structure (Belsky, Zavodnik & Vozzhennikov, 1984). The only significant differences are again in the C(9)—C(10) and C(10)—C(11) bond lengths, which are 1·504 Å in both the low-temperature and room-temperature structures. Also the C(12)—C(13) bond length in this study is 1·467 (7) Å, which agrees well with the low-temperature structure [1·472 (3) Å] and not very well with the room-temperature structure (1·491 Å).

The remainder of the anion, consisting of the 2′,3′-*O*-acetal of 1′,5′-anhydroribose, contains three five-membered rings each in an envelope conformation. In the 1′,5′-anhydroribose segment the two five-membered rings share three atoms which causes the six-membered ring of C(1′), C(2′), C(3′), C(4′), C(5′) and O(4) to be forced into a boat conformation. The conformation, bond lengths, and bond angles of this 1′,5′-anhydroribose fragment agree well with the structural results for this same fragment within the 2,6-anhydro-β-D-fructofuranose molecule (Dreissig & Luger, 1973).

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Structure of Tetramethylammonium Tetrabromomanganate in its Low-Temperature Phase

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Abstract. $[N(CH_3)_4]_2MnBr_4$, $M_r = 522{\cdot}8$, monoclinic, $P2_1/c$, $a = 9{\cdot}236$ (4), $b = 15{\cdot}983$ (9), $c = 12{\cdot}641$ (7) Å, $\beta = 90{\cdot}26$ (4)°, $V = 1866$ Å^3, $Z = 4$, $D_x = 1{\cdot}861$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 91{\cdot}49$ cm^{-1}, $F(000) = 1004$, $T = 223$ K, final $R = 0{\cdot}052$ for 1639 independent reflections with $F > 3\sigma(F)$. Compared with the high-temperature phase, a large decrease in the thermal parameters and in the degree of the distortion of NC_4 tetrahedra are found. The structure is characterized by two kinds of chains composed of $MnBr_4$ and $N(1)(CH_3)_4$; one is along [001] and the other is along [100].

Introduction. It is well known that among insulators of the A_2MX_4 family the compounds $[N(CH_3)_4]_2MX_4$, with M = Zn, Co, Ni, Fe, Mn, Cu, Hg and X = Cl, Br, I, exhibit a wide variety

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of successive phase transitions including incommensurate–commensurate phase transitions (Sawada, Shiroishi, Yamamoto, Takashige & Matsuo, 1978*a*,*b*) and they have received a great amount of attention (Shimizu, Oguri, Abe, Yasuda, Fujimoto, Sawada, Shiroishi & Takashige, 1979; Gesi, 1986, and references therein). As for the structural aspects, each of their highest-temperature phases has *Pmcn* symmetry and is characterized by large thermal parameters (Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967; Clay, Murray-Rust & Murray-Rust, 1975; Kamenar & Nagl, 1976; Kallel, Bats & Daoud, 1981; Trouélan, Lefebvre & Derollez, 1984, 1985; Hasebe, Mashiyama & Tanisaki, 1985; Hasebe, Mashiyama, Koshiji & Tanisaki, 1987; Asahi, Hasebe & Gesi, 1988; Mashiyama & Koshiji, 1989). However, an important difference has been found among modulated phases in these members; in $[N(CH_3)_4]_2MCl_4$, condensed wavenumbers are along **c***, while in $[N(CH_3)_4]_2CuBr_4$ and in $[N(CH_3)_4]_2ZnI_4$ (Werk, Chapuis & Perret, 1987) they are along **b***. Compared with $[N(CH_3)_4]_2MCl_4$ members, $[N(CH_3)_4]_2MBr_4$ compounds have not been widely studied; for the structure of $M = $ Cu and Zn see Trouélan *et al.* (1984, 1985), Hasebe *et al.* (1985) and Asahi *et al.* (1988).

A previous paper has reported the structure of $[N(CH_3)_4]_2MnBr_4$ in the high-temperature phase (Hasebe & Asahi, 1989). Unusually large thermal parameters suggested disorder of constituent ions, but this was not definitely established. This compound undergoes one phase transition at 276·7 K (Gesi, 1983, 1986). The present paper reports the structure in its low-temperature phase in order to investigate the mechanism of the phase transition.

