

## SHORT STRUCTURAL PAPERS

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## Cannizzarite

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**Abstract.**  $\text{Pb}_{46}\text{Bi}_{54}\text{S}_{127}$  (Vulcano, Italy), monoclinic,  $P2_1/m$ ,  $a = 189.8$  (2),  $b = 4.09$  (1),  $c = 74.06$  (7) Å,  $\beta = 11.93$  (8)°,  $Z = 2$ ,  $D_x = 6.95$ ,  $D_m = 6.7$  Mg m<sup>-3</sup>. The structure is characterized by alternating layers *A* [(Pb,Bi)<sub>46</sub>S<sub>46</sub>] and *B* [(Pb,Bi)<sub>54</sub>S<sub>81</sub>] parallel to (001). Pseudotranslation according to statistical substructures in each layer is responsible for order–disorder phenomena.

**Introduction.** Graham, Thompson & Berry (1953) derived two monoclinic lattices for natural and synthetic cannizzarite from two systems of reflexions with relatively high intensity. These differed only by the relation  $a_A : a_B = 7 : 12$ . The authors determined  $D_m$  with limited accuracy and found Bi, Pb and S to be the only chemical constituents. The chemical formula is based on these results combined with the present structure determination and the assumption of stoichiometry. Two different statistical substructures *A* [(Pb,Bi)<sub>2</sub>S<sub>2</sub>] and *B* [(Pb,Bi)<sub>4</sub>S<sub>6</sub>] were determined by Matzat (1972) (Fig. 1). Lattice relations were interpreted in connexion with structural data (Matzat, 1977). Cell dimensions of the sublattices are  $a_A = 4.13$ ,  $a_B = 7.03$ ,  $b_A = b_B = 4.09$ ,  $c_A = 15.48$ ,  $c_B = 15.46$  Å,  $\beta_A = 98.56$ ,  $\beta_B = 98.00$ °. The common space group is  $P2_1/m$ .

Precise orthogonalization of data measured on a scanning microdensitometer from Weissenberg films (50 μm raster) made it possible to order all observed reflexions on reciprocal-lattice points corresponding to the given unit cell, which can be described as 46 *A* and 27 *B* subcells combined in the *a* direction and penetrating each other as indicated in Fig. 1. Cell parameters and e.s.d.'s were determined within the orthogonalization process.

Space-group determination is based on the systematic absence of reflexions  $0k0$ ,  $k = 2n + 1$  allowing  $P2_1$  and the relative identity of intensities for  $hkl$  and  $h(k + 2)l$ . When  $I_{h0l} \approx I_{h2l}$  centres of Patterson peaks can be

located at  $y = 0$  or  $y = \frac{1}{2}$ . Patterson density  $p_{(xyz)}$  projected parallel to *b* will be  $p_{0(xz)}$  calculated from  $I_{h0l}$ . The cosine-modulated projection  $p_{2(xz)}$  calculated from  $I_{h2l}$  has identical relative values. Since  $p_{0(xz)} = p_{2(xz)} \times \sum_j \cos(2\pi ky_j)$  summed over *N* peaks, the relation is valid for  $y_j = 0, \frac{1}{2}$ . Atom parameters of the structure are then  $y$  or  $y + \frac{1}{2}$  corresponding to positions on mirror planes at  $y = \frac{1}{4}$  and  $y = \frac{3}{4}$ , and allow the space group to be defined as  $P2_1/m$ .  $I_{hkl} \approx I_{h(k+2)l}$  is valid in this case for all *k*. The difference between corresponding intensities is generally very small and given by a function of  $\sin \theta$  mainly determined by scattering factors and thermal parameters.

