

## Structure of Potassium Sodium Digermanate $\text{Na}_7(\text{Na}_{1-4}\text{K}_{0-6})\text{K}_3[\text{Ge}_2\text{O}_7]_2$

BY E. HALWAX AND H. VÖLLENKLE

*Institut für Mineralogie, Kristallographie und Strukturchemie, Technische Universität, Getreidemarkt 9, A-1060 Wien, Austria*

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**Abstract.**  $\text{K}_{3.6}\text{Na}_{8.4}[\text{Ge}_2\text{O}_7]_2$ ,  $M_r = 848.22$ , monoclinic,  $P2_1/c$ ,  $a = 5.939$  (1),  $b = 15.062$  (3),  $c = 19.904$  (3) Å,  $\beta = 93.31$  (1)°,  $V = 1777.5$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.170$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 77$  cm<sup>-1</sup>,  $F(000) = 1604$ ,  $T = 298$  K,  $R = 0.033$ ,  $wR = 0.038$  for 3184 independent reflections. The structure is made up of ditetrahedral  $\text{Ge}_2\text{O}_7$  groups linked by Na and K atoms. Two of the twelve alkali metal sites were found to have mixed Na/K occupancies.

**Introduction.** To date more than a dozen crystal structure determinations have been reported for compounds of the general composition  $M_a[\text{Ge}_2\text{O}_7]_b$ . These include  $\text{Al}_2\text{Ge}_2\text{O}_7$  (Agafonov, Kahn, Michel & Perez y Jorba, 1986), digermanates of the alkali metals or a combination of them (see below),  $\text{In}_2\text{Ge}_2\text{O}_7$  (Vavilin, Gladikh, Soldatov, Kuz'min, Ilyukhin & Belov, 1974) and a few rare-earth compounds such as those where  $M = \text{La}$  (Smolin, Shepelev & Upatova, 1970),  $\text{Nd}$  (Vetter, Queyroux, Labbe & Goreaud, 1982),  $\text{Eu}$  (Chiragov, Mamedov & Kulieva, 1983),  $\text{Gd}$  (Smolin, Shepelev & Butikova, 1971),  $\text{Tb}$  (Geller & Gaines, 1987) and  $\text{Er}$  (Smolin, 1970). In addition to these are known digermanates such as  $\text{Ba}_2\text{FeGe}_2\text{O}_7$  (Malinovskii, Pobedimskaja & Belov, 1976),  $\text{Na}_2\text{ZrGe}_2\text{O}_7$  (Ilyushin, 1989) and  $\text{NdGaGe}_2\text{O}_7$  (Jarchow, Klaska & Schenk-Strauss, 1985). A structural feature common to all known digermanates, except for some of the rare-earth compounds, is that they contain discrete  $\text{Ge}_2\text{O}_7$  units.

Of the digermanates of univalent metals, the crystal structures have been determined for  $\text{Li}_6\text{Ge}_2\text{O}_7$  (Völlenklee, 1980),  $\text{Na}_4\text{K}_2\text{Ge}_2\text{O}_7$  (Halwax & Völlenklee, 1987) and  $\text{K}_6\text{Ge}_2\text{O}_7$  (Halwax & Völlenklee, 1986). The rubidium and caesium compounds have been reported to crystallize in the structure of  $\text{K}_6\text{Ge}_2\text{O}_7$  (Schartau & Hoppe, 1973). The structure of  $\text{Na}_6\text{Ge}_2\text{O}_7$  is not known.  $\text{Ag}_6\text{Ge}_2\text{O}_7$  (Jansen, 1982) and  $\text{Tl}_6\text{Ge}_2\text{O}_7$  (Touboul, Feutelais & Hebrard, 1976) have been inferred from Guinier and Weissenberg photographs to be isostructural with the respective silicates. As part of a continuing study of alkali germanates, we present here a further new digermanate with  $\text{Ge}_2\text{O}_7$  groups.

