The Crystal Structure of Sodium 12-Niobomanganate(IV), $Na_{12}MnNb_{12}O_{38} \cdot 50H_2O$[1]

BY C. M. FLYNN, JR., AND G. D. STUCKY

Sodium 12-niobomanganate(IV), $Na_{12}MnNb_{12}O_{38} \cdot 50H_2O$, is monoclinic, $a = 24.18 \pm 0.03$ Å, $b = 12.69 \pm 0.02$ Å, $c = 14.14 \pm 0.02$ Å, $\beta = 92.1 \pm 0.2°$, $Z = 2$, $\rho_{exptl} = 2.31$ g/cm³, $\rho_{calcd} = 2.26$ g/cm³, space group P2₁/n, all at 24–25°. Data were collected photographically. The structure was refined by Fourier, difference Fourier, and full-matrix least-squares methods to an R value of 11.7% for 3263 observed reflections. The structure is composed of sodium ions, water molecules, and anions $MnNb_{12}O_{38}{}^{12-}$. The anion consists of a manganese atom octahedrally coordinated by oxygen atoms from two Nb_6O_{19} groups, the latter having first been found by Lindqvist in $Na_7HNb_6O_{19} \cdot 15H_2O$. The anion has a crystallographic center of symmetry, but approximates D_{3d} symmetry. The Mn–O distances are equal within experimental error ($\sigma = 0.03$ Å), averaging 1.87 Å, but the MnO₆ octahedron is stretched along the pseudo-threefold axis of the anion. The Nb–O distances range from 1.75 to 2.43 Å ($\sigma = 0.03$ Å), depending on the chemical environment of the oxygen atom. The packing of the anions correlates with the optical properties of the compound. The unit cell of trigonal $Na_2Li_{10}MnNb_{12}O_{38} \cdot 44H_2O$ was also determined.

Introduction

Since Keggin first described the structure of the $PW_{12}O_{40}{}^{3-}$ ion,[2] the structures of several isopoly and heteropoly complexes have been reported. A review of these structures published in 1956[3] has been augmented by a recent general review of isopoly complexes.[4] Wells also reviews them in his book.[5] However, in most of these studies, only heavy-atom positions were determined, and anion oxygen atom positions were inferred qualitatively from packing considerations. Recent advances in data collection and computation have made complete determinations feasible—examples include two salts of the $V_{10}O_{28}{}^{6-}$ anion[6,7] and $Na_3[H_6CrMo_6O_{24}] \cdot 8H_2O$.[8]

In some studies of transition metal heteropolyniobates,[1,9] we have obtained several salts of a manganese-(IV) complex. To establish the structure of the anion, we have carried out a single-crystal X-ray structure determination of the sodium salt, $Na_{12}MnNb_{12}O_{38} \cdot 50H_2O$, which we report here. In the course of this work, we also determined the unit cell of $Na_2Li_{10}MnNb_{12}O_{38} \cdot 44H_2O$.

Experimental Section

Compounds.—The 12-niobomanganate(IV) complex is prepared by the reaction of manganese(II)–EDTA complex and a stoichiometric quantity of sodium 6-niobate with hydrogen peroxide in a hot aqueous solution. Details are given elsewhere.[9]

Unit Cell and Space Group of $Na_2Li_{10}MnNb_{12}O_{38} \cdot 44H_2O$.—Fragments of the thin plates of this optically uniaxial compound were mounted with epoxy cement in 0.5-mm diameter thin-walled

glass capillaries filled with 1:2 v/v ethanol–water to prevent loss of water of crystallization and sealed with epoxy cement. Since decomposition of the crystals occurred at room temperature, the rotation and zero-level Weissenberg photographs were taken at 0–4°, using Cu Kα radiation (λ 1.5418 Å, Ni filter). The c axis was perpendicular to the rotation axis, and the [$\bar{1}2\bar{1}0$] direction was parallel to it. The photographs showed that the crystal was not single, but unit cell data could still be obtained. Attempts to obtain a single crystal were unsuccessful.

The unit cell constants obtained were $a = 12.03 \pm 0.03$ Å and $c = 3 \times (14.76 \pm 0.03)$ Å $= 44.3 \pm 0.1$ Å. The density at 27° (flotation in 1,2-$C_2H_4Br_2$–CH_2I_2) was 2.40 ± 0.02 g/cm³; that calculated for three formula weights per unit cell is 2.41 g/cm³.

Under the microscope, etch pits were observed on the (0001) faces of the crystals as they dissolved while the ethanol evaporated from the ethanol–water immersion medium. These had trigonal symmetry. Pits on one side of a plate were oriented oppositely from those on the other side. Where two of these merged, a hexagonal hole formed. These observations require that the crystal be trigonal, without a mirror perpendicular to c. The possible point groups are thus 3, $\bar{3}$, 32, 3m, and $\bar{3}$m. From zero-level Weissenberg photographs ($I(h0\bar{h}l) = I(h0\bar{h}\bar{l})$), oscillation photographs, and the etch pit data, the Laue group was determined to be $\bar{3}$m. The possible point groups are now 32 and $\bar{3}$m. For reflections 000l, systematic absences were observed to occur for $l \neq 3n$. The possible space groups are therefore the enantiomorphous set P3₂12 and P3₁12.

Unit Cell and Space Group of $Na_{12}MnNb_{12}O_{38} \cdot 50H_2O$.—The rod crystals of the compound cleave easily perpendicular to the long direction. Cleaved fragments were mounted in 1:3 v/v ethanol–water as immersion medium to prevent loss of water of crystallization. Rotation and Weissenberg photographs were taken at 25° using Cu Kα radiation (Ni filter). The length of the rod was aligned parallel to the rotation axis. Precession photographs were also taken, using Mo Kα radiation (λ 0.7107 Å, Zr filter), at 25°. The rod length was aligned parallel to the dial axis. The precession camera was calibrated with a single crystal of NaCl, $a = 5.6280$ Å.

Sodium 12-niobomanganate(IV)–50-water is monoclinic with the rod length parallel to b. Unit cell constants from $hk0$ and $0kl$ precession photographs are $a = 24.18 \pm 0.03$ Å, $b = 12.69 \pm 0.02$ Å, $c = 14.14 \pm 0.02$ Å, and $\beta = 92.1 \pm 0.2°$. The density measured at 24° (flotation in 1,2-$C_2H_4Br_2$–CH_2I_2) was 2.31 ± 0.02 g/cm³; because of efflorescence, measurements were made rapidly using large (up to 2-mm) crystals. The density calculated for two formula weights per unit cell is 2.26 g/cm³. The high observed density relative to the calculated density is attributed to loss of water from the crystals during the density determination.

(1) Taken from the Ph.D. dissertation of C. M. Flynn, Jr., University of Illinois, 1967.

(2) J. F. Keggin, *Proc. Roy. Soc.* (London), **A144**, 75 (1934).

(3) A. A. Babad-Zakhryapin, *Usp. Khim.*, **25**, 1373 (1956).

(4) K. F. Jahr and J. Fuchs, *Angew. Chem.*, **78**, 725 (1964).

(5) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, pp 443–453.

(6) H. T. Evans, Jr., *Inorg. Chem.*, **5**, 967 (1966).

(7) A. G. Swallow, P. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, **21**, 397 (1966).

(8) A. Perloff, Ph.D. Dissertation, Georgetown University, 1967; presented at the American Crystallographic Association Meeting, Georgia Institute of Technology, Atlanta, Ga., Jan 25–28, 1967.

(9) C. M. Flynn, Jr., and G. D. Stucky, *Inorg. Chem.*, **8**, 332 (1969).

Comparison of the Weissenberg $h0l$ and $h1l$ photographs shows that the unit cell is primitive. For reflections $h0l$ there were systematic absences for $h + l = 2n + 1$. The zero-level precession photographs revealed systematic absences for reflections $0k0$ of the type $k = 2n + 1$. The space group is therefore uniquely $P2_1/n$.

Collection and Reduction of Data for the Sodium Salt.—Data were collected at room temperature using Mo Kα radiation (λ 0.7107 Å, Zr filter, 32.5 kV, 20 mA) and multiple-film equi-inclination Weissenberg technique (Supper camera). Crystals were mounted in the same way as for the unit cell measurements. Two crystals were used, each of roughly cylindrical dimensions, about 0.30 mm long and about 0.10 mm in diameter. For the first crystal, two exposures (18 and 72 hr) of six-film packs were made for each of the levels $h0l$ through $h6l$. For the second crystal (used owing to a mishap), one exposure (96 hr) of a six-film pack was taken for each of the levels $h6l$ through $h14l$.