Weissenberg film data were collected with Cu  $K_{\alpha}$  radiation (graphite monochromator) from a crystal  $0.036 \times 0.006 \times 0.5$  mm with exposure times of up to 20 d for layers  $h0l$  to  $h4l$ . The intensities of 2965 observable reflexions for layers  $h0l$  and  $h1l$  in the range  $(\sin \theta)/\lambda \leq 0.625$  Å<sup>-1</sup> (13 954 accessible) were visually

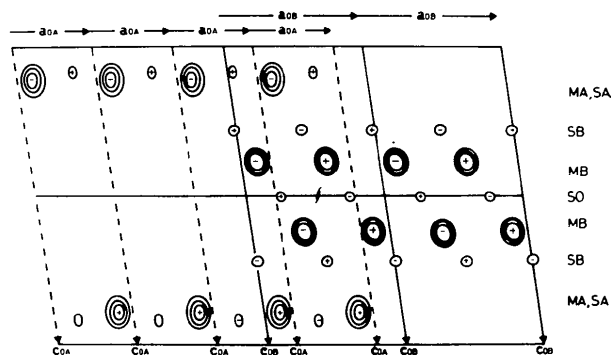


Fig. 1. Cannizzarite. Sine-modulated electron density projection ( $h1l$ ) parallel to  $[010]$  of statistical substructures *A* and *B* in space group  $P2_1/m$  and lattice parameters. The penetration of the combined substructures is indicated near a common  $2_1$  axis. Metal positions are named *MA* and *MB*, sulphur positions *SA* and *SB*, *SO* for substructures *A* and *B* respectively. Contours are at  $\pm 16$ ,  $\pm 32$  and  $\pm 64$  e Å<sup>-2</sup>.

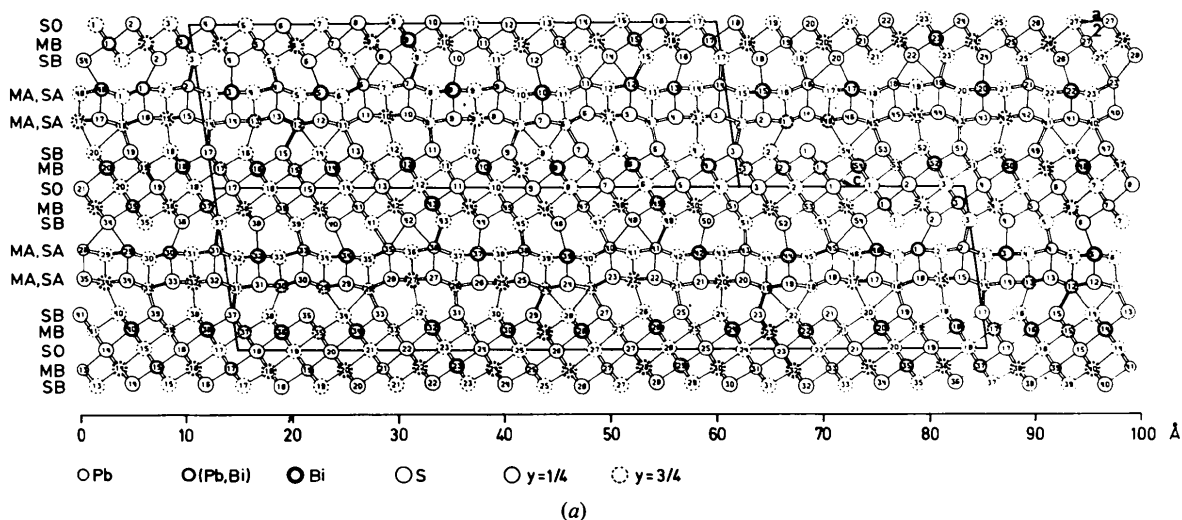


Fig. 2. (a) Projection of the structure of cannizzarite parallel to [010]. Substructural units of (12A)  $\approx$  (7B) and (17A)  $\approx$  (10B) are framed (compare b). One half of the (12A) plus the (17A) unit represents the contents of the asymmetric unit.

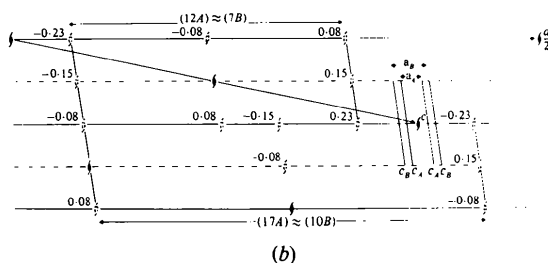


Fig. 2 (cont.). (b) Lattice geometry of cannizzarite.  $2_1$  axes common to substructures A and B are symbolized. Positional differences in the  $a$  direction for selected  $2_1$  axes of sublattices A and B are given in Å at positions where they nearly coincide (dashed symbol). Sublattice unit cells are shown around a common  $2_1$  axis as in Fig. 1.

estimated and corrected for Lorentz-polarization and absorption [ $\mu(\text{Cu } K\alpha) = 147.5 \text{ mm}^{-1}$ ] with a program written by Paulus (unpublished), and were used for the structure determination.

