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A Neutron Diffraction Study of Potassium Sulphamate, KSO₃NH₂

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A single-crystal neutron diffraction investigation of potassium sulphamate has been made in which the intensities of 501 reflexions were measured. The structure was refined by a least-squares technique with individual anisotropic temperature factors. The non-hydrogen atom positions obtained agree well with those of Jeffrey & Stadler (J. Chem. Soc. 1951, p. 1467). The hydrogen atom positions differ substantially from those postulated from the X-ray work and the nitrogen atom is in sp^3 configuration. The sulphamate ions are packed one above the other with hydrogen bonds linking them in infinite chains parallel to the c axis.

Introduction

The crystal structure of potassium sulphamate has been studied by Brown & Cox (1940) and by Jeffrey & Stadler (1951) by X-ray methods. In both cases the authors suggest that the nitrogen valency directions are coplanar and that the hydrogen atoms lie in the mirror plane of symmetry of the molecule.

Experimental procedure

Crystals of potassium sulphamate were grown by slow evaporation from a solution of pure sulphamic acid neutralized with pure potassium hydroxide. The crystal data (from Jeffrey & Stadler) are given in Table 1. Large crystals can be grown easily and a specimen of size $4 \times 3 \times 3$ mm was cut and mounted on a two-circle goniometer set so that the c axis of the crystal was along the φ axis of the goniometer and the scattering vector remained in the γ plane for all reflexions. The intensity data were collected on a neutron diffractometer on the Australian Atomic Energy Commission's reactor HIFAR. The beam current at the specimen was approximately 6×10^6 neutrons cm⁻²sec⁻¹, at a wavelength of 1.09 Å. The integrated intensities of 501 reflexions with $\sin \theta / \lambda < 0.65$ were measured. Of these, 81 were recorded as unobserved. There was no evidence of severe extinction effects. The crystal angles were set by hand and the intensity data recorded by

step scanning through the peak in the $\theta - 2\theta$ mode. The scan was made in steps of 0.03° of 2θ under monitor control.

Table 1. Crystal data

Crystal system: Orthorhombic Space group: *Pbcm* (D_{2h}^{11}) (no.57) Cell parameters a = 5.907, b = 8.333, c = 8.302 Å Z = 4 molecules per unit cell $D_x = 2.2$ g.cm⁻³ Mass = 32.5 mg Linear absorption coefficient, $\mu = 0.702$ cm⁻¹

Dimensions of crystal

	Perpendicular distance of face from
Miller indices of face	an origin inside the crystal

	mm
0 0 1	1.70
0 0 - 1	1.70
-1 0 0	1.14
0 1 0	1.49
1 2 0	1.04
1 1 0	0.97
1 0 0	1.14
1 - 2 0	1.68
0 - 1 0	1.75
-1 - 1 0	0.69

Volume calculated from dimensions, 15.85 mm³ Volume calculated from mass, 14.77 mm³

Analysis of data

The data were corrected for absorption and reduced to F_o and $\sigma(F_o)$ by the program CDRABS written by one of us (G.W.C.). The absorption cross sections were taken as the sum of the cross section due to true absorption and that due to incoherent scattering. The

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value used for the incoherent scattering cross section for hydrogen was 34 barns, which is the value found by Melkonian (1949) for hydrogen in water for 0.069 eV neutrons. An estimated standard deviation was assigned to every observed intensity according to expressions $\sigma^2(P) = \sigma_1^2(P) + \sigma_2^2(P)$, $\sigma_1(P) = (P+2B)^{\pm}$ where *P* is the total intensity in the peak less the background intensity *B*, $\sigma_2(P) = \alpha + \beta P$ and where α and β are constants chosen to allow for errors in crystal setting and background determination. Experience has shown that, for data collected under the conditions of this experiment, appropriate values are $\alpha = 200$, $\beta = 0.02$. The unobserved reflexions were assigned an intensity of $P_{\min}/2$ and a standard deviation of $P_{\min}/2$, where P_{\min} is the intensity of the weakest observed reflexion.

Before initial parameters were selected for the leastsquares refinement, structure factors were calculated with the non-hydrogen atom positions found by Jeffrey & Stadler (whose notation is used throughout this work) and the hydrogen atoms in the S–N–O(1) mirror plane. Comparison with the observed structure factors showed immediately that these positions were incorrect, so an intermolecular interaction $N-H \cdots O(2')$ was assumed. Jeffrey & Stadler remark that this distance is shorter than that usually associated with molecular packing in crystals but attribute the shortening to an electrostatic attraction between N^+ and O^- .

