

In general, X-ray photographs were recorded for several specimens about at least two crystallographic axes for each compound. For 2-methyltriphenylene, however, the thin acicular habit of the crystals allowed them to be mounted only about the *c* axis. Since precession photographs were too weak to confirm the presence or absence of odd *00l* reflexions, a space-group ambiguity remains for this compound. The monoclinic form of what is designated 1,3-dimethyltriphenylene was recognized in only one small specimen and it is possible that this was an isolated crystal of another dimethyltriphenylene.

Table 1 also includes a calculated volume per additional methyl group derived, by comparison with triphenylene itself, from the expression

$$v = n^{-1} [(V/Z) - (1159/4)] \text{ \AA}^3.$$

Here *V* is the cell volume of the substituted triphenylene and 1159 Å that of triphenylene; *n* is the degree of methyl-substitution; *Z* is the number of molecules per unit cell. Although there is a small tendency for *V* to decrease with

increasing substitution, its near constancy implies a remarkable similarity in efficiency of packing for these substituted triphenylenes.

We are grateful to Drs C. C. Barker, H. Heaney and P. Lees for samples and Bradford University for a research scholarship to J.Y.

References

- AHMED, F. R. & TROTTER, J. (1963). *Acta Cryst.* **16**, 503.
- BARKER, C. C., EMMERSON, R. G. & PERIAM, J. G. (1958). *J. Chem. Soc.* p. 1077.
- BARTLE, K. D., HEANEY, H., JONES, D. W. & LEES, P. (1965). *Tetrahedron*, **21**, 3289.
- BARTLE, K. D., HEANEY, H., JONES, D. W. & LEES, P. (1966). *Spectrochim. Acta*, **22**, 941.
- BARTLE, K. D. & JONES, D. W. (1967). *Trans. Faraday Soc.* **63**, 2868.
- BARTLE, K. D. & JONES, D. W. (1969). *J. Chem. Soc.* p. 437.
- HEANEY, H. & LEES, P. (1968). Private communication.

Acta Cryst. (1969). **B25**, 2650

Refinement of the structure of magnesium thiosulphate hexahydrate, MgS₂O₃.6H₂O. By S. BAGGIO, L. M. AMZEL* and L.N. BECKA,* *Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela*

(Received 7 April 1969)

The structure of MgS₂O₃.6H₂O, determined by Nardelli, Fava & Giraldi (*Acta Cryst.* (1962), **15**, 225) has been refined with the use of more extensive data. The refinement by the full-matrix least-squares method with anisotropic temperature factors gives the dimensions of the thiosulphate ion as: S-S distance = 2.013 Å, S-O distance = 1.468 Å, O-S-O angle = 110.1°. Hydrogen atoms have been located in the three-dimensional difference Fourier synthesis.

The most accurate dimensions of the thiosulphate ion reported so far are those published by Nardelli *et al.* (1962) in their paper on the structure of MgS₂O₃.6H₂O. However, since the reported estimated standard deviations are too high to establish whether there is a significant change in dimensions of the thiosulphate moiety when it coordinates to a transition metal, we decided to refine that structure with more data. We also wanted to locate the positions of the hydrogen atoms to confirm the hydrogen bonding scheme predicted by Nardelli *et al.* (1962) and supported by the nuclear magnetic resonance studies of El Saffar (1968, 1969), the latter being in conflict with the n.m.r. results reported by Visweswaramurthy (1963).

The cell data are: *a* = 9.397 ± 0.010, *b* = 14.455 ± 0.015, *c* = 6.864 ± 0.009 Å, *V* = 932.4 Å³, *D_o* = 1.740 (Z = 4), *D_w* = 1.730 g.cm⁻³ (by flotation); μ = 7.0 cm⁻¹ for Mo K α radiation; space group = *Pnma*. We determined the unit-cell dimensions from the $K_{\alpha I}$ - $K_{\alpha II}$ splitting of 89 independent high angle reflexions (recorded on levels *hk0* to *hk5* by the equi-inclination Weissenberg method with Cu K α

radiation) by the least-squares procedure proposed by Alcock & Sheldrick (1967). Intensity data were collected with Zr-filtered Mo radiation on a cylinder shaped crystal of 0.9 mm length × 0.25 mm diameter. Absorption corrections were neglected. We obtained 1589 independent reflexions of measurable intensity (70% of the reflexion sphere of $\sin \theta/\lambda = 0.90$) from mechanically integrated Weissenberg and precession photographs. The intensities were measured with a microdensitometer, and the different layers put on the same scale using the method of Hamilton, Rollett & Sparks (1965). The ratio of maximum observable intensity was 2500:1, and the discrepancy index ($R = \sum |A| / \sum F_o$) for equivalent reflexions measured on different layers is 0.06.