The spot (13, 0, 3) was photographed for measured numbers of oscillations (time series $(1.3)^n$) to furnish calibrated intensity strips for visual estimation of intensities. Only spots on the top halves of the films were measured, these all being symmetry independent.

For a given level, all films were scaled to the most intense one in the series. The data were first all scaled together by exposure times and data common to the two crystals. The observed intensities (numbering over 3300) were corrected for Lorentz, polarization, and spot-extension effects. The absorption coefficient μ/ρ was calculated using data from the "International Tables for X-Ray Crystallography."[10] The value obtained was $\mu/\rho = 8.0$ cm^2/g. From the calculated density of 2.26 g/cm^3, the value of μ is 18 cm^{-1}. For a cylinder of radius 0.05 mm, $\mu R = 0.09$. An absorption correction was therefore considered unnecessary. To the accuracy that the crystal can be described as a cylinder, the maximum error in the data made by neglecting absorption is 2%.

About 100 reflections were discarded to beam-stop interference or bad streaking. These were mostly of the types $1k0$, $2k0$, $0kl$, $1kl$, $\bar{1}kl$, $2kl$, and $\bar{2}kl$. There remained 3264 independent observed reflections.

Structure Solution

Calculations were performed on the IBM 7094 computer of the University of Illinois Department of Computer Science. A three-dimensional Patterson map was calculated using the fast ERFR3 program of Sly, Shoemaker, and van den Hende.[11] The most prominent feature was a group of 18 strong peaks symmetrically arranged about the origin. Another set of strong peaks appeared about the point ($1/2$, $1/2$, $1/2$). Because of the complexity of the Patterson function, indications of the structure of the 12-niobomanganate(IV) anion were obtained by indirect means.

The structure of the 12-niobomanganate(IV) ion was suggested by considering the structural features of known isopoly and heteropoly complexes and the physicochemical properties of the 12-niobomanganate(IV) compounds. The former considerations suggested a compact, symmetrical structure in which the niobium atoms were octahedrally coordinated by oxygen atoms. Further, these octahedra would be packed together sharing edges and corners but not faces. The properties of the 12-niobomanganate(IV) compounds are

consistent with 38 oxygen atoms per complex anion and support octahedral coordination of the manganese atom. Two models were found which satisfied all of these conditions. In one model, which has ideal symmetry O_h, the niobium atoms are arranged in a cuboctahedron about the manganese atom. The other, having ideal symmetry D_{3d}, consists of two Nb_6O_{19} groups[12] coordinated to the manganese atom.

The positions of the manganese atoms in the unit cell, which are completely fixed by symmetry, were taken as (0, 0, 0; $1/2$, $1/2$, $1/2$). From the Patterson map, the distance between niobium atoms across edge-shared octahedra was about 3.3 Å; this distance agrees with Lindqvist's results for sodium 6-niobate[12] (Nb–Nb = 3.3–3.4 Å). All the heavy metal–heavy metal vectors of the Patterson map were found to give excellent agreement with the proposed D_{3d} model, with the pseudo-threefold axis of the anion lying approximately in the ab plane at an angle of about 20° to a.

This model is consistent with the following observations. (1) The length of the D_{3d} ion is about 14 Å, using a closest metal–metal distance of 3.3 Å[12] across edge-shared octahedra, metal–oxygen distances of 2.0 Å, and a van der Waals radius of 1.4 Å for oxygen. Since this is longer than the b cell edge (12.69 Å), the anion cannot be aligned in this direction. (2) The ease of formation of the complex from alkali $Nb_6O_{19}^{8-}$ salts, manganese(II), and oxidizing agent[9] is consistent with the presence of Nb_6O_{19} groups in the heteropolyanion. (3) The infrared spectrum of the potassium sodium 12-niobomanganate is very similar to that of sodium or potassium 6-niobate in the 500–1000-cm^{-1} region where the metal–oxygen vibrations occur.[9] (4) The optical anisotropy of crystals of this complex implies deviation from cubic symmetry in the crystal field about the manganese atom. (5) Since the trigonal lithium–sodium salt contains three formula weights per unit cell, there is no proof of threefold symmetry in the anion. The space group requires only twofold symmetry. However, the unit cell dimensions still constrain the anions to lie with their threefold axes more nearly parallel to c than to a. Under polarized light these crystals are bright orange with the polarization plane perpendicular to c and light orange-yellow in parallel orientation. Crystals of the sodium salt are bright orange when the a axis is most nearly perpendicular to the polarization plane and yellow in the other two principal orientations. Combination of all of these data suggests that in the sodium salt the anions lie with their threefold axes close to the a axis.

Refinement

Fourier calculations were done with the ERFR3 program.[11] Structure factors were initially calculated using a routine taken from the UCLA least-squares program of Gantzel, Sparks, and Trueblood.[13] Scale factors were obtained initially for each layer by the rela-

(10) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, p 162.

(11) W. G. Sly, D. P. Shoemaker, and J. H. van den Hende, "A Two and Three Dimensional Fourier Program for the IBM 709/7090, ERFR-2," Esso Research Report CBRL22M-62, Linden, N. J., 1962.

(12) I. Lindqvist, *Arkiv Kemi*, **5**, 247 (1953).

(13) P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLAS1, 1961.

tion $K_{\text{layer}} = \Sigma(F_o)_{\text{layer}}/\Sigma(F_c)_{\text{layer}}$. Later this program was rewritten by the authors to take better advantage of symmetry elements, thereby saving computer time. Least-squares calculations were done with ORFLSD, a modification of the full-matrix least-squares program ORFLS of Busing, Martin, and Levy.[14] During refinement, interatomic distances were calculated with DISTAN, a bond distance and angle program by Shoemaker,[15] with local modifications.

Owing to storage limitations, a complete refinement cycle consisted of refinement of the more than 220 variable parameters in two or three batches. One complete refinement cycle required about 1 hr of IBM 7094 computer time. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with w always set equal to 1 for all observed reflections. Unobserved reflections were not included in the refinement.

Scattering factors for neutral Nb, Mn, and O atoms and for Na$^+$ and F$^-$ were taken from the "International Tables".[16] Real and imaginary corrections for anomalous scattering (Mo Kα radiation) were applied to Mn and Nb. Trial initial isotropic temperature factors B were (in Å^2): 3.0 for Mn, 4.0 for Nb, and 4.5 for light atoms.

Trial niobium positions obtained from well-resolved Patterson peaks were refined using only the 378 strongest reflections, after having discarded one reflection (002) which appeared to be badly affected by extinction. The value of R[17] fell to 24% during this refinement. With 575 high-angle reflections temporarily omitted, Fourier calculations using the 2688 remaining reflections then revealed 19 anionic oxygen atoms in their expected positions, as well as 31 other prominent peaks. These 31 atoms, called X atoms below, were assigned fluoride ion scattering factors at this point, since distinction between sodium ions and water molecules could not be made reliably on the basis of peak heights. The value of R over the 2688 reflections was 34% including only the heavy atoms and dropped to 29% on including the light atoms. Next, the X atom positions and the heavy-atom isotropic temperature factors were refined, giving $R = 21\%$.

