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SYNTHESIS AND MOLECULAR STRUCTURE OF TPPSn-Mn(CO)$_4$-Hg-Mn(CO)$_5$.1/2CH$_2$Cl$_2$: A BENT Sn-Mn-Hg-Mn ARRAY EXTENDED OVER A PORPHYRIN RING

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The title compound was synthesized by the reaction of TPPSnCl$_2$ with NaMn(CO)$_5$ which was prepared by Na-Hg reduction of Mn$_2$(CO)$_{10}$ in THF. The Molecular structure was solved by X-ray diffraction techniques. The molecule possesses a Sn-Mn-Hg-Mn unit and the unit is bound to TPP through the tin atom. The Mn-Hg-Mn unit is almost linear, but the Sn-Mn-Hg unit is bent at a right angle.

Metalloporphyrin chemistry is one of the most active fields of current investigation.1) In particular, metal-metal interactions in metalloporphyrins have attracted increasing interest not only from the biological aspect,2) but also from the potential use of the compounds as starting materials to synthesize linear metal-chain derivatives, which are candidates for a superconductor at room temperature. The reason to employ metalloporphyrins as constituents of such materials is twofold: first, many metalloporphyrin derivatives have axial ligands which are easily substituted by metal complexes as ligands to construct metal-chain frameworks. Second, metalloporphyrins occasionally undergo facile oxidation-reduction, which should be also desirable to build up such frameworks and to endow significant electrical conductivity to the metal framework. Recently a paper appeared where metalloporphyrins were used to construct a linear framework4) and metalloporphyrin chemistry in such use seems a fruitful field of investigation. We, therefore, started to study this field of chemistry by synthesizing a new metal oligomer as a precursor of linear metal-chain derivatives which contain tetraphenylporphyrin, TPP. Here we wish to report the reaction of TPPSnCl$_2$ (1)5) with NaMn(CO)$_5$ prepared from Mn$_2$(CO)$_{10}$ and Na-Hg and the synthesis and characterization of a compound containing a bent Sn-Mn-Hg-Mn framework with TPP as a ligand.

One mmol (390 mg) of dimanganesedecacarbonyl was stirred over 1% sodium amalgam in 30 cm^3 of THF for 3h at room temperature under a nitrogen atmosphere. The supernatant greenish-gray solution which should contain a small amount of finely dispersed mercury globules was decanted into another flask which contained 1 mmol (800 mg) of (1) dissolved in 20 cm^3 of THF. The mixture was stirred at room temperature overnight. The solvent was evaporated at reduced pressure to leave a dark purple-green solid. The solid was extracted with each 20 cm^3 of n-hexane ten times and the combined extracts were evaporated to dryness under vacuum. The resulting solid was dissolved in 3 cm^3 of dichloromethane, an equal amount of petroleum ether was added, and the mixture was stored in a refrigerator for a week to afford dark purple distorted hexagonal prismatic crystals (yield: less than 30 mg). Anal. Calcd for $TPPSnMn(CO)_4 \cdot HgMn(CO)_5 \cdot 1/2CH_2Cl_2$ (2) ($C_{53.5}H_{29}ClHgMn_2N_4O_9Sn$): C, 48.08; H, 2.19; N, 4.19. Found: C, 47.56; H, 2.20; N, 3.83. The ir spectrum of (2) in a Nujol mull exhibits ν(CO) peaks at 2070(s), 2003(3), 1970(vs), 1960(s,sh), 1941(w), 1920(s), and 1905(m) cm^{-1}. $\lambda_{max}(CH_2Cl_2)$: 365, 418(Soret), 425(sh), 457, 520, 555, 597, 640(sh), and 656.

