

The Crystal and Molecular Structure of 2-Formylthiophene Thiosemicarbazone

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The compound 2-formylthiophene thiosemicarbazone, $C_6H_7N_3S_2$, forms pale yellow, lath-like, monoclinic crystals with cell dimensions of $a=13.580$, $b=5.839$, $c=24.024$ Å and $\beta=117.69^\circ$. The space group is $P2_1/c$; there are 8 molecules per unit cell and hence two per asymmetric unit. The four sulphur atoms were located using the symbolic addition method and the light atoms from Fourier syntheses. The structure was refined by least-squares methods to an R index of 0.052 for the 2848 observed reflections measured with a diffractometer.

The thiophene rings are planar but slightly distorted from mm symmetry, presumably due to a resonance interaction with the thiosemicarbazone side chain. The bond distances in the side chain are similar to those of other thiosemicarbazones. The planarities of the two molecules in the asymmetric unit are different. This difference can be related to different hydrogen bonding schemes for the molecules.

Introduction

The relationship between metal ions and cancer is intriguing and controversial. French & Freedlander (1958) suggested that one common property of some antitumor agents was their ability to function as chelating agents. Subsequently, French & Blanz (1966) prepared a large number of thiosemicarbazones and found that all the tumor inhibitors were potentially capable of acting as a tridentate N–N–S type ligand. A crystal structure study of bis-(1-formylisoquinoline-thiosemicarbazono)nickel(II) monohydrate by Mathew & Palenik (1969) confirmed the ability of the ligand to act as a tridentate chelate. The related compound 2-formylthiophene thiosemicarbazone (2FTTSC) shows no tumor inhibition although the possibility of an S–N–S type chelate exists. A knowledge of the conformation and bond distances of an inactive thiosemicarbazone is essential for a final explanation of the requirements for biological activity; thus, the crystal structure determination of 2FTTSC was undertaken.

Experimental

A sample of 2FTTSC was kindly supplied by F. A. French and slow evaporation of an ethanol solution produced pale yellow, lath-like crystals elongated along **b**. A crystal was cleaved to give a parallelepiped of dimensions $0.18 \times 0.15 \times 0.15$ mm which was mounted with the [010] direction parallel to the ϕ axis of a General Electric single-crystal orienter. The unit-cell dimensions were obtained from a least-squares fit of twenty 2θ values measured using a narrow beam (0.7° take-off angle) of Cu $K\beta$ ($\lambda=1.39217$ Å) radiation.

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$C_6H_7N_3S_2$, mol. wt. 185.3, monoclinic
 $a=13.580$ (6), $b=5.839$ (4), $c=24.024$ (9) Å,
 $\beta=117.69$ (4) $^\circ$, $D_m=1.450$ g.cm 3 , $D_c=1.459$ g.cm 3 ,
 $Z=8$, space group $P2_1/c$ (C_{2h}^5), from systematic
absences ($h0l$ with l odd and $0k0$ with k odd).

Alternate setting:

$a=13.580$, $b=5.839$, $c=21.410$ Å, $\beta=96.48^\circ$,
space group $P2_1/n$.

A take-off angle of 3.7° , which produces a wide beam, was used in measuring intensities. A 0.7 mil Ni foil was placed in front of the counter window. Each reflexion was counted for 20 sec with the crystal and counter stationary. All the reflexions for which $2\theta \leq 135^\circ$ (Cu radiation, $\lambda=1.54051$ Å) in a unique quadrant were measured first and then the entire hemisphere was surveyed, a total of 10260 intensity measurements. A small correction (maximum 4%) was applied to correct for a slight decline in the intensities of the 4 standard reflexions which were measured after every 100 reflexions. After averaging equivalent reflexions, a total of 3038 unique intensities was obtained of which the 2848 greater than 1.30 times the background counts were considered to be observed and were used in the structure analysis. No absorption correction was applied.

Structure determination and refinement

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966) using the computer programs *FAME-MAGIC-LINK-SYMP* of Dewar, Stone & Fleischer (1966). The computed distribution of E values is compared with the theoretical values in Table 1. Seven large E 's were assigned symbols and after 5 iterations, a total of 445 reflexions had their signs determined in terms of the seven symbols. After

choosing the signs of three reflexions to define the origin, the most consistent set of signs was used to calculate an E -map.

