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Complexation of DMF and DMSO by a Monodentate Organomercurial Lewis Acid

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*Summary: When crystallized from DMSO or DMF, pentafluorophenylmercury chloride (**1**) forms the Lewis acid−Lewis base adducts **1**·DMSO (**2**) and (**1**)$_2$·DMF (**3**), respectively. These adducts have been characterized by elemental analysis, IR spectroscopy, ^{13}C CP/MAS NMR (**3**) and X-ray single-crystal structure analysis. Compound **2** is a T-shaped complex. In the crystal, the individual molecules of **2** aggregate through formation of Hg_2Cl_2 bridges to form a ladder polymer. Compound **3** crystallizes with four independent molecules of **1** and two independent molecules of DMF in the asymmetric unit. While all molecules are part of a complex framework formed by Hg_2Cl_2 bridges, three molecules of **1** are involved in the binding of two formamide molecules, which form bridges between adjacent mercury centers.*

Monofunctional organomercurials such as phenylmercury chloride rarely form adducts with basic substrates.[1] In this paper we report that pentafluorophenylmercury chloride[2] behaves differently than its perprotio-analogue and complexes DMSO and DMF. This work is part of our ongoing coordination studies of mercury-based Lewis acids.[3]

Slow evaporation of the solvent from a DMSO or DMF solution of pentafluorophenylmercury chloride (**1**) affords in both cases a quantitative yield of large crystals whose respective compositions are **1**·DMSO (**2**) and (**1**)$_2$·DMF (**3**) as determined by elemental analysis. IR spectroscopy revealed a weakening of the sulfoxide (1019 cm^{-1} in **2** vs 1057 cm^{-1} in free DMSO) and carbonyl (1654 cm^{-1} in **3** vs 1675 cm^{-1} in free DMF) stretching bands, thus suggesting that in both cases there is coordination of the terminal oxygen to the mercury center of **1**. This conclusion was corroborated by the deshielded value of the ^{13}C CP/MAS NMR carbonyl carbon chemical shift in **3** (167.6 ppm vs 162.7 cm^{-1} in free DMF).

The results of the X-ray single-crystal analysis for **2** and **3** confirmed the nature of the complexes (Table 1). The structure of **2** approaches that of a T-shaped coordination complex (Figure 1) with O−Hg−Cl, O−Hg−C(1), and C(1)−Hg−Cl angles of 93.5(1)°, 96.8(2)°, and 169.7(2)°, respectively. The Hg−O distance of 2.542(4) Å is comparable to the distance found in the dibutylsulfoxide adduct of $HgCl_2$ (2.593(5) Å).[4] Examination of the cell-packing diagram indicates that the monomers are associated through formation of head-to-tail Hg_2Cl_2 bridges (Hg′−Cl 3.131, Hg′−Cl″ 3.450 Å) (Figure 2). Those intramolecular distances are shorter than the sum of the van der Waals radii of chlorine ($r_{\mathrm{vdw}}(\mathrm{Cl}) = 1.8$ Å)[5] and mercury ($r_{\mathrm{vdw}}(\mathrm{Hg}) = 1.7-2.0$ Å)[6] and substantiate the presence of moderate interactions. The resulting supramolecule is a ladder polymer similar to that found in phenylmercury chloride,[7] yet in the present case, solvated by DMSO molecules. The structure of **3** contains four independent molecules of **1** and two independent molecules of DMF. Interestingly, three molecules of **1** are involved in the binding of the two DMF molecules (Figure 3). While the DMSO molecule of **2** is terminal, the DMF molecules in **3** form bridges between the mercury centers of three different complexes and are thus doubly coordinated. The mercury center of these three molecules is linearly coordinated to its primary ligands, and the Hg−O bonds are approximately perpendicular to the C−Hg−Cl sequences. The Hg−O distances in **3** (Hg(1b)−O(1b) 2.663, Hg(3b)−O(1b) 2.776, Hg(3b)−O(2a) 2.852, Hg(2a)−O(2a) 2.666) are very similar to those found in the structure of 1,2-bis(chloromercurio)benzene·μ_2-DMF (2.681 and 2.777 Å), which contains a chelated DMF molecule.[8,9] It must be indicated that the fourth molecule of **1** cements the cluster by forming Hg···Cl intermolecular contacts with two of its closest neighbors (Hg(4a)−Cl(2a) 3.144,

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(1) Organomercurials sometimes form adducts with polydendate Lewis bases. See for example: (a) Onan, K.; Rebek Junior, J.; Costello, T.; Marshall L. *J. Am. Chem. Soc.* **1983**, *105*, 6759. (b) Ruiz-Amil, A.; Martinez-Carrera, S.; Garcia-Blanco, S. *Acta Crystallogr. Sect. B* **1978**, *34*, 2711. (c) Redhouse, A. D. *J. Chem. Soc., Chem. Commun.* **1972**, 1119. (d) Canty, A. J.; Gatehouse, B. M. *Acta Crystallogr. Sect. B* **1972**, *28*, 1872.