The characterization of this product (2) was made by an X-ray crystallographic study. The crystal was triclinic with cell constants a = 14.785(35), b = 14.870(30), c = 13.494(22) Å, α = 92.26(21), β = 111.33(16), and γ = 109.34(26)°. Intensity data were collected with a Rigaku automated four circle diffractometer, AFC-5, up to 2θ = 55° (Mo K_α). A total of 5419 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were obtained. The structure was solved and refined by standard heavy atom methods based on the $P\bar{1}$ space group to the present discrepancy indices of R = 0.096 and R_w = 0.113 for 73 nonhydrogen atoms with anisotropic temperature factors. The crystal packing in a unit cell is shown in Fig. 1 and the atom numbering scheme is exhibited in Fig. 2. The unit cell contains two molecules of $TPPSnMn(CO)_4HgMn(CO)_5$ (2') and one CH_2Cl_2 molecule, which is disordered and located at two sites related by the center of symmetry with 0.5 multiplicity (Fig. 1).

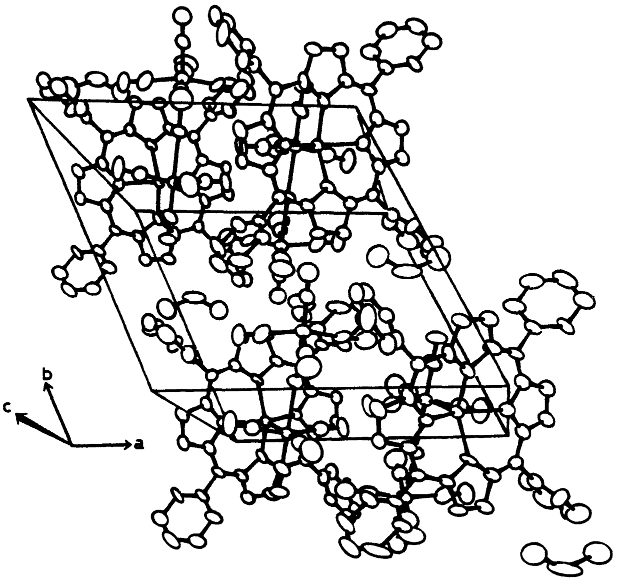

Fig. 1. Crystal packing in a unit cell of $TPPSnMn(CO)_4HgMn(CO)_5 \cdot 1/2CH_2Cl_2$

The striking feature of (2') is that there is a four-metal atom unit (Sn-Mn_1-Hg-Mn_2) on the TPP ring. The Mn_1-Hg-Mn_2 array (164.4(2)°) is only slightly bent upward from the porphyrin ring, while the

Sn-Mn_1-Hg skeleton is bent at virtually a right angle (94.6(2)°). The plane containing the Sn-Mn_1-Hg-Mn_2 array passes through two pyrrole rings close to C_{22}, N_2, N_4, and C_{42} atoms. However, Hg atom is too far from the C_{22} and N_2 atoms to expect any interaction. The observed Sn-Mn_1 (2.554(7) Å), Mn_1-Hg (2.579(11) Å), and Hg-Mn_2 (2.659(11) Å) distances are typical bond lengths for relevant metal-metal bonds.[6,7] The essentially equivalent Sn-N (pyrrole) distances (2.18(2) Å as an average) are shorter than those in stannic phthalocyanine (2.347(7) Å)[8] and longer than those in $TPPSn[Re(CO)_3(C)_2]_2$ (2.07(2) Å)[9] and $TPPSnCl_2$ (2.098(2) Å).[1] The average N-Sn-N bond angle is 81.3(9)°. The tin atom lies 0.85 Å from the plane defined by the four nitrogen atoms. Thus, the tin atom is five-coordinated in a square pyramidal array. The tin atom is reduced formally from 4+ in (1) to 2+ in (2') by oxidizing the Hg atom from 0 (amalgam) to 2+ in (2'). This change in oxidation state of the Sn atom should be responsible for significant elongation of the Sn-N bond and the deviation of the Sn atom from the plane of the four N atoms. The two Mn atoms are octahedrally coordinated with CO and metal atoms. The conformational arrangement of the equatorial carbonyl groups about the two Mn atoms is intermediate between eclipsed and staggered. The deviation from the eclipsed conformation is estimated by the intersecting angle of two planes which contain Hg-Mn_2-C_i (i = 202-205) and Hg-Mn_1-C_j (j = 102-104) and/or Hg-Mn_1-Sn. The angles average to 20.3(22)°. The observed Mn-C and C-O bond lengths compare well with similar manganese carbonyl derivatives.[6,7] All other bond lengths associated with TPP fall in the range reported for similar metalloporphyrin derivatives.[1,9]

