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Synthesis and Structure of Novel Organometallic Sulfide Cluster $[(\eta^5\text{-}C_5Me_5)MWO(\mu\text{-}S_2)(\mu\text{-}S)_2]_2$ (M=Rh,Ir) Containing High-Valent Tungsten Atoms

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Novel transition metal sulfide cluster $[(\eta^5\text{-}C_5Me_5)MWO(\mu\text{-}S_2)(\mu\text{-}S)_2]_2$ (M=Rh,Ir) was synthesized and the crystal structure of iridium complex was analyzed. The cluster consists of two fused double incomplete-cubane frameworks made of tungsten(VI) and iridium(III) atoms. There are no metal-metal direct interactions within the cluster core in spite of short W-Ir contact of 2.816(1) Å.

Condensed transition metal sulfide clusters have been interested for their various stereochemistry and electrochemical properties.[1] Especially these of early transition metals (Mo, W) have been widely investigated.[2] In most of these clusters transition metal atoms possess lower (+2~+4) oxidation state and have metal-metal direct interactions. There have been few examples containing high-valent tungsten atoms like polyoxometalates which have no d-electrons for metal-metal bondings. Mo or W atom may be easily reduced by sulfur atoms when the formation reaction of cluster occurs. We have synthesized novel neutral metal sulfide cluster of tungsten(VI) atoms with organorhodium(III) or organoiridium(III) groups and analyzed the crystal structure of the iridium complex.

To a suspension of $(NH_4)_2WS_4$ (0.13 g ; 0.5 mmol) in 30 cm^3 of methanol, a 0.05 g of $NaBH_4$ was added. The suspension soon turned to a clear yellow solution. An acetonitrile solution containing 0.15 g (0.25 mmol) of $[Cp^*IrCl_2]_2$ ($Cp^*=\eta^5\text{-}C_5Me_5$) was added dropwise to the thiotungstate solution under an Ar atmosphere. The color of the mixture became deep red. The solution was kept stirring for 5 h at 0°C and then evaporated to remove the solvent. The resulting brown solid was dissolved in 20 cm^3 of acetonitrile. Air stable deep red crystals[3] were obtained from the solution exposed to air. The corresponding rhodium complex was prepared by using $[Cp^*RhCl_2]_2$ as a starting material.

Single crystal X-ray structure analysis for the iridium complex[4] shows a tetranuclear metal sulfide cluster (Fig. 1). The molecule consists of two equivalent incomplete-cubane type frameworks related by an inversion center. The two units are fused by sharing a common plane W(1)-S(4)-W(1)*-S(4)*. W(1) atom is bound to an oxygen, two sulfur atoms, and a persulfido (S(3),S(6)) ligand and have distorted square-pyramidal geometry. The O atom is on the apex of the square-pyramid. The W-O bond distance of 1.708 Å corresponds to a double bond.[5)] A similar coordination geometry around the W atoms is found in the trinuclear tungsten sulfide $[WO(WS_4)_2]^{2-}$.[6)] The sixth coordinating site opposite to the O atom is occupied by S(4)* atom with long distance of 2.906(3) Å. The Ir atom with Cp* is bound to three S atoms to form octahedral geometry. Binding energies by X-ray photoelectron spectra[7)] support that the oxidation states of W and Ir are 6+ and 3+, respectively. There are no available d-electrons for W(1)-Ir(2) short contact of 2.816(1) Å. This is the first example for tungsten(VI) sulfide dimer structure with hexa-coordinate in the cluster.

