# Rational Synthesis and Crystal Structures of Heterometallic-Heterochalcogenido Cubane-Type Clusters $[(Cp^*M)_2(MoOCl_2)\{MoCl_2(dmf)\}(\mu_3\text{-}S)_2(\mu_3\text{-}Se)_2]$ (M = Rh, Ir)

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Reactions of $[\{MoO(dmf)_3\}_2(\mu_2\text{-}S)_2]I_2$ with $[(Cp^*MCl)_2(\mu_2\text{-}SeH)_2]$ (M = Rh, Ir) in the presence of $NMe_4Cl$ gave mixed-metal sulfido-selenido clusters $[(Cp^*M)_2(MoOCl_2)\{MoCl_2(dmf)\}(\mu_3\text{-}S)_2(\mu_3\text{-}Se)_2]$, whose cubane-type core structures have been demonstrated in detail by X-ray crystallography.

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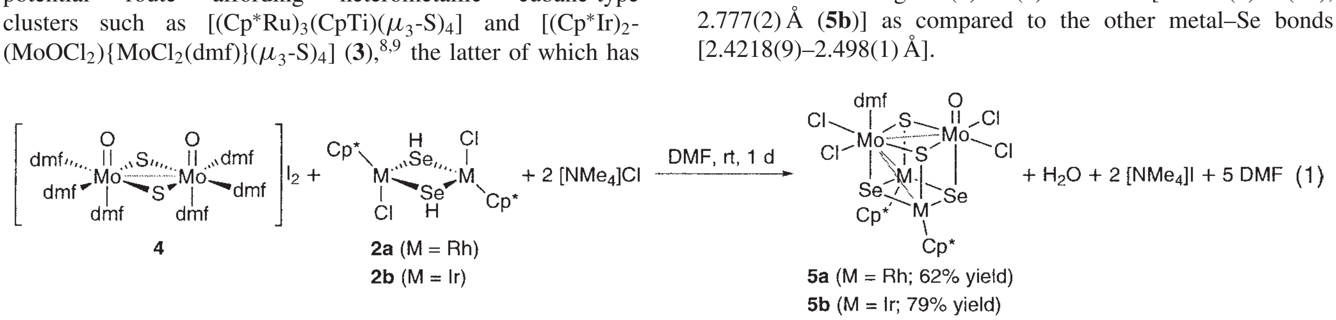
Transition metal sulfido clusters containing cubane-type $M_4S_4$ core are currently attracting much attention in connection with the bioinorganic chemistry, industrial catalysis, and material science.[1] A significant number of homo- and heterometallic cubane-type sulfido clusters have already been isolated and characterized in a well-defined manner. In contrast, as for the heavier chalcogenido analogues $M_4Se_4$ and $M_4Te_4$, fully characterized examples are still limited, and rational synthetic routes leading to these clusters are poorly developed.[2] Mixed chalcogenido clusters are of particular interest because of their possible unique properties.[3] However, the cubane-type mixed chalcogenido clusters, for example, are quite rare and few reliable methods to prepare these clusters are known to date.[4]

We have previously reported that the dinuclear bridging-hydrosulfido complexes $[(Cp^*MCl)_2(\mu\text{-}SH)_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Ru, Rh, Ir (**1**)) and $[\{(\eta^6\text{-}p\text{-cymene})RuCl\}_2(\mu\text{-}SH)_2]$ serve as good precursors to the sulfido clusters containing 3–5 metal centers.[5,6] For example, dehydrochlorination of these complexes affords the homometallic cubane-type clusters $[(Cp^*M)_4(\mu_3\text{-}S)_4]$ and $[\{(p\text{-cymene})Ru\}_4(\mu_3\text{-}S)_4]$. These reactions proceed via the dimerization of the intermediate stages $\{(L)M\}_2(\mu_2\text{-}S)_2$ ($L = Cp^*$, $\eta^6\text{-}p\text{-cymene}$). Recently, we have found that this method is applicable to the synthesis of the selenido clusters $[(Cp^*M)_4(\mu_3\text{-}Se)_4]$ and $[\{(\eta^6\text{-}p\text{-cymene})Ru\}_4(\mu_3\text{-}Se)_4]$ starting from the hydroselenido complexes $[(Cp^*MCl)_2(\mu\text{-}SeH)_2]$ (M = Rh (**2a**), Ir (**2b**)) and $[\{(\eta^6\text{-}p\text{-cymene})RuCl\}_2(\mu\text{-}SeH)_2]$.[6,7] Meanwhile, cross-condensation between different $M_2S_2$ fragments has proved to provide a potential route affording heterometallic cubane-type clusters such as $[(Cp^*Ru)_3(CpTi)(\mu_3\text{-}S)_4]$ and $[(Cp^*Ir)_2(MoOCl_2)\{MoCl_2(dmf)\}(\mu_3\text{-}S)_4]$ (**3**),[8,9] the latter of which has been synthesized from **1** and $[\{MoO(dmf)_3\}_2(\mu\text{-}S)_2]I_2$ (**4**) in the presence of $NMe_4Cl$. Here, we describe the results of the cross-condensation reactions between **2** and **4** to obtain novel heterometallic-heterochalcogenido clusters in high yields.