A preliminary structure proposal was made by extending the combination of substructures (Fig. 1) in the  $a$  direction and defining coincident  $2_1$  axes as possible origins (Fig. 2b). Metal atoms of the A layer (MA) were displaced from the statistical position parallel to  $c^*$ , so that the sum of displacements added to zero and the smallest interatomic distance to the nearest S atom of layer B (SB) was the same for all metal atoms ( $3.17 \text{ \AA}$ ). S atoms of layer A (SA) were displaced with the mean displacement of the neighbouring MA, coordinating them as a distorted square. Generally this kind of modulation was confirmed by the final results. Further refinement was achieved by Fourier syntheses. Full-matrix least-squares refinement of the metal positions revealed parameter shifts of up to  $1 \text{ \AA}$

due to strong correlation between pseudotranslational parameters. A weighting factor of  $0.05\text{--}0.1$  was used to compensate for this effect and fairly good convergence was achieved. Fourier syntheses (atom positions and overall temperature parameter) revealed parameter shifts up to  $0.15 \text{ \AA}$ . The final refinement was performed with difference syntheses (metal position and isotropic temperature parameters). Neutral-atom scattering factors with correction for anomalous dispersion for Bi, Pb and S (*International Tables for X-ray Crystallography*, 1974) yielded  $R = 0.099$  for the observed reflexions. Reflexions  $F_{hkl}$  with indices  $h \neq \pm n \times 46$  and  $h \neq \pm n \times 27$  ( $n = 0, 1, 2 \dots$ ) can be interpreted as satellite reflexions due to atom position modulation in the substructures over a period of  $46a_A$  or  $27a_B$ . The average intensity of such reflexions is smaller than that of sublattice reflexions, is dependent on the index  $h$ , and cannot be treated in the usual manner. Since the majority of the unobserved reflexions belong to this category it seems justified to scale them separately with a scale factor  $\sum |F_{o(\text{unobs})}| = \sum |F_{c(\text{unobs})}|$ . The residual  $R = 0.20$  for all accessible structure amplitudes is then an indication that the modulation principle is correct. Final positional and thermal parameters are listed in Table 1. Interatomic distances and bond angles\* and the occupation of metal positions by Pb and Bi based on these data are in good agreement with those in comparable Pb-Bi sulphosalt structures (Edenharter, 1976). Isomorphous replacement (Pb,Bi) has to be accepted at least as indicated in Fig. 2(a).

\* Lists of structure factors and interatomic distances and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33797 (79 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and isotropic thermal parameters ( $\text{\AA}^2$ ) for cannizzarite

The estimated temperature factor for S atoms is  $B = 1.6 \text{ \AA}^2$ . E.s.d.'s are  $0.006 \text{ \AA}$  and  $0.1 \text{ \AA}^2$  for metal atoms,  $M$ , and  $0.03 \text{ \AA}$  and  $0.3 \text{ \AA}^2$  for S atoms. Atoms in layer  $A$  are named  $MA$ ,  $SA$ , in layer  $B$   $MB$ ,  $SB$  and  $SO$ .

