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The Cubane-Type $Mo_2Ir_2S_4$ Cluster Containing an Organohydrazido(2−) Ligand on the Mo Site

Tadao Masumori,† Hidetake Seino,† Yasushi Mizobe,†,* and Masanobu Hidai‡,*

Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8558, Japan, and Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510 Japan

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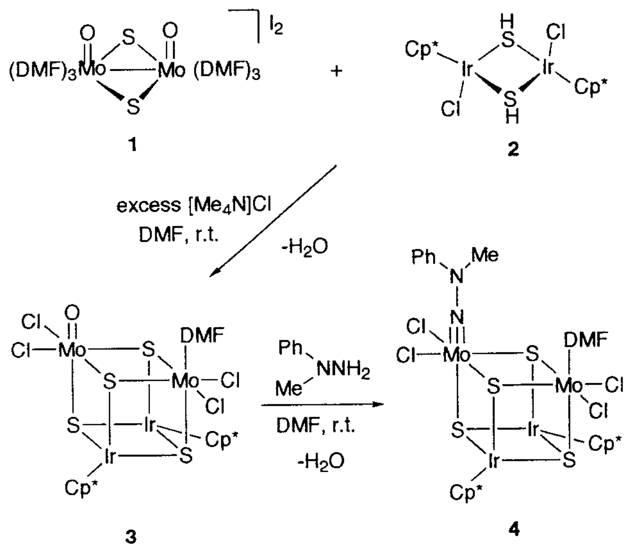
Metal−sulfur cubane-type clusters have been attracting significant attention owing to their unique structures and properties.[1] Recent X-ray crystallographic studies on nitrogenase have revealed the structure of the FeMo cofactor cluster, which consists of two incomplete cubane-type units connected by three bridging sulfides $\{(MoFe_3S_3)(\mu\text{-}S)_3(Fe_4S_3)\}$.[2] This has spurred on particularly the syntheses of the cuboidal clusters relevant to this active site core, including those with $\{(MoFe_3S_4)(\mu\text{-}S)(Fe_4S_4)\}$ or related Mo/Fe/S chromophores.[3] However, cuboidal metal−sulfides with a N_2 ligand are still unknown,[4] and even those with nitrogenous ligands relevant to N_2 reduction are unexplored except for a few examples having coordinated hydrazines.[3d,5]

Our research interest has focused recently on the exploitation of the rational pathways for preparing the metal−sulfido clusters, particularly the cubane-type clusters containing noble metals.[6] Now we have found that a new cubane-type $Mo_2Ir_2S_4$ cluster with a terminal oxo ligand can be obtained from the reaction of a sulfido-bridged dioxo dimolybdenum complex with a hydrosulfido-bridged diiridium complex. Importantly, this cluster has been shown to undergo the condensation reaction with $PhMeNNH_2$ at its Mo═O site to afford a novel cluster with a hydrazido(2−) ligand. Although mononuclear hydrazido(2−) complexes of Mo and W with tertiary phosphine coligands have been studied extensively in relevance to the mechanism of biological and industrial N_2 fixation,[7] cubane-type metal−sulfido clusters containing a hydrazido ligand are yet unknown[8] in spite of their potential to give some insight into the biological N_2-reducing system.

Scheme 1



Treatment of $[\{MoO(DMF)_3\}_2(\mu\text{-}S)_2]I_2$ (**1**)[9] with an equimolar amount of $[(Cp^*IrCl)_2(\mu\text{-}SH)_2]$[10] (**2**; $Cp^* = \eta^5\text{-}C_5Me_5$) in the presence of excess $[Me_4N]Cl$ gave $[(MoOCl_2)\{MoCl_2(DMF)\}(Cp^*Ir)_2(\mu_3\text{-}S)_4]$ (**3**) (Scheme 1).[11] It is to be noted that we have already reported that **2** and its Rh and Ru analogues can serve as versatile precursors for preparing a number of polynuclear homo- and heterometallic sulfido clusters.[12] An X-ray analysis (Figure 1)[13] has shown that **3** has a pseudo mirror plane defined by Mo(1), Mo(2), S(1), and S(4), which is consistent with the appearance of the Cp* resonance as one singlet in its ^1H NMR spectrum. In contrast to the equivalence of the two Ir sites, the nature of the two Mo atoms is significantly different; in addition to three sulfide and two chloride ligands, a DMF molecule is bound to Mo(1), while Mo(2) has a terminal oxo ligand. Hence, the tetrahedral Ir_2Mo_2 core is significantly distorted, in which three intermetallic distances, Ir(1)−Mo(1), Ir(2)−Mo(1), and Mo(1)−Mo(2), varying

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† The University of Tokyo.

‡ Science University of Tokyo.

