

Structure of Bis[2,3,4,5-tetrakis(trifluoromethylthio)pyrrolyl]mercury, $\text{Hg}[\text{N}(\text{CSCF}_3)_4]_2$

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[Received 29 January 1979; accepted 11 April 1979]

Abstract

The crystal structure of the title compound, $\text{Hg}[\text{N}(\text{C}_2\text{F}_3\text{S})_4]_2$, $\text{C}_{16}\text{F}_{24}\text{HgN}_2\text{S}_8$, has been determined from counter-measured X-ray data. The crystals belong to the monoclinic space group $C2/c$ with $a = 12.630$ (2), $b = 14.859$ (2), $c = 17.553$ (1) Å, $\beta = 102.917$ (7)°, $Z = 4$, $D_m = 2.33$ (1) and $D_x = 2.34$ Mg m^{-3} . Anisotropic refinement yielded a conventional R value of 0.029 based on 2295 reflections with $I > 2\sigma(I)$. The crystals consist of discrete molecules possessing crystallographic $\bar{1}$ symmetry. The two pyrrolyl rings as well as the S and Hg atoms are nearly coplanar while the S–C(CF₃) bonds are approximately perpendicular to this plane. The Hg–N bond length is 2.017 (5) Å. Variations in the S–C–F bond angles are discussed.

Introduction

Recent crystal structure investigations of the isostructural compounds $\alpha\text{-CF}_3\text{HgN}_3$ and CF_3HgNCO (Brauer, Bürger, Pawelke, Flegler & Haas, 1978) revealed short intramolecular Hg–N bond lengths compared to those reported for $\alpha\text{-Hg}(\text{N}_3)_2$ (Müller, 1973a), CH_3HgN_3 (Müller, 1973b) or $\text{KHg}(\text{NCO})_3$ (Thiele & Hilfrich, 1977). This shortening was attributed to the lower number of weak intermolecular Hg–(N₃) and Hg–(NCO) interactions in the CF₃ derivatives compared with those found in the other studies. A reliable value for an unperturbed Hg(*sp*)–N(*sp*²) bond length would test this formulation. Literature estimates, however, range from 2.04 Å (Thiele & Hilfrich, 1977) to 2.10 Å (Müller, 1973a). Our study of bis[2,3,4,5-tetrakis(trifluoromethylthio)pyrrolyl]mercury, (I), yields the desired bond length as well as new conformational information about the CF₃S groups.

Experimental

A block-shaped crystal of dimensions 0.28 × 0.24 × 0.16 mm was selected from a batch of (I) kindly supplied by Professor Haas (Haas, 1977) and sealed in a glass capillary. The $2/m$ Laue symmetry and systematic absences (hkl , $h + k = 2n + 1$ and $h0l$, $h =$

$2n + 1$, $l = 2n + 1$) revealed by Weissenberg photographs are indicative of space groups Cc (C_2^4) or $C2/c$ (C_{2h}^6), the latter being used in the refinement. Counter measurements were made at 293 K with a CAD-4 diffractometer equipped with a Mo tube ($K\alpha$, $\lambda = 0.71069$ Å) and a graphite monochromator. The crystal data, lattice constants being derived from 75 θ values, are $a = 12.630$ (2), $b = 14.859$ (2), $c = 17.553$ (1) Å, $\beta = 102.917$ (7)°, $Z = 4$, $D_m = 2.33$ (1), $D_x = 2.34$ Mg m^{-3} and $\mu(\text{Mo } K\alpha) = 5.45$ mm^{-1} .