**Experimental.** Crystals of the title compound were obtained in crucibles of  $\text{ThO}_2$  through the reaction of  $M_2\text{GeO}_3 + 2\text{MOH}$  where  $M = (60\% \text{ Na}, 40\% \text{ K})$  and subsequent annealing of the reaction product at 893 K for 60 h. The metagermanate,  $M_2\text{GeO}_3$ , was synthesized from  $\text{GeO}_2$  and the carbonates of sodium and potassium. Colourless crystals, sensitive to moisture. A plate-shaped crystal ( $0.12 \times 0.17 \times 0.35$  mm) was selected for a single-crystal study and sealed in a glass capillary. Philips PW 1100 diffractometer, graphite-monochromated  $\text{Mo } K\alpha$  radiation. Lattice parameters from least-squares refinement of  $19 \cdot 2(\sin\theta)$  values determined in the range  $7 < 2\theta < 33^\circ$  using the LAT procedure of the PW 1100 control program. Data were collected using the  $\omega$ - $2\theta$  scan mode with  $\omega$ -scan width  $(0.7 + 0.3\tan\theta)^\circ$ , scan speed  $2^\circ \text{ min}^{-1}$ . 5072 reflections measured,  $(\sin\theta)/\lambda \leq 0.69 \text{ \AA}^{-1}$ ,  $-8 \leq h \leq 8$ ,  $0 \leq k \leq 20$ ,  $0 \leq l \leq 27$ . Three standard reflections (102, 231,  $\bar{1}35$ ), 13% decrease in intensity within 172 h of total X-ray exposure time due to slow decomposition of the crystal. Data were corrected for decrease in standard intensities, Lorentz and polarization effects. No absorption correction.  $R_{\text{int}} = 0.013$  (based on  $F$ ). 4731 unique reflections of which 3184 were used for refinement, those with  $F_o < 6\sigma(F_o)$  were considered unobserved. Structure solved by direct methods using the program *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement on  $F$ , all atoms anisotropic, 271 parameters. The formula assumed at this stage of the refinement was  $\text{Na}_9\text{K}_3[\text{Ge}_2\text{O}_7]_2$ . Owing to conspicuously small thermal parameters for two of the nine Na-atom sites, the structure was subsequently refined by assuming mixed Na/K occupancies for these two sites. The final sodium occupation numbers were 0.64 (2) and 0.74 (2). Final residuals  $R = 0.033$  and  $wR = 0.038$ , goodness-of-fit  $S = 0.96$ , weighting scheme  $w = 0.8559/[\sigma^2(F_o) + 0.0005F_o^2]$ . 15 reflections with  $w^{1/2}(F_o - |F_c|) > 4S$  were excluded during the final stage of refinement. At convergence max. shifts/e.s.d. were  $< 0.02$  and the lowest and highest difference Fourier peaks were  $-1.0$  and  $1.1 \text{ e \AA}^{-3}$ . Refinement was carried out using the program

*SHELX76* (Sheldrick, 1976). Scattering factors for neutral atoms, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

**Discussion.** The final atomic parameters are given in Table 1\* and bond lengths and bond angles are listed in Table 2. The structure of  $\text{Na}_7(\text{Na}_{1.4}\text{K}_{0.6})\text{K}_3[\text{Ge}_2\text{O}_7]_2$  consists of ditetrahedral  $\text{Ge}_2\text{O}_7$  groups linked by Na and K atoms. The asymmetric unit contains two independent digermanate groups, hereafter denoted by *A* and *B* (Fig. 1). Both groups adopt a conformation approximately staggered with respect to their terminal O atoms as can be seen from the three smallest O—Ge—Ge—O torsion angles. These are 47.8 (2), 52.1 (2) and 63.3 (2)° in *A* and -42.3 (2), -51.7 (2) and -61.6 (2)° in *B*. Ge—O—Ge bond angles are 128.3 (2)° in group *A* and 121.3 (2)° in group *B* and are comparable to the values of 128 and 132° observed for  $\text{Na}_4\text{K}_2\text{Ge}_2\text{O}_7$  (Halwax & Völlenk, 1987). In agreement with the observation that large coordination numbers of metal atoms *M* tend to accompany large X—O—X bond angles where X = Si, Ge (*cf.* Liebau, 1985), these are greater than the Ge—O—Ge angle of 125.7° in  $\text{Li}_6\text{Ge}_2\text{O}_7$  (Völlenk, 1980) and less than that of 157° found for  $\text{K}_6\text{Ge}_2\text{O}_7$  (Halwax & Völlenk, 1986). The conformation of both groups, *A* and *B*, is stabilized through cations bonding across both halves of each group [these are Na(7), K(2) and K(3) in group *A* and *M*(2), Na(4), K(1) and K(2) in *B* where *M*(2) is a site of mixed