Table 1. *Statistical data for the symbolic addition procedure*

A. Statistical averages for normalized structure factors, E .			
	$\langle E \rangle$	$\langle E^2 - 1 \rangle$	$\langle E ^2 \rangle$
Experimental	0.814	0.933	1.000
Theoretical: centric	0.798	0.968	1.000
acentric	0.886	0.736	1.000

B. Distribution of structure factors.

	Experimental	Theoretical	
		Centric	Acentric
$ E > 1$	32.4%	32.0%	37.0%
$ E > 2$	4.2	5.0	1.8
$ E > 3$	0.2	0.3	0.01

The E -map contained four large peaks which were assigned to the four sulphur atoms. A Fourier synthesis phased on the four sulphur atoms was calculated and used in conjunction with the E -map to locate the remaining light atoms. In retrospect, both molecules could have been found in the first E -map. Structure factors were calculated using all the atoms except the hydrogens to give an R index, the usual residual, of 0.22.

Five full-matrix least-squares cycles using individual isotropic thermal parameters reduced R to 0.12, and four additional cycles using anisotropic thermal parameters dropped R to 0.069. The positions of all the hydrogen atoms were located in a difference Fourier synthesis. Three cycles of block-diagonal (6×6 and 3×3) least-squares calculations were computed in which all heavy atoms were assigned anisotropic thermal parameters and the hydrogen atoms had isotropic thermal parameters. Two reflexions, 204 and $\bar{1}14$, which were apparently affected by extinction were not included in the final cycles. At this point the shifts were less than 0.3 of a standard deviation, and with R at 0.052, the refinement was considered completed. The weighting scheme used in all the calculations was:

$$\begin{aligned} w &= |F_o|/4F_{\min} \text{ if } |F_o| < 4F_{\min} \\ w &= 1 \text{ if } 4F_{\min} \leq |F_o| \leq 6F_{\min} \\ w &= 6F_{\min}/|F_o| \text{ if } |F_o| > 6F_{\min} \end{aligned}$$

where F_{\min} was 1.7 (on the same scale as Table 5). The quality $\sum w(|F_o| - |F_c|)^2$ was minimized in the least-squares calculations. The scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962).

The final atomic parameters along with their estimated standard deviations are given in Tables 2, 3 and 4. The observed and calculated structure amplitudes are listed in Table 5.

Table 2. *The final positional parameters ($\times 10^5$) of non-hydrogen atoms with their e.s.d.s. in parentheses*

	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$
S(A1)	-19957 (7)	22313 (16)	25049 (4)
S(A2)	15001 (6)	82623 (15)	50929 (4)
N(A1)	-2263 (18)	39008 (44)	37693 (11)
N(A2)	6236 (19)	49158 (45)	42801 (11)
N(A3)	-6228 (20)	73542 (49)	43452 (13)
C(A1)	-7639 (23)	9383 (48)	30134 (13)
C(A2)	-6364 (27)	-11452 (55)	27772 (15)
C(A3)	-15573 (31)	-16227 (66)	21805 (17)
C(A4)	-23403 (29)	290 (75)	19800 (16)
C(A5)	171 (23)	20266 (52)	35832 (13)
C(A6)	4134 (21)	67723 (49)	45377 (12)
S(B1)	48318 (6)	14481 (13)	16580 (3)
S(B2)	66400 (5)	90277 (12)	1396 (3)
N(B1)	52877 (17)	53045 (38)	9547 (10)
N(B2)	55016 (17)	70554 (38)	6404 (10)
N(B3)	68839 (19)	48522 (40)	6250 (12)
C(B1)	41450 (21)	40132 (45)	13960 (11)
C(B2)	33286 (24)	42634 (54)	15725 (13)
C(B3)	32618 (26)	23579 (67)	19160 (15)
C(B4)	40194 (28)	7287 (59)	19999 (14)
C(B5)	44451 (21)	56570 (46)	10545 (11)
C(B6)	63289 (20)	68171 (42)	4848 (11)