When **2a** or **2b** was reacted with an equimolar amount of **4** in the presence of 3 equiv of $NMe_4Cl$ in DMF at room temperature, $[(Cp^*M)_2(MoOCl_2)\{MoCl_2(dmf)\}(\mu_3\text{-}S)_2(\mu_3\text{-}Se)_2]$ (M = Rh (**5a**), Ir (**5b**)) were produced, which were isolated as dark brown crystals in 62% and 79% yields, respectively.[10] The stoichiometry of this reaction might be explained by concomitant formation of $H_2O$ as shown in eq 1, although the amount of generated $H_2O$ was not determined.

X-ray crystallographic analyses confirmed that the structures of **5a** and **5b** are essentially identical,[11] which are also in good agreement with that of **3**.[9] The ORTEP drawing is shown only for **5b** in Figure 1. As expected, the cubane-type cluster cores in **5a** and **5b** consist of two square $Mo_2(\mu_2\text{-}S)_2$ and $M_2(\mu_2\text{-}Se)_2$ fragments combined each other by four metal-chalcogen bonds. Existence of a pseudo mirror plane defined by two Mo and two Se atoms is consistent with the equivalence of two Cp*M moieties demonstrated by their $^1$H NMR spectra, each exhibiting the Cp* methyl proton resonance as one singlet. For the Mo atoms with a distorted octahedral geometry, two sites trans to $\mu_3$-S are occupied by the Cl ligand, while to the remaining site trans to $\mu_3$-Se is bound a DMF molecule for Mo(1) or a terminal oxo ligand for Mo(2), respectively. In the $Mo_2M_2$ core, three short intermetallic distances are observed corresponding to metal–metal single bonds: Mo(1)–Mo(2) [2.9626(9) Å (**5a**); 2.977(2) Å (**5b**)] and two Mo(1)–M [2.9347(8), 2.9512(8) Å (**5a**); 2.918(1), 2.949(1) Å (**5b**)], wheras the other three indicate no bonding interactions [3.5576(8)–3.6580(7) Å]. Two Mo(1)–M bonds are interpreted to result from electron donation from M with formal oxidation state of +3 to the empty d-orbitals of Mo with that of +5. In contrast, Mo(2) has no bonding interactions with the M atoms but accepts $\pi$-donation from the oxo ligand [Mo(2)–O(1): 1.685(4) Å (**5a**), 1.673(9) Å (**5b**)], and its strong trans influence is reflected on the long Mo(2)–Se(2) distances [2.7638(9) Å (**5a**), 2.777(2) Å (**5b**)] as compared to the other metal–Se bonds [2.4218(9)–2.498(1) Å].