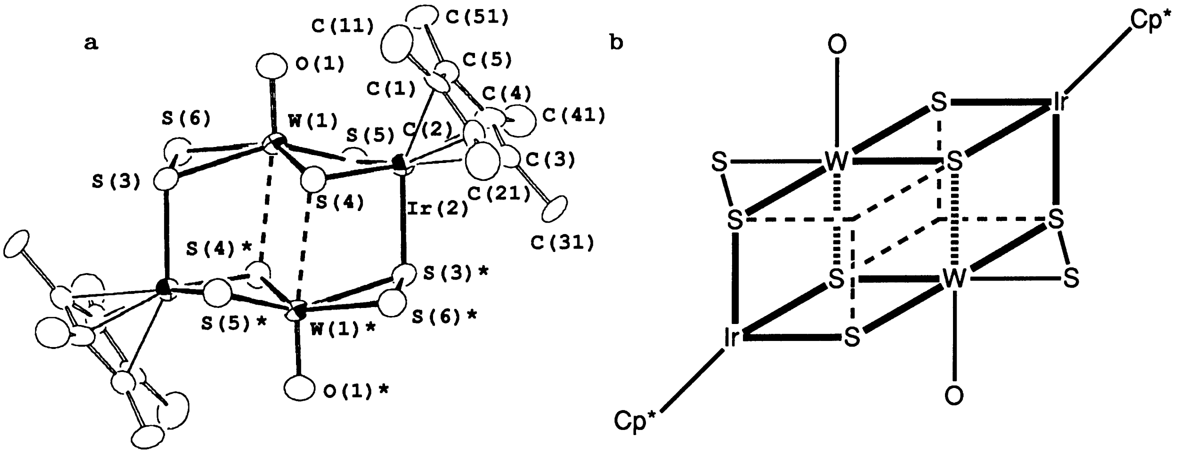

Fig. 1. Molecular structure of $[(\eta^5\text{-}C_5Me_5)IrWO(\mu\text{-}S_2)(\mu\text{-}S)_2]_2$: (a) ORTEP plotting and (b) schematic drawing of double incomplete-cubane framework. Selected bond distances (Å) and angles(°) : Ir(2)-W(1) 2.816(1), W(1)-W(1)* 3.890(1), Ir(2)-W(1)* 3.924(1), W(1)-S(4) 2.306(3), W(1)-S(5) 2.275(3), W(1)-S(3) 2.490(3), W(1)-S(6) 2.417(3), W(1)-O(1) 1.708(8), W(1)-S(4)* 2.906(3), Ir(2)-S(3)* 2.378(3), Ir(2)-S(4) 2.349(3), Ir(2)-S(5) 2.401(3), Ir(2)-Cp*(ring) 2.23(av.), S(3)-S(6) 2.089(5), S(4)-W(1)-S(5) 105.4(1), S(3)-W(1)-S(6) 50.4(1), S(4)-W(1)-O(1) 101.7(1), S(4)-W(1)-S(4)* 84.1(1), S(3)*-Ir(2)-S(4) 81.9(1), S(3)*-Ir(2)-S(5) 94.0(1), S(4)-Ir(1)-S(5) 100.2(1).

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2) A. Müller, E. Diemann, R. Jostes, and H. Bögge, Angew. Chem., Int. Ed. Engl., 20, 934 (1981); M. Daraganjac and T. B. Rauchfuss, ibid., 24, 742 (1985).
3) Elemental analysis for $Ir_2W_2O_2S_8C_{20}H_{30}$, C : 18.06(18.32), H : 2.34(2.31)%.
4) Crystallographic data for $[(\eta^5\text{-}C_5Me_5)IrWO(\mu\text{-}S_2)(\mu\text{-}S)_2]_2$: F.W.=1311.07, monoclinic $P2_1/n$, λ=0.71069 Å, a=9.708(1), b=17.773(4), c=8.609(1) Å, β=100.36(1)°, V=1461.2(4) Å^3, Z=2, D_c=2.98 g cm^{-3}, μ(MoKα)=176.37 cm^{-1}. Total 2263 independent reflections with $|F_o|>3.0\sigma(F_o)$ (2°<2θ<65°) were used for calculation. The metal atoms were located by Patterson function. The other non-hydrogen atoms were found from successive Fourier syntheses. R/R_w=0.031/0.035 was obtained by using block diagonal least-squares anisotropically for all non-H atoms.
5) The compound shows very strong IR band at 928 cm^{-1} from W=O stretch. W-S-Ir bands are observed at 500 and 416 cm^{-1}.
6) F. Sechersse, G. Lavigne, and Y. Jeannin, J. Coord. Chem., 11, 11 (1981); A. Müller, W. Rittner, A. Neumann, E. Koniger-Ahlborn, and R. G. Bhattacharya, Z. Anorg. Allg. Chem., 461, 91 (1980); A. Müller, H. Bögge, E. Krickemeyer, and B. Krebs, Z. Naturforsch., B, 37, 1014 (1982).
7) The binding energies for $[Cp^*IrWO(\mu\text{-}S_2)(\mu\text{-}S)_2]_2$ by X-ray photoelectron spectra : W 4f7/2, 32.6 eV, Ir 4f7/2, 62.1 eV, S 2p, 162.4 eV. The corresponding binding energies of starting materials, $(Ph_4N)_2WS_4$ (W 4f7/2, 32.5 eV), $[IrCp^*Cl_2]_2$ (Ir 4f7/2, 61.3 eV). These values are corrected by assuming C 1s binding energy in the compounds as 284.6 eV.

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