Journal of Organometallic Chemistry, 394 (1990) 757–764
Elsevier Sequoia S.A., Lausanne
JOM 20854

Dimethylsulfoxide coordination to methylmercury tetrafluoroborate *

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(Received February 2nd, 1990)

Abstract

Methyl(dimethylsulfoxide)mercury(II) tetrafluoroborate has been prepared from methylmercury(II) tetrafluoroborate and dimethylsulfoxide (DMSO) in dichloromethane solution in high yield as a colourless crystalline solid. IR and NMR spectra suggest the presence of a solely *O*-bonded DMSO ligand at mercury. The crystal has been shown to have an ionic structure made up of $MeHg(DMSO)^+$ cations and (disordered) BF_4^- anions by an X-ray diffraction study. The short Hg–O contact, 2.066(8) Å, and the values of the angles Hg–O–S, 119.3(5)°, and C–Hg–O, 178.7(5)°, are indicative of strong covalent DMSO coordination.

Introduction

Dimethylsulfoxide (DMSO) is an ambidentate ligand. Donor properties at both oxygen and sulfur allow it to coordinate to acceptor centers through a hard or a soft function [1], and structural investigations in recent years have revealed examples of both modes of interaction [1–5]. It should be noted, however, that DMSO can act not only as a monodentate donor (through oxygen or sulfur), but also as a 1,2-bidentate donor or as a bridging ligand between metals, with one or both of the chalcogen atoms involved, as shown in formulae **A**–**E**.

Pertinent studies have focused mainly on metals of the platinum group in the d^8 configuration [6–9], but systems involving other metals have also been considered [10], and the structural chemistry of the DMSO complexes of mercury(II) in particular is also quite well represented. Such complexes are of renewed interest owing to the growing concern about the complexation of mercury in the environ-

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[*] Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

[**] X-ray structure analysis.

ment, in which a wide variety of sulfur compounds are abundant as potential carrier and storage systems for trace elements [11]. Special attention has been given to methylmercury(II) compounds, which appear to be the most relevant mercury contaminant in environmental water, and complexation of which by natural sulfur-based complexing agents is of prime importance [12].

A literature survey has shown that DMSO is bound exclusively through oxygen to mercury(II) in all of the compounds whose structure have been determined to date. The mode of DMSO–Hg(II) interaction may be strictly terminal (end-on) *O*-monocoordination as in $[Hg(DMSO)_6](ClO_4)_2$ [13], terminal/bridging *O*-coordination as in $[Hg_2(DMSO)_8]^{4+}(ClO_4)_4$ [14], or solely *O*-bridging as in $[(HgCl_2)_3(DMSO)_2]$ [15]. With di-n-butyl- and diphenyl-sulfoxide, the ligands are found *O*-terminally coordinated in $HgCl_2 \cdot (n\text{-}C_4H_9)_2SO$ [16] and $HgCl_2 \cdot (C_6H_5)_2SO$, but with significant secondary interactions of mercury with the π-system of the phenyl groups in the latter [17]. It therefore appears that diorganosulfoxides are generally *O*-bonded to mercury(II) centers.

Surprisingly, only a very few organomercury(II) compounds have been structurally investigated, and information is restricted mainly to the tri- and tetramercuromethane derivatives. Crystals of $C(HgCl)_4$ obtained from DMSO solution contain dimers $[C(HgCl)_4 \cdot (DMSO)]_2$, in which the oxygen atoms of the DMSO molecules are in a triply-bridging position between three mercury atoms (of the two monomers), but where a very long (and therefore probably weak) *S*-contact to another mercury atom (3.578 Å) is also present [18]. In $(ClHg)_3C\text{–}COOH \cdot (DMSO)$ the sulfoxide has bridging *O*-contacts to two mercury atoms [19], and in an analogous aldehyde adduct $(BrHg)_3C\text{–}CHO \cdot (DMSO)$ the arrangement of the components is very similar [20].

Finally, 1,8-naphthalindiyl-bis[chloromercury(II)] crystallizes with one molecule of DMSO, which bridges the metals via its oxygen atom [21].