The high-angle reflections were then returned to the calculations, and niobium and light-atom positional parameters and the isotropic temperature factors were refined once. The R value was then 13%. The stereochemistry of three of the X atoms, combined with their low temperature factors, then indicated that they might be sodium ions. Two of these X atoms had coordination octahedra with a face in common. While this stereochemistry is not unknown for sodium salts,[18] it was intuitively dissatisfying here, because it was thought that a more uniform distribution of sodium ions would most effectively counter the high anion charges. However, additional Fourier calculations (including

one in which only anion atoms were input) only confirmed the arrangement of X atoms. The identities of three more expected sodium ions were still not evident. Another refinement cycle was carried out, with these three X atoms put in as sodium ions and the other 28 put in as oxygen atoms. The value of R was 12% and the value of wR[19] was 14.3%. A difference map was then calculated, in which several X atoms were omitted because their temperature factors were excessively high, casting doubt on their positions. The result indicated that two of these X atoms were probably spurious or were subject to disorder. Because these two atoms also had the highest temperature fac-

TABLE I

POSITIONAL PARAMETERS AND ISOTROPIC
TEMPERATURE FACTORS OF ATOMS[a]

Atom	x	y	z	B
Mn	0	0	0	0.57 (12)
Nb(1)	0.2187 (1)	−0.0249 (3)	−0.0132 (2)	0.83 (6)
Nb(2)	0.1076 (1)	−0.0259 (3)	0.1170 (2)	0.70 (6)
Nb(3)	0.0962 (1)	−0.0173 (3)	−0.1312 (2)	0.68 (5)
Nb(4)	0.0626 (1)	0.2086 (3)	0.0003 (2)	0.60 (6)
Nb(5)	0.1870 (1)	0.1885 (3)	0.1111 (2)	0.73 (6)
Nb(6)	0.1769 (1)	0.1956 (3)	−0.1241 (2)	0.85 (6)
O(1)	0.0420 (10)	0.0817 (19)	0.0870 (17)	0.7 (4)
O(2)	0.0336 (10)	0.0846 (20)	−0.0890 (18)	1.2 (6)
O(3)	0.1397 (19)	0.0863 (18)	−0.0048 (16)	0.2 (3)
O(4)	0.1458 (10)	0.0861 (20)	0.1882 (17)	1.0 (4)
O(5)	0.1290 (11)	0.0935 (21)	−0.2047 (18)	1.4 (5)
O(6)	0.2415 (10)	0.0755 (19)	0.0889 (16)	0.9 (4)
O(7)	0.2308 (10)	0.0819 (19)	−0.1104 (16)	0.8 (4)
O(8)	0.0063 (12)	0.2972 (25)	0.0055 (21)	2.1 (6)
O(9)	0.1114 (10)	0.2554 (21)	0.1017 (18)	1.1 (5)
O(10)	0.1030 (9)	0.2618 (19)	−0.1011 (16)	0.6 (4)
O(11)	0.2058 (11)	0.2598 (22)	−0.0053 (19)	1.5 (5)
O(12)	0.2232 (14)	0.2652 (29)	0.1953 (25)	3.8 (7)
O(13)	0.2088 (12)	0.2827 (25)	−0.2077 (21)	2.5 (6)
O(14)	0.0651 (10)	−0.0780 (20)	−0.0065 (17)	0.7 (4)
O(15)	0.0839 (12)	−0.1084 (24)	0.2095 (20)	2.3 (6)
O(16)	0.0655 (12)	−0.0941 (24)	−0.2245 (20)	2.1 (6)
O(17)	0.1734 (10)	−0.0931 (19)	0.0818 (17)	0.8 (4)
O(18)	0.1642 (11)	−0.0901 (21)	−0.1044 (18)	1.3 (5)
O(19)	0.2782 (11)	−0.1063 (21)	−0.0160 (20)	1.9 (5)
Na(1)	0.1278 (7)	−0.0437 (14)	0.4906 (12)	2.3 (3)
Na(2)	0.2572 (7)	0.0646 (16)	0.4273 (14)	2.7 (4)
Na(3)	0.3620 (7)	0.0674 (15)	0.2963 (13)	2.6 (4)
Na(4)	0.3494 (15)	0.1064 (32)	−0.3179 (27)	14.7 (9)
Na(5)	0.0483 (18)	0.3401 (32)	0.3610 (78)	13.8 (7)
W(1)	0.0360 (18)	−0.0057 (38)	0.4287 (32)	5.9 (10)
W(2)	0.2733 (11)	0.4282 (23)	−0.0330 (20)	1.8 (5)
W(3)	0.2710 (13)	−0.0207 (27)	0.2711 (22)	2.5 (6)
W(4)	0.2716 (13)	−0.0027 (28)	−0.2844 (24)	3.4 (7)
W(5)	0.4340 (27)	0.0066 (58)	0.0396 (47)	10.7 (19)
W(6)	0.3515 (14)	0.0005 (30)	0.4556 (25)	3.6 (7)
W(7)	0.1635 (11)	0.0900 (22)	0.3805 (20)	1.7 (5)
W(8)	0.1337 (14)	0.0970 (28)	−0.3949 (24)	3.1 (7)
W(9)	0.3515 (14)	0.1165 (29)	−0.1333 (25)	3.1 (7)
W(10)	0.3468 (25)	0.1360 (52)	−0.1037 (42)	11.1 (5)
W(11)	0.0432 (14)	0.1623 (28)	0.2851 (29)	3.4 (7)
W(12)	0.0189 (19)	0.1595 (40)	−0.2930 (34)	6.2 (11)
W(13)	0.2420 (13)	0.1783 (28)	−0.4411 (23)	2.8 (7)
W(14)	0.3887 (20)	0.1986 (43)	−0.4545 (34)	6.4 (11)
W(15)	0.4401 (14)	0.1852 (29)	0.3302 (24)	3.2 (6)
W(16)	0.4581 (26)	0.1736 (60)	−0.2723 (47)	12.6 (16)
W(17)	0.2960 (10)	0.2060 (21)	0.3426 (18)	1.3 (4)
W(18)	0.3118 (15)	0.2596 (30)	−0.2624 (26)	3.6 (7)
W(19)	0.3496 (13)	0.3412 (26)	0.1406 (23)	2.6 (6)
W(20)	0.4041 (16)	0.3380 (31)	−0.1015 (27)	4.0 (8)
W(21)	0.0833 (16)	0.4183 (34)	0.2170 (28)	4.4 (8)
W(22)	0.4101 (23)	−0.0383 (51)	−0.3366 (41)	9.2 (13)
W(23)	0.1528 (18)	0.3146 (37)	0.3729 (31)	5.2 (10)
W(24)	0.1372 (19)	0.3590 (38)	−0.3654 (34)	5.9 (10)

[a] In this and succeeding tables, the number in parentheses after each quantity is its standard deviation in units of the last significant figure.

(14) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
(15) D. P. Shoemaker, Massachusetts Institute of Technology, 1963.
(16) Reference 10, pp 202, 203, 210, 211, 215, 216.
(17) $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$.
(18) P. B. Jamieson and L. S. D. Glasser, *Acta Cryst.*, **22**, 507 (1967).

(19) $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$; $w = 1$.

TABLE II

Observed and Calculated Structure Factors in Electrons for $Na_{12}MnNb_{12}O_{38}\cdot 50H_2O$

TABLE II (*Continued*)

tors, they were eliminated from the structure. This decision was reinforced by the fact that some excessively short (less than 2.3 Å) interatomic distances were eliminated simultaneously. In addition, the distances between peaks suggested that two more X atoms were sodium ions, despite their low peak heights, which were then attributed to partial site occupation. The stereochemistry failed to indicate the identity of an expected sixth sodium ion; this is attributed to disorder and will be discussed below.

The last two refinement cycles were run with five X atoms input as sodium ions. In the first cycle, the layer scale factors and all niobium and anion oxygen atom positions were varied in the first round of calculations, then the layer scale factors and all sodium and water-oxygen positions in the second round, and finally all of the isotropic temperature factors in the third round. In the second cycle, the first 115 parameters

were varied and then the final 117 parameters. The largest value in the correlation matrices for any of these runs was 0.20. The final value of R was 11.6% and of wR, 14.0% for the 3263 observed reflections. In the last refinement, none of the 162 varied positional parameters shifted by more than 0.01 of its standard deviation. The final shifts of the scale factors were all less than half their standard deviations, which ranged from 0.7 to 2.2%. Of the 55 isotropic temperature factors, none shifted by more than 0.8 of its standard deviation. A final difference Fourier showed no peaks greater than 0.75 e/Å^3 or about 35% the average water-oxygen peak height. It should be reemphasized that because of the large number of heavy atoms, the instability of the crystals, and the existence of interstitial holes in the water matrix which readily permits a statistical disordering of sodium ions, a portion of the sodium–water matrix is not well defined. In particular, the errors
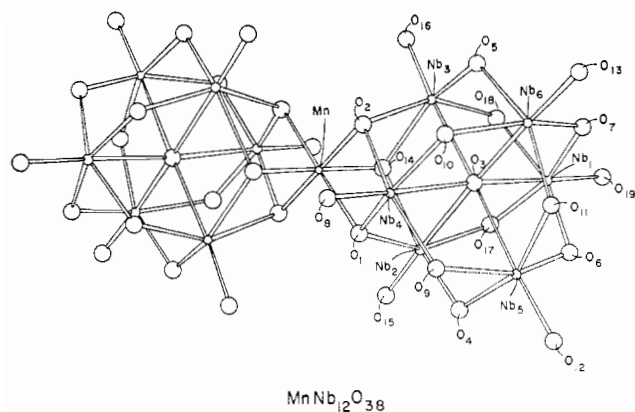
$MnNb_{12}O_{38}$

Figure 1.—Structure of the $MnNb_{12}O_{38}{}^{12-}$ anion.

stated for Na(4) and Na(5) and their coordinated water molecules should be taken as a lower limit.