(2) Chambers, R. D.; Coates, G. E.; Livingstone, J. G.; Musgrave, W. K. R. *J. Chem. Soc.* **1962**, 4367−4371.

(3) See for example: (a) Tschinkl, M.; Schier, A.; Riede, J.; Gabbaï, F. P. *Organometallics*, in press. (b) Tschinkl, M.; Schier, A.; Riede, J.; Mehltretter, G.; Gabbaï, F. P. *Organometallics* **1998**, *17*, 2921−2923. (c) Tschinkl, M.; Schier, A.; Riede, J. Gabbaï, F. P. *Inorg. Chem.* **1997**, *36*, 5706−5711.

(4) Biscarini, P.; Fusina, L.; Nivellini, G. D.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1981**, 1024−1027.

(5) Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr. Sect. B* **1985**, *41*, 274−279.

(6) Canty, A. J.; Deacon, G. B. *Inorg. Chim. Acta* **1980**, *45*, L225−L227.

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(8) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *Organometallics* **1987**, *6*, 153−156.

(9) Bridging DMF molecules have been observed in the solid state of inorganic alkali salts. See for example: (a) Markley, T. J.; Toby B. H.; Pearlstein, R. M.; Ramprasad, D. *Inorg. Chem.* **1997**, *36*, 3376−3378. (b) Ramprasad, D.; Pez, G. P.; Toby, B. H.; Markley, T. J.; Pearlstein, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 10694−10701.

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Table 1. Crystal Data, Data Collection, and Structure Refinement for 2 and 3

	2	**3**
	Crystal Data	
formula	$C_8H_6ClF_5HgOS$	$C_{7.5}H_{3.5}ClF_5HgN_{0.5}O_{0.5}$
M_r	481.23	439.65
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	13.693(1)	10.445(1)
b (Å)	6.292(1)	12.962(3)
c (Å)	14.120(1)	15.404(3)
α (deg)	90	101.37(1)
β (deg)	105.41(1)	95.97(1)
γ (deg)	90	92.78(1)
V (Å^3)	1172.8(2)	2028.4(6)
ρ_{calc} (g cm^{-3})	2.725	2.879
Z	4	8
F(000) (e)	880	1584
μ(Mo Kα)(cm^{-1})	135.7	154.8
	Data Collection	
T (°C)	−70	−97
scan mode		
hkl range	0→16, −7→7, −17→16	−12→12, −15→15, 0→18
no. of measured reflns	4555	7891
no. of unique reflns, [R_{int}]	2297, [$R_{int} = 0.0214$]	7891, [$R_{int} = 0.000$]
no. of reflns used for refinement	2222	7154
abs corr	DIFABS	DIFABS
	Refinement	
no. of refined params	154	559
final R values [$I > 2\sigma(I)$]		
R1[a] (%)	0.0318	0.0356
wR2[b] (%)	0.0833	0.0874
ρ_{fin} (max/min) (e Å^{-3})	1.496/−2.926, at Hg atom	1.375/−2.364, at Hg atoms

[a] $R1 = \sum(F_o - F_c)/\sum F_o$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0692$ (**2**), 0.0642 (**3**); $b = 0.5606$ (**2**), 4.4107 (**3**).

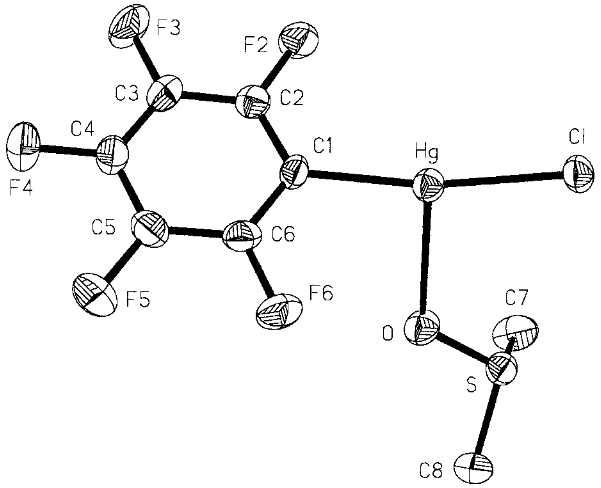

Figure 1. ORTEP drawing of **2** with 50% probability ellipsoids; H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Hg−C(1) 2.081(6), Hg−Cl 2.322(2), Hg−O 2.542(4), S−O 1.516(4); C(1)−Hg−Cl 169.7(2), O−Hg−C(1) 96.8(2), O−Hg−Cl, 93.5(1), S−O−Hg 119.3(2).