Owing to this limited number of examples it was an open question whether DMSO could also be *S*-coordinated to organomercurial(II) cations RHg^+, especially in cases where a positive inductive effect of the organic group R would reduce the acceptor properties of the metal and change its character from hard to soft. To test this possibility we have prepared and structurally characterized, as a simple reference compound, the DMSO complex of $CH_3Hg^+BF_4^-$. In this smallest possible example, steric effects should not be important so that electronic effects should be the dominant.

The crystal structure of the free ligand DMSO was determined at two different temperatures. The results obtained at 5 °C (space group $P2_1/c$) [22] and at −60 °C [23] ($P2_1/a$) are similar, but with the expected shortenings of bonds as the temperature is lowered (see reference data in Table 1 below). Gas phase data are also available [24], but are not considered here.

Preparation of the complex

Methylmercury(II) tetrafluoroborate was generated previously from the reaction of methylmercury(II) chloride and silver oxide in water solution followed by treatment with HBF_4, but was not isolated [25,26]. When this reaction is carried out in methanol, a methanol solvate of CH_3HgBF_4 can be obtained (after filtration and evaporation of the volatiles from the filtrate) as a colorless viscous liquid.

Treatment of this solvate with an equivalent of DMSO in dichloromethane gives a high of yield the DMSO complex, m.p. 78° C, crystals, which glitter like white mother of pearl. The product is soluble in most polar organic solvents.

$$CH_3HgCl + AgBF_4 \rightarrow AgCl + CH_3Hg^+BF_4^- (solv.)$$

$$CH_3Hg^+BF_4^- (solv.) + DMSO \rightarrow CH_3Hg(DMSO)^+ BF_4^-$$

The IR spectrum of the crystalline compound (in KBr) has a strong absorption at 953 cm^{-1} for ν(S=O). This value is more than 100 cm^{-1} lower than that reported for free DMSO (1055 cm^{-1}) and is thus indicative of *O*-coordination. It should be noted that for *S*-bonded DMSO an increase of the frequency is to be expected [27].

The ^{1}H NMR spectrum (in CD_2Cl_2) shows the CH_3S resonance at 2.97 ppm (*J*(CH) 142.5 Hz) and the CH_3Hg resonance at 1.25 ppm (*J*(CH) 144.3, *J*(HgH) 249.7 Hz). In the ^{13}C NMR spectrum the corresponding ^{13}C signals appear at 39.2 ppm and 1.8 ppm (*J*(HgC) 1639 Hz), respectively. The values for the CH_3Hg moiety are not very different from those for the methanol solvate of $CH_3Hg^+BF_4^-$, and thus the DMSO coordination seems to have little effect on the organometallic group. The downfield shift of the DMSO ^{H} resonance upon coordination ($\Delta\delta = 0.44$ ppm) again indicates *O*-coordination [2]. NMR data for the solid and solution state therefore favour a structure with DMSO exclusively *O*-bonded to the methylmercury(II) cation.

The crystal structure of $CH_3Hg[OS(CH_3)_2]^+BF_4^-$

The title compound crystallizes in monoclinic needles (space group $P2_1/c$) with $Z = 4$ molecules in the unit cell. The results of the structure determination are summarized in Tables 1–3, Fig. 1 shows the structure of the cation $CH_3Hg[OS(CH_3)_2]^+$, Fig. 2 a drawing of the unit cell.

Table 1

Fractional atomic coordinates and isotropic displacement parameters for the crystals of $[CH_3Hg(DMSO)]^+ BF_4^-$

Atom	*x*	*y*	*z*	U_{eq}
Hg	0.06039(6)	0.14295(3)	0.41917(4)	0.065
C1	0.303(2)	0.063(1)	0.397(2)	0.132
O	−0.187(1)	0.2214(6)	0.4384(8)	0.080
S	−0.1826(4)	0.3191(2)	0.5306(3)	0.057
C2	−0.271(2)	0.4250(9)	0.428(1)	0.076
C3	−0.381(2)	0.295(1)	0.614(1)	0.079
B	0.188(1)	0.3878(8)	0.269(1)	0.056
F11	0.185(3)	0.363(1)	0.397(1)	0.052
F12	0.223(3)	0.491(1)	0.252(2)	0.067
F13	0.012(2)	0.364(1)	0.202(1)	0.053
F14	0.315(3)	0.324(2)	0.218(2)	0.095
F21	0.220(3)	0.355(2)	0.396(1)	0.069
F22	0.143(3)	0.494(1)	0.267(2)	0.072
F23	0.050(3)	0.326(1)	0.203(2)	0.086
F24	0.354(2)	0.374(2)	0.215(2)	0.087

