Synthesis and X-ray Crystal Structure of a Heptametallic Complex Containing the Unbridged FeSnFeHgFeSnFe Skeleton

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The reaction between $[NEt_4]_2[Cl_2Sn\{Fe(CO)_4\}_2]$ and $[ClHgMo(CO)_3(\eta\text{–}C_5H_5)]$ affords the air-stable compound $[NEt_4]_2[\{(OC)_4FeSnCl_2Fe(CO)_4\}_2Hg]$ **1** with high yields; X-ray crystallography has proved that the anion contains the novel unsupported heptametallic FeSnFeHgFeSnFe skeleton.

Interest in the synthesis and study of polynuclear metal complexes by rational procedures continues to be an active research area.[1] Although chain-type complexes containing up to eleven bridged metal atoms have been described,[2] analogous complexes with unsupported metal–metal bonds are unknown. This is because this class of derivatives tends to break up giving mixtures of compounds with fewer metal atoms.[1b] In spite of this, in this communication we report the synthesis and structural characterization of the heptametallic complex $[NEt_4]_2[\{(OC)_4FeSnCl_2Fe(CO)_4\}_2Hg]$ **1**, which is to our knowledge the longest unbridged metallic chain described so far.†

Compound **1** is formed in 70% yield, within a few minutes, by the reaction of $[NEt_4]_2[Cl_2Sn\{Fe(CO)_4\}_2]$ with $ClHgMo(CO)_3(\eta\text{–}C_5H_5)$ in a 1:1 molar ratio in tetrahydrofuran (THF) at −20 °C. Slow addition of hexane afforded the crude product **1** and from the resulting solution was precipitated, after further addition of hexane, the trimetallic compound $[Mo(CO)_3(\eta\text{–}C_5H_5)]_2Hg$, identified by its IR and ^1H NMR spectra. Recrystallization from acetone–hexane solutions yield analytically pure samples of **1**,‡ which is an air-stable orange, crystalline solid.

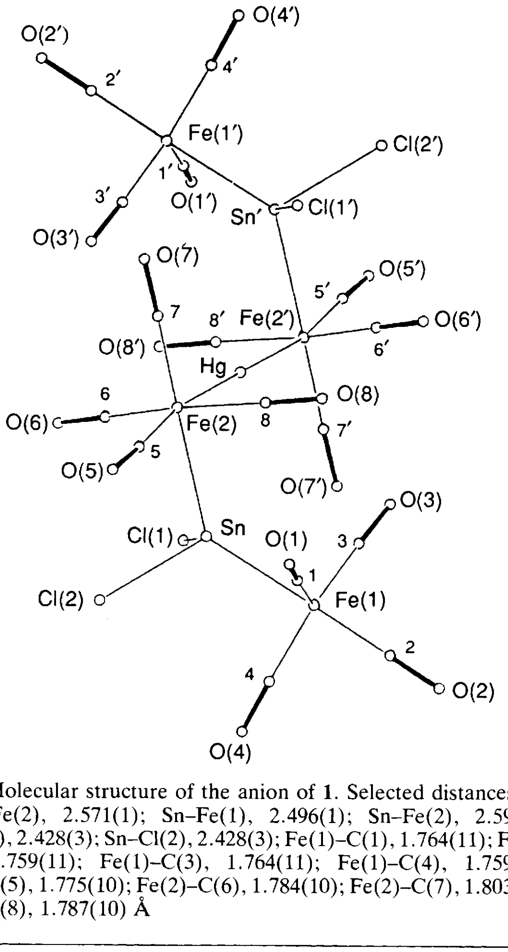

Fig. 1 Molecular structure of the anion of **1**. Selected distances are. Hg(1)–Fe(2), 2.571(1); Sn–Fe(1), 2.496(1); Sn–Fe(2), 2.593(1); Sn–Cl(1), 2.428(3); Sn–Cl(2), 2.428(3); Fe(1)–C(1), 1.764(11); Fe(1)–C(2), 1.759(11); Fe(1)–C(3), 1.764(11); Fe(1)–C(4), 1.759(11); Fe(2)–C(5), 1.775(10); Fe(2)–C(6), 1.784(10); Fe(2)–C(7), 1.803(11); Fe(2)–C(8), 1.787(10) Å