The observed and calculated structure factors are given in Table 1.

The final parameters for the non-hydrogen atoms were obtained by full-matrix least-squares refinement of the observed reflexions, minimizing $\sum w||F_o - |F_c||^2$. The weights, *w*, are chosen to make *wA²* approximately constant in the range of *F_o* and $\sin \theta/\lambda$. The form factors for S, O, Mg²⁺ and H are from *International Tables for X-ray Crystallography* (1962); the oxygen atoms of the S₂O₃²⁻ ion were given a fractional charge of $-\frac{2}{3}$ each and their form factor was

* Present address: Department of Biophysics, Johns Hopkins School of Medicine, The Johns Hopkins University, Baltimore, Md. 21205, U.S.A.

Table 1. Observed and calculated structure factors

Values listed are h , $10F_O$, and $10F_C$. Intensities that could not be distinguished from the background are indicated by the letter U following h . The values of F_C correspond to the parameters listed in the text with the origin shifted by $\frac{1}{2}$ along z .

h	$10F_O$	$10F_C$
0 0 0	0	0
0 1 0	0	0
0 2 0	0	0
0 3 0	0	0
0 4 0	0	0
0 5 0	0	0
0 6 0	0	0
0 7 0	0	0
0 8 0	0	0
0 9 0	0	0
0 10 0	0	0
0 11 0	0	0
0 12 0	0	0
0 13 0	0	0
0 14 0	0	0
0 15 0	0	0
0 16 0	0	0
0 17 0	0	0
0 18 0	0	0
0 19 0	0	0
0 20 0	0	0
0 21 0	0	0
0 22 0	0	0
0 23 0	0	0
0 24 0	0	0
0 25 0	0	0
0 26 0	0	0
0 27 0	0	0
0 28 0	0	0
0 29 0	0	0
0 30 0	0	0
0 31 0	0	0
0 32 0	0	0
0 33 0	0	0
0 34 0	0	0
0 35 0	0	0
0 36 0	0	0
0 37 0	0	0
0 38 0	0	0
0 39 0	0	0
0 40 0	0	0
0 41 0	0	0
0 42 0	0	0
0 43 0	0	0
0 44 0	0	0
0 45 0	0	0
0 46 0	0	0
0 47 0	0	0
0 48 0	0	0
0 49 0	0	0
0 50 0	0	0
0 51 0	0	0
0 52 0	0	0
0 53 0	0	0
0 54 0	0	0
0 55 0	0	0
0 56 0	0	0
0 57 0	0	0
0 58 0	0	0
0 59 0	0	0
0 60 0	0	0
0 61 0	0	0
0 62 0	0	0
0 63 0	0	0
0 64 0	0	0
0 65 0	0	0
0 66 0	0	0
0 67 0	0	0
0 68 0	0	0
0 69 0	0	0
0 70 0	0	0
0 71 0	0	0
0 72 0	0	0
0 73 0	0	0
0 74 0	0	0
0 75 0	0	0
0 76 0	0	0
0 77 0	0	0
0 78 0	0	0
0 79 0	0	0
0 80 0	0	0
0 81 0	0	0