Discussion

There are two molecules in the asymmetric unit; hence, we have two determinations of the dimensions of 2FTTSC. The atomic numbering, average bond distances and average bond angles are given in Fig. 1. The individual bond distances and angles together with their estimated standard deviations are given in Table 6. Excluding the bonds C(1)-C(2) and C(6)-N(3), the differences in bond lengths in the two molecules average 0.006 Å, with none of the differences being statistically significant. However, following the criteria of Cruickshank & Robertson (1953), the difference between the C(1)-C(2) bonds of 0.020 Å ($t_0 = 3.1$) is significant and the difference between the C(6)-N(3) bonds of 0.021 Å ($t_0 = 3.7$) is highly significant. The difference in the C(6)-N(3) bonds may be related to hydrogen bonding (see below).

Both thiophene rings are planar (see Table 7) but the side chains are bent out of the planes of the rings. A survey of bond distances in thiophene rings has been given by Rychnovsky & Britton (1968). However, only two of the compounds reported there contain asymmetrically substituted thiophene rings. The two C-S distances in the thiophene ring of 2FTTSC are significantly different ($t_0 = 3.0$). The lengthening of the C(1)-S(1) bond relative to the C(4)-S(1) bond is easily explained in terms of the double-bond character in the C(1)-C(5) bond. The difference in the C(1)-C(2) compared to the C(3)-C(4) bond also reflects the double-bond character in the C(1)-C(5) bond. A similar effect was observed by Bartlett, Schreiber & Palenik (1969) in bis-(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato)-copper(II) where the C-S bond lengths were found to be 1.691 and 1.710 Å.

A comparison of the bond distances in the side chain with the corresponding values in other thiosemicarbazones and in thiosemicarbazide is presented in Table 8. The bond distances in thiosemicarbazones show a lengthening of the C(6)–N(2) and a shortening of the N(1)–N(2) and C(6)–N(3) bonds compared to thiosemicarbazide. The decrease in the N(1)–N(2) bond length was discussed by Restivo & Palenik (1970) who attributed the effect to an interaction between the ring and the side chain. A structural study of acetone thiosemicarbazone currently in progress may resolve the question. The distances in 2FTTSC and KTS [2-keto-3-ethoxybutyraldehydebis(thiosemicarbazone), Gabe, Taylor, Glusker, Minkin & Patterson (1969)] are in excellent agreement but both sets of values differ from the distances in 4FPYTSC (4-formylpyridine thiosemicarbazone). The C(1)–C(5) distances in 2FTTSC and 4FPYTSC are significantly different ($t_0=6.0$) suggesting less interaction between the ring and side chain in

4 FPYTSC compared to 2 FTTSC. The significantly shorter C–S bond ($t_0=4.4$) in 4FPYTSC supports this conclusion. The C–S bonds in all three compounds are shorter than in the thiosemicarbazone ligand reported by Mathew & Palenik. The changes in the bond lengths resulting from the formation of the metal complex suggest that the thiosemicarbazones are a highly delocalized system, in agreement with previous observations.

An *ORTEP* drawing of the two molecules is given in Fig. 2. The thermal ellipsoids are surprisingly isotropic, a fact which is presumably related to the hydrogen bonding. The conformation of the side chain is the same in both molecules with the S atom *trans* to N(1). The same conformation was found in 4FPYTSC, KTS and thiosemicarbazide. However, in the formation of metal complexes where the thiosemicarbazone acts as a bidentate chelate, the S and N atoms must be *cis*. Therefore, a change in conformation about the

Table 3. *Final thermal parameters with their e.s.d.s. in parentheses*

The temperature factor is of the form $\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl) \}$.