On this basis the initial hydrogen coordinates were chosen as (0.279, 0.396, 0.152) and the parameters refined by full-matrix least-squares based on F, using the ORFLS program (Busing, Martin & Levy, 1962*a*) weighting each reflexion as $1/\sigma^2(F)$. The scattering lengths of each atom were fixed at the values given by Bacon (1962) and the overall scale factor, positional and anistropic thermal parameters of each atom were varied. After two cycles it was evident that this model was correct (with hydrogen atoms out of plane), but the observed F values for reflexions 004, 006, 200, 355 and 423 were much lower than calculated. These were strong reflexions and it was assumed they were affected by extinction or setting errors. They were dis-

Table 2. Observed and calculated structure amplitudes with the estimated standard deviation of F_o (×100) Unobserved reflexions are marked with an asterisk.

H = 0, K = 0 • 9 129 159 13 • 2 189 -171 9 • 0 205 -209 7	• 5 203 203 8 • 6 425 -453 8 • H = 4, K = 9 • H = 6, K = 0
2 291 353 4 • 10 110 91 15 • 3 145 155 11 • 1 92 -89 12	• 6• 35 4 35 • 8 81 81 19 • 0 369 403 8 • 0 84 · -73 17
6 367 676 9 • H * 1, K = 2 • 4 80 51 19 • 2 55 46 20	• 7 103 -105 14 • H = 4, K = 1 • 1 135 -157 12 • 2 71 46 20
	• 8 158 -156 11 • 0 48 43 22 • 2 225 -220 9 • 4 106 115 14
n = 0 $k = 2 + 1$ $307 = 300 = 5 + 6$ $170 = 156 10 + 6$ $288 = 261 7$	• 9 146 147 12 • 1 262 254 7 • H = 5, K = 0 • 6 297 311 8
	- H = 3, K = 3 - 2 107 93 11 - 0 408 - 447 8 - H = 6, K = 1
2 313 290 5 4 78 72 12 0 17 386 8 7 95 100 16	
3 335 -339 6 . 5 263 -258 7 . 1 195 -172 9 . 8 122 -124 13	• 1* 31 -10 31 • • 133 12/ 10 • • 194 -191 9 • 1* 30 -34 30 - 2 134 142 0 • 5 257 250 8 • 4 100 102 0 3 246 -234 0
4 691 -673 9 . 6 84 72 14 . 2 54 9 27 . 9 53 -55 29	
5 221 193 7 . 7 181 185 9 . 3 434 415 8 . H = 2, K = 6	• 4 170 -157 9 • 7 108 -110 14 • H = 5 K = 1 • 4 201 190 9
6 71 -75 15 . 8 36 35 36 . 4 37 41 37 . 0 101 109 13	• 5 91 106 15 • 8• 38 38 38 • 0• 34 19 34 • 5 75 -81 20
7 245 215 7 • 9 158 -165 11 • 5 117 -152 14 • 1 144 -135 10	• 6 328 - 332 8 • 9 155 155 11 • 1 56 - 66 22 • 6 199 - 192 1ú
8 186 -195 9 • 10 • 38 33 38 • H = 1, K = 10 • 2 353 326 7	• 7 133 -138 12 • H = 4, K = 2 • 2 266 -256 8 • H = 6, K = 2
9 49 35 28 • H = 1, K = 3 • 0 107 -108 15 • 3 270 267 8	• 8 77 77 20 • 0 193 189 8 • 3 427 - 398 8 • 0 180 - 186 10
10 266 287 8 • 0 225 - 262 5 • 1 • 38 38 38 • 4 309 - 297 8	• 9• 38 -44 38 • 1 110 -108 11 • 4• 36 21 36 • 1 204 204 9
H = 0, K = 4 . 1 304 -288 6 . 2 189 190 10 . 54 36 -22 36	• H = 3, K = 4 • 2 226 206 7 • 5 228 216 8 • 2 175 -158 10
	• 0 88 109 13 • 4 184 -184 8 • 6• 37 -32 37 • 3 122 127 13
	• 1 255 -249 7 • 5 253 280 8 • 7 58 58 26 • 4• 37 56 37