Intensity data (hkl , $\bar{h}kl$, $2^\circ \leq 2\theta \leq 50^\circ$) were measured with ω - 2θ scans from 0.5° below to $0.5^\circ + 0.34^\circ \tan \theta$ above $\omega(K\alpha_1)$. In order to keep the total number of counts constant for each reflection which had significant intensity, a scan rate in the range 0.87–10° min^{-1} in 2θ was chosen for each reflection which gave more than a precount number of impulses during a fast scan. Backgrounds were measured by scanning $0.25^\circ + 0.085^\circ \tan \theta$ before and after the measurement of each peak. To prevent coincident losses, several strong reflections were measured with a nickel attenuator inserted before the counter window. The intensities of three standard reflections, which were measured periodically, varied less than $\pm 2\%$ during the collection of 3061 data. The intensity data were corrected for absorption (the transmission varying between 0.236 and 0.334) and converted to structure factor amplitudes. Of the 2949 unique reflections, only the 2295 with $I > 2\sigma(I)$ were given weights w of $1/\sigma^2(|F_o|)$, $\sigma(|F_o|)$ being derived from $\sigma^2(I) = \sigma_{\text{counting}}^2(I) + (0.04I)^2$, and were used in the refinement. The remaining $|F_o|$'s were assigned $w = 0$.

All calculations were carried out assuming space group $C2/c$ since the E statistics favored this choice and since the refinement progressed smoothly. The structure was solved by Patterson and Fourier methods and refined by large-block least-squares techniques. The function minimized was $w\Delta^2$ where $\Delta = ||F_o| - |F_c||$. The programs used have been described elsewhere (Brauer & Krüger, 1975). Relativistic neutral-atom scattering factors (Cromer & Waber, 1965) were used for all atoms, real and imaginary anomalous-dispersion corrections (Cromer & Liberman, 1970) being included for the Hg and S atoms. Anisotropic refinement converged with $R = \sum \Delta / \sum |F_o| = 0.029$ and $R_w = [\sum w\Delta^2 / \sum w|F_o|^2]^{1/2} = 0.046$. The final

difference map contained only six peaks above the $\sim 0.4 \text{ e } \text{Å}^{-3}$ background level, the largest ($0.95 \text{ e } \text{Å}^{-3}$) being near the Hg atom, and thus confirmed the structure. A plot of $w\Delta^2$ against $|F_o|$, $\sin\theta$ and the Miller indices showed no significant trends. Positional parameters are given in Table 1, the numbering being defined in Fig. 1.* Bond distances and angles are listed in Tables 2 and 3 respectively.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34400 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ($\times 10^4$) for $\text{Hg}[\text{N}(\text{CSCF}_3)_4]_2$

	x	y	z
Hg	2500	2500	0
S(1)	2802 (2)	4132 (1)	-1371 (1)
S(2)	2616 (1)	6346 (1)	-654 (1)
S(3)	2090 (1)	6074 (1)	1230 (1)
S(4)	1999 (1)	3717 (1)	1515 (1)
F(1)	4607 (4)	3468 (4)	-527 (3)
F(2)	4762 (4)	4796 (4)	-917 (4)
F(3)	4564 (5)	3722 (4)	-1734 (4)
F(4)	1267 (5)	7193 (4)	-1703 (4)
F(5)	988 (4)	5796 (3)	-1752 (3)
F(6)	513 (4)	6525 (4)	-882 (4)
F(7)	89 (4)	5521 (4)	730 (4)
F(8)	285 (5)	6920 (4)	710 (5)
F(9)	376 (5)	6286 (5)	1757 (4)
F(10)	4012 (4)	3218 (4)	1634 (3)
F(11)	3854 (4)	4375 (4)	2271 (3)
F(12)	3424 (5)	3105 (5)	2659 (3)
N	2415 (3)	3851 (4)	73 (3)
C(1)	2572 (4)	4466 (4)	-463 (3)
C(2)	2430 (4)	5329 (4)	-196 (4)
C(3)	2210 (4)	5215 (4)	556 (3)
C(4)	2218 (4)	4313 (4)	707 (3)
C(5)	4232 (7)	4033 (6)	-1134 (5)
C(6)	1290 (6)	6464 (4)	-1266 (5)
C(7)	646 (6)	6176 (5)	1089 (5)
C(8)	3395 (6)	3592 (5)	2036 (4)