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[11] A mixture of **1** (1.27 g, 1.29 mmol), **2** (1.02 g, 1.29 mmol), and $[Me_4N]Cl$ (0.423 g, 3.86 mmol) in DMF (50 mL) was stirred at room temperature for 2 days. The filtrate of the resultant mixture was dried up, and the residue was extracted with CH_2Cl_2 (20 mL × 2). After addition of ether with stirring, the mixture kept at −20 °C for 12 h was filtered and ether (200 mL) was added again to the filtrate slowly, giving black needles of $\mathbf{3}\cdot CH_2Cl_2$ (1.32 g, 78%). ^1H NMR ($CDCl_3$): δ 2.02 (s, 30H, Cp*), 2.72 and 2.93 (s, 3H each, NMe_2), 5.30 (s, 2H, CH_2Cl_2), 7.76 (s, 1H, CHO). IR (KBr): ν(Mo═O), 930 cm^{-1}. Anal. Calcd for $C_{24}H_{39}NO_2Cl_6S_4Ir_2Mo_2$: C, 22.33; H, 3.05; N, 1.09. Found: C, 22.52; H, 3.17; N, 1.10.

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[13] Single crystals suitable for X-ray analysis were obtained by recrystallizing $\mathbf{3}\cdot CH_2Cl_2$ from DMF−ether. X-ray data for $\mathbf{3}\cdot$DMF: monoclinic, $P2_1/n$ (No. 14), $a = 10.782(3)$ Å, $b = 22.056(3)$ Å, $c = 17.219(3)$ Å, $\beta = 107.77(2)°$, $V = 3899(1)$ Å^3, $Z = 4$, $D_{calc} = 2.178$ g cm^{-3}, μ(Mo Kα) = 79.68 cm^{-1}, $R = 0.049$ and $R_w = 0.054$ for 5902 unique reflections ($I > 3.00\sigma(I)$).

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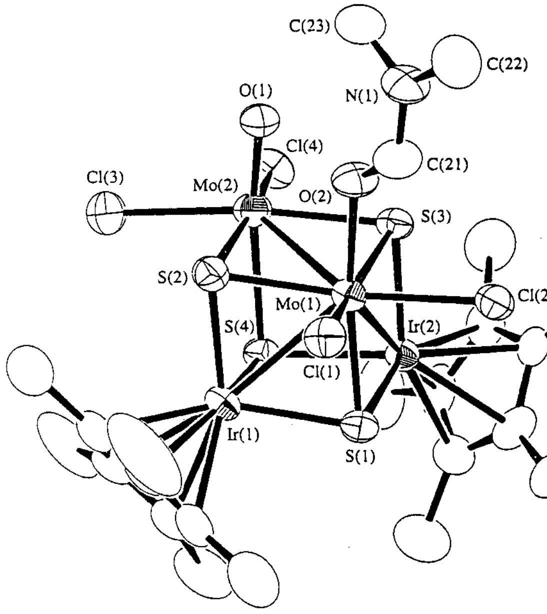

Figure 1. ORTEP diagram of **3**. Hydrogen atoms are omitted. Metal−metal distances (Å): Ir(1)−Ir(2), 3.552(1); Ir(1)−Mo(1), 2.894(1); Ir(1)−Mo(2), 3.496(2); Ir(2)−Mo(1), 2.893(1); Ir(2)−Mo(2), 3.542(1); Mo(1)−Mo(2), 2.960(2).

from 2.893(1) to 2.960(2) Å, correspond to those of the metal−metal single bond, while the remaining three are those without any bonding interaction (3.496(2)−3.552(1) Å). With respect to the metal−sulfur bonds in **3**, only the Mo(2)−S(4) bond at 2.611(3) Å is exceptionally elongated from the other Mo−S and Ir−S bonds in the range 2.304(3)−2.391(3) Å, reflecting unambiguously the strong trans influence of the oxo ligand. The Mo(2)−O(1) bond length at 1.679(9) Å is not unusual for the terminal oxo group bound to the high-valent Mo atom surrounded by the sulfide coligands[14] and is comparable also to that in the organometallic Mo(V) complex Cp*Mo(O)Cl_2 (1.683(2) Å).[15]