Experimental. Single crystals of $[N(CH_3)_4]_2MnBr_4$ were grown by the slow-evaporation method from an aqueous solution containing stoichiometric proportions of $[N(CH_3)_4]Br$ and $MnBr_2$. D_m was not determined. Spherical specimen with radius 0·109 mm; automatic four-circle diffractometer (Rigaku AFC-5), graphite-monochromated Mo $K\alpha$ radiation. Temperature of the sample kept at 223 ± 0·3 K by controlled nitrogen gas flow. Cell dimensions from 24 reflections, $9·2 < \theta < 10·5°$; ω-scan mode up to $(\sin\theta)/\lambda \le 0·591$ Å^{-1} ($-10 \le h \le 10$, $0 \le k \le 19$, $0 \le l \le 15$), scan speed 5°min^{-1} in θ, scan width $1·9° + 0·5°\tan\theta$; three standard reflections (413, 163 and 235) monitored every 100 reflections, no significant variation detected. 3573 reflections measured, 3237 unique reflections; $R_{\rm int} = 0·047$. Absorption correction was made by numerical integration (local program); transmission-factor ranges from 0·248 to 0·262. 1639 independent reflections with $F > 3\sigma(F)$ were used for the analysis.

From systematic absences of observed reflections ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$), the space group $P2_1/c$ was assigned. This space group is the same as that of $[N(CH_3)_4]_2CuBr_4$ in its lowest-temperature phase (Hasebe, Mashiyama, Tanisaki & Gesi, 1982) and that of $[N(CH_3)_4]_2ZnBr_4$ in its low-temperature phase (Hasebe, Mashiyama, Tanisaki & Gesi, 1984).

When the single crystal was cooled down to its low-temperature phase, single peaks of Bragg reflections split into two due to the formation of monoclinic domains with the (001) plane in common. Because of the small deviation of β from 90°, each measured intensity contains contributions from hkl reflections from the first domain and from $h\bar{k}\bar{l}$ from the second. If the volume fraction of the first domain to the total volume is denoted by x, then the measured intensity can be expressed as follows: $I = xF^2(hkl) + (1 - x)F^2(h\bar{k}\bar{l})$. It can be noticed that $F^2(hkl)$ and $F^2(h\bar{k}\bar{l})$ may be estimated by using the observed intensities of hkl and $h\bar{k}\bar{l}$ reflections when the volume fraction x is known and is not equal to 1/2. The block-diagonal-matrix least-squares program of *UNICS*3 (Sakurai & Kobayashi, 1979) was rewritten to include the volume fraction as a parameter, where $\sum w(\Delta F)^2$ was minimized.

H atoms were neglected. The positional parameters obtained for the isomorphous $[N(CH_3)_4]_2ZnBr_4$ (Asahi *et al.*, 1988) were used as the starting parameters. Least-squares refinement with anisotropic thermal parameters and a total of 138 variable parameters converged to $R = 0·052$, $wR = 0·044$, $S = 0·65$, $w = [\sigma^2(F_o)]^{-1}$, $(\Delta/\sigma)_{\max} < 0·03$. Atomic scattering factors for neutral atoms, dispersion corrections for Mn and Br were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are listed in Table 1.* Bond lengths and angles are given in Table 2. The crystal structure is shown in Figs. 1 and 2. The volume fraction x was 0·393 (2) in this study. The value is rather near to 1/2 so the precision of the estimation of $|F_o|$ would be low. Therefore the estimation of $|F_o|$ and the subsequent difference Fourier synthesis were not made.

Compared with the parameters in the high-temperature phase (Hasebe & Asahi, 1989), values of equivalent isotropic thermal parameters of Br and C atoms decreased by a factor 1/2 or 1/3 in the low-temperature phase, though the value of C(4) is still large. In the harmonic approximation, the degree of decrease can be expected to be equal to the ratio of

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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 52544 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2 × 10^2) *at* 223 K *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Mn	0·2694 (3)	0·4072 (2)	0·2509 (2)	3·2 (1)
Br(1)	0·2286 (2)	0·4046 (1)	0·0552 (2)	4·4 (1)
Br(2)	0·2980 (3)	0·5520 (1)	0·3204 (2)	6·0 (1)
Br(3)	0·0539 (2)	0·3416 (2)	0·3355 (2)	6·4 (1)
Br(4)	0·4952 (3)	0·3260 (2)	0·2960 (2)	5·5 (1)
N(1)	0·2381 (17)	0·0973 (9)	0·1518 (11)	5·0 (6)
C(1)	0·2928 (26)	0·0981 (16)	0·2673 (15)	8·3 (10)
C(2)	0·2549 (31)	0·0126 (12)	0·1058 (18)	9·5 (12)
C(3)	0·3342 (23)	0·1580 (16)	0·0832 (16)	8·2 (12)
C(4)	0·0928 (28)	0·1290 (23)	0·1402 (20)	13·8 (17)
N(2)	0·2505 (17)	0·8302 (9)	0·4885 (9)	3·5 (6)
C(5)	0·2619 (24)	0·7373 (11)	0·4549 (17)	6·1 (9)
C(6)	0·1880 (20)	0·8853 (14)	0·4007 (15)	5·7 (9)
C(7)	0·3929 (19)	0·8606 (14)	0·5155 (17)	5·0 (9)
C(8)	0·1580 (21)	0·8348 (15)	0·5879 (17)	7·2 (10)