3 197 - 181 7 . 5 375 - 380 7 . 4 129 - 120 8 4 4 7 . 5 7 . 5 375 - 380 7 . 4 129 - 120 8 4 4 7 . 5 7 .	• 2 112 91 8 • 0• 30 -41 30 • 8• 38 -7 38 • 5• 37 -44 37
4 363 -334 7 . 6 237 255 8 . 6 574 573 8 . 0 284 206 4	• 3 140 147 7 • 7 37 24 37 • H = 57 K = 2 • 68 58 11 38
5 89 -111 13 . 7 366 359 8 . 8 315 -315 8 18 35 13 35	• • 100 122 0 • 0 11 (3 20 • 0 140 100 10 • H = 0; K = 3
6 573 534 8 8 158 -158 11 . 10 223 -246 9 . 2 114 -117 13	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
7 439 433 3 • 9 80 -99 19 • H = 2 • K = 1 • 3 82 -69 17	- 7 239 238 8 . 1 538 -528 8 . 2 248 234 8 . 2 37 4 24
7 438 433 4 . 10 385 -423 8 . 0 156 148 5 . 4 287 279 8	• 8 122 118 9 • 2 253 -249 7 • 4 270 266 8 • 1 136 -134 12
8 67 -49 20 . H = 1, K = 4 . 1 24 -19 24 . 5 55 49 26	· 9 144 -142 12 · 3 477 460 8 · 5 162 -161 10 · 4 155 -143 11
9 37 34 37 0 220 -228 6 2 378 -337 6 6 101 -97 15	+ H = 3, K = 5 . 4 159 154 10 . 6 84 -93 18 . 5 113 120 14
10 147 141 11 • 1 256 237 6 • 3 95 86 9 • 7• 38 25 38	• 0 86 72 14 • 5 425 -402 8 • 7 66 54 23 • H = 6, K = 4
H = 0, K = 6 • 2 101 103 9 • 4 62 64 16 • H = 2, K = 8	• 1 384 - 356 7 • 6 193 - 193 9 • H = 5, K = 3 • 0 54 29 26
0 138 130 9 • 3 201 -188 7 • 5 61 -51 19 • 0 466 523 8	- 2 370 374 7 • 7 366 365 8 • 0 • 35 30 15 • 1 63 62 23
7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	• 3• 35 -4 24 • 8• 38 -7 38 • 1 259 -247 8 • 2 84 82 18
2 - 120 - 112 - 10 - 7 - 191 - 170 - 0 - 7 - 30 - 22 - 36 - 2 - 197 - 176 - 9 - 3 - 37 - 176 - 9 - 75 - 40 - 70 - 7 - 176 - 9 - 75 - 70 - 7 - 176 - 9 - 75 - 70 - 7 - 176 - 9 - 75 - 70 - 7 - 176 - 9 - 75 - 70 - 7 - 176 - 70 - 7 - 176 - 7 - 7 - 7 - 7 - 7 - 7 - 7 - 7 - 7 -	• 4 555 -586 8 • H = 4, K = 4 • 2 97 -97 14 • 3 208 216 9
4 567 539 R 7 106 -185 0 00 12 -3 20 4 707 -174 0	• 6 111 100 9 • 0 87 91 15 • 3 212 200 9 • 4 173 157 16
5 178 182 9 . 8 151 -155 11 - 10 153 -167 17 5 114 -170 14	• 1 186 184 1 • 1 314 -355 1 • 4 211 262 8 • 54 31 -47 31
6 233 - 230 8 . 9 133 124 13 - H = 2 . K = 2 . 6 311 - 307 B	• $3 + 9 - 22 - 30 + 2 - 115 - 122 - 12 + 5 - 269 - 266 - 8 + H = 6, K = 5$
7 41 -37 33 • H = 1 • K = 5 • 0 48 -51 15 • H = 2 • K = 9	• $\Pi = 3$; $K = 0$ • 3 108 -97 13 • 0 235 239 9 • 0 69 -95 21
8 120 126 13 0 179 -153 7 1 85 88 9 0 207 -216 9	
H = 0, K = 8 • 1 564 553 8 • 2 192 -182 6 • 1+ 37 -12 37	\sim 2 265 -267 8 . 64 37 51 37 . () 63 36 21 . 3 45 0 1 4
0 469 -487 8 . 2 160 -171 8 . 3 606 621 8 . 2 37 28 37	• 3 86 -57 16 • 7 326 321 8 • 1 265 241 8 • 4 172 • 194 16
1 40 -44 32 . 3 97 -102 12 . 4 469 424 7 . 3* 38 -38 38	• 4 105 110 14 • 8 • 38 9 38 • 2 84 -83 16 • H = 6 K = 6
2 243 209 8 4 704 665 10 5 451 -441 8 4 150 -152 11	• 5 75 56 20 • H = 4, K = 5 • 3 114 -119 13 • 0 55 -2/27