	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^5$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^4$
S(A1)	679 (6)	368 (3)	231 (2)	8 (2)	226 (5)	-51 (1)
S(A2)	489 (5)	363 (3)	238 (2)	-33 (2)	284 (5)	-79 (1)
N(A1)	493 (15)	314 (8)	179 (5)	-16 (5)	224 (15)	-35 (3)
N(A2)	460 (15)	337 (9)	213 (6)	1 (6)	193 (15)	-58 (4)
N(A3)	547 (17)	363 (10)	268 (7)	4 (7)	290 (17)	-68 (4)
C(A1)	621 (20)	257 (9)	204 (6)	-33 (6)	387 (19)	-23 (4)
C(A2)	770 (23)	309 (10)	249 (7)	-29 (8)	501 (23)	-40 (4)
C(A3)	1000 (30)	398 (12)	283 (9)	-110 (9)	670 (28)	-95 (6)
C(A4)	803 (26)	499 (15)	242 (8)	-85 (10)	374 (24)	-85 (6)
C(A5)	633 (20)	290 (9)	185 (6)	-1 (7)	329 (18)	-16 (4)
C(A6)	487 (17)	294 (9)	181 (6)	5 (6)	293 (17)	-17 (4)
S(B1)	732 (5)	247 (2)	200 (2)	28 (2)	349 (5)	14 (1)
S(B2)	495 (4)	225 (2)	200 (2)	-17 (1)	290 (4)	22 (1)
N(B1)	541 (15)	221 (6)	163 (5)	-35 (5)	257 (14)	3 (3)
N(B2)	502 (15)	224 (7)	193 (5)	-19 (5)	333 (14)	5 (3)
N(B3)	621 (17)	224 (7)	246 (6)	18 (6)	377 (17)	17 (3)
C(B1)	507 (17)	244 (8)	137 (5)	-31 (6)	198 (16)	-9 (3)
C(B2)	576 (19)	346 (11)	188 (6)	-4 (7)	306 (18)	12 (4)
C(B3)	698 (23)	455 (13)	202 (7)	-51 (9)	374 (21)	30 (5)
C(B4)	901 (27)	336 (11)	191 (7)	-66 (9)	306 (22)	28 (4)
C(B5)	527 (18)	245 (8)	153 (5)	-37 (6)	267 (16)	-11 (3)
C(B6)	461 (16)	207 (7)	135 (5)	-36 (5)	162 (15)	-10 (3)

Table 4. *Parameters of the hydrogen atoms and their estimated standard deviations*

	Bonded to	$x(\sigma_x) \times 10^3$	$y(\sigma_y) \times 10^3$	$z(\sigma_z) \times 10^3$	$B(\text{\AA}^2)$
H(A1)	N(A2)	134 (3)	439 (7)	442 (2)	3.8 (4)
H(A2)	N(A3)	-80 (3)	854 (7)	450 (2)	4.1 (4)
H(A3)	N(A3)	-117 (3)	630 (7)	409 (2)	4.6 (4)
H(A4)	C(A2)	-4 (3)	-202 (7)	299 (2)	3.3 (5)
H(A5)	C(A3)	-166 (3)	-302 (7)	196 (2)	3.4 (5)
H(A6)	C(A4)	-310 (3)	13 (7)	157 (2)	4.1 (4)
H(A7)	C(A5)	70 (3)	125 (7)	380 (2)	3.5 (5)
H(B1)	N(B2)	508 (3)	837 (7)	51 (2)	2.7 (6)
H(B2)	N(B3)	663 (3)	371 (6)	75 (2)	2.9 (6)
H(B3)	N(B3)	734 (3)	451 (7)	44 (2)	3.9 (4)
H(B4)	C(B2)	289 (3)	574 (7)	150 (2)	3.2 (5)
H(B5)	C(B3)	268 (3)	221 (8)	206 (2)	4.5 (4)
H(B6)	C(B4)	407 (3)	-70 (8)	216 (2)	4.3 (4)
H(B7)	C(B5)	396 (3)	703 (7)	89 (2)	2.9 (6)

Table 5. Observed and calculated structure amplitudes

The three columns in each group contain the values, reading from left to right of I, 10F₀ and 10F_c. A negative F₀ indicates an unobserved reflexion which was not included in the least-squares refinement.

Table with multiple columns for h, k, l, F₀, F_c, and I. The table lists observed and calculated structure amplitudes for various reflections, including observed values, calculated values, and differences. The data is organized into groups based on the h, k, l indices.

