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Synthesis and Characterization of an Oligomeric Mercury-Bridged Phthalocyanine

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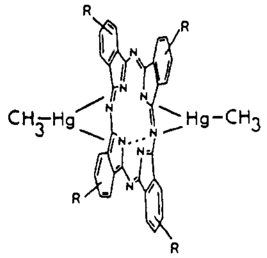
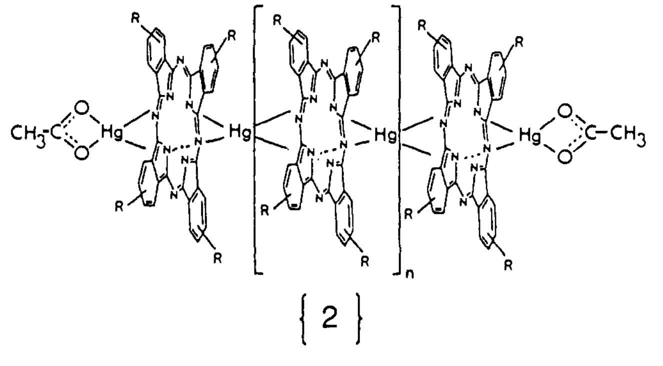
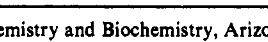
Mercury phthalocyanine exhibits anomalous bonding characteristics compared with other metallophthalocyanines (MPc's). Years ago, Barrett and Linstead[1] reported HgPc with the "normal" 1:1 Hg:Pc stoichiometry from an exchange reaction between Li_2Pc and $HgCl_2$. More recently, a 2:1 Hg:Pc phthalocyanine has been reported from the reaction of H_2Pc with $CH_3HgN(Si(CH_3)_3)_2$.[2] In this case, the structure may be represented by two CH_3Hg groups complexed to opposite faces of the macrocycle, as in {1}. In the present study, we synthesized both 1:1 and 2:1 Hg:Pc phthalocyanines by reaction of $H_2Pc(CP)_4$[3] with mercuric acetate ($Hg(OAc)_2$) and methylmercuric acetate (CH_3HgOAc), respectively. Our results show that the 1:1 $Hg{:}Pc(CP)_4$ compound forms a new type of MPc polymer with a highly perturbed electronic structure. As represented by structure {2}, this phthalocyanine polymer is unique in that no bridging group is axially coordinated in the polymer chain as is common for known Pc polymers.[4] Here, we present characterization demonstrating the polymeric nature of $HgPc(CP)_4$ and the effect of its polymeric linkage on the Q-band (π–π^* transition).



{1}



{2}



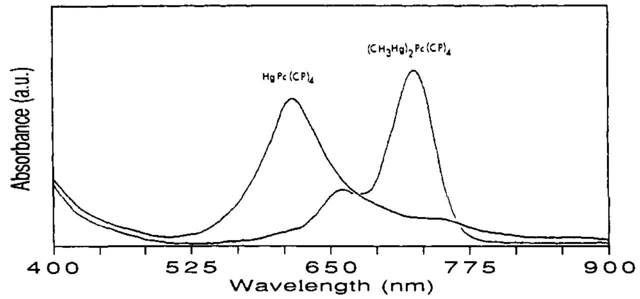


Figure 1. Visible absorption spectra of $HgPc(CP)_4$ (λ_{max} 618 nm; log ϵ 4.32) and $(CH_3Hg)_2Pc(CP)_2$ (λ_{max} 724 nm; log ϵ 5.11) in THF solution. The spectra are plotted on different intensity scales so that the line shapes can be easily compared.

Soluble 1:1 and 2:1 Hg:Pc complexes are formed by addition of the cumylphenoxy-substituted (CP-substituted) $H_2Pc(CP)_4$[3] to a stirred THF solution of $Hg(OAc)_2$ or CH_3HgOAc at 23 °C, followed by refluxing for 4 h. Reprecipitation into rapidly stirred methanol appears to free the crude product of excess $Hg(OAc)_2$, although the IR spectrum indicates detectable residual acetate (1580 cm^{-1}), possibly chemically bound, unlike the corresponding acetates of other metal–$Pc(CP)_4$ complexes. The IR spectrum also shows a total disappearance of the $H_2Pc(CP)_4$ N–H band (3290 cm^{-1}). The Q-band (λ_{max} 618 nm; log ϵ 4.34/$CHCl_3$) is very broad and without resolved vibronic satellite bands. The ^1H and ^{13}C NMR spectra are extremely broadened, unlike spectra of other metal–$Pc(CP)_4$ complexes. Elemental analysis indicates a 1:1 Hg:Pc ratio. (Anal. Calcd for CH_3CO_2-$[C_{92}H_{72}N_8O_4Hg]_{11}$-$HgCO_2CH_3$: C, 70.08; H, 4.59; N, 7.08; Hg, 13.84. Found: C, 71.26; H, 4.82; N, 7.09; Hg, 12.37.)