3 106 114 13 · 5 139 157 10 · 6 122 126 11 · 5 · 38 34 38	• 6 203 - 199 9 • 0 98 - 99 14 • 4• 37 - 25 37 • 1• 37 39 37
- 203 276 8 . 6 72 83 19 . 7 36 19 36 . H = 2, K = 10	• 7 • 3 8 -13 38 • 1 188 177 9 • 5 145 146 11 • 2• 37 40 37
	• H = 3, K = 7 • 2 187 188 9 • 6 • 38 -53 18 • 3 • 37 40 37
7 99 96 16 9 16 147 11 10 260 201 11 1 206 211 9	• 0 403 425 8 • 3 139 -117 11 • / 236 -239 9 • H = 7, K = 0
H = 0.6 K = 10 $H = 1.6 K = 6$ $H = 2.6 K = 3$ $H = 2.6 K = 3$	• 1• 36 46,36 • 4• 36 35 36 • H = 5, K = 5 • 0 168 99 14
	• 2 282 -275 6 • 5 158 156 10 • 0 437 -481 8 • 2 91 -63 17
1 257 -241 8 - 1 100 92 12 - 1 117 107 8 - 2 78 -59 12	
2* 38 4 38 . 2* 33 -29 33 . 2 175 161 7 . 4 195 193 7	-5 73 71 21 -1 -1 6 -1 6 -2 -5 7 -7 -7 -7 -7 7 7 7 7 7 7 7 7 7
3 431 421 8 . 3 55 -62 22 . 3 66 -80 15 . 6 82 -42 16	• 6 161 -156 11 • 0 • 36 -34 36 • 4 • 37 18 37 • 1 96 99 16
4* 38 -34 38 . 4 112 109 12 . 4* 32 -5 32 . 8 269 253 8	• 7 94 88 17 • 1 43 16 31 • 5• 37 -23 57 • 2 1/1 177 10
H= 1.K=0.5 55 51 24.5 71 74 17. H= 3.K= 1	H = 3, K = 8 . 2 112 -118 13 . 6 141 143 12 . 3 148 168 11
0 52 54 6 6 36 -19 36 6 150 135 10 0 338 393 6	0 183 -199 10 . 3 139 -130 11 . H = 5, K = 6 . 4. 18 -35 38
2 241 - 228 5 . 7 62 - 53 23 . 7 93 - 85 16 . 1 398 371 7	1 34 77 40 • 4 267 269 8 • 0 98 -112 15 • H = 7, K = 2
4 125 110 8 . 8 109 101 14 . 8 79 71 19 . 2 303 -291 6	• 2 307 319 8 5 • 37 - 47 37 1 • 37 - 44 37 0 54 30 37
6 197 - 175 8 . H = 1, K = 7 . 9 90 89 17 . 3 368 328 7	• 3 98 -51 25 • H = 4• K = 7 • 2 280 265 8 • 1 248 245 a
8• 36 18 36 • 0 456 -555 8 • H = 2, K = 4 • 4 360 353 7	• 4 94 -98 16 • 0 218 -236 8 • 3 128 107 13 - 2 125 110 14
10 133 -122 13 . 1 85 68 15 . 0 252 -226 7 . 5 132 -121 10	• 5 89 84 17 • 1 229 231 8 • 4 250 -238 8 • 3 249 400 8
H = 1, K = 1 . 2 204 184 8 . 1 586 600 8 . 6 488 -484 8	• H = 3, K = 9 . 2 90 97 16 . 5 88 -106 17 . H = 7. K = 1
0 169 -191 4 . 3 312 288 8 . 2 31 -4 31 . 7 266 -247 8	• 0 173-161 10 • 3 94-123 16 • H = 5, K = 7 • 3• 37 2/ 37
1 238 -284 4 . 4 116 -141 13 . 3* 32 -2 32 . 8 278 260 8	• 1• 38 0 38 • 4 238 -232 9 • 0 115 -75 14 • H = 7, K = 4
2 350 327 5 5 36 3 36 4 120 185 11 9 38 -74 38	• 2• 38 - 23 38 • 5 121 126 13 • 1 232 236 9 • 0• 37 - 57
3 342 +350 / • 6 / 9 60 19 • 5 250 253 8 • H = 3, K = 2	• 3 223 -215 9 • H = 4, K = 8 • 2 98 108 16 • 0• 38 10 38
7 107 172 r r 1 175 181 10 r 6 225 224 8 r 0 220 216 7	• • 114 100 14 • 0 446 -459 8 • 3• 37 -7 37 • 1• 38 • 38
- 567 574 F H = 1, K = 8 F 7 52 - 512 8 1 209 213 F	• H = 4, K = 0 • 1 113 117 14 • 4 143 137 12 • 2• 38 24 36
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	• U 183 167 8 - 20 37 39 37 - H = 5, K = 8 - 1 291 -285 8
	• 4• 34 -3 34 • 3 10 -12 21 • 0 226 253 9 •