Hg(4a)−Cl(3b) 3.101, Hg(2a)−Cl(4a) 3.136, Hg(3b)−Cl(4a) 3.455 Å). In addition, the three juxtaposed perfluorinated phenyl groups are close enough to be involved in $\pi-\pi$ interactions (C(34b)−C(14b) 3.479 Å and C(34b)−C(24a) 3.370 Å). In the crystal, the tetranuclear clusters aggregate through formation of additional Hg···Cl intermolecular interactions to form a complex ribbon (Figure 4) whose structure differs markedly from the simple ladder observed in the structure of phenylmercury chloride.

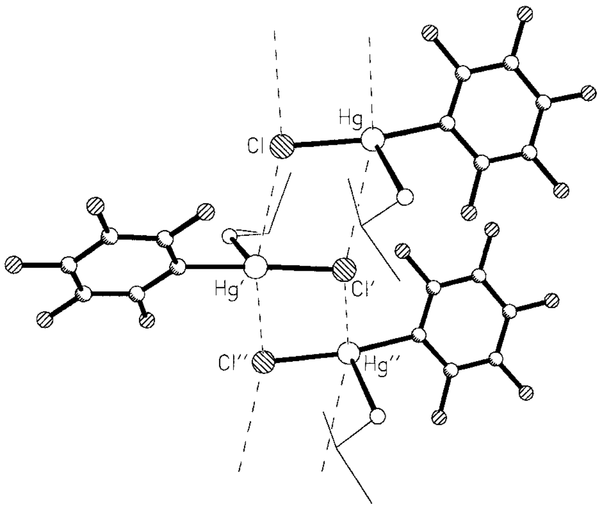

Figure 2. Stick and ball diagram showing the formation of ladders solvated by DMSO molecules in the structure of **2**. The DMSO molecules are represented by thin lines for clarity.

The present results show that when electron-withdrawing substituents are present, monodentate organomercurials can form adducts with neutral bases such as formamides and sulfoxides. We also demonstrate that, at least in the solid state, the double coordination of a carbonyl function can be achieved by two independent monodentate organomercurials and does not necessitate the use of a bifunctional Lewis acid.[10] A study of the behavior of **1** in solution is presently under way.

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[10] Wuest, J. D. *Acc. Chem. Res.* **1998**, *32*, 81−89.