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53658 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters with *e.s.d.*'s

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{\AA}^2)$
Na(1)	0.3586 (3)	0.3995 (1)	0.1904 (1)	0.019 (1)
<i>M</i> (2)†	0.1113 (3)	0.2594 (1)	0.0495 (1)	0.021 (1)
Na(3)	0.3794 (3)	0.0873 (1)	0.0263 (1)	0.018 (1)
Na(4)	0.0132 (3)	0.1442 (1)	0.4008 (1)	0.019 (1)
Na(5)	0.6151 (3)	0.2222 (1)	0.1379 (1)	0.021 (1)
Na(6)	0.7802 (3)	0.3142 (1)	0.2666 (1)	0.020 (1)
Na(7)	0.5546 (3)	0.5024 (1)	0.3254 (1)	0.017 (1)
<i>M</i> (8)‡	0.2233 (3)	0.4680 (1)	0.0384 (1)	0.025 (1)
Na(9)	0.8200 (4)	0.4058 (2)	0.1239 (1)	0.023 (1)
K(1)	0.2819 (2)	0.3192 (1)	0.3643 (1)	0.0241 (7)
K(2)	0.5451 (2)	0.1229 (1)	0.3232 (1)	0.0214 (6)
K(3)	0.9349 (2)	0.0333 (1)	0.0880 (1)	0.0277 (7)
Ge(1)	0.01547 (8)	0.02035 (3)	0.27021 (3)	0.0108 (2)
Ge(2)	0.18671 (8)	0.20251 (3)	0.20108 (3)	0.0103 (2)
Ge(3)	0.58259 (9)	0.17034 (4)	0.50574 (3)	0.0146 (2)
Ge(4)	0.78048 (9)	0.34725 (4)	0.44414 (3)	0.0126 (2)
O(1)	-0.1814 (6)	-0.0122 (3)	0.2077 (2)	0.023 (2)
O(2)	0.2733 (5)	-0.0353 (2)	0.2698 (2)	0.015 (2)
O(3)	-0.0968 (6)	0.0090 (2)	0.3495 (2)	0.014 (2)
O(4)	0.0721 (6)	0.1384 (2)	0.2680 (2)	0.018 (2)
O(5)	-0.0290 (6)	0.2716 (2)	0.1698 (2)	0.019 (2)
O(6)	0.4139 (6)	0.2604 (2)	0.2388 (2)	0.016 (2)
O(7)	0.2856 (6)	0.1342 (2)	0.1382 (2)	0.016 (2)
O(8)	0.8413 (6)	0.1161 (3)	0.5034 (2)	0.024 (2)
O(9)	0.4695 (6)	0.1489 (2)	0.5836 (2)	0.019 (2)
O(10)	0.3803 (7)	0.1470 (3)	0.4427 (2)	0.037 (3)
O(11)	0.6430 (6)	0.2893 (2)	0.5112 (2)	0.021 (2)
O(12)	0.7965 (6)	0.2771 (2)	0.3762 (2)	0.020 (2)
O(13)	1.0461 (6)	0.3756 (3)	0.4775 (2)	0.027 (2)
O(14)	0.6068 (6)	0.4400 (2)	0.4318 (2)	0.020 (2)

† Site of mixed occupancy: s.o.f. (Na) = 0.64 (2), s.o.f. (K) = 0.36 (2).

‡ Site of mixed occupancy: s.o.f. (Na) = 0.74 (2), s.o.f. (K) = 0.26 (2).