Table 2

Selected interatomic distances (Å) and angles (°) in crystalline $[CH_3Hg(DMSO)]^+ BF_4^-$ (at −50 °C) and reference data for DMSO (at 5 °C) [22] and −60 °C [23]. (Standard deviations between parentheses.)

	Complex −50 °C	Ligand	
		5 °C	−60 °C
Hg–C1	2.05(1)		
Hg–O	2.066(8)		
S–O	1.556(8)	1.521(5)	1.471(8)
S–C2	1.78(1)	1.766(8)	1.81(1)
S–C3	1.78(1)	1.82(1)	1.80(1)
C1–Hg–O	178.7(5)		
Hg–O–S	119.3(5)		
O–S–C2	103.8(5)	106.7(4)	107.0(6)
O–S–C3	102.6(6)	107.5(4)	107.4(6)
C2–S–C3	99.9(6)	97.4(4)	97.9(5)

Table 3

Crystal and data collection parameters for $CH_3Hg[OS(CH_3)_2]BF_4$ [a]

emp. formula	$C_3H_9HgOSBF_4$
fw	380.56
crystal system	monoclinic
space group	$P2_1/c$ (No.14)
a [Å]	7.194(1)
b [Å]	12.566(2)
c [Å]	10.445(2)
β [°]	97.44(1)
V [Å^3]	936.2(3)
Z	4
ρ_{calc} [g/cm^3]	2.70
μ(Mo-K_α) [cm^{-1}]	160.53
$F(000)$ [e]	688
diffractometer	Syntex $P2_1$
radiation, λ [Å]	0.71069
temperature [°C]	−50
scan technique	ω
scan with [° in ω]	0.9
scan speed [°/min]	0.7–29.3
hkl range	$\pm 8, \pm 15, +12$
$[(\sin\theta)/\lambda]_{max}$ [Å^{-1}]	0.62
measured reflections	3837
unique reflections	1838
R_{int}	0.02
observed reflections [$F_o \geq 4\sigma(F_o)$]	1547
refined parameters	102
R [b]	0.0437
R_w [c]	0.0452
(shift/error)$_{max}$	−0.002
$\Delta\rho_{fin}$(max/min) [e/Å^3]	+1.93/−1.98

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[a] Estimated standard deviations of the last significant digit are given in parentheses. [b] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c] $R_w = [\Sigma(w|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$

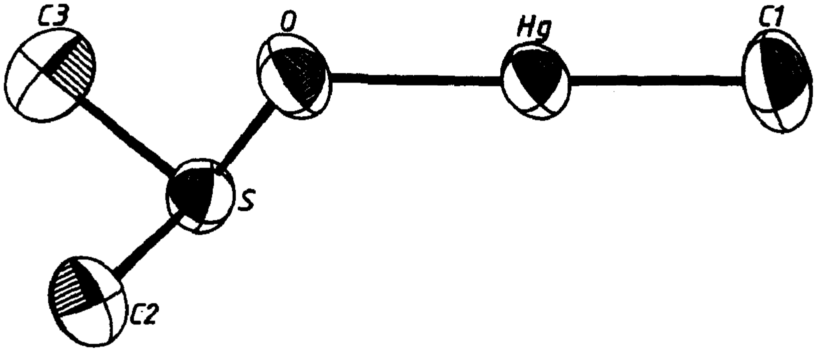

Fig. 1. Structure of the cation $\{CH_3Hg[OS(CH_3)_2]\}^+$ in the crystals of the tetrafluoroborate salt with atomic numbering. (ORTEP, 50% probability ellipsoids.)

It is apparent from Fig. 1 that the DMSO ligand is *O*-bonded to mercury. The mercury atom is linearly two-coordinate with an angle of 178.7(5)° at the metal atom. The Hg–O bond is rather short at 2.066(8) Å, a value very close to the Hg–O distance in mercuric oxide (2.03 Å), indicating a strong donor–acceptor bond in the cation.