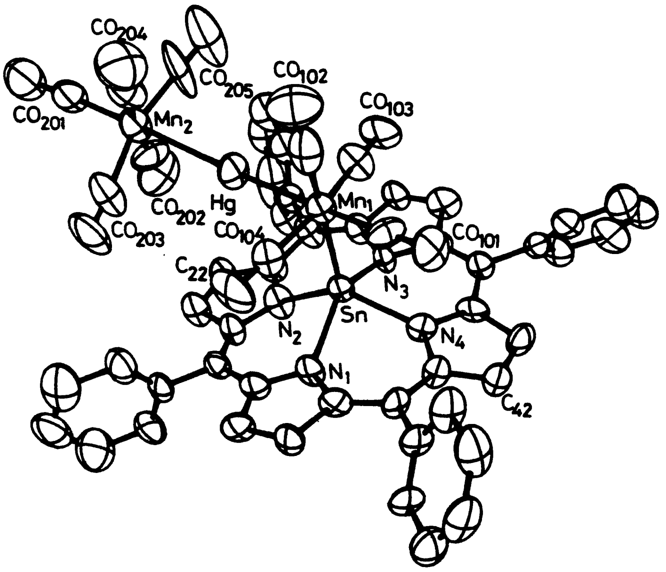

Fig. 2. Atom numbering scheme for TPPSnMn-$(CO)_4HgMn(CO)_5$. The thermal ellipsoids are drawn at the 50% probability level.

As was described in the introduction, we have aimed to construct a linear metal framework, but we obtained a bent metal framework instead. Therefore, it's pertinent to allude to the problem of why the Sn-Mn_1-Hg-Mn_2 skeleton is bent, although a linear arrangement of this skeleton seems desirable to minimize steric repulsion between CO groups and the phenyl groups of the TPP ring. The detected Sn-Mn_1 bond lengths is the shortest one yet observed[6] and the Mn_1-Hg distance is significantly shorter than that of $Hg[Mn(CO)_5]_2$ (2.610(2) Å),[7] whereas the $Hg-Mn_2$ distance is significantly longer than that of $Hg[Mn(CO)_5]_2$. The result suggests the presence of π interactions between Sn and Mn_1 and between Mn_1 and Hg.[6] If π interaction makes an important contribution to the $Sn-Mn_1$ and Mn_1-Hg bonds, a bent array is rationalized by the following reason: in a linear array, the Sn atom should compete with the Hg atom for π electrons in two different 3d orbitals of Mn_1, leading to inevitable reduction of the π interaction in either the $Sn-Mn_1$ bond or the Mn_1-Hg bond[10]; in a bent array at a right angle, however, the Sn atom and the Hg atom can exploit one 3d orbital of Mn_1 independently for π bonding, even though the Sn atom still competes with the Hg atom for the π electron in one 3d orbital of Mn_1.

In conclusion, we would like to emphasize that the present work is the first report on the metalloporphyrin derivative which possesses a four-metal-atom unit with unequivocal metal-metal bonds.[1] We also discovered quite recently that (2) can be synthesized in somewhat better yield by reacting $TPPSnCl_2$ with $Hg[Mn(CO)_5]_2$ in hot o-dichlorobenzene. Apparently this method is promising to extend this chemistry to other combinations of metal atoms such as Sn-Mn-Cd-Mn which is bound to TPP and this program is in progress in our laboratory.

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