The large number of atoms relative to the amount of data did not justify refinement of anisotropic temperature factors. The financial expense of computations did not justify this either, as well as further attempts to improve the values of the parameters. Final positional parameters and isotropic temperature factors are given in Table I. Observed and final calculated structure factors, in electrons, are given in Table II.

Discussion of the Structure

Final interatomic distances and bond angles, with their standard deviations, were calculated with the ORFFE program of Busing, Martin, and Levy.[20] The DISTAN program[16] was used to obtain distances connecting anionic and nonanionic atoms. Illustrations of the structure were prepared with the aid of the program ORTEP.[21]

The bond lengths and angles in the $MnNb_{12}O_{38}{}^{12-}$ anion, with their standard deviations, are given in Tables III and IV. Mean values for quantities equivalent by the pseudo-threefold symmetry are also given with the approximate maximum deviations of individual values from them.

The anion consists of a manganese(IV) atom coordinated to two Nb_6O_{19} groups[13] as shown in Figure 1. The anion has symmetry D_{3d} within two standard deviations with respect to interatomic distances, but the deviations of some individual bond angles from their pseudo-symmetry mean values appear significant.

The mean Mn–O distance of 1.87 ± 0.01 Å is about the same as the Mn–O distances in two forms of MnO_2 ($1.87-1.94$ Å[22]) and in $Na_7H_4Mn(IO_6)_3 \cdot 17H_2O$ (mean, 1.90 Å).[23] The mean O–Mn–O bond angle across the plane perpendicular to the pseudo-threefold axis is

$96.7 \pm 0.3°$; *i.e.*, the MnO_6 octahedron is stretched along a threefold axis. This stretching of the MnO_6 octahedron is attributed to electrostatic repulsion of the two Nb_6O_{19} groups. Consistent with this, the mean closest approach of oxygen atoms (not bonded to manganese) of the two niobate groups is 3.29 ± 0.02 Å across the plane perpendicular to the pseudo-threefold axis. This is about 0.5 Å longer than the usual van der Waals contact distance.

Nine of the twelve niobium–niobium distances are in the range 3.3–3.4 Å, in agreement with Lindqvist's results for $Na_7HNb_6O_{19} \cdot 15H_2O$.[13] Three niobium–niobium distances are longer, about 3.53 Å, and these are bound to the face of the Nb_6 octahedron which faces the manganese atom. These three longer niobium–niobium distances are attributed to the additional electrostatic repulsion contributed by the manganese atom core.

The niobium–oxygen distances vary according to the number of bonds from the metal atoms to a given oxygen atom. The shortest Nb–O distances ($1.75-1.79$ Å) correspond to terminal oxygen atoms, which each have only one bond to a niobium atom. Distances to oxygen atoms which bridge two niobium atoms range from 1.88 to 2.05 Å. For oxygen atoms which bridge two niobium atoms and the manganese atom, the Nb–O distances average 2.10 Å. The longest Nb–O distances connect the niobium atoms to the oxygen atom in the center of the Nb_6O_{19} group (O(3)) and average about 2.4 Å. These long distances are a consequence of the niobium–niobium electrostatic repulsions. This variation of metal–oxygen distances has recently been found in two compounds containing the $V_{10}O_{28}{}^{6-}$ anion,[7,8] in $K_5Co^{III}W_{12}O_{40} \cdot 20H_2O$,[24] and in $Na_3H_6Cr^{III}Mo_6O_{24} \cdot 8H_2O$.[9] In the 6-molybdochromate(III), the Mo–O distances range from 1.70 to 2.35 Å. The niobium–oxygen distances in a high-temperature form of Nb_2O_5 and in compounds of Nb_2O_5 with TiO_2 and WO_3 range from 1.7 to 2.2 Å.[25] In these ReO_3-based structures, however, no good correlation of Nb–O distances with oxygen atom bonding was noted.

In the 12-niobomanganate(IV), the niobium atoms all have octahedral coordination of oxygen atoms. The shortest contacts to other oxygen atoms are about 3.7 Å (Nb(2)–W(11) and Nb(3)–W(12)), too long for bonds. Niobium–oxygen coordination in oxides is nearly always octahedral; however, coordination number 7 has recently been found in the hydrothermally synthesized $NaNb_6O_{15}(OH)$.[26] In a high-temperature form of Nb_2O_5 there is some tetrahedrally coordinated niobium, but tetrahedral sites in some Nb_2O_5–WO_3 compounds[25] are probably occupied mainly by tungsten, in view of the stability of $WO_4{}^{2-}$.

(20) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge, National Laboratory, Oak Ridge, Tenn., 1964.

(21) C. K. Johnson, Report ORNL-3794 TID-4500, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(22) Yu. D. Kondrashev and A. I. Zaslavskii, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **15**, 179 (1951).

(23) A. Linek, *Czech. J. Phys.*, **13**, 398 (1963).

(24) K. Eriks, N. F. Yannoni, U. C. Ararivala, V. E. Simmons, and C. W. Baker, *Acta Cryst.*, **13**, 1139 (1960); N. F. Yannoni, Ph.D. Dissertation, Boston University, 1961.

(25) A. D. Wadsley, *Acta Cryst.*, **14**, 660, 664 (1961); B. M. Gatehouse and A. D. Wadsley, *ibid.*, **17**, 1545 (1964); R. S. Roth and A. D. Wadsley, *ibid.*, **19**, 32, 38, 42 (1965); S. Anderson, W. G. Mumme, and A. D. Wadsley, *ibid.*, **21**, 802 (1966).

(26) S. Anderson, *Acta Chem. Scand.*, **19**, 2285 (1965).

TABLE III

INTERATOMIC DISTANCES IN THE ANION (Å)[a]

Metal–Metal Distances

Mn–Nb(2)	3.045 (7)
Mn–Nb(3)	3.035 (7)
Mn–Nb(4)	3.049 (5)
Mean	3.04 (1)
Nb(2)–Nb(3)	3.511 (7)
Nb(2)–Nb(4)	3.552 (7)
Nb(3)–Nb(4)	3.527 (7)
Mean	3.53 (2)

Metal–Oxygen Distances

Mn–inner bridging O

Mn–O(1)	1.88 (3)
Mn–O(2)	1.86 (3)
Mn–O(14)	1.86 (3)
Mean	1.87 (1)

Inner Nb–inner bridging O

Nb(2)–O(1)	2.12 (2)
Nb(2)–O(14)	2.10 (3)
Nb(3)–O(2)	2.09 (3)
Nb(3)–O(14)	2.09 (3)
Nb(4)–O(1)	2.09 (3)
Nb(4)–O(1)	2.10 (3)
Nb(4)–O(2)	2.12 (3)
Mean	2.10 (2)

Outer Nb–outer bridging O

Nb(1)–O(6)	1.99 (3)
Nb(1)–O(7)	1.96 (3)
Nb(5)–O(6)	1.98 (3)
Nb(5)–O(11)	1.95 (3)
Nb(6)–O(7)	1.94 (3)
Nb(6)–O(11)	1.97 (3)
Mean	1.97 (3)

Inner Nb–middle bridging O

Nb(2)–O(4)	1.96 (3)
Nb(2)–O(17)	1.88 (3)
Nb(3)–O(5)	1.93 (3)
Nb(3)–O(18)	1.91 (3)
Nb(4)–O(9)	1.92 (3)
Nb(4)–O(10)	1.89 (3)
Mean	1.92 (4)