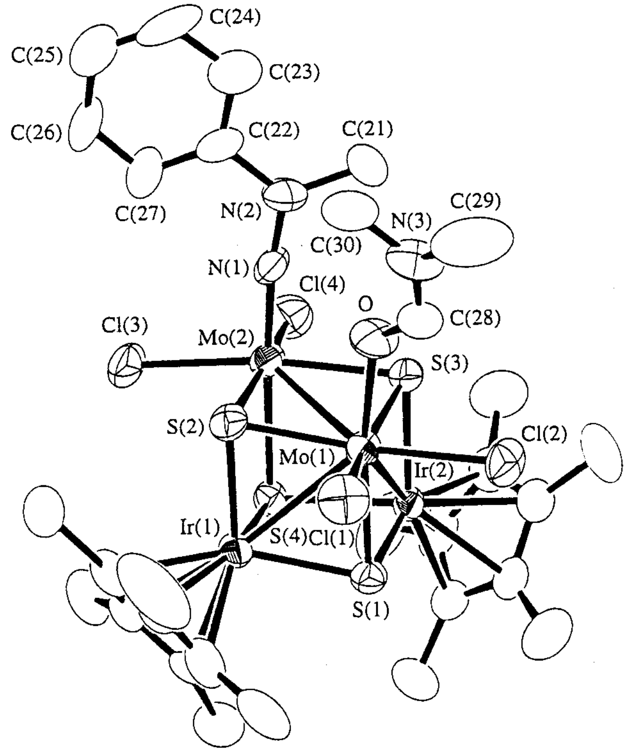

Figure 2. ORTEP diagram of **4**. Hydrogen atoms are omitted. Metal−metal distances (Å): Ir(1)−Ir(2), 3.563(1); Ir(1)−Mo(1), 2.884(2); Ir(1)−Mo(2), 3.474(2); Ir(2)−Mo(1), 2.896(2); Ir(2)−Mo(2), 3.496(2); Mo(1)−Mo(2), 2.974(2).

Condensation reactions of oxo complexes with hydrazine or organic hydrazines are often employed to prepare dinitrogen (or hydrazido(4−)) and hydrazido(2−) complexes,[16] which include several Mo and W hydrazido(2−) complexes.[17] Although the reaction of **3** with N_2H_4 was found to be elusive, treatment of **3** with $PhMeNNH_2$ has turned out to give the desired condensation product [{Mo(NNPhMe)Cl_2}{MoCl_2(DMF)}$(Cp^*Ir)_2(\mu_3\text{-}S)_4$] (**4**) (Scheme 1),[18] whose structure has also been determined by X-ray analysis (Figure 2).[19] In **4**, the metrical parameters associated with the $Ir_2Mo_2S_4$ core are in good agreement with those in **3**. The PhMeNN ligand is bound to Mo(2) in an end-on fashion, where the Mo−N−N linakge is almost linear (172(1)°) and the Mo−N and N−N bond distances are 1.74(1) and 1.32(2) Å, respectively. All non-hydrogen atoms in the hydrazido(2−) ligand as well as Mo(2) are essentially coplanar, where the plane defined by these atoms is oriented toward the direction nearly coincident with the Mo(2)−S(3) vector. The structural features associated with the MoNN moiety are well comparable to those in the other hydrazido(2−) complexes.[20] A strong trans influence of this organohydrazido(2−) ligand is implicated by the much longer Mo(2)−S(4) bond (2.541(4) Å) than the other M−S bonds (2.308(4)−2.385(4) Å) in **4**.

Further studies are now in progress to clarify the reactivities of the hydrazido(2−) ligand in **4** toward protonation, preliminary results of which revealed, for example, the formation of PhMeNH in 21% yield by treatment with 2,6-lutidine hydrochloride and Cp_2Co as the proton and electron sources, respectively. Details will be reported in a subsequent paper.

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Supporting Information Available: Details of X-ray crystallography for **3**·DMF and **4**·$2CH_2Cl_2$. X-ray crystallographic data file for **3**·DMF and **4**·$2CH_2Cl_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Into a DMF solution (15 mL) of **3** (298 mg, 0.231 mmol) was added $PhMeNNH_2$ (27 μL, 0.23 mmol), and the mixture was stirred at room temperature for 24 h. After volatile materials were evaporated in vacuo, the residue was extracted with CH_2Cl_2 (15 mL). Addition of ether to the extract deposited black needles of **4**·$2CH_2Cl_2$ (236 mg, 69%). ^1H NMR ($CDCl_3$): δ 2.02 (s, 30H, Cp*), 2.11 and 2.64 (s, 3H each, $CONMe_2$), 4.31 (s, 3H, NNMe), 5.30 (s, 4H, CH_2Cl_2), 6.88 (t, J = 7.6 Hz, 1H, *p*-H in Ph), 7.22 (d, J = 7.6 Hz, 2H, *o*-H in Ph), 7.31 (t, J = 7.6 Hz, 2H, *m*-H in Ph), 7.70 (s, 1H, CHO). Anal. Calcd for $C_{32}H_{49}N_3OCl_8S_4Ir_2Mo_2$: C, 25.97; H, 3.34; N, 2.84. Found: C, 26.33; H, 3.48; N, 2.94.

(19) X-ray data for **4**·$2CH_2Cl_2$: monoclinic, $P2_1/c$ (No. 14), $a = 14.334(4)$ Å, $b = 15.625(2)$ Å, $c = 21.365(3)$ Å, $\beta = 91.51(2)°$, $V = 4783(1)$ Å^3, $Z = 4$, $D_{calc} = 2.055$ g cm^{-3}, μ(Mo Kα) = 67.24 cm^{-1}, $R = 0.049$ and $R_w = 0.050$ for 4957 unique reflections ($I > 3.00\sigma(I)$).

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