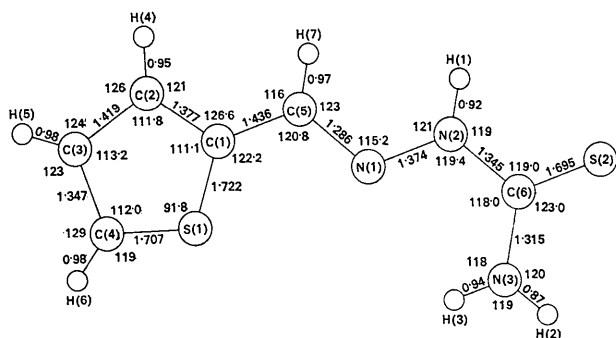


Fig. 1. The atomic numbering, average bond distances and average bond angles in 2-formylthiophene thiosemicarbazone.

N-H...S hydrogen bonds quoted by Srinivasan & Chacko (1967); the other two N...S distances of 3.484 and 3.489 Å are longer. The two shorter and presumably stronger N-H...S bonds involve hydrogen atoms from the *A* molecule. A consideration of various least-squares planes through the two molecules which are given in Table 7 indicates that the *A* molecule is much less planar than the *B* molecule. Apparently the *A* molecule is twisted as a result of the two stronger N-H...S hydrogen bonds. The shortening of the C(6)-N(3) bond distance in the *A* molecule may be a result of the N-H...S hydrogen bonds.

The molecular packing can be viewed as chains of dimer-like molecules held together by two N-H...S hydrogen bonds. There are only five intermolecular contacts less than 3.5 Å. These are 3.355 Å between C(B6) and N(B1) (in molecule 1-x, 1-y, -z), 3.439 Å between N(B3) and N(B2) (in molecule 1-x, 1-y, -z), 3.454 Å between C(B3) and N(A3) (in molecule

-x, y-½, ½-z), 3.454 Å between C(A3) and C(A5) (-x, ½+y, ½-z) and 3.475 Å between C(B2) and N(A3) (in molecule -x, y-½, ½-z). Therefore, all the contacts between the chains are normal van der Waals contacts.

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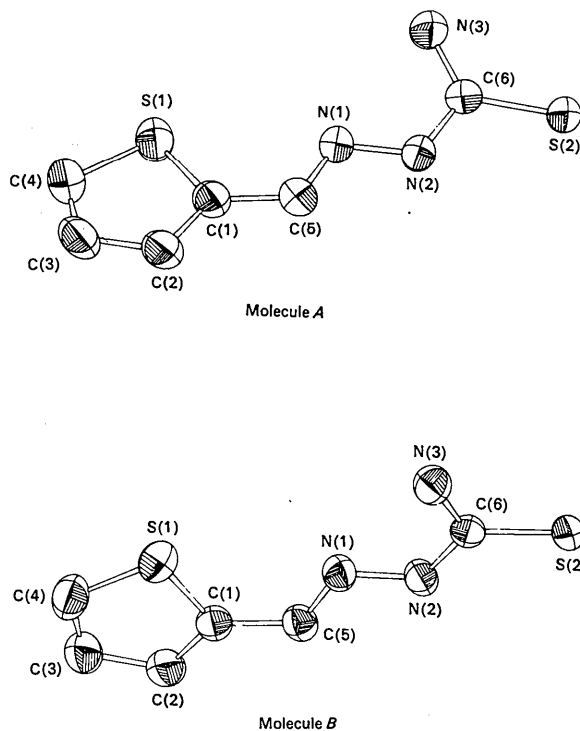


Fig. 2. An ORTEP drawing showing the conformation and thermal ellipsoids in the two independent molecules.