Q-bands of $HgPc(CP)_4$ and $(CH_3Hg)_2Pc(CP)_4$ are contrasted in Figure 1. The $(CH_3Hg)_2Pc(CP)_4$ Q-band is characteristic of monomeric metal phthalocyanines and is in good agreement with the 721-nm Q-band reported for peripherally unsubstituted $(CH_3Hg)_2Pc$.[2] The $HgPc(CP)_4$ Q-band is very broad and blue-shifted from the $(CH_3Hg)_2Pc(CP)_4$ absorption. This behavior is associated with the close approach of one phthalocyanine ring to another. This occurs for cofacial aggregation in a dynamically equilibrating system[3] and for axial covalent linkage through a bridging atom such as in the $(SiPc\text{-}O)_n$ polymeric system.[5] The former case does not appear applicative to the $HgPc(CP)_4$ system because both the effects of dilution (10^{-3}–10^{-7} M) and addition of disaggregating solvents[6] did not shift the Q-band to a spectrum of the monomeric form. This indicates that the binding forces between $HgPc(CP)_4$ units are much stronger than those associated with normal phthalocyanine aggregation. In the latter case, covalent bonding should determine the magnitude of the π–π^* perturbation by controlling the approach distance and number of rings. For a series of monodisperse $(SiPc\text{-}O)_n$ compounds (n = 1, 2, 3, 4), a limiting blue shift with increasing number of rings (665, 630, 618, and 615 nm, respectively) has been reported.[5] This overall blue shift energy difference (1230 cm^{-1}) is smaller than the difference between the $HgPc(CP)_4$ and $(CH_3Hg)_2Pc(CP)_4$ Q-bands (2210 cm^{-1}) and is evidence that the $HgPc(CP)_4$ units are bonded at closer approach distances.

Our hypothesis is that $HgPc(CP)_4$ exists as a cofacially bonded oligomer as represented in structure {2}. A vapor pressure osmometer number average molecular weight measurement is 17 200 g mol^{-1}, corresponding to a polymer chain length of 11 $HgPc(CP)_4$ units. Broadened NMR spectra correlate with a very large, slowly tumbling $HgPc(CP)_4$ oligomer. This type of sandwich structure has been proposed for mercury–porphyrin complexes.[7] However, the interaction between Hg^{2+} and the Pc macrocycle appears to be stronger and leads to polymerization. The Hg:Pc reaction

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stoichiometry may regulate the polymer chain length if the chain length correlates with the Q-band blue shift. Experimentally, for Hg:Pc reactant ratios of 40:1, 20:1, 10:1, 5:1, and 2:1, the Q-band shifts progressively from 643 to 625 nm. At a 1:1 reactant ratio, the observed Q-band is a combination of $HgPc(CP)_4$ and unreacted $H_2Pc(CP)_4$. Currently, the $HgPc(CP)_4$ polymer structural features (chain length control, end group analysis, inter-ring distance, and coplanarity) and physical properties (electrical[4] and nonlinear optical[8] effects attributable to the linear polymer structure induced by mercury bonding) are being investigated.

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Synthesis of Mixed-Metal Sulfido Clusters with a Cuboidal Mo_3PdS_4 Core Which Coordinate Alkene to the Unique Palladium Site Surrounded by Sulfido Ligands

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Extensive studies on the reactivities of the incomplete cubane-type cluster $[Mo_3S_4(H_2O)_9]^{4+}$ (**1**)[2] have revealed that **1** is a highly potential precursor for synthesizing mixed-metal sulfido clusters with a cuboidal Mo_3MS_4 core. This transformation generally takes place by the direct interaction of **1** with metallic Fe,[3] Co,[4] Ni,[5] Cu,[6] Sn,[7] and Hg[4] under mild conditions, and the corresponding single or double cubane-type mixed-metal clusters have been isolated. However, the reaction of **1** with noble metals has not yet been clarified, despite much interest in the exploitation of catalytic reactions promoted at a noble metal site embedded in metal–sulfur aggregates. Here we report the syntheses and characterization of novel single and double cubane-type clusters with a Mo_3PdS_4 core derived from **1**, which coordinate an alkene ligand to the unique Pd site in η^2-fashion. It is to be noted that no such reactivities have been reported to date for any other mixed-metal cuboidal clusters of this type cited above, although several precedents for η^1-binding of substrates such as CN^-, RNC, N_3^-, N_2H_4, etc. to the unique Fe or Mo sites in Fe_4S_4[8] or Fe_3MoS_4[9] cores have appeared already.

