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Structure of a Complex of Midaflur (a Central Nervous System Depressant) and Dimethyl Sulfoxide

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Abstract

A structural study on a complex of midaflur [4-amino-2,2,5,5-tetrakis(trifluoromethyl)-3-imidazoline] ($C_7H_3F_{12}N_3$) and dimethyl sulfoxide (C_2H_6OS) has been carried out by X-ray diffraction. The crystals (M_r = 435·15) belong to the monoclinic space group $P2_1/c$ with $a = 11·977$ (3), $b = 16·527$ (3), $c = 17·211$ (3) Å, $\beta = 108·44$ (1)°, $\rho_c = 1·776$ Mg m^{-3} and $Z = 8$; μ(Mo $K\alpha$) = 0·3447 mm^{-1}. The structure was solved by direct methods and refined by least-squares techniques to a final residual of 0·075 for 2936 independent reflections. The S atom in the dimethyl sulfoxide molecule is disordered. The plane of the imidazole ring is an approximate mirror. The hydrogen-bonding scheme involves both N—H···O and N—H···N hydrogen bonds.

Introduction

Midaflur has skeletal-muscle-relaxant and CNS-depressant properties (Clark *et al.*, 1971). From the NMR evidence, Middleton & Krespan (1970) indicated that the compound exists as an amino tautomer with restricted rotation about the C—N bond because of the solvation. At 283 K in dimethyl sulfoxide solution, two separate peaks appear in the spectrum. The formation of a complex between midaflur and Me_2SO causes the restricted rotation of the amine group. A 1:1 complex of midaflur and Me_2SO (Fig. 1) was isolated by Middleton & Krespan (1970). The X-ray structural study of midaflur itself was by Guggenberger (1973). Crystal structure studies have been carried out on the complex to see the effect of the solvation on the structure of midaflur and also to study the hydrogen bonding.

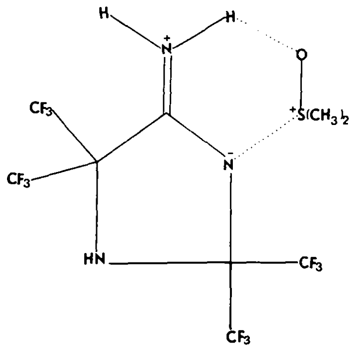

Fig. 1. The structure of the complex as proposed by Middleton & Krespan.

Experimental

Needle-shaped, colorless crystals of the complex were kindly supplied to us by Dr Carl G. Krespan of DuPont. Preliminary photographs indicated that the crystals belong to monoclinic space group $P2_1/c$. The intensity data were collected from a crystal 0·1 × 0·1 × 0·2 mm on a Syntex $P2_1$ four-circle computer-controlled diffractometer with a graphite monochromator (Mo $K\alpha$, $\lambda = 0·71069$ Å) and a pulse-height analyzer. The intensities of 6016 reflections with $2\theta < 50·0°$ were scanned using the θ–2θ scan technique, a variable scan rate (0·5–29·3° min^{-1}), a scan range of 2·0° and a background to scan ratio of 0·8. Of these, 2936 with $I \geq 3\sigma(I)$ were considered observed. The intensities were corrected for Lorentz and polarization effects but no correction was made for absorption and extinction effects. The structure was solved using the direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) with E's > 1·6. The E map revealed only one molecule of midaflur and both molecules of the dimethyl sulfoxide in the asymmetric unit. The second molecule of midaflur in the asymmetric unit was located in a difference map. Two cycles of isotropic refinement of nonhydrogen atoms reduced R to 0·20. A difference map at this stage revealed that the S atom of the dimethyl sulfoxide molecule was disordered. The refinement of the occupancy factors of the S atoms gave values of 0·67 and 0·33 for molecule (I) and 0·75 and 0·25 for molecule (II). Further isotropic refinement reduced R to 0·157. Anisotropic refinement of positional and thermal parameters brought R to 0·080.

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The H atoms belonging to the midaflur molecules were located from a difference map but the methyl H atoms could not be located because of disorder. The final anisotropic refinement of nonhydrogen atoms and isotropic refinement of the H atoms of the midaflur molecules gave a final R of 0·075. The refinement was based on F_o, the quantity minimized being $\sum w(F_o - F_c)^2$. The scattering factors used were those of Hanson, Herman, Lea & Skillman (1964).* The weighting scheme used was based on counter statistics as defined by Corfield, Doedens & Ibers (1967); the value of p was 0·04.

