 1. Sensitivity and resolution. Inorg. Chem. **18** (1979) 93-103.
2. Pope, M. T.: Heteropoly and Isopoly Oxometalates. Springer, Berlin 1983.
3. Pope, M. T.; Müller, A.: Polyoxometalate Chemistry: An Old Field with New Dimensions in Several Disciplines. Angew. Chem., Int. Ed. **30** (1991) 34-48.
4. Flynn, C. M.; Stucky, G. D.: Sodium 6-niobo(ethylenediamine)-cobaltate(III) and its chromate(III) analog. Inorg. Chem. **8** (1969) 178-180.
5. Flynn, C. M.; Stucky, G. D.: Heteropolyniobate complexes of manganese(IV) and nickel(IV). Inorg. Chem. **8** (1969) 332-334.
6. Flynn, C. M.; Stucky, G. D.: The Crystal Structure of Sodium 12-Niobomanganate(IV), $Na_{12}MnNb_{12}O_{38} \cdot 50H_2O$. Inorg. Chem. **8** (1969) 335-344.
7. Nyman, M.; Bonhomme, F.; Alam, T. M.; Rodriguez, M. A.; Cherry, B. R.; Krumhansl, J. L.; Nenoff, T. M.; Sattler, A. M.: A General Synthetic Procedure for Heteropolyniobates. Science **297** (2002) 996-998.
8. Nyman, M.; Bonhomme, F.; Alam, T. M.; Parise, J. B. M.; Vaughan, G. M. B.: Residual Dipolar Couplings – A Valuable NMR Parameter for Small Organic Molecules. Angew. Chem., Int. Ed. **43** (2004) 2787-2792.
9. Bonhomme, F.; Larentzos, J. P.; Alam, T. M.; Maginn, E. J.; Nyman, M.: Synthesis, Structural Characterization, and Molecular Modeling of Dodecaniobate Keggin Chain Materials. Inorg. Chem. **44** (2005) 1774-1785.
10. Brown, D.; Altermatt, D.: Bond-Valance Parameters Obtained from a Systematic Analysis of the Inorganic Crystal Structure Database. Acta Crystallogr. **B41** (1985) 244-247.
11. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
12. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.