Table 2. *Bond lengths* (Å) *and angles* (°) *at* 223 K *with e.s.d.'s in parentheses*

Mn—Br(1)	2·501 (4)	N(1)—C(1)	1·54 (3)	N(2)—C(5)	1·55 (3)
Mn—Br(2)	2·488 (4)	N(1)—C(2)	1·48 (3)	N(2)—C(6)	1·53 (3)
Mn—Br(3)	2·496 (4)	N(1)—C(3)	1·58 (3)	N(2)—C(7)	1·44 (3)
Mn—Br(4)	2·521 (4)	N(1)—C(4)	1·44 (4)	N(2)—C(8)	1·53 (3)

Br(1)—Mn—Br(2)	112·4 (1)
Br(1)—Mn—Br(3)	107·5 (1)
Br(1)—Mn—Br(4)	109·6 (1)
Br(2)—Mn—Br(3)	108·8 (1)
Br(2)—Mn—Br(4)	108·2 (1)
Br(3)—Mn—Br(4)	110·3 (1)

C(1)—N(1)—C(2)	110·2 (18)	C(5)—N(2)—C(6)	112·3 (15)
C(1)—N(1)—C(3)	109·4 (16)	C(5)—N(2)—C(7)	109·0 (16)
C(1)—N(1)—C(4)	113·2 (20)	C(5)—N(2)—C(8)	108·2 (15)
C(2)—N(1)—C(3)	106·6 (17)	C(6)—N(2)—C(7)	108·6 (16)
C(2)—N(1)—C(4)	112·4 (21)	C(6)—N(2)—C(8)	111·1 (16)
C(3)—N(1)—C(4)	104·7 (20)	C(7)—N(2)—C(8)	107·6 (16)

absolute temperature, *i.e.* about 0·76. The excess decrease strongly suggests the disorder of constituent ions in the high-temperature phase. The disorder has been reported in isomorphous compounds $[N(CH_3)_4]_2ZnCl_4$ (Hasebe *et al.*, 1987) and $[N(CH_3)_4]_2CuBr_4$ (Hasebe *et al.*, 1985).

The distortion of the $MnBr_4$ tetrahedron is small in both phases. On the other hand, distortions of the NC_4 tetrahedra are much reduced in this phase: in the high-temperature phase, C—N(1)—C angles range from 96 (2) to 119 (3)° and C—N(2)—C angles from 106 (2) to 120 (2)°.

The structure shown in Fig. 1 was induced by the second-order phase transition through the loss of the mirror plane m_x in the high-temperature phase. In the following, the terminology of displacive-type phase transitions is used in order to describe the structural characteristics. Three kinds of displacements are relevant for each tetrahedral ion; a translation along [100] and rotations about axes along [010] and [001]. The characteristic features exhibited in Fig. 1 are counterclockwise rotations along [010] of all ions, and the same sense of rotations along [001] for each linear chain of $MnBr_4$ and $N(1)(CH_3)_4$ along [001]. The same feature has been found in $[N(CH_3)_4]_2ZnBr_4$ (Asahi *et al.*, 1988) and $[N(CH_3)_4]_2MnCl_4$ (Mashiyama & Koshiji, 1989). For the less distorted $MnBr_4$, the value of translation along [100] and angles of rotation along [010] and [001] were estimated to be 0·179 (3) Å, 8·4 (1) and 6·5 (1)° respectively. The displacement of Mn was taken as the first value, the first angle was defined as the **b** projection of the angle between the Br(1)—Mn direction and the **c*** direction, and the second angle the **c** projection of the angle between the Mn—Br(2) direction and [010].

Another important feature is the existence of zigzag chains along [100] as shown in Fig. 2, where

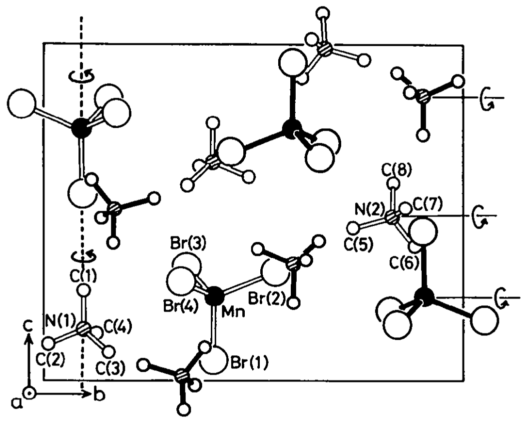

Fig. 1. The **a** projection of the structure of $[N(CH_3]_4]_2MnBr_4$. The dashed line represents a chain along the c axis. Each arrow indicates the sense of rotation along the b or c axis.