0 82 0	0	0
0 83 0	0	0
0 84 0	0	0
0 85 0	0	0
0 86 0	0	0
0 87 0	0	0
0 88 0	0	0
0 89 0	0	0
0 90 0	0	0
0 91 0	0	0
0 92 0	0	0
0 93 0	0	0
0 94 0	0	0
0 95 0	0	0
0 96 0	0	0
0 97 0	0	0
0 98 0	0	0
0 99 0	0	0
0 100 0	0	0
0 101 0	0	0
0 102 0	0	0
0 103 0	0	0
0 104 0	0	0
0 105 0	0	0
0 106 0	0	0
0 107 0	0	0
0 108 0	0	0
0 109 0	0	0
0 110 0	0	0
0 111 0	0	0
0 112 0	0	0
0 113 0	0	0
0 114 0	0	0
0 115 0	0	0
0 116 0	0	0
0 117 0	0	0
0 118 0	0	0
0 119 0	0	0
0 120 0	0	0
0 121 0	0	0
0 122 0	0	0
0 123 0	0	0
0 124 0	0	0
0 125 0	0	0
0 126 0	0	0
0 127 0	0	0
0 128 0	0	0
0 129 0	0	0
0 130 0	0	0
0 131 0	0	0
0 132 0	0	0
0 133 0	0	0
0 134 0	0	0
0 135 0	0	0
0 136 0	0	0
0 137 0	0	0
0 138 0	0	0
0 139 0	0	0
0 140 0	0	0
0 141 0	0	0
0 142 0	0	0
0 143 0	0	0
0 144 0	0	0
0 145 0	0	0
0 146 0	0	0
0 147 0	0	0
0 148 0	0	0
0 149 0	0	0
0 150 0	0	0
0 151 0	0	0
0 152 0	0	0
0 153 0	0	0
0 154 0	0	0
0 155 0	0	0
0 156 0	0	0
0 157 0	0	0
0 158 0	0	0
0 159 0	0	0
0 160 0	0	0
0 161 0	0	0
0 162 0	0	0
0 163 0	0	0
0 164 0	0	0
0 165 0	0	0
0 166 0	0	0
0 167 0	0	0
0 168 0	0	0
0 169 0	0	0
0 170 0	0	0
0 171 0	0	0
0 172 0	0	0
0 173 0	0	0
0 174 0	0	0
0 175 0	0	0
0 176 0	0	0
0 177 0	0	0
0 178 0	0	0
0 179 0	0	0
0 180 0	0	0
0 181 0	0	0
0 182 0	0	0
0 183 0	0	0
0 184 0	0	0
0 185 0	0	0
0 186 0	0	0
0 187 0	0	0
0 188 0	0	0
0 189 0	0	0
0 190 0	0	0
0 191 0	0	0
0 192 0	0	0
0 193 0	0	0
0 194 0	0	0
0 195 0	0	0
0 196 0	0	0
0 197 0	0	0
0 198 0	0	0
0 199 0	0	0
0 200 0	0	0
0 201 0	0	0
0 202 0	0	0
0 203 0	0	0
0 204 0	0	0
0 205 0	0	0
0 206 0	0	0
0 207 0	0	0
0 208 0	0	0
0 209 0	0	0
0 210 0	0	0
0 211 0	0	0
0 212 0	0	0
0 213 0	0	0
0 214 0	0	0
0 215 0	0	0
0 216 0	0	0
0 217 0	0	0
0 218 0	0	0
0 219 0	0	0
0 220 0	0	0
0 221 0	0	0
0 222 0	0	0
0 223 0	0	0
0 224 0	0	0
0 225 0	0	0
0 226 0	0	0
0 227 0	0	0
0 228 0	0	0
0 229 0	0	0
0 230 0	0	0
0 231 0	0	0
0 232 0	0	0
0 233 0	0	0
0 234 0	0	0
0 235 0	0	0
0 236 0	0	0
0 237 0	0	0
0 238 0	0	0
0 239 0	0	0
0 240 0	0	0
0 241 0	0	0
0 242 0	0	0
0 243 0	0	0
0 244 0	0	0
