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A Reinvestigation of Sodium Metagermanate

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Abstract. Na_2GeO_3, $Cmc2_1$, a = 10·845 (3), b = 6·224 (3), c = 4·918 (1) Å. In the Ge–O chains the mean Ge–O(bridging) = 1·800 (3) Å, Ge–O(non-bridging) = 1·712 Å, and Ge–O–Ge = 124·6°. Na has a distorted trigonal-bipyramidal coordination.

Introduction. The structure was first determined by Ginetti (1954) with R = 0·28. Vollenkle, Wittman & Nowotny (1971) published a refinement with 169 reflexions from integrated Weissenberg photographs using Cu $K\alpha$ radiation. Their R was 0·044; however, due to the small number of reflexions the reported e.s.d.'s for the bond lengths were around 0·01 Å, while the average Ge–O length was somewhat longer than might have been expected. In 1969 we had measured 565 reflexions photographically with Mo $K\alpha$ radiation, but were not satisfied with the quality of the results of a refinement. Through the kindness of Mr R. Faggiani and the late Professor C. Calvo crystals were regrown, and 1083 reflexions were collected with a suitable crystal on a Syntex diffractometer at McMaster University. The cell constants were obtained directly on the diffractometer from the accurate location of 15 reflexions and by least-squares fitting of the reflexion angles and Miller indices. We now, somewhat tardily, report the results of a refinement with these diffractometer data.

Table 1. *Fractional coordinates, vibration tensor components* (Å^2 × 10^4) *and e.s.d.'s*

	x	y	z
Na	0·16760 (8)	0·33982 (12)	0
Ge	0	0·16296 (3)	0·53641 (30)
O(1)	0·13596 (14)	0·29444 (23)	0·47603 (43)
O(2)	0	0·10277 (30)	0·89613 (52)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Na	121 (3)	129 (3)	118 (9)	−8 (8)	−4 (4)	0 (4)
Ge	68 (1)	49 (1)	54 (1)	2 (2)	0	0
O(1)	91 (5)	112 (5)	132 (6)	30 (8)	−0 (8)	−54 (8)
O(2)	169 (8)	59 (6)	63 (6)	14 (10)	0	0

With a weighting function $w = (2{\cdot}120 - 0{\cdot}1101|F_o| + 0{\cdot}00556|F_o|^2 - 0{\cdot}0000241|F_o|^3)^{-1}$, the refinement converged smoothly to a residual on $|F|$ of 0·0264 and to the atomic parameters of Table 1. The refinement used form factors for Na and Ge which were corrected for the real and imaginary components of anomalous dispersion. As data had been collected for positive and negative l values, the numerous Friedel pairs enabled the positive sense for x to be determined unambiguously. The bond lengths and angles are given in Table 2; O(1) is the non-bridging oxygen and O(2) bridges two germanate tetrahedra. The bond-length e.s.d.'s from the least-squares matrix are approximately 0·002 Å, but these estimates should be increased by about 50% to allow for other uncertainties.*

Discussion. The structure is isostructural with Na_2SiO_3 (McDonald & Cruickshank, 1967). The diagrams and much of the description in the latter paper serve well for the metagermanate. In both structures Na has four bonds with O at distances within 0·06 Å of 2·35 Å and a fifth longer bond (2·62 Å in the germanate, 2·55 Å in the silicate). The mean Ge–O bond length is 1·756 Å, and the Ge–O(bridging) bonds are 0·088 Å longer than the Ge–O(non-bridging) bonds (0·080 Å in the silicate). [In both structures, libration corrections of about 0·004 Å are estimated for the T–O bonds, but these are ignored in the following discussion.]

As is common, though not invariable, the Ge–O(bridging)–Ge angle (124·6°) is several degrees smaller than the angle (133·7°) in the corresponding

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33271 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

silicate. The O(2)–T–O(2′) and O(1)–T–O(1′) angles are more distorted from the regular tetrahedral value when T = Ge than when T = Si, despite the greater T–O lengths in the germanate. Louisnathan & Gibbs (1972) have defined triple-angle averages $\langle O-T-O_i\rangle_3$ as the average of the angles O–T–O_i made by a given O with the other three O_i of a tetrahedron. This is a simple measure of the angular space about T required by a given T–O bond. The triple-angle averages in the germanate are 112·2° for T–O(non-bridging) and 104·0 and 108·2° for T–O(bridging), and in the silicate 111·6, and 105·7 and 108·2°. In both structures the shorter T–O(non-bridging) bonds require the greater angular space, as is consistent with several valence theories. With T–O and Na–O bond strengths calculated from the lengths by the method of Brown & Shannon (1973), the bond-strength sums are close to the valences on all atoms in both structures. The similarity of the two structures is emphasized by the closeness of the bond strengths shown in Table 2.

Other determinations of metagermanate structures include $CoGeO_3$ (Peacor, 1968) and $MnGeO_3$ (Fang, Townes & Robinson, 1969). The germanate dimensions are non-bridging 1·727 Å, bridging 1·792 Å and 119·4° in $CoGeO_3$, and 1·714, 1·803 Å and 123·4° in one chain and 1·716, 1·795 Å and 129·7° in the other chain of $MnGeO_3$. These structures have average Ge–O distances of 1·759 and 1·757 Å respectively, which are practically identical with the present average of 1·756 Å. As expected from the silicates, these metagermanate averages are longer than that of 1·739 Å in GeO_2 (Smith & Isaacs, 1964) and a little shorter than the 1·76–1·77 Å typically found in structures with isolated GeO_4 tetrahedra. These values are near the 1·77 Å included for Ge by Kálmán (1971) in his empirical codification of lengths in tetrahedral oxyanions. Bond-length and bond-angle variations in tetrahedral germanates have been carefully reviewed by Hill, Louisnathan & Gibbs (1977).

In the isolated gas-phase molecule $(GeH_3)_2O$ (Glidewell, Rankin, Robiette, Sheldrick, Beagley & Cradock, 1970), Ge–O(bridging) = 1·766 (4) Å and Ge–O–Ge = 126·5 (4)°. These values are quite close to those found in solid sodium metagermanate (where there are, in addition, two weak Na–O bonds), and suggest that similar explanations of the bonding are needed for both structures.

Note added in proof: In crystalline $(GePh_3)_2O$ (Glidewell & Liles, 1978) Ge–O(bridging) = 1·767 (2) Å and Ge–O–Ge = 135·2 (2)°.

Table 2. *Bond lengths* (Å), *angles* (°) *and Brown–Shannon bond strengths*

	Length in Na_2GeO_3	Bond strength in Na_2GeO_3	Bond strength in Na_2SiO_3
Na–O(1)	2·383	0·19	0·20
Na–O(1′)	2·305	0·23	0·23
Na–O(1″)	2·292	0·24	0·25
Na–O(1‴)	2·615	0·12	0·13
Na–O(2)	2·395	0·19	0·18
Ge–O(1)	1·712 (×2)	1·13	1·10 (Si–O)
Ge–O(2)	1·808	0·84	0·87
Ge–O(2′)	1·792	0·88	0·89

		Bond-strength sums		Bond-strength sums	
O(1)–Ge–O(1′)	118·9	Na	0·97	Na	0·99
O(1)–Ge–O(2)	105·6	Ge	3·98	Si	3·96
O(1)–Ge–O(2′)	112·0	O(1)	1·91	O(1)	1·91
O(2)–Ge–O(2′)	100·7	O(2)	2·10	O(2)	2·12
Ge–O(2)–Ge′	124·6				

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