Computer programs used in refinement: *SHELX*76 (Sheldrick, 1976) and *XFLS* (Busing, Martin & Levy, 1977). Computers used: MicroVAX II and CONVEX C1-XP. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Our structure analysis of $Na_2|Fe(CN)_5NO|.2H_2O$ based on neutron data completes the information concerning the light atoms, *i.e.* hydrogen. The atomic positions and equivalent isotropic thermal parameters are given in Table 1, bond lengths and angles in Table 2.*

The structure (Fig. 1) is in reasonable agreement with that determined by Bottomley & White, (1979) from X-ray data. As expected there are some discrepancies between the atomic positions of the water molecule and of the NO group where the largest thermal parameters of the nitroprusside anion are also found. The Fe—N—O angle (176·2°) is slightly closer to 180° than that (175·7°) found from X-ray diffraction, whilst the distance from the Fe atom to the least-squares mean plane of the *cis* C atoms (0·189 Å, as opposed to 0·182 Å) is slightly greater.

The water oxygen atoms are tetrahedrally coordinated [Na(1)···O(2) = 2·536 (2), Na(2)···O(2) = 2·504 (2) Å]; the corresponding angles centered at O(2) are: Na(1)···O(2)···Na(2) = 95·7 (1), Na(1)···O(2)—H(1) = 119·9 (3), Na(1)···O(2)—H(2) = 117·5 (3), Na(2)···O(2)—H(1) = 114·3 (2) and Na(2)···O(2)—H(2) = 102·6 (2)°.

Both cations are in a similar environment; Na(1) is coordinated to O(2), N(2) and N(3) [Na(1)···N(2) = 2·508 (2), Na(1)···N(3) = 2·498 (2) Å] and Na(2)

to O(2), N(1) and N(2) [Na(2)···N(1) = 2·490 (2), Na(2)···N(2) = 2·538 (2) Å] (Fig. 2).

The polar axis of the nitroprusside anion |N(1)—C(1)—Fe(1)—N(4)—O(1)| (almost parallel to the —N=O direction) lies on the crystallographic mirror plane (Manoharan & Hamilton, 1963), making an angle of 30·3 (2)° with the *a* axis of the cell.

* Lists of observed and calculated structure factors, anisotropic thermal parameters and mean plane equations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51616 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Tetramethylammonium Tetrabromomanganate at Room Temperature

BY KATSUHIKO HASEBE AND TAKANAO ASAHI

Department of Physics, Faculty of Liberal Arts, Yamaguchi University, Yamaguchi 753, Japan

Abstract. $|N(CH_3)_4|_2MnBr_4$, $M_r = 522·8$, orthorhombic, *Pmcn*, $a = 9·301$ (1), $b = 16·182$ (3), $c = 12·750$ (3) Å, $V = 1919$ (1) Å^3, $Z = 4$, $D_x = 1·810$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·7107$ Å, $\mu = 95·20$ cm^{-1}, $F(000) = 1028$, $T = 297$ K, final $R = 0·060$ for 741 independent reflections. The $MnBr_4$ is slightly distort-

ed, while the distortion of $N(CH_3)_4$ is large. Large thermal parameters for Br and C suggest the possibility of the disordering of the constituent ions.

Introduction. Recently the group of compounds $|N(CH_3)_4|_2MCl_4$, with $M = Zn$, Co, Cu, Ni, Fe and Mn, has been of interest because of successive phase transitions and numerous investigations on this group of compounds have been performed (Gesi, 1986, and many references therein). The crystal structures of the compounds with $M = Zn$, Co and Ni have been reported (Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967). $[N(CH_3)_4]_2MCl_4$ and $|N(CH_3)_4|_2$-$CuBr_4$ are known to have incommensurate phase and to have the orthorhombic space group $Pmcn$ in the highest-temperature phase. In $|N(CH_3)_4|_2MCl_4$, condensed wavenumbers are along $\mathbf{c}^*$, while in $[N(CH_3)_4]_2$-$CuBr_4$ the wavenumber is along $\mathbf{b}^*$. $[N(CH_3)_4]_2MBr_4$ members have not been studied in detail; for the structures for $M = Cu$ and Zn see Trouélan, Lefebvre & Derollez (1984, 1985) and for $M = Cu$ Hasebe, Mashiyama & Tanisaki (1985). The present paper reports the structure of $[N(CH_3)_4]_2MnBr_4$ in the high-temperature phase. The crystal shows one phase transition at $276 \cdot 7$ K (Gesi, 1983, 1986).