Results and discussion

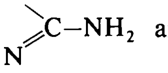
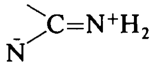
The atomic coordinates and B_{eq} for both the independent molecules in the asymmetric unit are given in Table 1. Fig. 2 shows the thermal ellipsoid plots of molecules (I) and (II) of midaflur and of the disordered dimethyl sulfoxide molecules. The bond distances and angles in the midaflur molecules (I) and (II) are shown in Fig. 3(a,b). The bond distances and angles in the dimethyl sulfoxide molecules are given in Table 2. The bond lengths anu angles in midaflur agree well with those observed by Guggenberger (1973) and the literature values. Because of disorder, some of the bond lengths and angles of the two molecules of Me_2SO differ. The midaflur molecule has an approximate mirror plane. The C(1)—N(1) distances of 1·32 (1) and 1·32 (1) Å and C(1)—N(2) distances of 1·27 (1) and 1·29 (1) Å indicate that the two resonance hybrids  $\overset{\diagdown}{\underset{\text{N}\diagup\!\!\!\diagup}{}}\text{C}-\text{NH}_2$ and  $\overset{\diagdown}{\underset{\bar{\text{N}}\diagup}{}}\text{C}=\text{N}^+\text{H}_2$ do exist, a similar

Table 2. *Bond distances* (Å) *and angles* (°) *in dimethyl sulfoxide molecules* (I) *and* (II)

The standard deviations are of the order of 0·01 Å in distances and 0·7° in angles.

	(I)	(II)		(I)	(II)
S—S′	1·37	1·04	O—S—C(8)	107·8	105·6
S—O	1·51	1·50	O—S′—C(8)	103·1	112·5
S′—O	1·57	1·52	O—S—C(9)	103·3	109·5
S—C(8)	1·75	1·74	O—S′—C(9)	110·1	116·7
S′—C(8)	1·79	1·59	C(8)—S—C(9)	98·3	100·4
S—C(9)	1·85	1·73	C(8)—S′—C(9)	104·5	113·7
S′—C(9)	1·65	1·59			

Table 1. *Fractional coordinates and* B_{eq} *values* (Å^2) *with standard deviations in parentheses*

$B_{eq} = 8\pi^2(U_{11}.U_{22}.U_{33})^{1/3}$, where U_{11}, U_{22}, U_{33} are the amplitudes along the principal axes of the thermal ellipsoid. The occupancy factors for disordered S atoms (S and S′) are 0·67 and 0·33 for molecule (I) and 0·75 and 0·25 for molecule (II).