Metal–Metal Distances

Nb(1)–Nb(5)	3.334 (7)
Nb(1)–Nb(6)	3.348 (7)
Nb(5)–Nb(6)	3.327 (7)
Mean	3.34 (1)
Nb(1)–Nb(2)	3.310 (8)
Nb(1)–Nb(3)	3.348 (8)
Nb(2)–Nb(5)	3.332 (7)
Nb(3)–Nb(6)	3.333 (8)
Nb(4)–Nb(5)	3.350 (8)
Nb(4)–Nb(6)	3.335 (8)
Mean	3.33 (2)

Metal–Oxygen Distances

Outer Nb–middle bridging O

Nb(1)–O(17)	1.98 (3)
Nb(1)–O(18)	1.99 (3)
Nb(5)–O(4)	1.99 (3)
Nb(5)–O(9)	2.01 (3)
Nb(6)–O(5)	2.06 (3)
Nb(6)–O(10)	2.01 (3)
Mean	2.01 (4)

Inner Nb–center O

Nb(2)–O(3)	2.39 (3)
Nb(3)–O(3)	2.43 (3)
Nb(4)–O(3)	2.42 (3)
Mean	2.41 (2)

Outer Nb–center O

Nb(1)–O(3)	2.39 (3)
Nb(5)–O(3)	2.35 (3)
Nb(6)–O(3)	2.39 (3)
Mean	2.38 (3)

Inner Nb–inner terminal O

Nb(2)–O(15)	1.78 (3)
Nb(3)–O(16)	1.77 (3)
Nb(4)–O(8)	1.76 (3)
Mean	1.77 (1)

Outer Nb–outer terminal O

Nb(1)–O(19)	1.77 (3)
Nb(5)–O(12)	1.75 (4)
Nb(6)–O(13)	1.76 (3)
Mean	1.76 (1)

Oxygen–Oxygen Distances

Inner bridging, edges of MnO6 octahedron

O(1)–O(2)	2.49 (4)
O(1)–O(14)	2.49 (4)
O(2)–O(14)	2.47 (4)
Mean	2.48 (1)

Edges of MnO6 octahedron

O(2)–O(14)*	2.79 (4)
O(1)–O(14)*	2.79 (3)
O(1)–O(2)*	2.79 (4)
Mean	2.79 (1)

Other contacts across center

O(1)–O(16)*	3.31 (4)
O(2)–O(15)*	3.27 (4)
O(14)–O(8)*	3.28 (4)
Mean	3.29 (2)

Inner bridging–inner terminal

O(1)–O(8)	3.07 (4)
O(1)–O(15)	3.12 (4)
O(2)–O(8)	3.09 (4)
O(2)–O(16)	3.08 (4)
O(14)–O(16)	3.09 (4)
O(14)–O(15)	3.09 (4)
Mean	3.09 (3)

Inner terminal–middle bridging

O(8)–O(9)	2.89 (4)
O(8)–O(10)	2.86 (4)
O(15)–O(4)	2.91 (4)
O(15)–O(17)	2.87 (4)
O(16)–O(5)	2.83 (4)
O(16)–O(18)	2.87 (4)
Mean	2.87 (4)

Inner bridging–middle bridging

O(1)–O(4)	2.85 (3)
O(1)–O(9)	2.77 (4)
O(2)–O(5)	2.88 (4)
O(2)–O(10)	2.82 (4)
O(14)–O(17)	2.86 (3)
O(14)–O(18)	2.82 (4)
Mean	2.83 (6)

Middle bridging–outer terminal

O(4)–O(12)	2.92 (4)
O(5)–O(13)	3.01 (4)
O(9)–O(12)	2.97 (5)
O(10)–O(13)	2.93 (4)
O(17)–O(19)	2.94 (4)
O(18)–O(19)	2.99 (4)
Mean	2.96 (5)

Oxygen–Oxygen Distances

Middle bridging–outer bridging

O(4)–O(6)	2.76 (4)
O(5)–O(7)	2.76 (4)
O(9)–O(11)	2.78 (4)
O(10)–O(11)	2.79 (4)
O(17)–O(6)	2.71 (4)
O(18)–O(7)	2.72 (4)
Mean	2.75 (4)

Outer bridging–outer terminal

O(12)–O(6)	2.88 (5)
O(12)–O(11)	2.86 (4)
O(13)–O(7)	2.95 (4)
O(13)–O(11)	2.87 (4)
O(19)–O(6)	2.90 (4)
O(19)–O(7)	2.95 (4)
Mean	2.90 (5)

Outer bridging

O(6)–O(7)	2.83 (4)
O(6)–O(11)	2.82 (4)
O(7)–O(11)	2.78 (4)
Mean	2.81 (3)

Center–middle bridging

O(3)–O(4)	2.73 (3)
O(3)–O(5)	2.83 (4)
O(3)–O(9)	2.72 (4)
O(3)–O(10)	2.74 (4)
O(3)–O(17)	2.70 (3)
O(3)–O(18)	2.73 (4)
Mean	2.74 (5)

Center–inner bridging

O(3)–O(1)	2.74 (3)
O(3)–O(2)	2.79 (3)
O(3)–O(14)	2.76 (3)
Mean	2.76 (3)

Center–outer bridging

O(3)–O(6)	2.76 (3)
O(3)–O(7)	2.71 (3)
O(3)–O(11)	2.72 (4)
Mean	2.73 (3)

Middle bridging

O(4)–O(9)	2.59 (4)
O(5)–O(10)	2.67 (4)
O(17)–O(18)	2.64 (4)
Mean	2.63 (4)

Middle bridging

O(9)–O(10)	2.88 (4)
O(5)–O(18)	2.84 (4)
O(4)–O(17)	2.82 (4)
Mean	2.85 (3)

[a] Quantities equivalent by the pseudo-threefold symmetry of the anion are grouped together, and their average values are given with the approximate maximum range of individual values in units of the last significant figure.

Within an Nb_6O_{19} group, the oxygen–oxygen distances corresponding to edges of NbO_6 oxtahedra are generally in the range 2.7–2.9 Å. Qualitatively, the niobium atoms are electrostatically repelled away from the centers of slightly distorted oxygen octahedra, the bridging atoms being pulled inward. The temperature factors of the anionic oxygen atoms show some correlation with their chemical environment, being greatest for terminal oxygen atoms (one Nb–O bond) and least for the oxygen atom at the center of an Nb_6O_{19} group.

The packing of the anions in the unit cell is shown in Figure 2. The pseudo-threefold axes are canted 19.4 ± 0.2° to the a axis, 70.6 ± 0.2° to the b axis, and 1.7 ± 0.2° to the normal to the ab plane. The anion centered at ($^1/_2$, $^1/_2$, $^1/_2$) is canted oppositely to that at (0, 0, 0),

Table IV
Bond Angles in the Anion (deg)[a]