Experimental. Crystals provided by Dr K. Gesi, a spherical specimen with radius $0 \cdot 109$ mm; an automatic four-circle diffractometer (Rigaku AFC-5), graphite-monochromated Mo $K\alpha$ radiation; cell dimensions from 24 reflections, $9 \cdot 2^\circ < \theta < 11 \cdot 5^\circ$; θ–2θ mode up to $(\sin\theta)/\lambda < 0 \cdot 595$ Å^{-1} $(0 \le h \le 11,\ 0 \le k \le 19,\ 0 \le l \le 15)$, scan speed 5° min^{-1} in θ, scan width $1 \cdot 4^\circ + 0 \cdot 4^\circ \tan\theta$; three standard reflections (511, 163 and 235) monitored every 100 reflections, no significant variation detected. After absorption, Lorentz and polarization corrections, 748 independent reflections with $F > 2\sigma(F)$ out of 1962 reflections were used for the analysis.

Systematic absences of observed reflections $(h0l, l = 2n+1;\ hk0, h+k = 2n+1)$ suggested $Pmcn$ and $Pmc2_1$ as possible space groups. As the former has previously been reported in this phase (Gesi, 1986), $Pmcn$ was assigned. The setting of the crystal axes chosen by Sawada, Shiroishi, Yamamoto, Takashige & Matsuo (1978) was adopted in this paper. Starting parameters of non-hydrogen atoms (Wiesner *et al.*, 1967); atomic scattering factors for neutral atoms, dispersion corrections for Mn and Br from *International Tables for X-ray Crystallography* (1974); full-matrix least-squares refinement with anisotropic thermal factors. At the final stage of the refinement, seven reflections (400, 040, 260, 111, 021, 002 and 013) were removed because of the possibility of extinction effects. $wR = 0 \cdot 051$, $S = 1 \cdot 29$, $w = [\sigma^2(F_o)]^{-1}$, $(\Delta/\sigma)_{max} < 0 \cdot 2$; $(\Delta\rho)_{max}$ and $(\Delta\rho)_{min}$ $0 \cdot 6$ and $-0 \cdot 5$ e Å^{-3}. H atoms could not be found. When the

Table 1. *Positional parameters and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^2)$ *at* 297 K *with e.s.d.'s in parentheses*

U_{eq} = trace $\mathbf{U}/3$.

	x	y	z	U_{eq}
Mn	0·25	0·4084 (2)	0·2485 (3)	5·5 (2)
Br(1)	0·25	0·4030 (2)	0·0539 (2)	9·5 (2)
Br(2)	0·25	0·5516 (2)	0·3178 (3)	12·3 (3)
Br(3)	0·0314 (2)	0·3373 (1)	0·3144 (2)	11·9 (2)
N(1)	0·25	0·0972 (15)	0·1501 (15)	8·1 (15)
C(1)	0·25	0·1020 (23)	0·2575 (22)	20·1 (36)
C(2)	0·25	0·0199 (22)	0·1035 (31)	28·4 (55)
C(3)	0·3666 (31)	0·1475 (21)	0·1076 (21)	26·7 (36)
N(2)	0·25	0·8292 (12)	0·4837 (15)	6·5 (14)
C(4)	0·25	0·7413 (17)	0·4491 (25)	14·0 (27)
C(5)	0·25	0·8911 (21)	0·4097 (24)	21·1 (40)
C(6)	0·3677 (27)	0·8426 (16)	0·5431 (22)	22·2 (29)

Table 2. *Bond lengths* (Å) *and angles* ($^\circ$) *at* 297 K *with e.s.d.'s in parentheses*

Each atom with primed number corresponds to the atom obtained from the original one by a mirror reflection at $x = 1/4$.

Mn–Br(1)	2·483 (5)	N(1)–C(3)	1·46 (4)
Mn–Br(2)	2·480 (5)	N(2)–C(4)	1·49 (4)
Mn–Br(3)	2·483 (4)	N(2)–C(5)	1·38 (4)
N(1)–C(1)	1·37 (4)	N(2)–C(6)	1·35 (3)
N(1)–C(2)	1·39 (5)		

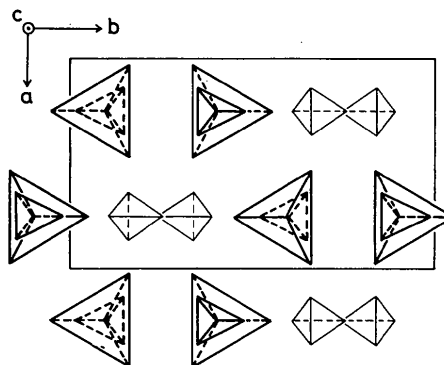|			
Br(1)–Mn–Br(2)	112·9 (2)	Br(2)–Mn–Br(3)	108·2 (2)
Br(1)–Mn–Br(3)	108·8 (2)	Br(3)–Mn–Br(3')	110·0 (1)
C(1)–N(1)–C(2)	118·6 (28)	C(4)–N(2)–C(5)	119·5 (23)
C(1)–N(1)–C(3)	109·8 (26)	C(4)–N(2)–C(6)	108·6 (21)
C(2)–N(1)–C(3)	110·1 (26)	C(5)–N(2)–C(6)	105·6 (23)
C(3)–N(1)–C(3')	96·3 (23)	C(6)–N(2)–C(6')	108·5 (22)