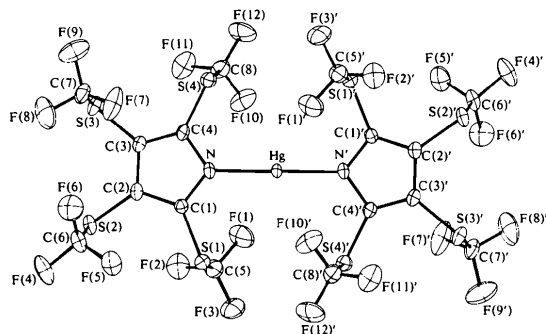


Fig. 1. A perspective drawing of $\text{Hg}[\text{N}(\text{CSCF}_3)_4]_2$ showing 20% probability thermal ellipsoids.

Table 2. Bond distances (Å) in $\text{Hg}[\text{N}(\text{CSCF}_3)_4]_2$

Hg-N	2.017 (5)	S(3)-C(7)	1.791 (8)
N-C(1)	1.358 (7)	S(4)-C(8)	1.805 (8)
N-C(4)	1.377 (7)	$\langle \text{S}-\text{C}(sp^3) \rangle$	1.787 (15)
$\langle \text{N}-\text{C} \rangle^*$	1.368 (13)	C(5)-F(1)	1.356 (10)
C(1)-C(2)	1.391 (9)	C(5)-F(2)	1.329 (11)
C(2)-C(3)	1.419 (9)	C(5)-F(3)	1.304 (11)
C(3)-C(4)	1.367 (8)	C(6)-F(4)	1.324 (9)
C(1)-S(1)	1.754 (6)	C(6)-F(5)	1.309 (9)
C(2)-S(2)	1.752 (7)	C(6)-F(6)	1.312 (9)
C(3)-S(3)	1.769 (6)	C(7)-F(7)	1.282 (9)
C(4)-S(4)	1.747 (6)	C(7)-F(8)	1.318 (10)
$\langle \text{C}(sp^2)-\text{S} \rangle$	1.756 (9)	C(7)-F(9)	1.303 (11)
S(1)-C(5)	1.768 (9)	C(8)-F(10)	1.288 (9)
S(2)-C(6)	1.785 (8)	C(8)-F(11)	1.325 (10)
		C(8)-F(12)	1.305 (10)
		$\langle \text{C}-\text{F} \rangle$	1.313 (20)

* These are average values with $\sigma = \left[\sum_{i=1}^N (l_i - \bar{l})^2 / (N - 1) \right]^{1/2}$.