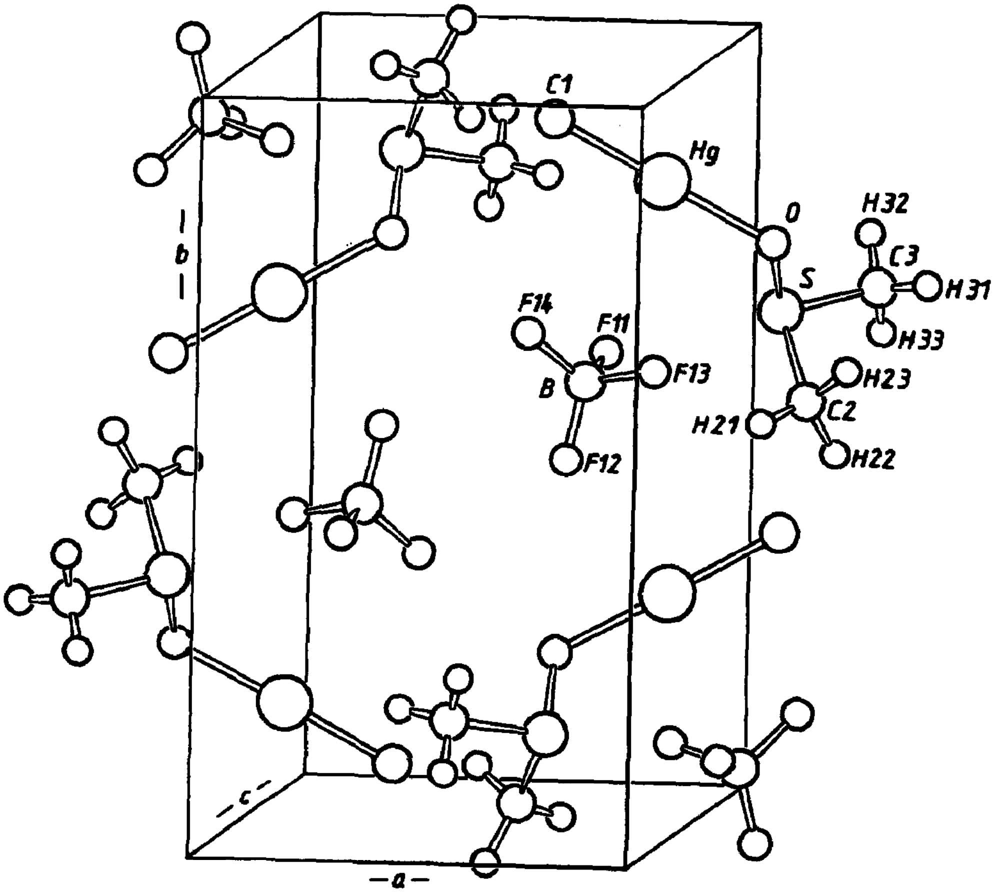

Fig. 2. Unit cell of crystalline $\{CH_3Hg[OS(CH_3)_2]\}^+BF_4^-$.

The geometry of the DMSO ligand is changed very little upon coordination to the CH_3Hg^+ site, as shown by a comparison of the data for the free ligand with those for the complex in Table 2. A small decrease of the C–S–O angles and a small increase of the C–S–C angle lead to a very minor reduction in the sum of valence angles at sulfur for the complex (306.4°, compared with 310.9° for the 5°C structure of DMSO). The change in the S=O bond distance is also surprisingly small (Δ = 0.02 Å). The absolute values of the S=O distance (1.556(8) Å) and the S–O–Hg angle (119.3(5)°) are not unusual, and similar to those found in the Hg^{II} complexes of DMSO [13–21].

The structure of the unit cell (Fig. 2) shows no short contacts between cations and anions. The compound can thus be described as a largely ionic system, in which the DMSO ligand is fully able to satisfy the acceptor properties of the CH_3Hg^+ cation. This result is in good agreement with the solubility properties and spectral data of the material.