Table 7. *Least-squares planes*

Planes and deviations from plane (Å × 10³)

	I		II		III		IV	
	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>
S(1)	-1*	0*			529	22	216*	3*
S(2)	548	406	+1*	3*	132	30	362*	100*
N(1)	-14	126			0*	0*	-63*	-11*
N(2)	212	193	+1*	3*	0*	0*	51*	-4*
N(3)	-537	150	+1*	3*	-415	-173	-392*	-53*
C(1)	1*	-1*			150	45	-62*	-47*
C(2)	-1*	3*			90	151	-169*	-9*
C(3)	0*	-3*			363	203	-15*	45*
C(4)	0*	2*			613	150	195*	62*
C(5)	69	32			0*	0*	-95*	-78*
C(6)	29	228	-2*	-9*	-119	-66	-26*	-3*

Parameters of the plane†

<i>A</i> × 10 ⁴	7618	2904	4055	2584	6044	2189	6455	2674
<i>B</i> × 10 ⁴	4267	4397	5722	3575	5167	4342	5421	4092
<i>C</i> × 10 ⁴	-4534	8499	-7129	8975	-6065	8738	-5380	8724
<i>D</i> (Å)	-6.007	4.738	-6.443	4.438	-6.415	4.458	-5.931	4.686

* Deviations of atoms which were used to define the plane.

† Equation of the plane in the form: Deviation (Å) = *AX* + *BY* + *CZ* + *D* with *X*, *Y*, *Z* the coordinates of the atom in Å with respect to *a*, *b*, *c**

Table 8. Comparison of bond distances (Å) of various thiosemicarbazones

	C(1)–C(5)	C(5)–N(1)	N(1)–N(2)	N(2)–C(6)	C(6)–S	C(6)–N(3)	Reference
2-Formylthiophene thiosemicarbazone	1.433 (4) 1.439 (4)	1.282 (4) 1.290 (4)	1.369 (4) 1.380 (3)	1.343 (4) 1.346 (4)	1.698 (3) 1.691 (3)	1.306 (4) 1.327 (4)	1
4-Formylpyridine thiosemicarbazone	1.467 (3) 1.447 (6)	1.275 (3) 1.285 (6)	1.365 (3) 1.371 (6)	1.354 (3) 1.351 (6)	1.678 (2) 1.692 (4)	1.329 (3) 1.310 (6)	2
2-Keto-3-ethoxybutyral- dehyde bis(thiosemi- carbazone)	1.447 1.445 1.445	1.294 1.284 1.290	1.371 1.379 1.365	1.359 1.351 1.352	1.687 1.689 1.682	1.305 1.314 1.311	3
Bis(isoquinoline-1- carboxaldehyde thio- semicarbazono) nic- kel(II) monohydrate thiosemicarbazide	1.446 (12) 1.457	1.295 (9) 1.279	1.356 (8) 1.357 1.399 (6)	1.328 (9) 1.331 1.337 (6)	1.735 (7) 1.719 1.685 (5)	1.350 (9) 1.345 1.316 (6)	4 5

References: (1) Present study;
(4) Mathew & Palenik (1969);

(2) Restivo & Palenik (1970); (3) Gabe *et al.* (1969);
(5) Domino, Gasparri, Nardelli & Sgarabotto (1969).

Table 9. Hydrogen bonds and close contacts

A. Hydrogen bonds				D–H	H···A	D···A	D–H···A angle
Bond	Position of A			(Å)	(Å)	(Å)	(°)
D–H···A*							
N(A2)–H(A1)···S(B2)	1–x	y–½	½–z	0.92	2.45	3.348 (3)	165
N(B2)–H(B1)···S(B2)	1–x	2–y	–z	0.92	2.61	3.484 (3)	159
N(A3)–H(A2)···S(A2)	–x	2–y	1–z	0.88	2.49	3.360 (3)	174
N(B3)–H(B3)···S(A2)	1–x	y–½	½–z	0.93	2.55	3.489 (3)	175
B. Close contacts							
N(B3)–H(B2)···N(B1)	x	y	z	0.86	2.29	2.644 (4)	104
N(A3)–H(A3)···N(A1)	x	y	z	0.94	2.26	2.639 (4)	103
N(B3)–H(B2)···S(B2)	x	y–1	z	0.86	3.10	3.560 (3)	115
C(B2)–H(B4)···S(A2)	x	½–y	z–½	1.01	3.05	3.562 (3)	113