0 245 0	0	0
0 246 0	0	0
0 247 0	0	0
0 248 0	0	0
0 249 0	0	0
0 250 0	0	0
0 251 0	0	0
0 252 0	0	0
0 253 0	0	0
0 254 0	0	0
0 255 0	0	0
0 256 0	0	0
0 257 0	0	0
0 258 0	0	0
0 259 0	0	0
0 260 0	0	0
0 261 0	0	0
0 262 0	0	0
0 263 0	0	0
0 264 0	0	0
0 265 0	0	0
0 266 0	0	0
0 267 0	0	0
0 268 0	0	0
0 269 0	0	0
0 270 0	0	0
0 271 0	0	0
0 272 0	0	0
0 273 0	0	0
0 274 0	0	0
0 275 0	0	0
0 276 0	0	0
0 277 0	0	0
0 278 0	0	0
0 279 0	0	0
0 280 0	0	0
0 281 0	0	0
0 282 0	0	0
0 283 0	0	0
0 284 0	0	0
0 285 0	0	0
0 286 0	0	0
0 287 0	0	0
0 288 0	0	0
0 289 0	0	0
0 290 0	0	0
0 291 0	0	0
0 292 0	0	0
0 293 0	0	0
0 294 0	0	0
0 295 0	0	0
0 296 0	0	0
0 297 0	0	0
0 298 0	0	0
0 299 0	0	0
0 300 0	0	0
0 301 0	0	0
0 302 0	0	0
0 303 0	0	0
0 304 0	0	0
0 305 0	0	0
0 306 0	0	0
0 307 0	0	0
0 308 0	0	0
0 309 0	0	0
0 310 0	0	0
0 311 0	0	0
0 312 0	0	0
0 313 0	0	0
0 314 0	0	0
0 315 0	0	0
0 316 0	0	0
0 317 0	0	0
0 318 0	0	0
0 319 0	0	0
0 320 0	0	0
0 321 0	0	0
0 322 0	0	0
0 323 0	0	0
0 324 0	0	0
0 325 0	0	0
0 326 0	0	0
0 327 0	0	0
0 328 0	0	0
0 329 0	0	0
0 330 0	0	0
0 331 0	0	0
0 332 0	0	0
0 333 0	0	0
0 334 0	0	0
0 335 0	0	0
0 336 0	0	0
0 337 0	0	0
0 338 0	0	0
0 339 0	0	0
0 340 0	0	0
0 341 0	0	0
0 342 0	0	0
0 343 0	0	0
0 344 0	0	0
0 345 0	0	0
0 346 0	0	0
0 347 0	0	0
0 348 0	0	0
0 349 0	0	0
0 350 0	0	0
0 351 0	0	0
0 352 0	0	0
0 353 0	0	0
0 354 0	0	0
0 355 0	0	0
0 356 0	0	0
0 357 0	0	0
0 358 0	0	0
0 359 0	0	0
0 360 0	0	0
0 361 0	0	0
0 362 0	0	0
0 363 0	0	0
0 364 0	0	0
0 365 0	0	0
0 366 0	0	0
0 367 0	0	0
0 368 0	0	0
0 369 0	0	0
0 370 0	0	0
0 371 0	0	0
0 372 0	0	0
0 373 0	0	0
0 374 0	0	0
0 375 0	0	0
0 376 0	0	0
0 377 0	0	0
0 378 0	0	0
0 379 0	0	0
0 380 0	0	0
0 381 0	0	0
0 382 0	0	0
0 383 0	0	0
0 384 0	0	0
0 385 0	0	0
0 386 0	0	0
0 387 0	0	0
0 388 0	0	0
0 389 0	0	0
0 390 0	0	0
0 391 0	0	0
0 392 0	0	0
0 393 0	0	0
0 394 0	0	0
0 395 0	0	0
0 396 0	0	0
0 397 0	0	0
0 398 0	0	0
0 399 0	0	0
0 400 0	0	0
0 401 0	0	0
0 402 0	0	0
0 403 0	0	0
0 404 0	0	0
0 405 0	0	0
0 406 0	0	0
0		