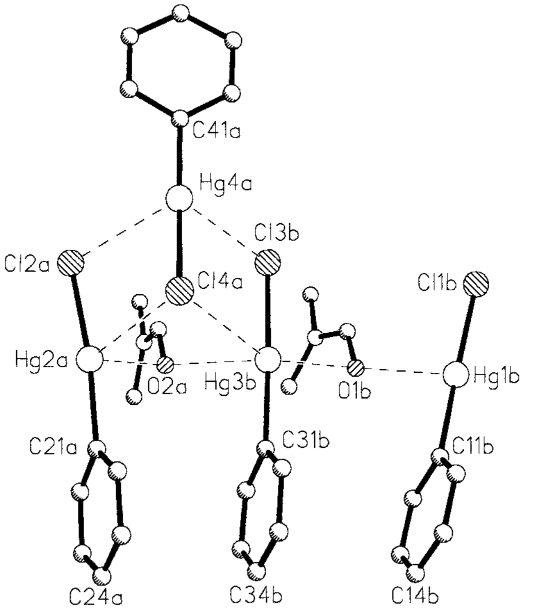

Figure 3. Stick and ball diagram of **3**. H and F atoms omitted for clarity. Selected intramolecular bond lengths (Å) and angles (deg): Hg(1b)−C(11b) 2.054(9), Hg(2a)−C(21a) 2.059(9), Hg(3b)−C(31b) 2.086(8), Hg(4a)−C(41a) 2.063(8), Hg(1b)−Cl(1b) 2.312(2), Hg(2a)−Cl(2a) 2.301(3), Hg(3b)−Cl(3b) 2.316(2), Hg(4a)−Cl(4a) 2.338(2); C(11b)−Hg(1b)−Cl(1b) 177.1(3), C(21a)−Hg(2a)−Cl(2a) 173.4(3), C(31b)−Hg(3b)−Cl(3b) 178.0(2), C(41a)−Hg(4a)−Cl(4a) 177.3(2). Selected intermolecular bond lengths (Å) and angles (deg): Hg(1b)−O(1b) 2.663, Hg(3b)−O(1b) 2.776, Hg(3b)−O(2a) 2.852, Hg(2a)−O(2a) 2.666, Hg(1b)−O(1b) 2.663, Hg(3b)−O(1b) 2.776, Hg(3b)−O(2a) 2.852, Hg(2a)−O(2a) 2.666; Cl(2a)−Hg(2a)−O(2a) 89.3, C(21a)−Hg(2a)−O(2a) 95.2, Cl(3b)−Hg(3b)−O(1b) 84.4, C(31b)−Hg(3b)−O(1b) 97.7, Cl(3b)−Hg(3b)−O(2a) 84.5, C(31b)−Hg(3b)−O(2a) 94.6, Cl(1b)−Hg(1b)−O(1b) 88.6, C(11b)−Hg(1b)−O(1b) 93.6.

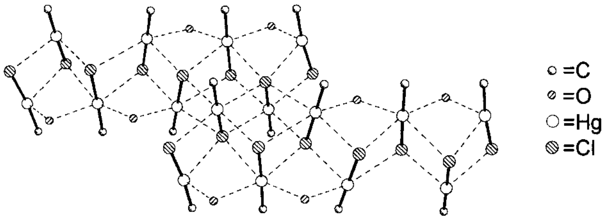

Figure 4. Stick and ball diagram showing a portion of the polymeric aggregate formed in the supramolecular structure of **3**. All H, C, F, and N have been omitted (with the exception of the C_{ipso} atoms).

Experimental Section

General Procedures. The solid-state ^{13}C CP/MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer operating at a field strength of 7.05 T. Cross-polarization and high-power proton decoupling were applied with a 90° pulse time of 5 ms, a contact time of 5 ms, and a recycle delay of 8 s. ^{13}C NMR shifts are referenced to an external sample of adamantane, with the signal at low frequency being set to 29.472 ppm relative to TMS. Approximately 50 mg of the sample was packed into 4 mm ZrO_2 Bruker rotors with Kel-F caps. The rotor spinning speed was 7 kHz for **3**. All NMR measurements were carried out at 25 °C. The Laboratory for Microanalysis at Technische Universität München performed the elemental analyses. The infrared spectra were recorded in KBr pellets. All melting points were measured on samples in sealed capillaries and are uncorrected. DMSO and DMF were distilled prior to use and stored over molecular sieves. All commercially available starting materials were purchased from Aldrich Chemicals and used as provided. Compound **1** was prepared according to the published procedure.[2]

Pentafluorophenylmercury Chloride·DMSO (2). A 50 mg sample of **1** was placed in a vial and dissolved in 0.5 mL of DMSO. The solvent was then allowed to evaporate in a well-aerated fume hood over a period of 3 weeks. A quantitative amount of crystalline **2** could then be collected. mp 54 °C. Anal. Calcd for $C_8H_6ClF_5HgOS$: C, 19.95; H, 1.25. Found: C, 20.22; H, 1.37. IR: 3427, 1642, 1509, 1474, 1374, 1315, 1081, 1069, 1019, 965, 807 cm^{-1}.

(Pentafluorophenylmercury chloride)$_4$·(DMF)$_2$ (3). A 50 mg sample of **1** was placed in a vial with a small aperture and dissolved in 0.5 mL of DMF. The solvent was then allowed to evaporate in a well-aerated fume hood. After a week colorless crystals of **3** could be isolated in a quantitative yield, mp 98 °C. Anal. Calcd for $C_{15}H_7Cl_2F_{10}Hg_2NO$: C, 20.47; H, 0.79; N, 1.52. Found: C, 20.32; H, 0.79; N, 1.45. ^{13}C CP/MAS NMR (7.05 T) for **3**: δ 31.0, 35.7 (CH_3), 120−155 (br, C-aryl), 168.2 (CO). IR: 3427, 1654, 1642, 1522, 1474, 1384, 1374, 1328, 1097, 1011, 965, 807 cm^{-1}.

Crystal Structure Determination of 2 and 3. Single crystals of suitable quality and size were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo Kα radiation, λ(Mo Kα) = 0.710 73 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for all compounds. Lp correction was applied, and intensity data were corrected for absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5U_{eq}$ of the attached C atom). Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important bond lengths and angles have been gathered in the figure captions of Figures 1−3.

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and thermal parameters for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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