Oxygen-Metal-Oxygen		Oxygen-Metal-Oxygen		Metal-Oxygen-Metal		Metal-Oxygen-Metal	
O(1)-Mn-O(2)*	96.6 (11)	O(14)-Nb(2)-O(17)	91.6 (11)	Nb(1)-O(17)-Nb(2)	118.5 (13)	Nb(1)-O(3)-Nb(4)	176.6 (11)
O(1)-Mn-O(14)*	96.4 (11)	O(14)-Nb(3)-O(18)	89.6 (11)	Nb(1)-O(18)-Nb(3)	118.0 (14)	Nb(2)-O(3)-Nb(6)	176.7 (11)
O(2) Mn-O(14)*	97.0 (11)	O(2)-Nb(4)-O(10)	88.9 (11)	Nb(2)-O(4)-Nb(5)	115.0 (13)	Nb(3)-O(3)-Nb(5)	176.0 (12)
Mean	96.7 (3)	Mean	90.0 (14)	Nb(3)-O(5)-Nb(6)	113.3 (13)	Mean	176.4 (4)
O(15)-Nb(2)-O(1)	105.4 (12)	O(3)-Nb(1)-O(17)	76.0 (9)	Nb(4)-O(9)-Nb(5)	116.8 (14)	Nb(1)-O(3)-Nb(5)	89.5 (8)
O(15)-Nb(2)-O(14)	105.1 (12)	O(3)-Nb(1)-O(18)	76.7 (10)	Nb(4)-O(10)-Nb(6)	117.2 (13)	Nb(5)-O(3)-Nb(6)	89.3 (8)
O(16)-Nb(3)-O(2)	105.5 (12)	O(3)-Nb(5)-O(4)	77.6 (9)	Mean	116.5 (26)	Nb(1)-O(3)-Nb(6)	89.1 (8)
O(16)-Nb(3)-O(14)	105.9 (12)	O(3)-Nb(5)-O(9)	76.6 (10)	Nb(1)-O(6)-Nb(5)	114.0 (12)	Mean	89.3 (2)
O(8)-Nb(4)-O(1)	105.3 (13)	O(3)-Nb(6)-O(5)	78.8 (10)	Nb(1)-O(7)-Nb(6)	117.9 (13)	Nb(2)-O(3)-Nb(3)	93.6 (8)
O(8)-Nb(4)-O(2)	105.0 (13)	O(3)-Nb(6)-O(10)	76.6 (9)	Nb(5)-O(11)-Nb(6)	116.2 (15)	Nb(2)-O(3)-Nb(4)	95.2 (8)
Mean	105.4 (5)	Mean	77.1 (14)	Mean	116.0 (20)	Nb(3)-O(3)-Nb(4)	93.1 (8)
O(15)-Nb(2)-O(4)	102.1 (13)	O(6)-Nb(1)-O(7)	91.2 (11)	Nb(2)-O(14)-Nb(3)	114.0 (12)	Mean	94.0 (11)
O(15)-Nb(2)-O(17)	102.7 (13)	O(6)-Nb(5)-O(11)	91.6 (11)	Nb(2)-O(1)-Nb(4)	114.7 (11)	Nb(1)-O(3)-Nb(2)	87.9 (8)
O(16)-Nb(3)-O(5)	99.4 (13)	O(7)-Nb(6)-O(11)	90.4 (11)	Nb(3)-O(2)-Nb(4)	113.7 (12)	Nb(1)-O(3)-Nb(3)	88.0 (8)
O(16)-Nb(3)-O(18)	102.1 (13)	Mean	91.0 (6)	Mean	114.1 (5)	Nb(2)-O(3)-Nb(5)	89.5 (8)
O(8)-Nb(4)-O(9)	103.2 (13)	O(7)-Nb(1)-O(18)	86.7 (11)	Mn-O(1)-Nb(2)	99.1 (11)	Nb(3)-O(3)-Nb(6)	87.5 (8)
O(8)-Nb(4)-O(10)	102.9 (13)	O(4)-Nb(5)-O(6)	88.0 (11)	Mn-O(1)-Nb(4)	100.1 (11)	Nb(4)-O(3)-Nb(5)	89.2 (8)
Mean	102.1 (19)	O(5)-Nb(6)-O(7)	87.2 (11)	Mn-O(2)-Nb(3)	100.4 (12)	Nb(4)-O(3)-Nb(6)	87.8 (8)
O(3)-Nb(2)-O(1)	74.5 (9)	Mean	87.3 (7)	Mn-O(2)-Nb(4)	99.8 (12)	Mean	88.3 (10)
O(3)-Nb(2)-O(14)	75.6 (9)	O(17)-Nb(1)-O(18)	83.7 (11)	Mn-O(14)-Nb(2)	100.4 (12)		
O(3)-Nb(3)-O(2)	75.0 (9)	O(4)-Nb(5)-O(9)	80.7 (11)	Mn-O(14)-Nb(3)	100.3 (12)		
O(3)-Nb(3)-O(14)	74.8 (9)	O(5)-Nb(6)-O(10)	82.0 (11)	Mean	100.0 (7)		
O(3)-Nb(4)-O(1)	74.1 (9)	Mean	82.1 (15)				
O(3)-Nb(4)-O(2)	75.3 (9)	O(6)-Nb(1)-O(17)	86.2 (10)				
Mean	75.0 (8)	O(9)-Nb(5)-O(11)	89.3 (11)				
O(3)-Nb(2)-O(4)	77.2 (9)	O(10)-Nb(6)-O(11)	89.0 (11)				
O(3)-Nb(2)-O(17)	77.5 (10)	Mean	88.2 (17)				
O(3)-Nb(3)-O(5)	80.0 (10)	O(1)-Nb(2)-O(4)	88.3 (10)				
O(3)-Nb(3)-O(18)	76.9 (10)	O(2)-Nb(3)-O(5)	91.2 (11)				
O(3)-Nb(4)-O(9)	76.4 (10)	O(1)-Nb(4)-O(9)	87.3 (11)				
O(3)-Nb(4)-O(10)	77.8 (10)	Mean	88.9 (20)				
Mean	77.6 (18)	O(3)-Nb(4)-O(8)	179.3 (12)				
O(3)-Nb(1)-O(6)	77.5 (9)	O(3)-Nb(3)-O(16)	178.8 (11)				
O(3)-Nb(1)-O(7)	76.3 (9)	O(3)-Nb(2)-O(15)	179.3 (12)				
O(3)-Nb(5)-O(6)	78.7 (9)	Mean	179.1 (3)				
O(3)-Nb(5)-O(11)	77.9 (10)	O(3)-Nb(1)-O(19)	178.0 (11)				
O(3)-Nb(6)-O(7)	76.7 (9)	O(3)-Nb(5)-O(12)	179.0 (13)				
O(3)-Nb(6)-O(11)	76.5 (10)	O(3)-Nb(6)-O(13)	176.5 (12)				
Mean	77.3 (12)	Mean	177.8 (13)				
O(19)-Nb(1)-O(6)	100.6 (12)	O(1)-Nb(2)-O(17)	150.4 (10)				
O(19)-Nb(1)-O(7)	104.4 (13)	O(4)-Nb(2)-O(14)	150.0 (11)				
O(12)-Nb(5)-O(11)	101.3 (15)	O(2)-Nb(3)-O(18)	150.3 (11)				
O(12)-Nb(5)-O(16)	100.8 (14)	O(5)-Nb(3)-O(14)	152.6 (11)				
O(13)-Nb(6)-O(7)	105.4 (13)	O(1)-Nb(4)-O(10)	149.3 (10)				
O(13)-Nb(6)-O(11)	100.6 (13)	O(2)-Nb(4)-O(9)	148.6 (11)				
Mean	102.2 (24)	Mean	150.2 (20)				
O(19)-Nb(1)-O(17)	103.4 (13)	O(6)-Nb(1)-O(18)	153.8 (11)				
O(19)-Nb(1)-O(18)	105.2 (13)	O(7)-Nb(1)-O(17)	152.1 (10)				
O(12)-Nb(5)-O(4)	103.2 (14)	O(4)-Nb(5)-O(11)	155.1 (11)				
O(12)-Nb(5)-O(9)	104.0 (14)	O(6)-Nb(5)-O(9)	154.6 (11)				
O(13)-Nb(6)-O(5)	104.0 (13)	O(5)-Nb(6)-O(11)	155.1 (12)				
O(13)-Nb(6)-O(10)	101.6 (12)	O(7)-Nb(6)-O(10)	152.6 (11)				
Mean	103.6 (18)	Mean	153.9 (15)				
O(1)-Nb(2)-O(14)	72.4 (10)						
O(2)-Nb(3)-O(14)	72.4 (10)						
O(1)-Nb(4)-O(2)	72.2 (10)						
Mean	72.3 (1)						

[a] Quantities equivalent by the pseudo-threefold symmetry of the anion are grouped together, and their average values are given with the approximate maximum range of individual values in units of the last significant figure.

the two being related by the glide and twofold screw operations. The anions do not contact each other but are separated by water molecules. The shortest interanion distances are (in Å): 4.2_0 (O(13)-O(19)), 4.34 (O(12)-O(17)), 4.5_2 (O(13)-O(18)), and 4.8_1 (C(13)-O(19)).

Interatomic distances and angles involving sodium ions and water molecules are given in Tables V and VI. The identification of sodium ions and water molecules is based on stereochemistry and temperature factors, as described under refinement of the structure.

Sodium–water distances vary from 2.3 to 2.8 Å. The coordination polyhedra of Na(1), Na(2), and Na(3) are distorted octahedra. The octahedra about Na(1) and Na(2) have an edge in common, and the octahedra

about Na(2) and Na(3) have a face in common. (The distance Na(2)-Na(3) is 3.20 ± 0.03 Å.) Face sharing by sodium–water octahedra has recently been found in $Na_2GeO_3 \cdot 6H_2O$ and in the isomorphous silicate.[18] Edge sharing by sodium–water octahedra is fairly common in highly hydrated sodium salts.[27–30] The coordination of Na(4) is irregular. Atom Na(5) is surrounded by five water molecules at the corners of a distorted square pyramid. There are indications from difference maps that a sixth water molecule is sometimes

(27) P. B. Jamieson and L. S. D. Glasser, *Acta Cryst.*, **20**, 688 (1966).
(28) D. Bedlivy and A. Preisinger, *Z. Krist.*, **121**, 114 (1965).
(29) P. N. Meulendijk, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **B59**, 403 (1956).
(30) N. Morimotio, *Mineral J.* (Sapporo), **2**, 1 (1956).