In summary, the results have shown that DMSO is bonded as a *O*-coordinate ligand not only to Hg^{2+} centers but also to the CH_3Hg^+ cation. There is no indication that alkylmercury species have acceptor properties for diorganosulfoxides very different from mercuric cation. The sulfoxide sulfur atoms are not sufficiently polarizable (soft) to compete favourably with the hard oxygen donor sites for mercury. Of various hard ligands, such as the solvents water, methanol, or halomethanes, or counter ions such as halide or complex halide, DMSO is the preferred donor system.

Experimental

General

The experiments were carried out under purified dry nitrogen. Solvents and glassware were treated appropriately. Light was excluded in experiments in which silver salts were present.

Methyl(dimethylsulfoxide)mercury(II) tetrafluoroborate

A solution of methylmercury chloride (4.40 g, 17.5 mmol) in methanol (90 ml) is treated with one of silver tetrafluoroborate (3.41 g, 17.5 mmol) in 30 ml of the same solvent. The mixture is stirred for 2 h and filtered to leave silver chloride (2.46 g, 98% yield). The solvent is removed from the filtrate under a vacuum to leave a colourless viscous residue, which is dissolved in dichloromethane (30 ml). The solution is again filtered and the filtrate treated dropwise with DMSO (1.43 g, 1.30 ml, 18.3 mmol). Exothermal formation of crystals occurs immediately. The product is filtered off and dried in vacuum at 20°C. Yield 6.34 g (95%), m.p. 78°C.

Found: C, 9.80; H, 2.50. Analysis. $C_3H_9BF_4HgOS$ (380.6) calc.: C, 9.47; H, 2.38%. ^1H NMR (CD_2Cl_2, 25°C): δ 2.97 ppm (s, J(CH) 142.5 Hz, CH_3S), 1.25 (s, J(CH) 144.3, J(HgH) 249.7 Hz, CH_3Hg). $^{13}C\{^1H\}$ NMR (above): δ 39.2 ppm (s, CH_3S), 1.8 (s, J(HgC) 1639 Hz, CH_3Hg). IR (KBr): ν(S=O) 953 cm^{-1}.

Crystal structure determination

Suitable crystals were obtained by recrystallisation from dichloromethane. A crystal with the dimension 0.1 × 0.2 × 045 mm^3 was selected and mounted in a glass capillary under argon. The intensities $\pm h, \pm k, l$ were measured for the monoclinic cell (space group $P2_1/c$) with a 7.194(1), b 12.566(2), c 10.445(2) Å, β 97.44(1)° at −50 °C (ω-scan, Mo-K_α, λ 0.72069 Å, graphite monochromator). During data collection three intensity check reflections were measured every 2 h (1 0 0, 0 4 0, 0 0 2), and no appreciable decomposition was observed. The data were corrected for absorption and polarization effects. The positional parameters of the mercury atom were calculated from the Patterson map (SHELXS-86). A difference Fourier map (SHELX-76) based on the metal atom phases revealed the positions of all non-hydrogen atoms in the asymmetric unit. The positional parameters were refined by full matrix least squares methods with anisotropic thermal parameters for all non-hydrogen atoms, except for the four fluorine atoms. The BF_4^- anion was found to be disordered, but by fixing the B–F distances and interatomic angles two possible arrangements for the anion were found. Five hydrogen atoms of the methyl groups at sulfur were located, the position of the remaining hydrogen was calculated. These hydrogen atoms were assigned fixed thermal parameters (U_{iso} 0.05 Å^2), and the positions were improved by rigid group refinement. The positions of the methyl hydrogens of the cation were neither found nor was it possible to calculate them. Atomic coordinates are listed in Table 1, selected interatomic distances and angles in Table 2. Calculated and observed structure factor amplitudes together with a complete list of atomic coordinates and thermal parameters have been deposited. Further details of the structure determination are available from Fachinformationszentrum Karlsruhe GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the reference number CSD 54600, the names of the authors, and the full literature citation.

Acknowledgement

This work was supported by Deutsche Forschungsgemeinschaft (Leibniz-Programm) and by Fonds der Chemischen Industrie. We thank Mr. J. Riede for obtaining the X-ray diffraction data.

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