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Rational Preparation and Characterization of Tandem Tetrametal Clusters. Crystal Structure of Tetrakis(6-diphenylphosphino-2-pyridonato)dimolybdenum

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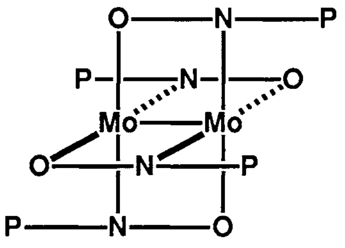
Dinuclear molybdenum complex $Mo_2(pyphos)_4$, pyphos = 6-diphenylphosphino-2-pyridonato, was treated with transition metal complexes such as $Mo(CO)_3(CH_3CN)_3$, $PdCl_2(PhCN)_2$, and $PtBr_2(cod)$ to form one-dimensional tetranuclear cluster complexes $Mo_2(pyphos)_4(ML_n)_2$ (**3**) (**a**: ML_n = $Mo(CO)_3$, **b**: ML_n = $PdCl_2$, and **c**: ML_n = $PdBr_2$). Iodine—doped material of **3a** showed semi-conducting property.

Recently the chemistry of assembled molecules has been of much interest.[1—3] Metal cluster complexes with low-dimensional structure have been expected to have new class of collective properties instead of the simple summation of each units. We report here that tandem tetranuclear transition metal complexes were prepared by using a unique tridentate P-N-O ligand, 6-diphenylphosphinopyridone (**2**), and a complex **3a** with linear Mo_4 cluster exhibited electronic semi-conducting properties upon exposure to iodine.

The ligand **2** was treated with one fourth equiv. of $Mo_2(OAc)_4$ and an equimolar amount of sodium methoxide in dichloromethane. After removal of the precipitated solid by filtration through Celite, the resulting deep red solution was concentrated to give red powder. Recrystallization from hexane—dichloromethane afforded $Mo_2(pyphos)_4$ (**1**)[4] in 54% yield as deep red crystals. $^{31}P\{^1H\}$ NMR spectrum of **1** showed that the phosphorus moiety is free for coordination of transition metal. Mass spectrum showed it to be monomeric. A single crystal X-ray analysis confirmed the structure of **1**, including the geometry around molybdenum.[5] An *ORTEP* drawing of



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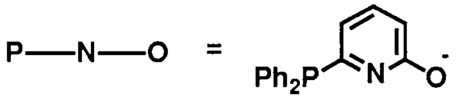


1 is shown in Fig. 1. Bond distance [2.103(1) Å] of Mo—Mo is comparable to those of Mo—Mo bonded complexes with a bond order of four; $Mo_2(mhp)_4$, 2.065(1) Å;[6] $Mo_2(map)_4$, 2.070(1) Å.[7]

The P-N-O ligand (**2**) coordinates to dimolybdenum(II,II) by N—O chelation keeping original dinuclear structure. Each two phosphorus atoms of four ligands make two cis-chelating coordination sites available. Other known pyridonate N-O dinuclear transition metal complexes have exclusively trans arrangement[6] or a mixture of cis and trans structures.[8] Here, the diphenylphosphino group is too bulky to occupy trans positions at each edge of the Mo_2 moiety.

Both edges of the dinuclear complex **1** have coordination sites for transition metals, in which two phosphorus atoms and one molybdenum make unique facial geometry for coming metal atoms. The reaction of **1** with some transition metal complexes was expected to form tandem tri- and tetra-nuclear complexes, e.g. **3**. Treatment of **1** with a little excess amount of $Mo(CO)_3(CH_3CN)_3$ in toluene or THF afforded **3a** as orange crystalline solid in 50—64% yields.[9] Similarly, treatment of **1**