Table 1 (*cont.*)

Table 2. Final positional parameters ($\times 10^4$), and coefficients B_y ($\times 10^4$) in the expression $\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$, all with their standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{33}
Mg	0	0	0	31 (2)	11 (1)	58 (5)	0 (1)	-7 (3)	-6 (2)
S(1)	0411 (2)	2500	4406 (2)	57 (2)	11 (1)	43 (4)	0	-8 (3)	0
S(2)	2149 (2)	2500	6118 (2)	52 (2)	19 (1)	77 (5)	0	2 (3)	0
O(1)	-0421 (5)	1662 (3)	4778 (5)	96 (8)	29 (2)	106 (12)	-5 (4)	-4 (9)	-5 (5)
O(2)	0904 (7)	2500	2372 (7)	124 (13)	17 (2)	43 (13)	0	-12 (12)	0
O($W1$)	-1545 (3)	0807 (2)	1469 (4)	45 (5)	16 (1)	66 (10)	-2 (2)	-2 (6)	2 (3)
O($W2$)	1270 (4)	1141 (2)	-0295 (5)	74 (6)	17 (1)	95 (11)	-7 (3)	-6 (7)	-6 (4)
O($W3$)	-0982 (4)	0270 (2)	-2592 (5)	65 (6)	22 (2)	81 (11)	-3 (3)	5 (8)	-2 (4)

obtained by interpolation. After two cycles of refinement with isotropic temperature factors followed by three cycles with anisotropic temperature factors, no parameter shifted by more than 1/10 of the e.s.d. The final residual was $R=0.091$ and $R'(\Sigma w|F_0|/\Sigma w|F_c|)=0.105$. We applied the secondary extinction correction given by Zachariasen (1963) in the last two cycles of refinement, refining the parameter C together with the atomic parameters (C converged to a value of 0.032). With the final set of calculated structure factors we computed a three-dimensional difference Fourier synthesis on a mesh of $0.1 \times 0.1 \times 0.1 \text{ \AA}^{-3}$ using reflexions with $\sin \theta/\lambda < 0.40 \text{ \AA}^{-1}$. This map showed six peaks, of 0.5 e. \AA^{-3} , in the asymmetric unit. These peaks clearly correspond to hydrogen atoms since: (a) they are 5 times larger than the e.s.d. of the electron density and 3 times larger than the next highest peaks; (b) the positions are compatible with the hydrogen bonding scheme proposed by Nardelli *et al.* (1962) and less than twice the e.s.d. away from the positions calculated by El Saffar (1969) from his n.m.r. results; (c) when hydrogen atoms at these positions are included in the structure factor calculation R drops to 0.085 and R' to 0.101. The positional and thermal parameters used in the last cycle of least-squares refinement are shown in Table 2, the hydrogen atom coordinates formed in the difference Fourier synthesis are given in Table 3, and the interatomic distances and angles in Table 4. The atoms are named as in the paper by El Saffar (1969), which uses practically the same assignment as Nardelli *et al.* (1962).

Our results give essentially the same coordinates for the

Table 3. Coordinates ($\times 10^3$) and isotropic temperature factors of hydrogen atoms

Standard deviations are given in parentheses.

x/a	y/b	z/c	B
H(1a)	877 (15)	99 (9)	232 (21)
H(1b)	814 (14)	122 (9)	80 (21)
H(2a)	127 (14)	150 (9)	62 (20)
H(2b)	142 (15)	142 (10)	874 (21)
H(3a)	898 (15)	74 (9)	655 (20)
H(3b)	825 (15)	985 (9)	708 (20)

non-hydrogen atoms as those reported by Nardelli *et al.* (1962), and the hydrogen coordinates seen in the difference Fourier synthesis do not differ significantly from those obtained by El Saffar (1969). The agreement between these independent studies provides reliable additional structural data on the OH---S hydrogen bond, which has not been studied in detail so far. The dimensions of the S_2O_3 group have been determined by us with sufficient accuracy to ascertain that there is a significant lengthening of the S-S bond when the $S_2O_3^{2-}$ ion coordinates through its terminal S atom. This lengthening is about 10 times the e.s.d. in the compound $Na_{4n}[Cu(NH_3)_4]_n[Cu_n(S_2O_3)_{2n}]_2$ (Ferrari, Braibanti & Tiripichio, 1966) where each terminal S atom bridges two Cu atoms; and about 7 times the e.s.d. in the compound $[Pd(en)_2][Pd(en)(S_2O_3)_2]$ (Baggio, Amzel & Becka, 1969) where each terminal S atom is bonded to a Pd atom. In the compound $Ni[SC(NH_2)_2]_4S_2O_3 \cdot 4H_2O$ (Fava Gasparri, Musatti & Nardelli, 1966), the S_2O_3 group

Table 4. Distances and angles in $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$

E.s.d.'s are given in parentheses; these estimates take into account correlation and unit-cell errors.