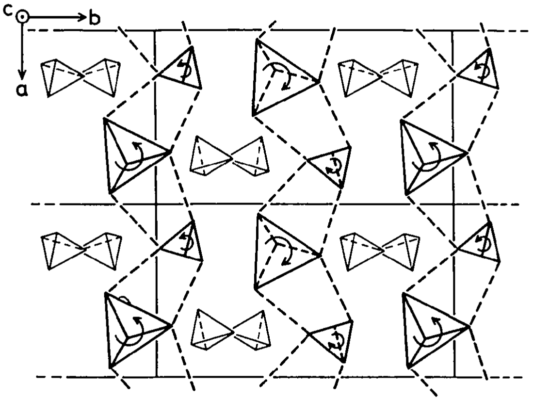

Fig. 2. Rotation of ions with $0 \leq z \leq 1/2$ projected along the c axis. The arrangements of $MnBr_4$ and $N(1)(CH_3)_4$ are indicated as bold large and small tetrahedra, while the light small tetrahedra represent $N(2)(CH_3)_4$; apices represent positions of Br or C atoms.

the sense of rotation changes chain by chain alternately just as in $[N(CH_3)_4]_2ZnBr_4$ (Asahi *et al.*, 1988) and in $[N(CH_3)_4]_2MnCl_4$ (Mashiyama & Koshiji, 1989).

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Structures of Nitratobis(4-nitropyridine *N*-oxide)silver(I) and Dinitratobis(4-nitropyridine *N*-oxide)copper(II)

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Abstract. $[Ag(NO_3)(C_5H_4N_2O_3)_2]$ (I), $M_r = 450{\cdot}1$, monoclinic, $C2/c$, $a = 24{\cdot}073\,(4)$, $b = 5{\cdot}295\,(1)$, $c = 23{\cdot}396\,(4)$ Å, $\beta = 98{\cdot}73\,(2)°$, $V = 2948\,(1)$ Å^3, $Z = 8$, $D_x = 2{\cdot}03$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 1{\cdot}41$ mm^{-1}, $F(000) = 1776$, $T = 299\,(1)$ K, final $R = 0{\cdot}042$ for 2309 observed unique reflections. $[Cu(NO_3)_2(C_5H_4N_2O_3)_2]$ (II), $M_r = 467{\cdot}8$, monoclinic, $P2_1$, $a = 10{\cdot}670\,(2)$, $b = 8{\cdot}1249\,(9)$, $c = 9{\cdot}699\,(2)$ Å, $\beta = 104{\cdot}71\,(2)°$, $V = 813{\cdot}3\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}91$ Mg m^{-3}, $\mu = 1{\cdot}43$ mm^{-1}, $F(000) = 470$, $T = 299\,(1)$ K, final $R = 0{\cdot}031$ for 1715 reflections. In (I), the Ag atom exhibits a distorted tetrahedral geometry to two *N*-oxide O atoms and two O atoms of a nitrate ion. In (II), the two *N*-oxide O atoms and the two O atoms of two nitrate ions coordinate to the Cu atom forming a square-planar *cis* complex. There are no contacts between the metal atoms and the nitro group of 4-nitropyridine *N*-oxide.

Introduction. Certain nitrobenzene derivatives have recently attracted much attention as organic nonlinear optical materials (Twieg & Jain, 1983). If the crystal structure has a center of symmetry, optical second harmonic generation cannot be expected. Accordingly, the control of the molecular arrangement in crystals is desirable. A solution to this problem may be polynuclear metal complex formation. In the present study, the structures of two metal complexes involving 4-nitropyridine *N*-oxide have been studied. Metal cations, Ag^+ and Cu^{2+}, were selected because of their relatively small coordination numbers.

Experimental. (I): Yellow needle-like crystals were obtained from ethanol solution of silver nitrate and 4-nitropyridine *N*-oxide (molar ratio 1/1). A crystal of dimensions $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}35$ mm was mounted on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Laue group $2/m$, systematic absences hkl, $h + k$ odd; $h0l$, h or l odd (Cc or $C2/c$), cell parameters refined by least squares for 25 2θ values ($20 < 2\theta < 30°$); intensity

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