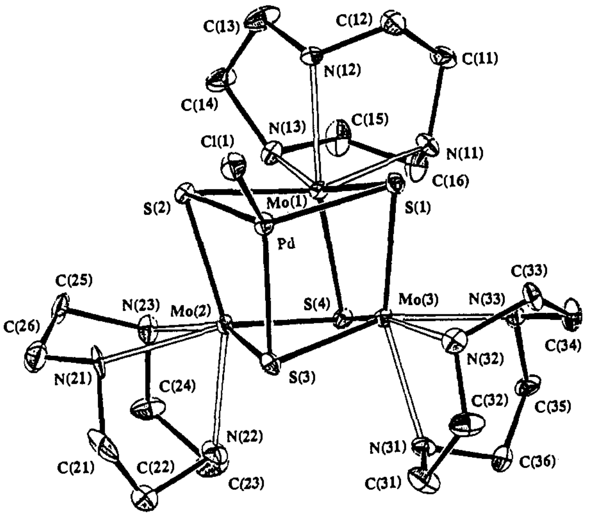

Figure 1. ORTEP drawing of the cation in **3**. Selected distances (Å): Pd–Mo(1), 2.790 (2); Pd–Mo(2), 2.792 (2); Pd–Mo(3), 2.798 (2); Mo(1)–Mo(2), 2.815 (2); Mo(1)–Mo(3), 2.817 (2); Mo(2)–Mo(3), 2.825 (2).

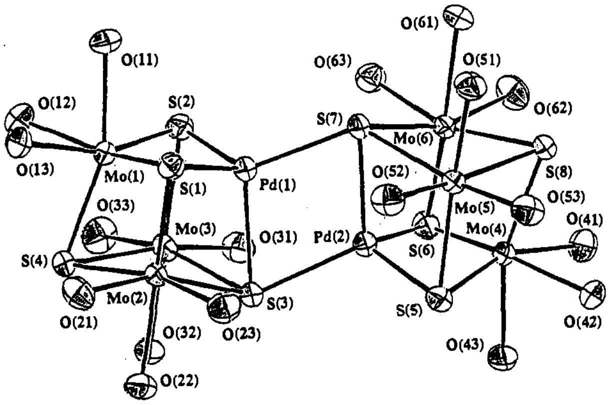

Figure 2. ORTEP drawing of the cation in **4**. Selected distances (Å): Pd(1)–Pd(2), 2.790 (1); Pd(1)–Mo(1), 2.746 (1); Pd(1)–Mo(2), 2.816 (1); Pd(1)–Mo(3), 2.820 (1); Mo(1)–Mo(2), 2.767 (1); Mo(1)–Mo(3), 2.777 (1); Mo(2)–Mo(3), 2.789 (1); Pd(2)–Mo(4), 2.759 (1); Pd(2)–Mo(5), 2.814 (1); Pd(2)–Mo(6), 2.836 (1); Mo(4)–Mo(5), 2.764 (1); Mo(4)–Mo(6), 2.759 (1); Mo(5)–Mo(6), 2.784 (1).

After stirring of a mixture of **1** and an excess of Pd black in 2 M HCl for 10 h at room temperature, the resultant blue solution was separated from unreacted Pd metal by filtration and then purified on a Dowex 50W-X2 column, which revealed that this solution contained essentially one product in addition to a small amount of unreacted **1**. Evaporation of all volatile materials from the eluted blue band afforded a solid that can be tentatively formulated as $[Mo_3PdS_4Cl(H_2O)_9]Cl_3$ (**2**) in ca. 90% yield.[10] However, we could not characterize **2** in detail because single crystals suitable for an X-ray analysis were not obtained. Further treatment of **2** with 3.3 equiv of 1,4,7-triazacyclononane (tacn) in MeOH at 60 °C and successive cooling of the solution resulted in deposition of a blue crystalline material. Recrystallization of

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(10) Anal. Calcd for **2**·HCl: H, 2.21; S, 14.86; Cl, 20.54. Found: H, 1.71; S, 13.60; Cl, 20.92. The presence of both Mo and Pd atoms is confirmed by electron-probe microanalysis using an energy dispersive type X-ray analyzer for all complexes reported here.

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