Table 3. Bond angles ($^\circ$) in $\text{Hg}[\text{N}(\text{CSCF}_3)_4]_2$

N-Hg-N'	180	S(1)-C(5)-F(3)	109.6 (6)
Hg-N-C(1)	127.5 (4)	F(1)-C(5)-F(2)	103.8 (7)
Hg-N-C(4)	124.7 (4)	F(1)-C(5)-F(3)	107.3 (7)
C(1)-N-C(4)	107.8 (5)	F(2)-C(5)-F(3)	107.5 (7)
N-C(1)-C(2)	109.7 (5)	S(2)-C(6)-F(4)	109.0 (5)
N-C(1)-S(1)	121.2 (4)	S(2)-C(6)-F(5)	114.5 (5)
C(2)-C(1)-S(1)	128.8 (5)	S(2)-C(6)-F(6)	114.0 (6)
C(1)-C(2)-C(3)	105.7 (5)	F(4)-C(6)-F(5)	106.1 (7)
C(1)-C(2)-S(2)	126.9 (5)	F(4)-C(6)-F(6)	108.6 (6)
C(3)-C(2)-S(2)	127.2 (5)	F(5)-C(6)-F(6)	104.2 (6)
C(2)-C(3)-C(4)	107.6 (5)	S(3)-C(7)-F(7)	115.7 (5)
C(2)-C(3)-S(3)	126.9 (5)	S(3)-C(7)-F(8)	111.6 (5)
C(4)-C(3)-S(3)	125.2 (5)	S(3)-C(7)-F(9)	110.5 (5)
C(3)-C(4)-N	109.1 (5)	F(7)-C(7)-F(8)	107.3 (7)
C(3)-C(4)-S(4)	131.3 (5)	F(7)-C(7)-F(9)	108.2 (7)
N-C(4)-S(4)	119.6 (4)	F(8)-C(7)-F(9)	102.6 (7)
C(1)-S(1)-C(5)	100.3 (4)	S(4)-C(8)-F(10)	114.1 (5)
C(2)-S(2)-C(6)	99.0 (3)	S(4)-C(8)-F(11)	112.2 (5)
C(3)-S(3)-C(7)	101.9 (3)	S(4)-C(8)-F(12)	108.8 (6)
C(4)-S(4)-C(8)	98.6 (3)	F(10)-C(8)-F(11)	105.9 (6)
S(1)-C(5)-F(1)	113.3 (6)	F(10)-C(8)-F(12)	108.2 (7)
S(1)-C(5)-F(2)	114.8 (6)	F(11)-C(8)-F(12)	107.3 (7)

* Coordinates of the primed atom are $0.5 - x$, $0.5 - y$, $-z$.

Results and discussion

Crystals of (I) are composed of discrete molecules with the Hg atom occupying an inversion center. Of the intermolecular distances, only F-F and F-S contacts are as short as the sums of the van der Waals radii (Bondi, 1964), the shortest being F(11)-F(11) ($1 - x$, y , $0.5 - z$), $2.827 (7) \text{ Å}$.

The pyrrolyl rings and the Hg atom are coplanar within $\pm 0.02 \text{ Å}$, the S atoms deviating less than 0.15 Å from this least-squares best plane. The endocyclic and

exocyclic bond angles and the bond lengths of the pyrrolyl ring show no significant deviations from those reported for pyrrole (Nygaard, Nielsen, Kirchheimer, Maltesen, Rastrup-Andersen & Sørensen, 1969). The directing of the S—C(sp^3) bonds nearly perpendicularly to the pyrrolyl ring, Fig. 1, minimizes steric interactions. Since C(5) and C(8) are below and C(6) and C(7) are above the ring plane in Fig. 1, the molecular symmetry is approximately $2/m$ (C_{2h}). The approximate non-crystallographic mirror plane, which includes the Hg—N bonds and is perpendicular to the pyrrolyl rings, is only seriously violated by the gearing of bonds radiating from C(6) and C(7). The mean C(sp^2)—S bond length, 1.756 (9) Å, is typical for such bonds, e.g., 1.767 (10) Å in (*p*-NO₂C₆H₄S)₂ (Ricci & Bernal, 1969). The average S—C(sp^3) bond distance, 1.787 (15) Å, is not significantly shorter than those reported for (CF₃)₂S, 1.828 (15) Å (Bowen, 1954), and CF₃SH, 1.800 (5) Å (Marsden, 1973). The average C—S—C bond angle, 100.0 (15)°, may be compared with that of (CF₃)₂S, 105.6 (30)° (Bowen, 1954).

The mean C—F bond length, 1.313 (20) Å, is not significantly shorter than the C—F distances in (CF₃)₂S, 1.328 (11) Å (Bowen, 1954), and CF₃SH, 1.335 (3) Å (Marsden, 1973). The spread of the C—F bond lengths does not seem to be unexceptionally large since the SCF₃ groups display large torsional motions, Fig. 1. Even bearing this in mind, the spread of the S—C—F bond angles is striking, 109.0 (5)—115.7 (5)°. A plot (Fig. 2) of these angles *versus* the moduli of the corresponding C—S—C—F torsion angles is reasonably linear, correlation coefficient —0.96. Since at least one F atom of each CF₃ group is within the van der Waals distance, 3.17 Å (Bondi, 1964), of a third nearest-neighbor pyrrolyl C atom, an explanation for the correlation in terms of 1–3 C···F repulsions seems plausible. That S(3) has the largest C—S—C bond angle while C(3)—S(3) and C(7)—F(7) are the only such bonds that are nearly eclipsed (Fig. 2) offers additional evidence for such interactions. Interestingly, while the