ATOM	x	y	z	B	ATOM	x	y	z	B	ATOM	x	y	z	B	ATOM	x	y	z	B
MA 1(PB)	.86432	1/4	.36321	2.90	MA26(PB)	.42771	1/4	.39291	2.50	MB 5(PB)	.04197	1/4	.12483	1.80	MB30(BI)	.50650	3/4	.11876	2.40
MA 2(PB)	.91171	1/4	.37601	2.50	MA27(BI)	.43510	1/4	.42892	1.75	MB 6(BI)	.05752	3/4	.13279	1.85	MB31(PB)	.52276	1/4	.12526	2.30
MA 3(BI)	.91763	1/4	.41511	2.00	MA28(PB)	.47666	1/4	.37628	2.45	MB 7(PB)	.08013	1/4	.12310	1.80	MB32(BI)	.53750	3/4	.13526	2.50
MA 4(PB)	.95152	1/4	.36334	2.35	MA29(PB)	.49487	1/4	.38679	2.35	MB 8(BI)	.10208	3/4	.11291	1.70	MB33(PB)	.56130	1/4	.12269	1.90
MA 5(BI)	.95896	1/4	.42261	1.65	MA30(PB)	.51204	1/4	.39611	3.20	MB 9(BI)	.12459	1/4	.10167	2.10	MB34(BI)	.58235	3/4	.11544	1.45
MA 6(PB)	.99744	1/4	.37644	2.40	MA31(PB)	.53977	1/4	.38227	2.95	MB10(BI)	.13594	3/4	.11946	1.95	MB35(BI)	.60390	1/4	.10808	2.20
MA 7(PB)	.02173	1/4	.37260	2.50	MA32(BI)	.54704	1/4	.41577	2.40	MB11(PB)	.15227	1/4	.12571	1.80	MB36(BI)	.62129	3/4	.11059	2.00
MA 8(BI)	.02842	1/4	.41050	1.70	MA33(PB)	.58267	1/4	.38442	2.60	MB12(BI)	.16694	3/4	.13631	1.65	MB37(BI)	.63949	1/4	.11090	2.50
MA 9(PB)	.05856	1/4	.39129	2.40	MA34(BI)	.59048	1/4	.41982	2.30	MB13(PB)	.19111	1/4	.12209	1.70	MB38(BI)	.65187	3/4	.12722	2.15
MA10(BI)	.06541	1/4	.42369	1.35	MA35(PB)	.62697	1/4	.37858	2.45	MB14(BI)	.21259	3/4	.11349	1.80	MB39(PB)	.67132	1/4	.12570	2.30
MA11(PB)	.10718	1/4	.37522	2.70	MA36(PB)	.65240	1/4	.37765	3.00	MB15(BI)	.23419	1/4	.10562	1.70	MB40(BI)	.68792	3/4	.13104	1.85
MA12(PB)	.12766	1/4	.38646	1.70	MA37(BI)	.65865	1/4	.41006	2.00	MB16(BI)	.24958	3/4	.11321	2.00	MB41(PB)	.71108	1/4	.11971	2.00
MA13(PB)	.13558	1/4	.46453	2.70	MA38(PB)	.68958	1/4	.39958	2.80	MB17(BI)	.26684	1/4	.11657	2.10	MB42(BI)	.73206	3/4	.11212	1.35
MA14(PB)	.16648	1/4	.38767	2.75	MA39(BI)	.69633	1/4	.42758	1.75	MB18(BI)	.27966	3/4	.13176	2.00	MB43(BI)	.75441	1/4	.10139	1.85
MA15(BI)	.17593	1/4	.42345	2.00	MA40(PB)	.73740	1/4	.37516	2.60	MB19(PB)	.30080	1/4	.12605	1.90	MB44(BI)	.76571	3/4	.11951	2.10
MA16(PB)	.21378	1/4	.36226	2.45	MA41(PB)	.75870	1/4	.37573	1.90	MB20(BI)	.31948	3/4	.12578	1.65	MB45(PB)	.78242	1/4	.12486	2.40
MA17(BI)	.22446	1/4	.41095	3.40	MA42(BI)	.76848	1/4	.40563	1.90	MB21(PB)	.34186	1/4	.11676	1.90	MB46(BI)	.79721	3/4	.13475	1.55
MA18(PB)	.25115	1/4	.33164	2.40	MA43(PB)	.79773	1/4	.39133	2.50	MB22(BI)	.36304	3/4	.10897	2.15	MB47(PB)	.82119	1/4	.12130	2.00
MA19(BI)	.26146	1/4	.37427	2.65	MA44(BI)	.80522	1/4	.42709	1.60	MB23(BI)	.38394	1/4	.10204	2.05	MB48(BI)	.84273	3/4	.11254	1.80
MA20(PB)	.26890	1/4	.41116	2.00	MA45(PB)	.84535	1/4	.37702	2.90	MB24(BI)	.39525	3/4	.12002	2.60	MB49(BI)	.86427	1/4	.10398	2.00
MA21(BI)	.32742	1/4	.36612	2.15	MA46(PB)	.86202	1/4	.39297	3.45	MB25(PB)	.41225	1/4	.12477	2.05	MB50(BI)	.88475	3/4	.11707	2.10
MA22(BI)	.32751	1/4	.42523	1.75	PS 1(BI)	.77337	1/4	.11110	2.30	MB26(BI)	.42734	3/4	.13399	1.65	MB51(PB)	.89412	1/4	.12264	2.20
MA23(PB)	.36766	1/4	.37513	2.50	PS 2(BI)	.99274	3/4	.10655	1.90	MB27(PB)	.45087	1/4	.12146	1.50	MB52(BI)	.90802	3/4	.13483	1.50
MA24(PB)	.39645	1/4	.37426	2.15	PS 3(BI)	.01253	1/4	.10641	1.90	MB28(BI)	.47229	3/4	.11281	1.40	MB53(PB)	.93062	1/4	.12542	1.80
MA25(BI)	.39515	1/4	.41137	1.65	PS 4(BI)	.02402	3/4	.12254	1.35	MB29(BI)	.49394	1/4	.10410	2.20	MB54(BI)	.95069	3/4	.12122	2.25