Na/K occupancy]. In either group the bridging O atoms enter into the primary coordination of the alkali atoms (see below). The mean Ge—O bond length is 1.760 Å in each of the two groups. This value lies well within the range of average Ge—O distances known from  $\text{Ge}_2\text{O}_7$  groups of other accurately determined crystal structures: 1.770 Å in  $\beta\text{-Mn}_2\text{GeO}_4$  (Morimoto, Tokonami, Koto & Nakajima, 1972), 1.766 Å in  $\text{Eu}_2\text{Ge}_2\text{O}_7$  (Chiragov, Mamedov & Kulieva, 1983), 1.763 Å in  $\text{Li}_6\text{Ge}_2\text{O}_7$  (Völlenk, 1980), 1.754 Å in  $\text{Tb}_2\text{Ge}_2\text{O}_7$  (Geller & Gaines, 1987), 1.750 Å in  $\text{NdGaGe}_2\text{O}_7$  (Jarchow, Klaska & Schenk-Strauss, 1985), 1.748 Å in  $\text{Na}_2\text{-ZrGe}_2\text{O}_7$  (Ilyushin, 1989) and 1.736 Å in  $\text{Al}_2\text{Ge}_2\text{O}_7$  (Agafonov, Kahn, Michel & Perez y Jorba, 1986).

Except for the mixed-occupancy sites, *M*(2) and *M*(8), the Na atoms show a clear coordination to O atoms. The coordination numbers are 4 and 5, the mean Na—O distances being 2.321 (average over two atoms) and 2.405 Å (average over five atoms). The coordination polyhedra can be described as more or less distorted tetrahedra and trigonal dipyramids. The coordination about *M*(8) is a dipyramid, too, whereas that about *M*(2) is irregular. The sums of bond valences (Brown & Altermatt,

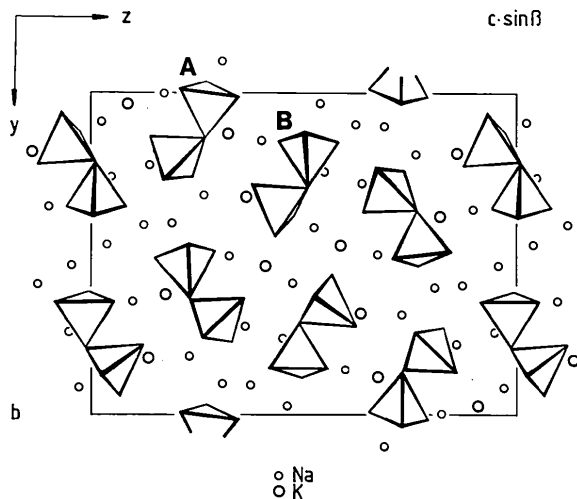


Fig. 1. Projection of the structure along  $[100]$ .