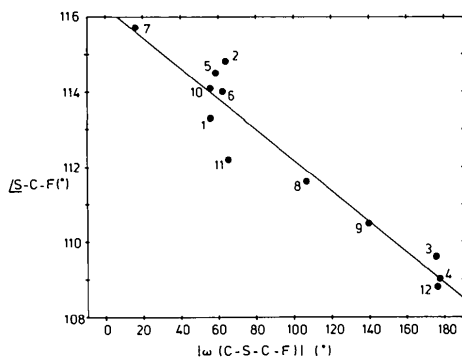


Fig. 2. A plot of the moduli of the C—S—C—F_{*i*} torsion angles *vs* the S—C—F_{*i*} bond angles. The subscript *i* refers to the F atom forming the angle.

mean F—C—F angle, 106.4 (19)°, is not significantly smaller than that found in CF₃SH, 107.7 (3)° (Marsden, 1973), in each CF₃ group the F—C—F angle formed by the two F atoms which have C—S—C—F torsion angles with moduli between 55 and 140° is the smallest of the three. Thus the symmetry of the SCF₃ groups is no higher than *m* (C_s) and the departure from $3m$ (C_{3v}) symmetry is not simply a tilt of the CF₃ threefold axis away from the S—C(sp^3) vector.

All intermolecular contacts with the Hg atom are too long (>3.50 Å) to be bonding. The conformation of the pyrrolyl ligands allows four Hg—S and four Hg—F intramolecular contacts to be shorter than 3.50 Å. The Hg—S(1) and Hg—S(4) distances, 3.391 (2) and 3.497 (2) Å respectively, however, are even longer than the shortest intermolecular Hg—S distances in (CH₃)₂Hg, 3.25 Å (Bradley & Kunchur, 1964). Similarly, the Hg—F(1) and Hg—F(10) contacts, 3.334 (5) and 3.251 (5) Å respectively, are even longer than the shortest intermolecular Hg—F distances in (CF₃)₂Hg, 3.181 (7) Å (Brauer, Bürger & Eujen, 1977). Thus the Hg—N bond length in (I), 2.017 (5) Å, should represent an essentially unperturbed measure of a Hg(sp)—N(sp^2) bond. Correspondingly, the observed length compares well with that (2.02 Å) interpolated from structural data on (CH₃)₂Hg (Kashiwabara, Konaka, Iijima & Kimura, 1973), (CH₃N)₂ (Chang, Porter & Bauer, 1970) and C₂H₆ (Bartell & Higginbotham, 1965). The Hg—N bond length in (I) is about as long as those in CF₃HgN₃ and CF₃HgNCO, 2.02 (2) and 2.03 (2) Å respectively (Brauer *et al.*, 1978) and probably shorter than those in α-Hg(N₃)₂, 2.04 (2) and 2.14 (2) Å (Müller, 1973*a*), CH₃HgN₃, 2.22 (14) Å (Müller, 1973*b*) and KHg(NCO)₃, 2.07 and 2.10 Å (Thiele & Hilfrich, 1977). Thus the above-mentioned dependence of the Hg—N bond length on intermolecular contacts appears to be confirmed.

Thanks are due to Dr C. Krüger of the Max-Planck-Institut für Kohlenforschung for the use of X-ray and computer facilities and to Professor Dr Haas of the Ruhr Universität Bochum for the compound.