	Molecule (I)				Molecule (II)			
	x	y	z	B_{eq}	x	y	z	B_{eq}
S	0·1223 (6)	0·5206 (4)	0·8390 (4)	4·51 (9)	0·6355 (6)	0·4639 (4)	0·3237 (4)	5·05 (9)
S′	0·1279 (10)	0·5106 (7)	0·9190 (6)	2·92 (9)	0·6532 (20)	0·4668 (13)	0·3868 (13)	5·21 (9)
F(1)	0·7261 (8)	0·8480 (5)	1·0852 (5)	6·86 (9)	0·2658 (6)	0·9009 (4)	0·6635 (4)	7·89 (9)
F(2)	0·6245 (7)	0·8397 (5)	1·1659 (5)	6·16 (9)	0·1008 (5)	0·8758 (4)	0·5733 (3)	7·42 (9)
F(3)	0·7831 (6)	0·7726 (5)	1·1922 (4)	5·60 (9)	0·2438 (5)	0·7930 (4)	0·5943 (3)	7·26 (9)
F(4)	0·5112 (7)	0·7086 (5)	1·1720 (5)	6·71 (9)	0·1249 (5)	0·6751 (3)	0·6282 (4)	7·57 (9)
F(5)	0·6591 (8)	0·6316 (6)	1·1873 (5)	7·89 (9)	−0·0262 (4)	0·7478 (3)	0·6069 (3)	6·23 (9)
F(6)	0·5028 (9)	0·6153 (5)	1·0855 (6)	8·21 (9)	0·0454 (5)	0·6883 (3)	0·7208 (4)	7·03 (9)
F(7)	0·7123 (8)	0·5564 (5)	0·9284 (5)	7·11 (9)	0·0902 (6)	1·0031 (3)	0·8301 (4)	7·34 (9)
F(8)	0·5617 (9)	0·6039 (6)	0·8378 (5)	8·29 (9)	0·2520 (6)	0·9641 (4)	0·9178 (4)	7·57 (9)
F(9)	0·5488 (9)	0·5619 (5)	0·9511 (7)	8·35 (9)	0·2411 (6)	0·9836 (4)	0·7936 (4)	7·89 (9)
F(10)	0·8352 (7)	0·6938 (6)	0·9378 (5)	7·50 (10)	0·0474 (6)	0·7608 (4)	0·8613 (4)	9·47 (10)
F(11)	0·6884 (8)	0·7332 (7)	0·8362 (5)	8·29 (10)	0·1122 (7)	0·8539 (5)	0·9476 (3)	9·23 (10)
F(12)	0·7540 (9)	0·8038 (6)	0·9442 (6)	8·29 (10)	−0·0395 (5)	0·8719 (4)	0·8414 (4)	8·91 (10)
O	0·1294 (9)	0·4336 (6)	0·8662 (7)	4·81 (9)	0·6285 (9)	0·3803 (6)	0·3566 (7)	4·89 (9)
N(1)	0·4323 (8)	0·7991 (6)	1·0089 (5)	2·84 (8)	0·3395 (5)	0·7308 (4)	0·7696 (4)	3·86 (8)
N(2)	0·5381 (8)	0·7326 (6)	0·9367 (5)	3·23 (8)	0·2494 (5)	0·8174 (4)	0·8381 (4)	3·71 (8)
N(3)	0·6973 (7)	0·6839 (5)	1·0416 (5)	3·63 (8)	0·0859 (5)	0·8587 (4)	0·7318 (3)	3·71 (8)
C(1)	0·5230 (9)	0·7566 (7)	1·0026 (6)	3·08 (8)	0·2558 (6)	0·7811 (5)	0·7731 (4)	3·86 (8)
C(2)	0·6454 (9)	0·6857 (7)	0·9542 (6)	2·76 (8)	0·1453 (7)	0·8675 (5)	0·8178 (5)	3·08 (8)
C(3)	0·6217 (9)	0·7289 (7)	1·0785 (6)	2·84 (8)	0·1488 (6)	0·8020 (5)	0·6983 (4)	3·11 (8)
C(4)	0·6915 (12)	0·7982 (8)	1·1305 (8)	4·10 (9)	0·1911 (9)	0·8432 (6)	0·6314 (6)	5·13 (9)
C(5)	0·5724 (14)	0·6694 (9)	1·1320 (9)	5·13 (8)	0·0714 (8)	0·7272 (6)	0·6640 (6)	4·34 (8)
C(6)	0·6158 (14)	0·5995 (10)	0·9179 (9)	5·52 (9)	0·1836 (10)	0·9564 (6)	0·8405 (6)	5·13 (9)
C(7)	0·7336 (13)	0·7310 (11)	0·9172 (8)	5·21 (9)	0·0637 (10)	0·8393 (7)	0·8673 (7)	6·39 (9)
C(8)	0·2424 (19)	0·5719 (12)	0·9052 (16)	7·34 (10)	0·5392 (21)	0·5227 (15)	0·3571 (25)	11·62 (10)
C(9)	0·0056 (17)	0·5632 (11)	0·8762 (13)	6·79 (9)	0·7686 (19)	0·5080 (13)	0·3780 (17)	8·91 (9)

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* Lists of structure factors, temperature factors and H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36124 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

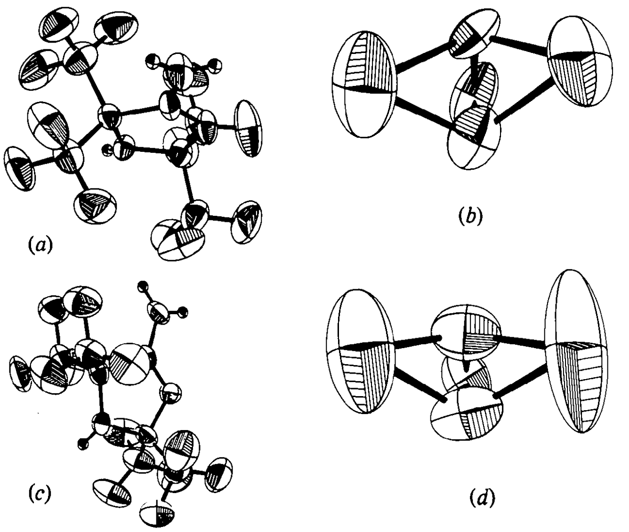

Fig. 2. Thermal ellipsoid plot of the (a) midaflur (I), (b) Me_2SO (I), (c) midaflur (II), (d) Me_2SO (II).