carded and the reliability factor converged to values of 0.079, 0.067 and 0.073 for all reflexions, excluding unobserved reflexions, and for weighted structure amplitudes respectively. The observed and calculated structure amplitudes are given in Table 2. The final positional parameters and their standard deviations are listed in Table 4. The coordinates of non-hydrogen atoms agree well with those reported from X-ray studies. A Fourier section of the nuclear density at z=0.25 is shown in Fig. 1, from which it is clear that the hydrogen atoms are not in the mirror plane.

Interatomic distances and bond angles were calculated from the parameters listed in Table 1, using the program ORFFE (Busing, Martin & Levy, 1962b). These values are given in Table 3, together with the values for sulphamic acid reported by Sass (1960).

Table 3. Bond lengths and bond anglesStandard deviations are shown in brackets.

Bond lengths					
C C	Potassium	Sulphamic			
	sulphamate	acid			
S –N	1·666 (0·006) Å	1·764 (0·02) Å			
S –O(1)	1.459 (0.007)	1.421 (0.02)			
S -O(2)	1.454 (0.004)	1.452 (0.02)			
N-H	1.007 (0.006)	1.024 (0.02) (average)			
$O(2) \cdots H$	2.147 (0.006)				
$N-H \cdots O(2)$	3.080 (0.006)				
Bond angles					
U U	Potassium	Sulphamic			
	sulphamate	acid			
H-N-H	110·1 (0·7)°	107.6° (average)			
H–N–S	110.2 (0.4)	111.3 (average)			
N-S-O(1)	108.5 (0.4)	103.2 (average)			
N-S-O(2)	103.9 (0.3)				
O(1) - S - O(2)	112.1 (0.3)	115.1 (average)			
O(2)-S - O(2')	115.5 (0.5)				
SN-O(2)	105.2 (0.1)				
N-H-O(2)	153-2 (0-5)				

Discussion

The nitrogen atom configuration

This investigation shows conclusively that the two hydrogen atoms do not lie in the plane containing the S, N and O(1) atoms. The bond angles around the nitrogen atom are S-N-H $110\cdot2^{\circ}$ and H-N-H $110\cdot1^{\circ}$. These are so close to the ideal tetrahedral angle of 109.5° that it must be assumed the nitrogen atom has an sp^3 configuration with a lone pair of electrons in the fourth tetrahedral position. This conclusion is in disagreement with the expected relationship between bond length and bond order for the S-N bond. The theoretical single and double bond lengths are 1.74 and 1.54 Å from the covalent radii given by Pauling (1945). A single bond is associated with a tetrahedral configuration and Sass has found that in sulphamic acid the bond length is 1.764 Å and the nitrogen has an sp^3 configuration. In most other substances (see review by Trueblood & Mayer, 1956) a shorter bond has been observed and attributed to the availability of p electrons from the nitrogen to form π bonds with sulphur d-orbitals (Sass & Donohue, 1958). The nitrogen is then expected to be trigonally bonded with sp² hybridization. Recently, O'Connor & Maslen (1965) have found the S–N bond to be 1.61 Å in β -sulphanilamide and the configuration sp² while Alléaume & Decap



Fig. 1. Fourier section of neutron scattering density at z=0.25. The full, broken and dotted lines represent positive, zero and negative densities respectively. The negative densities are plotted with half the contour interval of the positive ones.