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Acta Cryst. (1979). **B35**, 1773–1775

Double Conformation du Groupement Méthanedisulfonato à l'Intérieur d'un Même Cristal de Méthanedisulfonate d'Argent(I): $\text{Ag}_2(\text{SO}_3\text{CH}_2\text{SO}_3)$

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(Reçu le 20 novembre 1978, accepté le 19 mars 1979)

Abstract

Silver(I) methanedisulphonate, $\text{Ag}_2(\text{CH}_2\text{O}_6\text{S}_2)$, crystallizes in space group $Pmc2_1$ with $a = 8.578$ (3), $b = 7.387$ (2), $c = 9.954$ (2) Å, $Z = 4$, $D_x = 4.11$ Mg m $^{-3}$, $\mu = 6.56$ mm $^{-1}$ for Mo $K\alpha$. Intensities were collected on an automatic four-circle diffractometer (Mo $K\alpha$) and the structure was determined by means of the Patterson function and Fourier syntheses. An anisotropic full-matrix least-squares refinement was performed yielding a final R of 0.028 for the 876 measured reflections. Within the same crystal the methanedisulphonato group exhibits two different conformations which have m symmetry: the *syn* form has symmetry closely related to $mm2$ and the *anti* form is derived from this by a π rotation of an SO_3 group around its own C–S bond. There are two kinds of Ag atoms coordinated to six and five sulphonic O atoms in very distorted coordination polyhedra [Ag–O bond ranges: 2.460 (7) to 2.603 (7) Å, and 2.357 (8) to 2.494 (8) Å]. The *syn* and *anti* forms act respectively as deca- and dodeca-coordinating ligands; moreover, it is noteworthy that the *syn* form is a chelating agent for two Ag atoms of the same kind.

Introduction

Avec la structure du méthanedisulfonate d'argent(I), $\text{Ag}_2(\text{SO}_3\text{CH}_2\text{SO}_3)$, nous poursuivons l'étude de l'environnement de l'argent(I) dans ses composés de coordination avec différents coordinats organiques

dont en particulier ceux qui renferment des groupes sulfoniques. Les structures du méthanesulfonate d'argent(I), $\text{Ag}(\text{CH}_3\text{SO}_3)$, et du bromométhanesulfonate d'argent(I), $\text{Ag}(\text{BrCH}_2\text{SO}_3)$, ont été décrites récemment (Charbonnier, Faure & Loiseleur, 1977, 1978).

Résultats expérimentaux

Par action de l'acide méthanedisulfonique $\text{HSO}_3\text{CH}_2\text{SO}_3\text{H}$ sur l'oxyde Ag_2O , on obtient un composé qui cristallise facilement à partir de solutions aqueuses lentement évaporées à l'air et à l'abri de la lumière. L'analyse chimique a montré qu'il s'agissait du méthanedisulfonate d'argent $\text{Ag}_2(\text{SO}_3\text{CH}_2\text{SO}_3)$. Les clichés obtenus en chambres de Weissenberg et de précession révèlent la symétrie orthorhombique; l'extinction systématique des ordres $h0l$ pour $l = 2n + 1$ détermine l'appartenance soit aux groupes non centrosymétriques $Pmc2_1$ ou $P2cm$, soit au groupe centrosymétrique $Pmcm$. Au cours de la détermination de la structure, le groupe $Pmc2_1$ s'est imposé.

A partir d'un cristal taillé en parallélépipède (0,08 × 0,09 × 0,10 mm) les intensités de 2089 réflexions d'un octant de la sphère de réflexion ont été examinées en rayonnement $\lambda(\text{Mo } K\alpha)$ avec balayage ω – θ pour $1 \leq \theta \leq 45^\circ$, au moyen d'un diffractomètre CAD-4 Nonius (Centre de Diffractométrie de l'Université Claude Bernard). Seules 876 réflexions émergeant de plus de 30% du fond continu ont été réellement mesurées et prises en considération pour la détermination de la