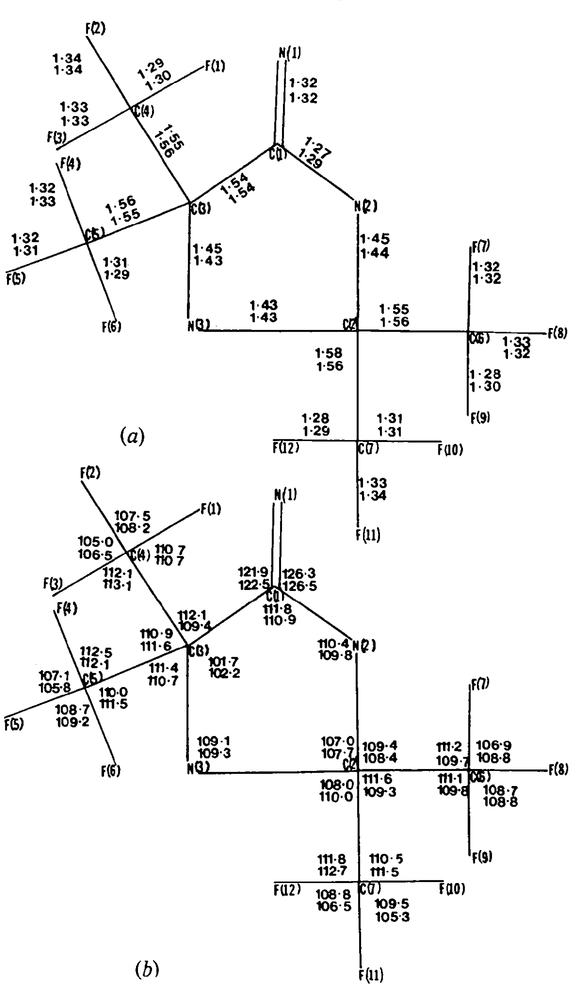

Fig. 3. (a) Bond distances (Å) in the midaflur molecules. The top values are for molecule (I). The standard deviations are of the order of 0·01 Å. (b) Bond angles (°) in the midaflur molecules. The top values are for molecule (I). The standard deviations are of the order of 0·5°.

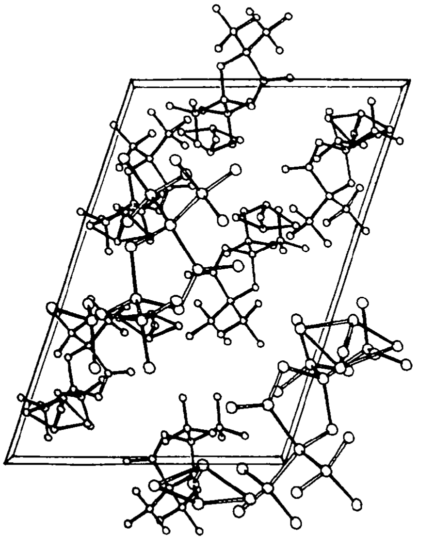

Fig. 4. Packing of the molecules in the unit cell as seen down the b axis.

Table 3. *Details of hydrogen bonds, D*—H···*A*

A prime refers to molecule (II). The standard deviations are of the order of 0·01 Å.

D	H	*A*	Symmetry position	*D*···*A*
N(1)	H(1)N(1)	O(1)′	$1-x, \frac{1}{2}+y, 1\frac{1}{2}-z$	2·96 Å
N(1)	H(2)N(1)	N(2)′	x,y,z	3·07
N(1)′	H(2)N(1)′	N(2)	x,y,z	3·10
N(1)′	H(1)N(1)′	O(1)′	$1-x, 1-y, 1-z$	2·96
N(3)	HN(3)	O(1)	$1-x, 1-y, 2-z$	2·92
N(3)′	HN(3)′	O(1)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	2·88

observation to that of Guggenberger (1973). The dihedral angles between the plane through C(3), C(4), C(5) and the ring plane are 89·2 (7) and 88·7 (7)° while those between the plane through C(2), C(6), C(7) and the ring plane are 88·6 (6) and 88·2 (7)° for molecules (I) and (II) respectively. This indicates that the orientations of the CF_3 group are the same.