The formation of **1** together with $[Mo(CO)_3(\eta\text{–}C_5H_5)]_2Hg$, (eqn. 1) can be speculatively explained in terms of a two-step process. First, the pentametallic salt $[NEt_4][(OC)_3(\eta\text{–}C_5H_5)MoHgFe(CO)_4SnCl_2Fe(CO)_4]$ is generated by a ligand-replacement reaction and secondly, this intermediate, not detected spectroscopically, undergoes a spontaneous ligand-redistribution process to give **1** and the trimetallic mercury compound. Both metathetical and ligand-redistribution reactions are well documented for the chemistry of mercury; in particular, ligand-redistribution reactions have been recently discussed for trimetallic chains[3] and cluster complexes.[4]

$$\begin{aligned}&[NEt_4]_2[Cl_2Sn\{Fe(CO)_4\}_2] + ClHgMo(CO)_3(\eta\text{–}C_5H_5) \rightarrow\\&\text{‘}[NEt_4][(OC)_3(\eta\text{–}C_5H_5)MoHgFe(CO)_4SnCl_2Fe(CO)_4]\text{’}\\&\qquad\qquad + NEt_4Cl \quad (1)\\&\qquad\qquad\downarrow\\&\tfrac{1}{2}[NEt_4]_2[\{(OC)_4FeSnCl_2Fe(CO)_4\}_2Hg]\\&\qquad\qquad + \tfrac{1}{2}[Mo(CO)_3(\eta\text{–}C_5H_5)]_2Hg\end{aligned}$$

The structure of the anion of **1** based on the X-ray analysis is shown in Fig. 1.§ The most remarkable feature is the unusual heptametallic unsupported FeSnFeHgFeSnFe skeleton. In this, the central mercury atom is linearly coordinated to two hexa-coordinated iron atoms. Each one of these is bonded to four carbonyl ligands and one tin atom, which displays a local tetrahedral geometry, being also surrounded by two chlorines and one almost pyramidal $Fe(CO)_4$ moiety. Consequently, two different Fe–Sn bond lengths are obtained, the Fe(hexa-coordinate)–Sn [2.593(1) Å] being longer than the Fe(penta-coordinate)–Sn [2.496(1) Å] as expected. The Fe–Hg bond distance [2.571(1) Å] agrees with those in related structures.[5] Interestingly the structure of the anion can be envisaged as the

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† Two germanium compounds containing a branched heptametallic chain have been described.[1a] $[Ph_3GeCdNi(\eta\text{–}C_5H_5)GePh_3]_2Cd$ and $[Ph_3GeHgNi(\eta\text{–}C_5H_5)GePh_3]_2Cd$.

‡ Compound **1**: IR(THF) ν_{max} (CO) in THF at 2045s, 2010m, 2000s, 1985s, 1935sh, 1910s and 1875s cm^{-1}.

§ *Crystal data* for **1**: $C_{32}H_{40}Cl_4Fe_4HgN_2O_{16}Sn_2$, M = 1511.3, monoclinic, space group $P2_1/n$, $a = 10.431(1)$, $b = 13.314(2)$, $c = 18.366(5)$ Å, $\beta = 93.55(3)$, $U = 2545.74(8)$ Å^3, $Z = 4$, $D_c = 2.23$ g cm^3, $F(000) = 1612$, μ(Mo-Kα) = 83.545 cm^{-1}. 7407 Measured reflections, $R = 0.063$ ($R_w = 0.042$) for 4152 unique, absorption-corrected intensities [298 K, $\omega -2\theta$ scans, $2 < \theta < 32$, $I > 2\sigma(I)$, Mo-Kα ($\lambda = 0.71069$ Å)]. Data were collected on an Enraf-Nonius CAD-4 diffractometer. The Hg atom was located on a Patterson map, and the structure was solved from subsequent Fourier syntheses and least-squares refinement. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

result of the condensation of two[6] $[Cl_2Sn\{Fe(CO)_4\}_2]^{2-}$ and one[5] $[(OC)_4FeHgFe(CO)_4]^{2-}$ anions, both of which have been structurally characterized in our laboratories.

In conclusion, the successful process described here seems to open an interesting route to long metallic chain-type complexes containing mercury as the central atom.

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