Table 2. Selected bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Digermanate group A	
Ge(1)—O(1)	1.728 (4)
Ge(1)—O(2)	1.746 (3)
Ge(1)—O(3)	1.756 (3)
Ge(1)—O(4)	1.810 (3)
O(1)—Ge(1)—O(2)	114.7 (2)
O(1)—Ge(1)—O(3)	110.0 (2)
O(1)—Ge(1)—O(4)	112.4 (2)
O(2)—Ge(1)—O(3)	109.6 (2)
O(2)—Ge(1)—O(4)	107.9 (2)
O(3)—Ge(1)—O(4)	101.4 (2)
Digermanate group B	
Ge(3)—O(10)	1.723 (4)
Ge(3)—O(8)	1.744 (4)
Ge(3)—O(9)	1.755 (4)
Ge(3)—O(11)	1.829 (4)
O(10)—Ge(3)—O(8)	117.6 (2)
O(10)—Ge(3)—O(9)	108.6 (2)
O(10)—Ge(3)—O(11)	111.7 (2)
O(8)—Ge(3)—O(9)	108.7 (2)
O(8)—Ge(3)—O(11)	106.9 (2)
O(9)—Ge(3)—O(11)	102.2 (2)
Na—O and K—O	
Na(1)—O(6)	2.322 (4)
Na(1)—O(3')	2.372 (4)
Na(1)—O(9 <sup>iii</sup> )	2.375 (4)
Na(1)—O(2 <sup>ii</sup> )	2.484 (4)
Na(1)—O(1')	2.690 (5)
Mean	2.449
Next nearest	3.01
M(2)*—O(13 <sup>iii</sup> )	2.504 (5)
M(2)*—O(5)	2.587 (4)
M(2)*—O(9 <sup>iii</sup> )	2.594 (4)
M(2)*—O(8 <sup>iii</sup> )	2.600 (5)
M(2)*—O(7)	2.745 (5)
M(2)*—O(11 <sup>iii</sup> )	2.934 (5)
M(2)*—O(10 <sup>iii</sup> )	3.074 (5)
Mean	2.720
Next nearest	3.37
Na(3)—O(13 <sup>iii</sup> )	2.225 (4)
Na(3)—O(14 <sup>iii</sup> )	2.370 (4)
Na(3)—O(14 <sup>iii</sup> )	2.413 (4)
Na(3)—O(7)	2.433 (4)
Na(3)—O(11 <sup>iii</sup> )	2.460 (4)
Mean	2.380
Next nearest	4.07
Na(4)—O(10)	2.289 (5)
Na(4)—O(3)	2.353 (4)
Na(4)—O(8 <sup>iii</sup> )	2.374 (5)
Na(4)—O(12 <sup>iii</sup> )	2.414 (4)
Na(4)—O(4)	2.687 (4)
Mean	2.423
Next nearest	3.81
Na(5)—O(5 <sup>iii</sup> )	2.296 (4)
Na(5)—O(9 <sup>iii</sup> )	2.362 (5)
Na(5)—O(7)	2.363 (4)
Na(5)—O(6)	2.464 (4)
Na(5)—O(11 <sup>iii</sup> )	2.542 (4)
Mean	2.405
Next nearest	3.85
Na(6)—O(12)	2.248 (5)
Na(6)—O(6)	2.357 (4)
Na(6)—O(5 <sup>iii</sup> )	2.380 (5)
Na(6)—O(2 <sup>ii</sup> )	2.396 (4)
Mean	2.345
Next nearest	3.16
Ge(2)—O(5)	1.738 (3)
Ge(2)—O(6)	1.740 (3)
Ge(2)—O(7)	1.747 (3)
Ge(2)—O(4)	1.810 (4)
O(5)—Ge(2)—O(6)	113.1 (2)
O(5)—Ge(2)—O(7)	111.5 (2)
O(5)—Ge(2)—O(4)	106.4 (2)
O(6)—Ge(2)—O(7)	108.6 (2)
O(6)—Ge(2)—O(4)	105.3 (2)
O(7)—Ge(2)—O(4)	111.7 (2)
Ge(4)—O(12)	1.723 (4)
Ge(4)—O(13)	1.730 (4)
Ge(4)—O(14)	1.746 (4)
Ge(4)—O(11)	1.827 (4)
O(12)—Ge(4)—O(13)	111.2 (2)
O(12)—Ge(4)—O(14)	116.1 (2)
O(12)—Ge(4)—O(11)	109.1 (2)
O(13)—Ge(4)—O(14)	112.0 (2)
O(13)—Ge(4)—O(11)	105.9 (2)
O(14)—Ge(4)—O(11)	101.6 (2)
Na(7)—O(2 <sup>ii</sup> )	2.277 (4)
Na(7)—O(1')	2.286 (4)
Na(7)—O(7 <sup>iii</sup> )	2.299 (4)
Na(7)—O(14)	2.321 (4)
Mean	2.296
Next nearest	3.61
M(8)*—O(8 <sup>iii</sup> )	2.402 (5)
M(8)*—O(9 <sup>iii</sup> )	2.429 (4)
M(8)*—O(3')	2.475 (4)
M(8)*—O(8 <sup>iii</sup> )	2.656 (5)
M(8)*—O(10 <sup>iii</sup> )	2.775 (5)
Mean	2.547
Next nearest	3.58
Na(9)—O(3 <sup>iii</sup> )	2.302 (4)
Na(9)—O(9 <sup>iii</sup> )	2.337 (4)
Na(9)—O(5 <sup>iii</sup> )	2.372 (4)
Na(9)—O(2 <sup>ii</sup> )	2.388 (4)
Na(9)—O(8 <sup>iii</sup> )	2.432 (5)
Mean	2.366
Next nearest	3.81
K(1)—O(6)	2.804 (4)
K(1)—O(13 <sup>iii</sup> )	2.851 (5)
K(1)—O(14)	2.923 (4)
K(1)—O(1')	2.959 (4)
K(1)—O(12 <sup>iii</sup> )	2.975 (4)
K(1)—O(10)	3.067 (5)
K(1)—O(12)	3.117 (4)
Mean	2.957
Next nearest	3.52
K(2)—O(10)	2.648 (5)
K(2)—O(6)	2.750 (4)
K(2)—O(3 <sup>iii</sup> )	2.758 (5)
K(2)—O(12)	2.924 (4)
K(2)—O(4)	2.966 (4)
K(2)—O(2)	3.036 (4)
Mean	2.847
Next nearest	3.39
K(3)—O(1 <sup>iii</sup> )	2.611 (5)
K(3)—O(13 <sup>iii</sup> )	2.706 (5)
K(3)—O(13 <sup>iii</sup> )	2.715 (5)
K(3)—O(7 <sup>iii</sup> )	2.722 (5)
K(3)—O(14 <sup>iii</sup> )	3.108 (5)
Mean	2.772
Next nearest	3.49