TABLE V
SODIUM–WATER DISTANCES (Å)

Na(1)–W(1)	2.40 (5)	Na(3)–W(9)	2.39 (4)
Na(1)–W(2)	2.47 (3)	Na(3)–W(15)	2.44 (4)
Na(1)–W(7)	2.48 (3)	Na(3)–W(17)	2.49 (3)
Na(1)–W(8)	2.42 (4)	Na(3)–W(21)	2.32 (5)
Na(1)–W(19)	2.44 (4)	Na(4)–W(4)	2.45 (5)
Na(1)–W(20)	2.34 (4)	Na(4)–W(14)	2.46 (6)
Na(2)–W(2)	2.43 (3)	Na(4)–W(16)	2.76 (7)
Na(2)–W(3)	2.49 (4)	Na(4)–W(18)	2.32 (6)
Na(2)–W(6)	2.44 (4)	Na(4)–W(22)	2.37 (7)
Na(2)–W(7)	2.36 (3)	Na(5)–W(5)	2.58 (7)
Na(2)–W(13)	2.41 (4)	Na(5)–W(11)	2.47 (5)
Na(2)–W(17)	2.37 (3)	Na(5)–W(16)	2.82 (7)
Na(3)–W(3)	2.49 (4)	Na(5)–W(21)	2.44 (5)
Na(3)–W(6)	2.43 (4)	Na(5)–W(23)	2.54 (5)

TABLE VI
WATER–SODIUM–WATER ANGLES (DEG)

W(1)–Na(1)–W(2)	172.2 (15)	W(16)–Na(4)–W(22)	73.6 (21)
W(1)–Na(1)–W(7)	88.7 (14)	W(18)–Na(4)–W(22)	162.9 (24)
W(1)–Na(1)–W(8)	97.4 (15)	W(5)–Na(5)–W(11)	169.1 (21)
W(1)–Na(1)–W(19)	94.0 (15)	W(5)–Na(5)–W(16)	121.4 (22)
W(1)–Na(1)–W(20)	92.9 (16)	W(5)–Na(5)–W(21)	92.4 (20)
W(2)–Na(1)–W(7)	84.1 (11)	W(5)–Na(5)–W(23)	84.1 (19)
W(2)–Na(1)–W(8)	84.7 (12)	W(11)–Na(5)–W(16)	69.4 (18)
W(2)–Na(1)–W(19)	82.0 (11)	W(11)–Na(5)–W(21)	92.0 (16)
W(2)–Na(1)–W(20)	94.5 (13)	W(11)–Na(5)–W(23)	87.5 (17)
W(7)–Na(1)–W(8)	84.3 (12)	W(16)–Na(5)–W(21)	76.4 (18)
W(7)–Na(1)–W(19)	80.8 (11)	W(16)–Na(5)–W(23)	142.0 (21)
W(7)–Na(1)–W(20)	175.9 (14)	W(21)–Na(5)–W(23)	74.7 (16)
W(8)–Na(1)–W(19)	160.9 (14)	W(6)–Na(2)–W(13)	104.0 (14)
W(8)–Na(1)–W(20)	91.7 (14)	W(6)–Na(2)–W(17)	87.1 (12)
W(19)–Na(1)–W(20)	102.9 (14)	W(7)–Na(2)–W(13)	88.0 (12)
W(2)–Na(2)–W(3)	107.2 (13)	W(7)–Na(2)–W(17)	98.5 (12)
W(2)–Na(2)–W(6)	88.1 (12)	W(13)–Na(2)–W(17)	90.4 (13)
W(2)–Na(2)–W(7)	87.8 (11)	W(3)–Na(3)–W(6)	81.3 (12)
W(2)–Na(2)–W(13)	83.7 (12)	W(3)–Na(3)–W(9)	85.3 (13)
W(2)–Na(2)–W(17)	171.3 (13)	W(3)–Na(3)–W(15)	167.9 (14)
W(3)–Na(2)–W(6)	81.1 (12)	W(3)–Na(3)–W(17)	77.1 (11)
W(3)–Na(2)–W(7)	88.2 (12)	W(3)–Na(3)–W(21)	97.1 (14)
W(3)–Na(2)–W(13)	168.3 (15)	W(6)–Na(3)–W(9)	166.6 (15)
W(3)–Na(2)–W(17)	79.2 (11)	W(6)–Na(3)–W(15)	97.9 (13)
W(6)–Na(2)–W(7)	166.9 (15)	W(6)–Na(3)–W(17)	84.7 (12)
W(4)–Na(4)–W(14)	137.6 (22)	W(6)–Na(3)–W(21)	82.1 (14)
W(4)–Na(4)–W(16)	150.4 (23)	W(9)–Na(3)–W(15)	95.0 (13)
W(4)–Na(4)–W(18)	93.6 (18)	W(9)–Na(3)–W(17)	91.5 (12)
W(4)–Na(4)–W(22)	92.8 (21)	W(9)–Na(3)–W(21)	100.5 (15)
W(14)–Na(4)–W(16)	70.7 (20)	W(15)–Na(3)–W(17)	90.8 (12)
W(14)–Na(4)–W(18)	92.2 (21)	W(15)–Na(3)–W(21)	94.7 (14)
W(14)–Na(4)–W(22)	93.7 (22)	W(17)–Na(3)–W(21)	166.3 (14)
W(16)–Na(4)–W(18)	93.3 (21)		

TABLE VII
ANION–WATER CONTACTS (Å)a

O(1)–W(11)	2.98	O(12)–W(3)	2.77
O(2)–W(12)	3.06	O(12)–W(17)	2.78
O(4)–W(7)	2.73	O(12)–W(19)	3.32
O(4)–W(11)	3.03	O(12)–W(23)	3.16
O(5)–W(8)	2.70	O(13)–W(14)	2.80
O(5)–W(12)	3.02	O(13)–W(18)	2.75
O(6)–W(3)	2.91	O(13)–W(24)	2.88
O(6)–W(6)	2.75	O(14)–W(14)	3.11
O(7)–W(4)	2.88	O(15)–W(12)	2.87
O(7)–W(10)	2.88	O(15)–W(15)	2.73
O(8)–W(14)	2.92	O(15)–W(19)	2.69
O(8)–W(15)	2.92	O(16)–W(11)	2.88
O(8)–W(16)	3.41	O(16)–W(16)	3.00
O(9)–W(6)	3.34	O(16)–W(20)	2.72
O(9)–W(11)	3.34	O(17)–W(14)	3.50
O(9)–W(21)	2.72	O(17)–W(17)	2.85
O(10)–W(6)	3.81	O(18)–W(14)	3.10
O(10)–W(12)	3.57	O(18)–W(18)	2.75
O(10)–W(22)	2.66	O(19)–W(13)	2.83
O(11)–W(2)	2.73	O(19)–W(23)	2.76
O(11)–W(6)	3.44	O(19)–W(24)	2.74

a Standard deviations are in the range 0.05–0.1 Å.