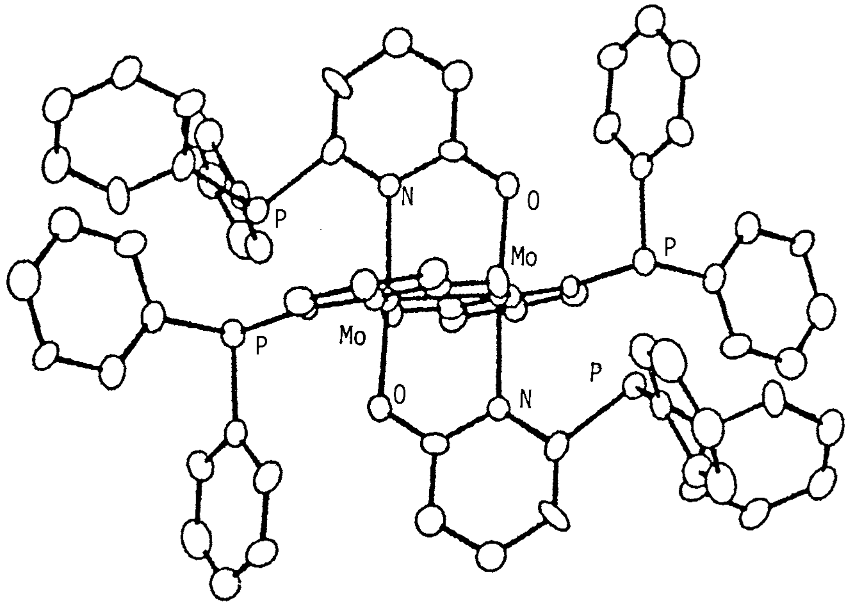
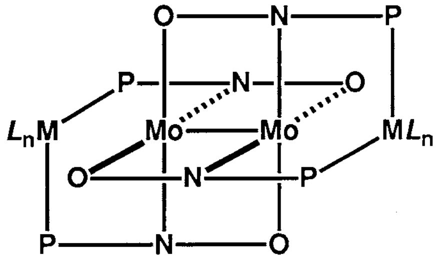


Fig. 1. *ORTEP* drawing of complex **1**.

with $PdCl_2(PhCN)_2$ and $PdBr_2(cod)$ afforded the corresponding tetranuclear complexes **3b** and **3c**, respectively, whose structures were confirmed by analytical and spectral data.[9] UV-vis spectrum of **3b** and **3c** in dichloromethane exhibited intense absorptions at 645 and 660 nm, respectively, which might suggest the formation of a dative Mo—>Pd bonding.[10]



a: $ML_n = Mo(CO)_3$
b: $ML_n = PdCl_2$
c: $ML_n = PdBr_2$

3

As a one-dimensional tetranuclear cluster complex **3a** has zero-valent transition metals at both edges, we studied the reaction of **3a** with iodine in order to prepare iodine-bridged one-dimensional polymeric materials, which were expected to have conducting properties. When **3a** was exposed to iodine, the room temperature conductivity of solid material of **3a** was $10^{-2}\ \Omega^{-1}cm^{-1}$.[11—13] These values are much higher than the conventional halogen-bridged metal complexes (e.g. $<10^{-8}\ \Omega^{-1}cm^{-1}$ for $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_2$ where en = ethylenediamine)[14] and even higher than halogen-bridged dinuclear complexes, which show comparatively high conductivity (10^{-3}—$10^{-4}\ \Omega^{-1}cm^{-1}$ for $K_4[Pt_2(pop)_4Br]$ where pop = $(HO_2P)_2O^{2-}$).[15]

The building of novel one-dimensional molecular wires based on the treatment of **1** with various kinds of low-valent metals is also our future target.