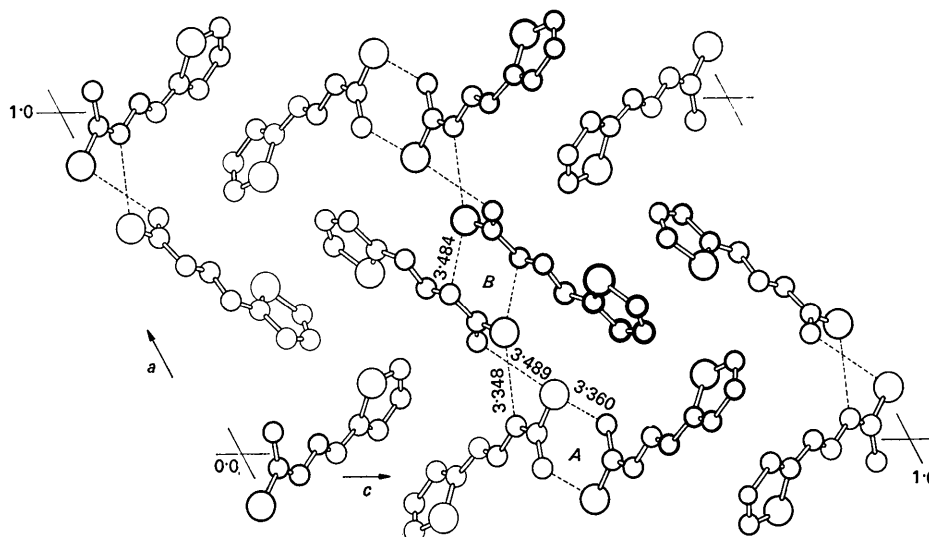


Fig. 3. A projection of the unit cell on the (010) plane. The hydrogen bonds are shown as dotted lines.

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The Structure of Manganese Dichloride Tetrahydrate: A Neutron-Diffraction Study*

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The hydrogen atoms in the room-temperature form of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ have been located by neutron-diffraction analysis. The data provide independent confirmation and refinement of the hydrogen positions and hydrogen-bonding scheme deduced by Baur by consideration of the electrostatic energy of the crystal, utilizing the results of the X-ray analysis of Zalkin and co-workers. The H-O-H angles in the 4 different water molecules are 104.3, 106.1, 111.4, and 112.4° (standard deviation about 0.3° for each). One hydrogen bond is clearly bifurcated, as deduced by Baur; in addition, there is another atomic configuration which may be regarded as a very unevenly bifurcated hydrogen bond. Among the remaining hydrogen bonds there are significant departures from linearity (by as much as 21°). The heavy-atom coordinates are not significantly different from those from the work of Zalkin *et al.*; however, some of the thermal parameters are significantly different. In the least-squares refinement scattering factors (relative to the factor for H) for Mn, O, and Cl were obtained which are slightly different from those previously tabulated.

Introduction

Neutron-diffraction analysis of the room-temperature (α) form of manganese dichloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) was undertaken to locate the hydrogen atoms as accurately as possible. Reliable hydrogen coordinates were required both for establishing the pattern of hydrogen bonding and for possible use in connection with nuclear magnetic resonance (n.m.r.) studies of the substance in its antiferromagnetic state.

The heavy-atom structure of the α form of manganese chloride tetrahydrate was determined precisely in an X-ray analysis by Zalkin, Forrester & Templeton (1964), and a set of approximate coordinates for the hydrogen atoms was obtained in the final stages of the analysis. A previous attempt at neutron-diffraction

analysis of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was reported briefly (Gardner, 1960), but final results have not been published. An n.m.r. study of the compound at room temperature (El Saffar, 1965) did not furnish proton-proton vectors; the spectrum is unusual, there being only a single bell-shaped peak with a width of about 12 gauss and no dipole-dipole splitting.

Because of an error in the use of a computer program, Zalkin *et al.* did not give a complete description of the hydrogen bonding. Baur (1965a) showed, however, that all of their eight experimental positions for the hydrogen atoms except the position for H(32) fit into a reasonable hydrogen bonding scheme. Baur also calculated the hydrogen positions of least electrostatic energy consistent with the known heavy-atom positions and with assumed values for the H-O-H angle and the O-H bond length, using a procedure with which he had previously been successful in predicting hydrogen positions in close agreement with those from neutron diffraction (Baur, 1965b). For atom H(32) a new position 0.73 Å from the X-ray position was

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