ATOM	x	y	z	ATOM	x	y	z	ATOM	x	y	z	ATOM	x	y	z	ATOM	x	y	z
SA 1	.85583	3/4	.43583	SA27	.41917	3/4	.44292	SB 7	.04917	3/4	.22167	SB33	.53083	3/4	.22000	SO 5	.08125	3/4	.00625
SA 2	.89063	3/4	.44041	SA28	.44222	3/4	.43542	SB 8	.07375	1/4	.20333	SB34	.55292	1/4	.20917	SO 6	.09792	1/4	.01083
SA 3	.90292	3/4	.42750	SA29	.47583	3/4	.40750	SB 9	.08917	3/4	.20875	SB35	.57042	3/4	.21125	SO 7	.11958	3/4	.00333
SA 4	.92750	3/4	.41792	SA30	.46750	3/4	.43333	SB10	.10458	1/4	.21666	SB36	.59042	1/4	.20709	SO 8	.14042	1/4	.99585
SA 5	.94292	3/4	.43667	SA31	.52050	3/4	.40417	SB11	.12042	3/4	.22583	SB37	.60583	3/4	.21458	SO 9	.16167	3/4	.98875
SA 6	.96125	3/4	.44333	SA32	.53208	3/4	.43125	SB12	.13792	1/4	.22917	SB38	.62208	1/4	.22083	SO10	.17708	1/4	.99625
SA 7	.00083	3/4	.39708	SA33	.55500	3/4	.42542	SB13	.16042	3/4	.22042	SB39	.64000	3/4	.22500	SO11	.19292	3/4	.90417
SA 8	.01292	3/4	.42542	SA34	.57500	3/4	.43208	SB14	.18292	1/4	.20792	SB40	.65750	1/4	.22708	SO12	.20750	1/4	.01417
SA 9	.03792	3/4	.41417	SA35	.59408	3/4	.44250	SB15	.20000	3/4	.21000	SB41	.67958	3/4	.21916	SO13	.22958	3/4	.00500
SA10	.04958	3/4	.44292	SA36	.63125	3/4	.39667	SB16	.21750	1/4	.21250	SB42	.70375	1/4	.20292	SO14	.25000	1/4	.99833
SA11	.07167	3/4	.43359	SA37	.64375	3/4	.42375	SB17	.23375	3/4	.21875	SB43	.71917	3/4	.20792	SO15	.27250	3/4	.98917
SA12	.10667	3/4	.40533	SA38	.66917	3/4	.41167	SB18	.24958	1/4	.22666	SB44	.73500	1/4	.21500	SO16	.28875	1/4	.99500
SA13	.11833	3/4	.43205	SA39	.68063	3/4	.44041	SB19	.27042	3/4	.22333	SB45	.75000	3/4	.22667	SO17	.30583	3/4	.99875
SA14	.14917	3/4	.40792	SA40	.70125	3/4	.44167	SB20	.28917	1/4	.22167	SB46	.76792	1/4	.22875	SO18	.32167	1/4	.00667
SA15	.16042	3/4	.43750	SA41	.73750	3/4	.40417	SB21	.31125	3/4	.21375	SB47	.78958	3/4	.22208	SO19	.34000	3/4	.00708
SA16	.18333	3/4	.43166	SA42	.75000	3/4	.43000	SB22	.33292	1/4	.20417	SB48	.81292	1/4	.20667	SO20	.35667	3/4	.01125
SA17	.20958	3/4	.42250	SA43	.77875	3/4	.41042	SB23	.34875	3/4	.20833	SB49	.82917	3/4	.21042	SO21	.38042	1/4	.99958
SA18	.22417	3/4	.43875	SA44	.78633	3/4	.44375	SB24	.36500	1/4	.21417	SB50	.84667	1/4	.21333	SO22	.40125	1/4	.99208
SA19	.26083	3/4	.39875	SA45	.81333	3/4	.43291	SB25	.38042	3/4	.22459	SB51	.86083	3/4	.22583	SO23	.42292	3/4	.98417
SA20	.27417	3/4	.42334	SA46	.84206	3/4	.41666	SB26	.39708	1/4	.22958	SB52	.87792	1/4	.23000	SO24	.43708	1/4	.99542
SA21	.29917	3/4	.41250	SA47	.94125	3/4	.21167	SB27	.41958	3/4	.22125	SB53	.90042	3/4	.22208	SO25	.45208	3/4	.00500
SA22	.31208	3/4	.43772	SB 2	.96167	1/4	.20625	SB28	.44333	1/4	.20500	SB54	.92167	1/4	.21375	SO26	.46833	3/4	.01042
SA23	.33042	3/4	.44417	SB 3	.97750	3/4	.21083	SB29	.45958	3/4	.20833	SO 1	.01125	3/4	.99542	SO27	.49000	1/4	.00292
SA24	.36917	3/4	.40035	SB 4	.99375	1/4	.21708	SB30	.47458	1/4	.21750	SO 2	.03125	1/4	.99125				
SA25	.38167	3/4	.42709	SB 5	.01000	3/4	.22542	SB31	.49083	3/4	.22542	SO 3	.04958	3/4	.99125				
SA26	.40875	3/4	.41125	SB 6	.02706	1/4	.22875	SB32	.50792	1/4	.22958	SO 4	.06625	1/4	.99667				