Table 2 (cont.)

## Shortest cation-cation contacts

Ge(3)···Ge(4)	3.186 (1)	Ge(4)···K(1)	3.306 (2)
Ge(1)···Na(9 <sup>iii</sup> )	2.852 (2)	K(1)···K(2)	3.464 (2)
K(3)···Na(3 <sup>iii</sup> )	3.085 (3)	Na(5)···Na(6)	3.026 (3)

Symmetry code: (i)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (ii)  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (iv)  $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (v)  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (vi)  $-1 + x, y, z$ ; (vii)  $1 + x, y, z$ ; (viii)  $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ .

\* Sites of mixed Na/K occupancies (See Table 1).

1985), weighted according to the respective occupation numbers, are calculated to be 1.00 for *M*(2) and 0.99 for *M*(8). For the remainder of the Na atoms,  $\sum s$  ranges from 0.92 to 1.10.

The three K atoms are five-, six- and seven-coordinate, their respective mean K—O distances being 2.772 ( $\sum s = 0.97$ ), 2.847 ( $\sum s = 0.93$ ) and 2.957 Å ( $\sum s = 0.78$ ). The coordination polyhedron about K(2) and K(3) is a distorted octahedron and a trigonal dipyramid, respectively. The coordination about K(1) is irregular.

Inspection of the coordination of O atoms to Ge, K and Na atoms reveals typical coordination numbers of 5 and 6. The bridging O atom, O(4), is coordinated to four atoms only (2Ge + 1K + 1Na), the other, O(11), is surrounded by five atoms (2Ge + 3Na). For the terminal oxygen atoms, the coordination ranges from 1Ge + 4Na for O(5) to 1Ge + 3K + 2Na for O(12) and O(13). On applying the site occupancy factors (s.o.f.'s) given in Table 1 to the calculation of bond strengths for those O atoms bonded to either *M*(2) or *M*(8), one obtains  $\sum s$  values ranging from 1.80 for O(1) to 2.16 for O(13) with an average over all O atoms of 1.95.

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## Di- $\mu$ -iodo-bis[tetracarbonylmanganese(I)]