Table 4. Atomic parameters and their estimated standard deviations Positional parameters are expressed as fractions of the lattice parameters. Thermal parameters are in the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. All parameters are given $\times 10^4$.

	x, $\sigma(x)$	$y, \sigma(y)$	z, $\sigma(z)$	$egin{array}{c} eta_{11}, \ \sigma(eta_{11}) \end{array}$	$\beta_{22}, \sigma(\beta_{22})$	$\beta_{33}, \sigma(\beta_{33})$	$egin{array}{c} eta_{12}, \ \sigma(eta_{12}) \end{array}$	$\beta_{13}, \sigma(\beta_{13})$	$egin{array}{c} eta_{23}, \ \sigma(eta_{23}) \end{array}$
S	1775 (10)	1370 (7)	2500	86 (17)	22 (7)	59 (9)	-9(9)	0	0
N	2914 (4)	3198 (3)	2500	141 (6)	39 (3)	59 (3)	-10(4)	0	0
O(1)	- 684 (6)	1532 (5)	2500	92 (10)	76 (6)	91 (6)	1 (6)	0	0
O(2)	2611 (5)	650 (3)	3981 (3)	201 (8)	67 (3)	43 (3)	10 (4)	-26(4)	17 (3)
K	6644 (10)	2500	0	136 (19)	51 (6)	44 (7)	0	0	8 (6)
н	2438 (10)	3803 (7)	1506 (7)	285 (20)	131 (7)	119 (9)	-23 (10)	-35 (10)	57 (7)

All parameter changes in the last cycle of least-squares refinement were less than 1×10^{-4} .

(1965) have made a similar observation for γ -sulphanilamide in which they have found an S–N bond of 1.67 Å. Sabine & Cox (1967) have found the S–N bond in S₄N₄H₄ to be 1.65 Å and a trigonal nitrogen configuration.

In potassium sulphamate the S–N bond is not significantly longer but the configuration is sp^3 . The sulphamate ion configuration is the same as that of the sulphamic acid molecule except for the absence of one of the hydrogen atoms from the nitrogen atom.

Hydrogen bonding

The intermolecular $O \cdots H$ distance of 2.15 Å is significantly less than the van der Waals contact distance of 2.8 Å and constitutes a weak hydrogen bond joining the suphamate molecules in infinite chains parallel to the *c* axis. The N-H bonds are staggered from the S-O bonds with respect to rotation about the S-N bond with a dihedral angle of 60.8° between the SNO(1) and SNH planes.

The potassium ion environment

The potassium ions are located between the chains of sulphamate molecules. Each potassium ion is surrounded by six oxygen atoms, two at each of the distances 2.729 (O(1)], 2.729 [O(2)] and 2.961 Å [O(2)]. The average S–O distance of 1.455 Å is close to the value 1.439 Å for sulphamic acid found by Sass.

Thermal vibrations

A detailed analysis of the thermal vibration parameters was not made; however, inspection of Table 4 shows that the maximum vibration is along a, which is normal to the direction of hydrogen bonding. This work was carried out during and immediately after an International Atomic Energy Agency Study Group Meeting on Research Reactor Utilization held at Sydney, in March 1966. Financial assistance was provided by the International Atomic Energy Agency, and the Australian Department of External Affairs through the Colombo Plan.

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The Crystal and Molecular Structure of a Dimethyl Sulfoxide Complex of Iron(III) Chloride

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A three-dimensional X-ray structure determination of the dimethyl sulfoxide (DMSO) compound of empirical formula FeCl₃(DMSO)₂ has shown it to be composed of *trans*-[FeCl₂(DMSO)₄]⁺ and FeCl₄⁻ ions. It crystallizes in the space group $I4_1/a$ of the tetragonal system with unit-cell dimensions $a=11.60 \pm 0.01$, $c=20.33\pm0.01$ Å. There are four of the true (ionic) formula units in each cell, with all iron atoms occupying positions of 4 symmetry. The DMSO molecules are coordinated through their oxygen atoms. The S-O distance $(1.541\pm0.006$ Å) is slightly but significantly greater than that in DMSO itself.

Introduction

The pronounced ability of dimethyl sulfoxide (hereafter abbreviated DMSO) to function as a donor or Lewis base toward a wide variety of acceptors or Lewis acids was clearly demonstrated by the isolation of a large number of complexes'several years ago (Cotton & Francis, 1960). Subsequent studies showed that other sulfoxides possess similar bonding capacities (Francis & Cotton, 1961; Francis, 1964) but not to the same degree as DMSO.