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.

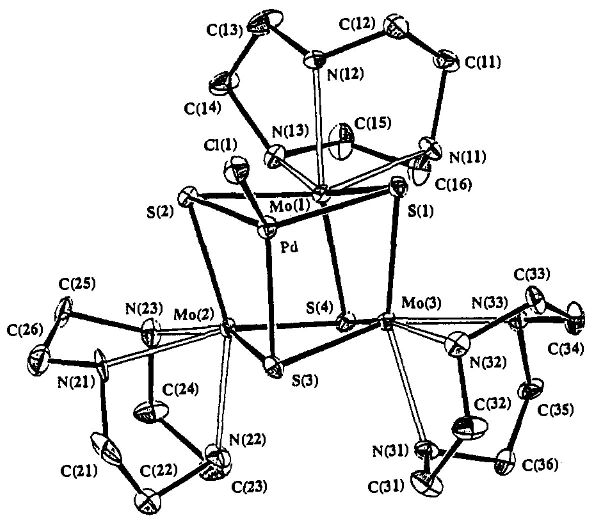

Figure 1. ORTEP drawing of the cation in **3**. Selected distances (Å): Pd–Mo(1), 2.790 (2); Pd–Mo(2), 2.792 (2); Pd–Mo(3), 2.798 (2); Mo(1)–Mo(2), 2.815 (2); Mo(1)–Mo(3), 2.817 (2); Mo(2)–Mo(3), 2.825 (2).

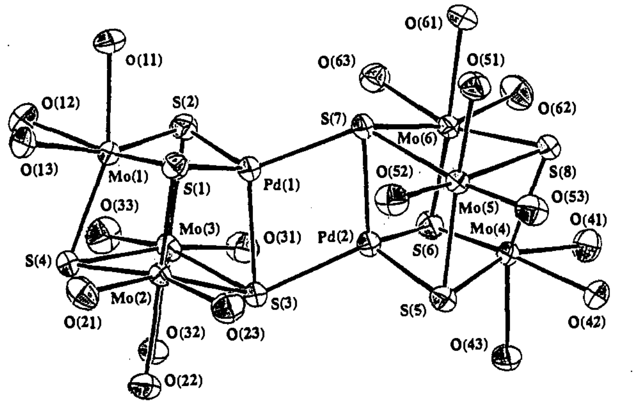

Figure 2. ORTEP drawing of the cation in **4**. Selected distances (Å): Pd(1)–Pd(2), 2.790 (1); Pd(1)–Mo(1), 2.746 (1); Pd(1)–Mo(2), 2.816 (1); Pd(1)–Mo(3), 2.820 (1); Mo(1)–Mo(2), 2.767 (1); Mo(1)–Mo(3), 2.777 (1); Mo(2)–Mo(3), 2.789 (1); Pd(2)–Mo(4), 2.759 (1); Pd(2)–Mo(5), 2.814 (1); Pd(2)–Mo(6),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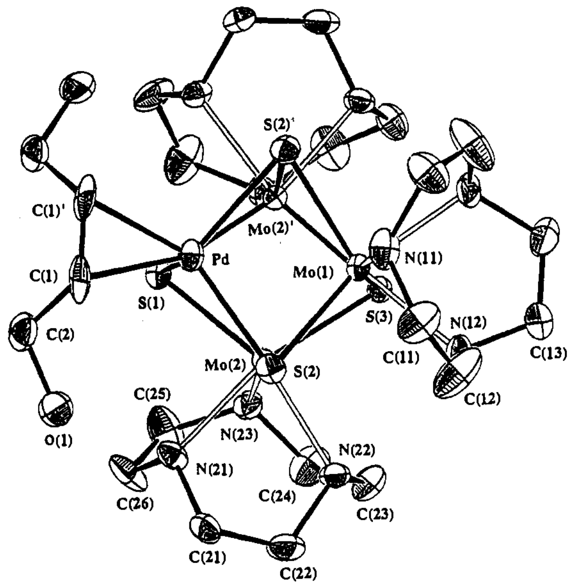

Figure 3. ORTEP drawing of the cation in **5**. Selected distances (Å): Pd–Mo(1), 2.815 (3); Pd–Mo(2), 2.830 (2); Mo(1)–Mo(2), 2.805 (2); Mo(2)–Mo(2)′, 2.787 (2); Pd–C(1), 2.26 (2); C(1)–C(1)′, 1.38 (3).

this product from 2 M HCl gave $[Mo_3PdS_4Cl(tacn)_3]Cl_3{\cdot}4H_2O$ (**3**) in 30–50% yield, the structure of which has been unambiguously determined by an X-ray analysis (Figure 1).[11] Complex **3** has a cubane-type Mo_3PdS_4 core with three tacn ligands coordinated to the Mo atoms and one Cl ligand on the Pd site, which totally comprises a pseudo-C_3 configuration around the Cl(1)–Pd–S(4) vector. An interesting feature observed in **3** is that the Pd atom has a tetrahedral structure not commonly observed in Pd(II) chemistry. The Pd–S distances (2.35–2.38 Å) are normal and not significantly different from those reported for the sulfido-bridged complex $[\{(\eta^3\text{-}C_3H_5)Pd\}_2WS_4]$ (2.33–2.35 Å).[12]