Fig. 4 shows the packing of the molecules in the unit cell. The molecules are held together in the crystal by hydrogen bonding and form channels parallel to the *ac* diagonal. Table 3 gives the details of the hydrogen-bonding scheme. All the hydrogen bonds are intermolecular. The O and N(2) atoms are the acceptor atoms while N(1) and N(3) are the donors. The dimethyl sulfoxide acts as a bridge between different midaflur molecules.

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Structure of Cadmium Selenate Monohydrate

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Abstract. $CdSeO_4.H_2O$, monoclinic, $P2_1/c$, a = 7·679 (2), b = 7·723 (2), c = 8·207 (3) Å, β = 120·96 (4)°, V = 417·37 Å^3, Z = 4, D_x = 3·78 Mg m^{-3}, μ(Mo $K\alpha$) = 12·6 mm^{-1}. For 1281 observed reflexions the final R = 0·023. The Cd atom is octahedrally coordinated by four selenate groups and two water molecules at Cd—O distances of 2·25–2·42 Å.

Introduction. The structures of $CdSeO_4.H_2O$ and $CdSO_4.H_2O$ are isomorphous with $HgSeO_4.H_2O$ (Stålhandske, 1978) but different from $HgSO_4.H_2O$ (Stålhandske, 1980). In order to understand better the differences in coordination of Hg^{II} and Cd^{II}, a structural study of Hg and Cd compounds with the same stoichiometry has been started. Isomorphous pairs investigated earlier are $CdSO_4$, $HgSO_4$ (Aurivillius & Stålhandske, 1981) and CdF(OH) (Stålhandske, 1979*a*), HgF(OH) (Stålhandske, 1979*b*).

Crystals of $CdSeO_4.H_2O$ were obtained by dissolving CdO in concentrated H_2SeO_4 according to Herpin & Bregéault (1968). A single crystal 0·11 × 0·11 × 0·26 mm was used for the data collection on a CAD-4 diffractometer with Zr-filtered Mo K radiation at room temperature. The ω–2θ scan technique was used with variable scan speeds and peak-scan intervals $\Delta\omega = (0{\cdot}75 + 0{\cdot}75\tan\theta)°$. The maximum time spent on a reflexion was 4 min. Intensities of the 1694 unique reflexions with $3° \le \theta \le 32{\cdot}5°$ were measured within one quadrant of reciprocal space. Of these, 1281 with $I > 3\sigma(I)$ were corrected for Lorentz–polarization and absorption effects and used in the analysis. The transmission factors, evaluated by numerical integration, varied from 0·27 to 0·36. Three standard reflexions were measured during the data collection. They showed a maximum deviation from the mean of 3%.

The atomic positions for the non-hydrogen atoms were taken from the structure of $HgSeO_4.H_2O$ and refined by full-matrix least squares with anisotropic temperature factors and a parameter to correct for secondary extinction (Zachariasen, 1967). The H-atom positions, as found in difference syntheses, could not be

Table 1. *Fractional atomic coordinates and* B_{eq} *values* (Å^2) *with estimated standard deviations in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cd	0·21101 (3)	0·23809 (3)	0·25817 (3)	1·19 (1)
Se	0·26096 (4)	0·61488 (4)	0·51574 (4)	0·87 (1)
O(1)	0·1209 (3)	0·4895 (3)	0·3326 (3)	1·46 (6)
O(2)	0·3410 (3)	0·5054 (3)	0·7136 (3)	1·40 (6)
O(3)	0·4554 (4)	0·6970 (3)	0·5158 (4)	1·58 (6)
O(4)	0·1056 (4)	0·7707 (3)	0·4990 (4)	1·43 (6)
O(W)	0·2700 (3)	0·1010 (3)	0·5378 (3)	1·24 (6)
H(1)	0·212	0·024	0·516	
H(2)	0·404	0·086	0·613	

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