**Discussion.** In connexion with the structural investigation and synthesis of Pb-Bi sulphosalts the determination of the crystal structure of cannizzarite was undertaken. The structure shows a predominant pseudotranslational component of  $\frac{17}{46} \approx \frac{10}{27}a$ , which fits within  $0.15 \text{ \AA}$ , when applied to the statistical subcells with  $a_A = \frac{1}{46}a$  and  $a_B = \frac{1}{27}a$ . The atomic positions (mean difference  $0.07 \text{ \AA}$ ) and interatomic coordination are also comparable according to this translation, so it has to be introduced as a partial symmetry operation in addition to those given by Dornberger-Schiff (1966). The consequences will be discussed in a separate paper. With multiple application of this partial operation it is possible to derive substructural units of  $\frac{17}{46}$ ,  $\frac{12}{46}$ ,  $\frac{5}{46}$  ... (*e.g.*  $3 \times \frac{17}{46} - 1 = \frac{5}{46}$ ) or geometrically described in subcells of  $(17A) \approx (10B)$ ,  $(12A) \approx (7B)$ .

These can be combined to form similar structures, all named cannizzarite but differing in unit-cell dimensions.

The determined structure is then comprised of geometrical units:  $2 \times (17A) + (12A) \approx 2 \times (10B) + (7B)$ . A synthetic specimen of cannizzarite kindly provided by Dr Mariolacos (Göttingen) shows lattice and intensity features which confirm the relative identity of the structures, but is probably combined of 41  $A$  subcells and 24  $B$  subcells or described in larger units of  $2 \times (12A) + (17A) \approx 2 \times (7B) + (10B)$ , with  $a \approx 169 \text{ \AA}$ . In Fig. 2 one possibility for separating the most probable larger structural and geometrical units of  $(17A) \approx (10B)$  and  $(12A) \approx (7B)$  is indicated. In accordance with the metal position occupation and pseudo  $2_1$  axes, space group  $P2_1/m$  is probable for all cannizzarite structures.