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References

1) M. C. Bohm, "One-Dimensional Organometallic Materials," Springer-Verlag, 1987; T. J. Marks, *Angew. Chem., Int. Ed. Engl.*, **29**, 857 (1990).
2) For examples: K. Sakai and K. Matsumoto, *J. Am. Chem. Soc.*, **111**, 3074 (1989); M.-S. Tsai and S.-M. Peng, *J. Chem. Soc., Chem. Commun.*, **1991**, 514; R. Usón, A. Laguna, M. Laguna, J. Jimenez, and P. G. Jones, *Angew. Chem., Int. Ed. Engl.*, **30**, 198 (1991).
3) R. H. Cayton and M. H. Chisholm, *J. Am. Chem. Soc.*, **111**, 8921 (1989); R. H. Cayton, M. H. Chisholm, J. C. Huffman, and E. B. Lobkovsky, *Angew. Chem., Int. Ed. Engl.*, **30**, 862 (1991).

4) **1**: Mp 245—251 °C (dec). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -8.3 ppm (s). Mass spectrum *m*/*z* (^{98}Mo), 1308 (M^+).
5) Crystal data for **1**: F.W. = 1474.83 (dichloromethane as solvent molecules), triclinic space group $P\bar{1}$, a = 15.516(5) Å, b = 11.381(4) Å, c = 9.396(3) Å, α = 93.35(3)°, β = 91.50(3)°, γ = 76.57(3)°, U = 1611.0(9) Å^3, Z = 1, d_{calcd} = 1.520, μ = 7.016 cm^{-1}, no. of parameters = 502, no. of reflection data with $|Fo|>3\sigma(Fo)$ = 2276, goodness of fit = 3.687, R = 0.050, R_w = 0.055. Half of complex **1** is independent and each halves of **1** are related by centrosymmetry. Molybdenum atom was located by the Patterson synthesis and the remaining non-hydrogen atoms were located by Fourier synthesis. Data was collected by Rigaku-AFC5 and was refined by UNICS-III (IMS).
6) mhp = anion of 2-hydroxy-6-methylpyridine: F. A. Cotton, P. E. Fanwick, R. H. Niswander, and J. C. Sekutowski, *J. Am. Chem. Soc.*, **100**, 4725 (1978).
7) map = anion of 2-amino-6-hydroxypyridine: F. A. Cotton, R. H. Niswander, and J. Sekutowski, *Inorg. Chem.*, **17**, 3541 (1978).
8) M. Berry, C. D. Garner, I. H. Hillier, A. A. MacDowell, and W. Clegg, *J. Chem. Soc., Chem. Commun.*, **1980**, 494; W. Clegg, *Acta Crystallogr., Sect. B*, **36**, 2437 (1980); F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, **20**, 584 (1981).
9) Spectral data for **3**. **3a**: Mp 152—159 °C (dec). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 35 (broad s). IR (KBr) 1930, 1840, 1814 cm^{-1} (ν_{CO}). **3b**: Mp 237—243 °C (dec). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 16 (s). **3c**: Mp 245—250 °C (dec). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 16 (s). $^{31}P\{^1H\}$ NMR spectrum of $PdCl_2(pyphos)_2$ in $CDCl_3$ exhibited a singlet at δ 17 ppm similar to those of **3b** and **3c**.
10) W. Micklitz, G. Müller, B. Huber, J. Ruede, F. Rashwan, J. Heinze, and B. Lippert, *J. Am. Chem. Soc.*, **110**, 7084 (1988).
11) IR spectrum of doped complexes showed no carbonyl absorptions.
12) The iodine bridging polymeric structure has been assumed for solid material; Some iodine-bridged molybdenum complexes have been reported. G. Schmid, R. Boese, and E. Welz, *Chem. Ber.*, **108**, 260 (1975); G. Schmid and R. Boese, *Chem. Ber.*, **109**, 2148 (1976).
13) When complex **1** was treated with iodine, the conductivity of resulting material was 10^{-6} $\Omega^{-1}cm^{-1}$.
14) Y. Hamaue, R. Aoki, M. Yamashita, and S. Kida, *Inorg. Chim. Acta.*, **54**, L13 (1981).
15) C.-M. Che, F. H. Herbstein, W. P. Schaefer, R. E. Marsh, and H. B. Gray, *J. Am. Chem. Soc.*, **105**, 4604 (1983).

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