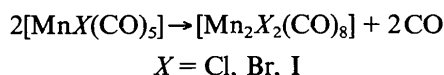
BY JULIAN A. DAVIES, MONIEM EL-GHANAM AND A. ALAN PINKERTON

*Department of Chemistry, University of Toledo, Toledo, OH 43606, USA*

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**Abstract.**  $[\text{Mn}_2\text{I}_2(\text{CO})_8]$ ,  $M_r = 587.77$ , monoclinic,  $P2_1/c$ ,  $a = 9.759$  (1),  $b = 12.252$  (2),  $c = 13.017$  (2) Å,  $\beta = 108.65$  (1)°,  $V = 1474.8$  (1.7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.65$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 58.2$  cm<sup>-1</sup>,  $F(000) = 1072$ ,  $T = 294$  (1) K,  $R = 0.032$  for 1877 unique reflections with  $F_o^2 > 3\sigma(F_o^2)$  of 3212 total data. The I atoms form the dimer. There is pseudo octahedral geometry around the Mn atoms. Ranges of bond lengths and angles: I—Mn 2.691 (1)–2.710 (1), Mn—C<sub>eq</sub> 1.797 (9)–1.815 (8), Mn—C<sub>ax</sub> 1.865 (9)–1.882 (8), Mn···Mn 3.986 (1), C<sub>eq</sub>—O 1.122 (9)–1.16 (1), C<sub>ax</sub>—O 1.108 (9)–1.127 (9) Å, Mn—C—O 177.6 (6)–180 (1), I—Mn—C<sub>ax</sub> 88.0 (2)–89.7 (2), I—Mn—C<sub>eq</sub> 91.2 (3)–92.7 (2), Mn—I—Mn 95.09 (3)–95.10 (3), I—Mn—I 84.61 (3)–85.16 (3)°.

**Introduction.** Since the first synthesis of manganese pentacarbonyl iodide in 1954 (Brimm, Lynch & Sesny, 1954), other carbonyl halides of manganese (Cl, Br) have been prepared and their utility in organometallic synthesis has become apparent (Wimmer & Snow, 1978). These compounds undergo thermal dissociation of coordinated carbon monoxide and dimerization to produce bis[halotetracarbonylmanganese(I)] (Brimm, Lynch & Sesny, 1954), according to the following stoichiometry



It is known that the thermal decomposition of manganese pentacarbonyl iodide to the correspond-

ing bis[iodotetracarbonylmanganese(I)] is easier (Abel & Wilkinson, 1959) than the corresponding dimerization of the rhenium analog, whose X-ray structure has been reported previously (Darst, Lenhart, Lukehart & Warfield, 1980). Although both  $[\text{Mn}_2\text{Cl}_2(\text{CO})_8]$  (Clegg & Morton, 1978) and  $[\text{Mn}_2\text{Br}_2(\text{CO})_8]$  (Dahl & Wei, 1963) have been characterized crystallographically  $[\text{Mn}_2\text{I}_2(\text{CO})_8]$  has not. In order to complete the series of manganese dimers and to allow comparisons with  $[\text{Re}_2\text{I}_2(\text{CO})_8]$ , we describe here the structural characterization of  $[\text{Mn}_2\text{I}_2(\text{CO})_8]$ .

**Experimental.** The complex  $[\text{Mn}_2\text{I}_2(\text{CO})_8]$  was prepared by the reaction of  $[\text{Mn}(\text{CO})_5]^-$  with diiodoacetylene as reported previously (Davies, El-Ghanam, Pinkerton & Smith, 1990). This compound was isolated with other products of the reaction and then separated.  $[\text{Mn}_2\text{I}_2(\text{CO})_8]$  was first identified by infrared and mass spectroscopy. IR (KBr disk):  $\nu(\text{CO})$  1844 (vw), 1868 (w), 1890 (w), 1951 (m), 1960 (w), 1978 (s), 2004 (m), 2026 (m), 2036 (m), 2087 (vs) cm<sup>-1</sup>; MS (70 eV; EI):  $M^+$  (558),  $M^+ - 3\text{CO}$  (504),  $M^+ - 4\text{CO}$  (476),  $M^+ - 5\text{CO}$  (448),  $M^+ - 6\text{CO}$  (420),  $M^+ - 7\text{CO}$  (392),  $\text{Mn}_2\text{I}_2^+$  (364),  $\text{Mn}_2\text{I}^+$  (237),  $\text{MnI}^+$  (182),  $\text{I}^+$  (127),  $\text{Mn}^+$  (55).  $[\text{Mn}_2\text{I}_2(\text{CO})_8]$  was crystallized from hexane to give a brown crystalline material found to be suitable for X-ray analysis. Crystal  $0.34 \times 0.14 \times 0.08$  mm; Enraf-Nonius CAD-4 computer-controlled  $\kappa$ -axis diffractometer, graphite monochromator; cell dimensions from setting angles of 25 reflections,  $10 < \theta <$