Code for superscripts:

	Atom at		
(None)	x	y	z
1	$x - \frac{1}{2}$	y	$\frac{1}{2} - z$
11	x	y	$z - 1$
111	$-\frac{1}{2} - x$	$-y$	$\frac{1}{2} + z$

(a) Dimensions of the $\text{S}_2\text{O}_3^{2-}$ group:			
S(1)—S(2)	2.013 (3) Å	S(2)—S(1)—O(1)	109.3 (4)°
S(1)—O(2)	1.471 (5)	S(2)—S(1)—O(2)	107.4 (4)
S(1)—O(1)	1.465 (5)	O(2)—S(1)—O(1)	109.5 (6)
O(1)---O(2)	2.398 (7)	O(1)—S(1)—O(1)	111.5 (6)

(b) Dimensions of the $\text{Mg}(\text{H}_2\text{O}_6)^{2+}$ group:			
Mg—O(W1)	2.118 (4) Å	O(W1)—Mg—O(W2)	89.8 (4)
Mg—O(W2)	2.046 (4)	O(W1)—Mg—O(W3)	90.0 (4)
Mg—O(W3)	2.042 (4)	O(W2)—Mg—O(W3)	88.6 (4)

(c) Hydrogen bonds:			
O(W1)---S(2')	3.263 (5) Å	O(W1)—H---S(2')	178°
O(W1)---O(1)	2.793 (6)	O(W1)—H---O(1)	174
O(W2)---S(2'')	3.255 (5)	O(W2)—H---S(2'')	169
O(W2)---O(2)	2.707 (6)	O(W2)—H---O(2)	165
O(W3)---O(1'')	2.753 (6)	O(W3)—H---O(1'')	160
O(W3)---O(W1''')	2.870 (6)	O(W3)—H---O(W1''')	171

coordinates as a bidentate ligand through S and O, there being no significant difference in the S-S bond distance with respect to the $\text{S}_2\text{O}_3^{2-}$ ion. A comparison of the S—O distances determined in all the above mentioned thiosulphate complexes with the S—O distance determined in the ionic thiosulphate shows that the largest difference is less than 3 times the e.s.d. of the bond distance (e.s.d. 0.01 Å in all the complexes). The S—O distances and O—S—O angles of the thiosulphate ion are significantly different (about 10 times the e.s.d.) from those determined in ionic sulphites (see Baggio & Becka, 1969 and references therein) and practically the same as those determined in ionic sulphates (see Baur (1965) and references therein).

The authors are grateful to the Departments de Calculo of the Universidad Central de Venezuela for assistance and generous allocation of computing time. We are also indebted to Drs F. R. Ahmed, B. Foxman, M. E. Pippy, C. T. Prewitt, D. P. Shoemaker and A. Zalkin, for making available to us the FORTRAN IV programs used in the calculations. Finally, we thank Dr El Saffar for providing us with a copy of his paper prior to publication.

References

- ALCOCK, N. W. & SHELDICK, G. M. (1967). *Acta Cryst.* **23**, 35.
- BAGGIO, S. & BECKA, L. (1969). *Acta Cryst.* **25**, 1150.
- BAGGIO, S., AMZEL, L. & BECKA, L. (1969). *Acta Cryst.* In the press.
- BAUR, W. H. (1965). *Acta Cryst.* **19**, 909.
- EL SAFFAR, Z. M. (1968). *Acta Cryst.* **B24**, 1131.
- EL SAFFAR, Z. M. (1969). *Acta Cryst.* **B25**, 1708.
- FAVA GASPARRI, G., MUSATTI, A. & NARDELLI, M. (1966). *Chem. Comm.* p. 602.
- FERRARI, A., BRAIBANTI, A. & TIRIPICCHIO, A. (1966). *Acta Cryst.* **21**, 605.
- HAMILTON, W. C., ROLLETT, J. S. & SPARKS, R. A. (1965). *Acta Cryst.* **18**, 129.
- International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
- NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.* **15**, 227.
- VISWESWARAMURTHY, S. (1963). *Acta Cryst.* **16**, 933.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.