Fig. 1. Projection of the structure of $[N(CH_3)_4]_2MnBr_4$ along the [001] direction. The pseudohexagonal arrangement of $MnBr_4$ and $N(1)(CH_3)_4$ is indicated by bold large and small tetrahedra, while the light small tetrahedra represent $N(2)(CH_3)_4$; the apices represent positions of Br or C atoms.

seven previously removed reflections were included, $R = 0 \cdot 066$, $wR = 0 \cdot 062$ and $S = 1 \cdot 61$ with the same weighting scheme. Computer calculations were carried out with *UNICS*3 (Sakurai & Kobayashi, 1979).

Discussion. The final atomic parameters are listed in Table 1,* bond lengths and angles in Table 2. As shown in Fig. 1, the structure projected along |001| shows a pseudohexagonal arrangement of tetrahedral ions, $MnBr_4$ and one kind of $N(CH_3)_4$ at $z \sim 1/4$ and 3/4; another kind of $N(CH_3)_4$ takes positions at the vacant places at $z \simeq 0$ and 1/2. The distortion of $MnBr_4$ is relatively small. For $N(CH_3)_4$ ions $C-N(1)-C$ angles range from 96° to 119° with standard deviations about 3°; the large distortion of tetrahedra is significant.

It is noticeable that values of the thermal parameters of Br and C atoms are unusually large. Large thermal parameters have been observed in many isomorphous materials (Wiesner et al., 1967; Clay, Murray-Rust & Murray-Rust, 1975; Trouélan et al., 1984). The present result strongly suggests the possibility of disordering of the constituent ions. The disordered-type model was studied by using a block-diagonal-matrix least-squares program, where each ion occupies two mirror-sym-metry-related positions with equal probability. However, no definite result without any assumptions has been obtained.

A study at low temperature is now in progress to study the structural changes accompanying the transition.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51633 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Sodium Alumino-Germanate Sodalites [Na8(Al6Ge6O24)A2, A = Cl, Br, I]

By Michael E. Fleet

Department of Geology, University of Western Ontario, London, Ontario, Canada N6A 5B7

Abstract. $Na_8(Al_6Ge_6O_{24})Cl_2$, $M_r = 1236.2$, cubic, $P\bar{4}3n$, $a = 9.0438 (7)$ Å, $V = 739.7$ Å^3, $Z = 1$, $D_x = 2.775$ g cm^{-3}, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 69.50$ cm^{-1}, $F(000) = 584$, room temperature, final $R = 0.013$ for 111 unique reflections. $Na_8(Al_6Ge_6O_{24})Br_2$, $M_r = 1325.1$, $a = 9.0949 (7)$ Å, $V = 752.3$ Å^3, $D_x = 2.925$ g cm^{-3}, $\mu = 94.71$ cm^{-1}, $F(000) = 620$, final $R = 0.019$ for 453 unique reflections. $Na_8(Al_6Ge_6O_{24})I_2$, $M_r = 1419.1$, $a = 9.1755 (10)$ Å, $V = 772.5$ Å^3, $D_x = 3.050$ g cm^{-3}, $\mu = 85.04$ cm^{-1}, $F(000) = 656$, final $R = 0.016$ for 461 unique reflections. The Na_8Br_2- and Na_8I_2-sodalite have completely ordered $(Al,Ge)O_4$ tetrahedral frameworks, but the Na_8Cl_2-sodalite, which was synthesized at the highest temperature investigated (1048 K), has incipient (12%) Al,Ge disorder. There is distortion of the $(Al,Ge)O_4$ tetrahedra with halide substitution, and the collapse of the alumino-germanate framework to accommodate the interframework ions is not controlled exclusively by simple rotation of the tetrahedral groups.

Introduction. Sodalite |Na8(Al6Si6O24)Cl2 (Pauling, 1930)| has a cuboctahedral framework of (Al,Si)O4 tetrahedral (T) units linked into six-membered rings parallel to |111| and four-membered rings parallel to |100| (Fig. 1). The framework cavity is large enough to accommodate $ClNa_4$ tetrahedral groups. The six-membered rings form continuous channels that allow diffusion of interframework ions (Barrer & Vaughan, 1971). Sodalite *sensu stricto* is a clathrosil framework silicate (Liebau, 1985) but the sodalite cage is used as a building unit in many zeolite structures (Meier, 1968).