Anion metathesis, which was performed by eluting **2** adsorbed on a Dowex 50W-X2 column with 4 M *p*-toluenesulfonic acid (TsOH), resulted in the formation of a purple-blue solution. When left for several weeks, dark blue single crystals of $[Mo_6Pd_2S_8(H_2O)_{18}](OTs)_8{\cdot}24H_2O$ (**4**) precipitated from this solution. The X-ray crystallography has also been undertaken for **4**, which disclosed the double cubane-type structure shown in Figure 2.[13] The X-ray structure of this cation is not centrosymmetric, and the Pd_2S_2 plane is slightly folded, with a dihedral angle of 168° along the Pd–Pd vector. Analogous interconversion between the double and single cubane-type structures depending on the nature of the anion has already been suggested for the Mo_3CuS_4 cluster in TsOH or HCl media, although only the double cubane-type structure has been clarified in detail by the X-ray analysis.[6]

Treatment of **2–4** with various alkenes in H_2O or MeOH resulted in a rapid color change from blue to red. However, we could not isolate any stable clusters with coordinated alkenes in pure form from these reaction mixtures. Alternatively, when the anion exchange of **3** by ClO_4^- was carried out followed by treatment with *cis*-$HOCH_2CH{=}CHCH_2OH$ in H_2O, the resultant reaction mixture afforded the stable single cubane-type cluster $[Mo_3PdS_4(tacn)_3(HOCH_2CH{=}CHCH_2OH)](ClO_4)_4{\cdot}2H_2O$ (**5**). The X-ray analysis of **5** has been performed, which clearly demonstrates that this alkene coordinates to the Pd site in a side-on manner (Figure 3).[14] The C–C bond distance in the coordinated alkene [1.38 (3) Å] is comparable to those in the other Pd(II) alkene complexes such as $[(COD)PdCl_2]$ (1.37–1.39 Å; COD = 1,4- or 1,5-cyclooctadiene),[15] $[(cyclooctatetraene)PdCl_2]$ [1.38 (1), 1.39 (1) Å],[16] and $[(norbornadiene)PdCl_2]$ [1.37 (1) Å].[17] Further study on the reactivity of the alkene ligand coordinated to the unique Pd site in this and analogous Mo_3PdS_4 clusters is now in progress.

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Supplementary Material Available: Tables listing detailed X-ray crystallographic data, positional and thermal parameters, and bond distances and angles for **3–5** and table presenting ^1H NMR data for **3** and **5** (26 pages); tables of structure factors for **3–5** (84 pages). Ordering information is given on any current masthead page.

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[11] Crystal data of **3**: orthorhombic, space group $P2_12_12_1$, $a = 17.549$ (3) Å, $b = 20.032$ (4) Å, $c = 10.256$ (2) Å, $V = 3605$ Å^3, $Z = 4$, $d_{calcd} = 2.05$ g cm^{-3}, μ(Mo Kα) = 20.44 cm^{-1}. Block-diagonal least-squares refinements of 389 parameters obtained by using 4014 reflections $[F_o > 3\sigma(F_o)]$ collected by a MAC MXC-18 diffractometer gave residuals of $R = 0.051$ and $R_w = 0.062$. Refinements obtained by inverting the coordinates of all atoms did not improve the *R* values. Anal. Calcd: C, 19.23; H, 4.76; N, 11.21; S, 11.41; Cl, 12.61. Found: C, 18.81; H, 4.57; N, 11.14; S, 10.70; Cl, 13.28.

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[13] Crystal data of **4**: triclinic, space group $P1$, $a = 15.799$ (4) Å, $b = 18.079$ (6) Å, $c = 11.873$ (1) Å, $\alpha = 108.75$ (2)°, $\beta = 108.73$ (1)°, $\gamma = 70.87$ (3)°, $V = 2944$ Å^3, $Z = 1$, $d_{calcd} = 1.79$ g cm^{-3}, μ(Mo Kα) = 10.78 cm^{-1}. Block-diagonal least-squares refinements of 1316 parameters obtained by using 10 089 reflections $[F_o > 5\sigma(F_o)]$ collected on a Nonius CAD4 diffractometer gave residuals of $R = 0.028$ and $R_w = 0.036$. Structure solutions and refinements were carried out by selecting the space group of both $P1$ and $P\bar{1}$, but only the choice of $P1$ resulted in the successful solution and refinement of all non-hydrogen atoms in the cation, OTs anions, and solvated H_2O molecules. Anal. Calcd: C, 21.21; H, 4.46; S, 16.18. Found: C, 22.10; H, 4.09; S, 16.16. The atomic ratio of Mo to Pd determined by inductively coupled plasma (ICP) emission spectroscopy was 3.09:1.

[14] Crystal data of **5**: monoclinic, space group $P2_1/m$, $a = 12.314$ (1) Å, $b = 12.732$ (2) Å, $c = 15.736$ (2) Å, $\beta = 94.01$ (1)°, $V = 2461$ Å^3, $Z = 2$, $d_{calcd} = 1.90$ g cm^{-3}. Block-diagonal least-squares refinements of 362 parameters obtained by using 2743 reflections $[F_o > 5\sigma(F_o)]$ collected on a Rigaku AFC5R diffractometer gave residuals of $R = 0.068$ and $R_w = 0.081$. Anal. Calcd: C, 18.66; H, 4.06; N, 8.90. Found: C, 19.02; H, 4.13; N, 8.97.

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Resolution and Asymmetric Synthesis of Ortho-Substituted (Benzaldehyde)tricarbonylchromium Complexes

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(π-Arene)tricarbonylchromium complexes play a very important role in stereoselective reactions, and some asymmetric syntheses

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