TABLE VIII
WATER–WATER CONTACTS (Å)

W(1)–W(1)*	2.73 (9)	W(7)–W(11)	3.29 (4)
W(1)–W(8)	3.62 (6)	W(7)–W(13)	3.31 (4)
W(1)–W(11)	2.96 (6)	W(7)–W(19)	3.19 (4)
W(1)–W(12)	3.00 (7)	W(7)–W(23)	2.86 (6)
W(1)–W(19)	3.54 (6)	W(8)–W(12)	3.26 (6)
W(1)–W(20)	3.43 (6)	W(8)–W(13)	2.92 (5)
W(2)–W(4)	2.89 (4)	W(8)–W(20)	3.41 (5)
W(2)–W(6)	3.38 (4)	W(8)–W(24)	3.37 (6)
W(2)–W(7)	3.32 (4)	W(9)–W(10)	3.40 (7)
W(2)–W(8)	3.29 (4)	W(9)–W(17)	3.50 (4)
W(2)–W(13)	3.23 (5)	W(9)–W(19)	2.86 (5)
W(2)–W(19)	3.22 (4)	W(10)–W(18)	2.87 (7)
W(2)–W(20)	3.54 (5)	W(10)–W(20)	2.99 (7)
W(3)–W(6)	3.21 (5)	W(10)–W(24)	3.44 (8)
W(3)–W(9)	3.31 (5)	W(11)–W(16)	3.03 (7)
W(3)–W(17)	3.10 (4)	W(11)–W(25)	3.46 (6)
W(3)–W(21)	3.61 (5)	W(12)–W(15)	3.28 (6)
W(3)–W(23)	3.52 (6)	W(13)–W(17)	3.39 (4)
W(4)–W(10)	3.47 (7)	W(13)–W(18)	3.13 (5)
W(4)–W(13)	3.25 (5)	W(14)–W(15)	3.33 (6)
W(4)–W(18)	3.48 (5)	W(14)–W(16)	3.03 (8)
W(4)–W(22)	3.49 (6)	W(14)–W(17)	3.57 (6)
W(4)–W(24)	3.47 (6)	W(14)–W(18)	3.44 (6)
W(5)–W(9)	2.78 (7)	W(15)–W(21)	3.50 (5)
W(5)–W(10)	3.30 (8)	W(16)–W(20)	3.46 (7)
W(5)–W(23)	3.43 (8)	W(16)–W(21)	3.27 (7)
W(5)–W(24)	3.51 (8)	W(16)–W(22)	3.09 (9)
W(6)–W(14)	2.94 (6)	W(18)–W(20)	3.28 (5)
W(6)–W(17)	3.32 (4)	W(20)–W(20)*	3.48 (12)
W(6)–W(21)	3.12 (5)	W(21)–W(23)	3.02 (6)
W(6)–W(22)	3.28 (6)	W(22)–W(24)	3.31 (7)
W(7)–W(8)	3.29 (4)		
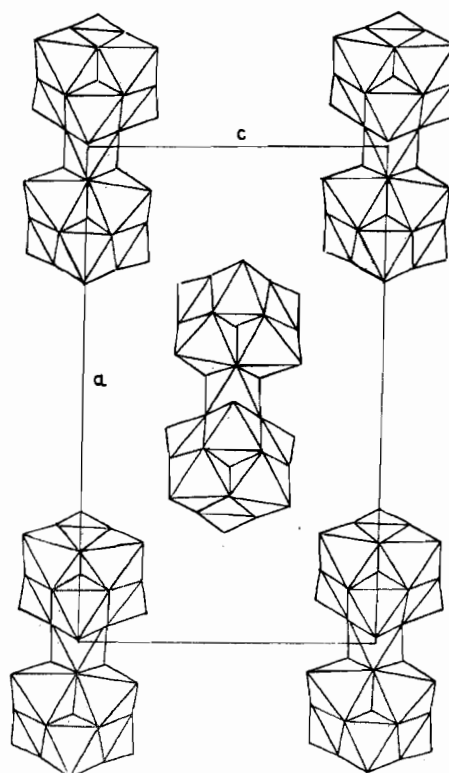
Figure 2.—Packing of the anions in the unit cell, in *ac* projection. The heavy-metal atoms are near the centers of the octahedra, and the oxygen atoms are at the corners. The *b* cell direction runs down into the page.

present, completing a distorted octahedron about Na(5).

Sodium–water distances in other compounds are comparable and vary widely, such that a standard sodium–water distance is difficult to ascertain. Sodium–water distances in some other highly hydrated sodium salts are 2.41–2.49 Å in $Na_2S \cdot 9H_2O$ and $Na_2Se \cdot 9H_2O$,[28] 2.41–2.50 Å in $Na_2SiO_3 \cdot 9H_2O$,[27] 2.36–2.82 Å in $Na_2SiO_3 \cdot 6H_2O$ and $Na_2GeO_3 \cdot 6H_2O$,[18] and 2.39–2.46 Å in $Na_2B_4O_7 \cdot 10H_2O$.[30] In the compound $2Co(en)_3Cl_3 \cdot NaCl \cdot 6H_2O$, isolated sodium–water octahedra are present; the sodium–oxygen distances are all equivalent, being 2.62 Å.[31]

The results of chemical analyses[10] require that six sodium ions exist in the asymmetric unit of the structure. That only five were found is attributed to disorder. In fact, difference maps show marked elongation of the Na(4) peak, and the Na(5) peak height is even lower than most oxygen peaks. The high calculated temperature factors of these two atoms are consistent with partial site occupation, since no allowance was made for the latter in the calculations. To satisfy stoichiometry and electrical neutrality, additional sodium ions would have to be disordered among interstices between water molecules or between anion oxygen atoms and water molecules. The contacts between anion atoms and water molecules, given in Table VII, and between water molecules, given in Table VIII, are

long enough to permit interstitial sodium ions. If such a site were occupied with 20% probability, the electron density therein would be comparable to that of a lithium ion and thus would not be detectable with certainty in the presence of so many heavy atoms.

The high temperature factors of some of the water molecules are attributed to partial site occupation, consistent with the efflorescence of the compound. Allowing for a sixth water molecule coordinated to Na(5), there are 25 water molecules in the asymmetric unit, in agreement with the stoichiometry.

The success of the structure determination supports the correlation of structure and properties used in the solution of the structure. The octahedral coordination of manganese(IV) is to be expected on the basis of its d^3 electron configuration, because of its high crystal field stabilization energy with respect to other geometries. It would be interesting to carry out a complete structure determination of the 9-molybdomanganate(IV) anion, $MnMo_9O_{32}{}^{6-}$, and then compare the geometries of the manganese(IV) in the niobate and molydate and correlate them with spectroscopic and magnetic data. (Only a two-dimensional heavy-atom determination of the $MnMo_9O_{32}{}^{6-}$ structure was carried out by Waugh, *et al.*[32]).

(31) K. Nakatsu, M. Shiro, Y. Saito, and H Kuroya, *Bull. Chem. Soc. Japan*, **30**, 158 (1957).

(32) J. L. T. Waugh, D. P. Shoemaker, and L. Pauling, *Acta Cryst.*, **7**, 438 (1954).

Contribution from the Department of Chemistry,
The University of Arizona, Tucson, Arizona 85721

Transition Metal Nitrosyls. VIII. Complexes of Chromium and Molybdenum

By ROBERT D. FELTHAM, W. SILVERTHORN,[1a] AND G. McPHERSON[1b]

Several new nitrosyl complexes of chromium and molybdenum have been synthesized including *trans*-[CrClNO(das)₂]ClO₄, *cis,cis*-MoCl₂(NO)₂(das), and *cis,cis*-MoCl₂(NO)₂(en). The chromium complex *trans*-CrClNO(das)₂⁺ has a doublet ground state and the esr spectrum shows hyperfine splitting due to both the nitrogen and arsenic nuclei. The measured values of the isotropic hyperfine parameters are $A_{As} = 35$ G and $A_N = 5$ G. The molybdenum compounds are diamagnetic and slowly isomerize to the mononitrosyl hyponitrito complexes {[MoClNO(das)]₂N₂O₂}Cl₂ and {[MoClNO(en)]₂N₂O₂}Cl₂. The first-order rate constants for these isomerization reactions at 25° are 1.10×10^{-4} and 1.13×10^{-5} sec⁻¹, respectively.

Introduction

The past several papers in this series have described the preparation and characterization of mononitrosyl derivatives of iron and cobalt.[2,3] These iron and cobalt

nitrosyl complexes, stabilized with *o*-phenylenebis-(dimethylarsine) (das) and ethylenediamine (en), have structures in which the metal, nitrogen, and oxygen atoms are not collinear.[4] The best *formalism* for discussing these compounds is the valence bond structure in which an N=O⁻ group is bound to the metal *via* the nitrogen atom. This description is explicit in demand-

(1) (a) Taken in part from the Ph.D. Thesis of W. S., University of Arizona, 1967; Shell Fellow, 1966–1967; (b) NSF Undergraduate Research Participant, 1965.
(2) W. Silverthorn and R. D. Feltham, *Inorg. Chem.*, **6**, 1662 (1967).
(3) R. D. Feltham and R. S. Nyholm, *ibid.*, **4**, 1334 (1965).

(4) L. Dahl, private communication.