The type of connexion between structural layers formally derived from the galena type is novel. Boundary planes of layers parallel to (001)(cannizzarite) are (100) and (111)(galena) of types  $A$  and  $B$  respectively;

the orientation parallel to [010](cannizzarite) is [110]-(galena) of both layers. The structure of phase 3 synthesized by Graham *et al.* (1953) can be proposed from the cannizzarite structure by adding one octahedral layer to the compact close-packed layer *B* in cannizzarite and this is in good agreement with the statistical lattice parameters given by the authors.

The author is grateful to Professor R. Huber and Dr P. Schwager for permission to use the scanning microdensitometer and for assistance during the measurements. All calculations were performed on a Univac 1108 computer of GWD, Göttingen, with programs

written by the author, except the intensity reduction program.

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## Ammonium Hexachlorotechnetate(IV)

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**Abstract.**  $(\text{NH}_4)_2\text{TcCl}_6$ , *Fm3m*, cubic,  $a = 9.9072$  (8) Å,  $U = 972.42$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.34$  Mg m<sup>-3</sup>,  $\mu = 2.97$  mm<sup>-1</sup> (Mo  $K\alpha$ ). The dianionic complex of technetium is octahedral with six Cl ligands bonded at a distance of 2.3531 (5) Å. The ammonium ions which occupy the eight tetrahedral sites ( $\bar{4}3m$ ) surrounding each complex anion are rotationally disordered. The structure was refined to an  $R$  of 0.033 using 115 independent, observed reflections.

**Introduction.** As part of an ongoing study of Tc complexes as radiopharmaceuticals, we are precisely determining the structures of a series of Tc complexes.

A nearly octahedral, yellow crystal, with edges ~0.25 mm was mounted on a glass fiber. Intensities were measured using Mo  $K\alpha$  radiation on a Syntex P1 diffractometer equipped with a graphite monochromator. The data supported the choice of space group *Fm3m* in agreement with the previous work of Schwocau (1964) and Elder, Fergusson, Gaines, Hickford & Penfold (1967) for various salts of hexahalotechnetium dianions. A total of 552 reflections ( $2.5 < 2\theta < 63.8^\circ$ ) were measured. After corrections for absorption, 115 unique reflections were obtained by averaging equivalent reflections. All 115 had  $I > 2\sigma(I)$  and were used in the subsequent refinement. Calculated transmission coefficients varied from 0.59 to 0.70.

The choice of space group requires the Tc atoms to be located at the fourfold position (0,0,0), the N atoms at the eightfold position  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and the Cl atoms at the

24-fold position of the type  $(x,0,0)$ . A sharpened, origin-removed Patterson map was used to locate the Cl atoms (0.24,0,0) and confirm the choice of the N-atom positions. Refinement of a scale factor, the Cl positional and anisotropic thermal parameters and Tc and N isotropic thermal parameters (six parameters total) converged with  $R = 0.033$  and  $R' = [\sum w(\Delta F)^2 / \sum w(F_o)^2] = 0.025$ .

The H atoms could not be located by examination of electron density or difference maps. Various models were tried placing H at the 32-fold position  $(x,x,x)$  with  $x = 0.19$  or  $x = 0.31$ . Since none of these resulted in improved agreement with the observations, we report here the results for the model without H atoms.\* The refined parameters are as follows: Cl,  $x = 0.23751$  (5),  $U_{11} = 0.0173$  (3),  $U_{22} = U_{33} = 0.0354$  (3) Å<sup>2</sup>; Tc,  $U = 0.0172$  (2) Å<sup>2</sup>; N,  $U = 0.0315$  (8) Å<sup>2</sup>. Neutral-atom scattering factors from Cromer & Mann (1968) were corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). A final difference synthesis was nearly featureless, exhibiting maxima of ~0.4 e Å<sup>-3</sup> at 0.08, 0.08, 0 and 0.48, 0.12, 0. Calculated positions for H had difference densities of ~0.2–0.1 e Å<sup>-3</sup>. Minima were observed ~0.1 Å from Cl (–1.4 e Å<sup>-3</sup>), ~0.6 Å from Tc (–1.0 e Å<sup>-3</sup>) and at

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33898 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.