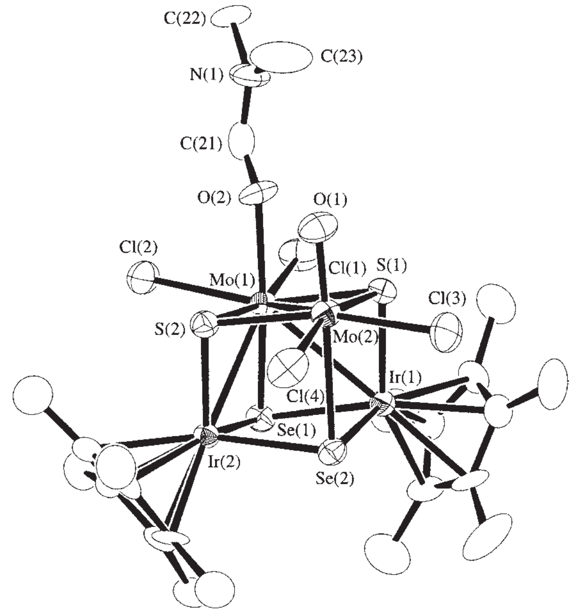


**Figure 1.** ORTEP drawing of **5b**. Hydrogen atoms are omitted for clarity. Important interatomic distances (Å) in **5a** (M = Rh)/**5b** (M = Ir) are as follows: M(1)–Mo(1), 2.9512(8)/2.949(1); M(2)–Mo(1), 2.9347(8)/2.918(1); Mo(1)–Mo(2), 2.9626(9)/2.977(2); M(1)$\cdots$M(2), 3.6529(8)/3.6580(7); M(1)$\cdots$Mo(2), 3.5806(8)/3.655(1); M(2)$\cdots$Mo(2), 3.5576(8)/3.622(1); M(1)–Se(1), 2.4326(9)/2.440(1); M(1)–Se(2), 2.4874(9)/2.493(1); M(1)–S(1), 2.317(2)/2.319(3); M(2)–Se(1), 2.4228(9)/2.434(1); M(2)–Se(2), 2.4943(9)/2.498(1); M(2)–S(2), 2.334(2)/2.321(3); Mo(1)–Se(1), 2.4218(9)/2.428(2); Mo(1)–S(1), 2.335(2)/2.340(3); Mo(1)–S(2), 2.338(2)/2.348(3); Mo(1)–Cl(1), 2.484(2)/2.493(3); Mo(1)–Cl(2), 2.484(2)/2.461(3); Mo(1)–O(2), 2.161(4)/2.151(8); Mo(2)–Se(2), 2.7638(9)/2.777(2); Mo(2)–S(1), 2.383(2)/2.402(3); Mo(2)–S(2), 2.380(2)/2.396(3); Mo(2)–Cl(3), 2.463(2)/2.455(4); Mo(2)–Cl(4), 2.450(2)/2.429(4); Mo(2)–O(1), 1.685(4)/1.673(9).

The metal–Se bonds in **5b** are about 0.11 Å longer than the corresponding metal–S distances in **3** except for Mo(2)–Se(2), which is longer by >0.17 Å. Accordingly, the intermetallic distances bridged by selenido ligand(s) are elongated from those in the sulfur analog. Although the Ir–Mo bond lengths are not so much influenced [2.893(1), 2.894(1) Å in **3**], differences in the non-bonded metal–metal distances are noteworthy [Ir$\cdots$Ir, 3.5521(8); Ir$\cdots$Mo, 3.496(2), 3.542(1) Å in **3**]. Other structural and spectroscopic features in **5b** and **3** are quite analogous: e.g. the $\nu(\mathrm{Mo}=\mathrm{O})$ values are 940 and 930 cm$^{-1}$, respectively.

Cyclic voltammetry studies showed that **5a** and **5b** underwent quasi-reversible one-electron reduction at $E_{1/2} = -0.24$ and $-0.38$ V, respectively (vs SCE in 0.1 mol/l DMF solution of $n$-$\mathrm{Bu_4N\ BF_4}$). The second reduction at $E_\mathrm{p} = -0.75$ and $-0.85$ V and oxidation at $E_\mathrm{p} = 1.00$ and 0.92 V for **5a** and **5b** were irreversible (peak potentials). Although the first reduction potential of the $\mathrm{Ir_2Mo_2S_2Se_2}$ cluster **5b** at $-0.24$ V is very close to or even slightly more positive than that of the $\mathrm{Ir_2Mo_2S_4}$ cluster **3** ($E_{1/2} = -0.41$ V), not only **5b** but also the $\mathrm{Rh_2Mo_2S_2Se_2}$ cluster **5a** are apparently more susceptible to oxidation than **3** (irreversible oxidation: $E_\mathrm{p} = 1.07$ V), reflecting higher electron-donating ability of the selenido ligand than the sulfido ligand.

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10 A mixture of **4** (209 mg, 0.213 mmol), **2a** (152 mg, 0.215 mmol), and $\mathrm{NMe_4Cl}$ (84 mg, 0.76 mmol) was stirred in DMF (20 ml) at room temperature for 1 d. The resultant mixture was concentrated to 12 ml under reduced pressure followed by addition of ether (8 ml), and filtered after stirring for 5 min. Slow diffusion of ether (20 ml) to the filtrate gave dark brown crystals of **5a**·2DMF (166 mg, 62% yield). $^1$H NMR ($\mathrm{CD_2Cl_2}$): $\delta$ 1.97 (s, 30H, Cp*), 2.58, 2.86 (s, 3H each, $\mathrm{NMe_2}$), 7.48 (s, 1H, CHO). IR (KBr): $\nu(\mathrm{Mo}=\mathrm{O})$, 930 cm$^{-1}$. Anal. Calcd for $\mathrm{C_{29}H_{51}N_3O_4S_2Cl_4Se_2Mo_2Rh_2}$: C, 27.49; H, 4.06; N, 3.32%. Found: C, 26.99; H, 3.95; N, 3.40%. Dark brown crystals of **5b**·DMF were similarly obtained in 79% yield. $^1$H NMR ($\mathrm{CD_2Cl_2}$): $\delta$ 2.00 (s, 30H, Cp*), 2.67, 2.90 (s, 3H each, $\mathrm{NMe_2}$), 7.64 (s, 1H, CHO). IR (KBr): $\nu(\mathrm{Mo}=\mathrm{O})$, 941 cm$^{-1}$. Anal. Calcd for $\mathrm{C_{26}H_{44}N_2O_3S_2Cl_4Se_2Mo_2Ir_2}$: C, 22.75; H, 3.23; N, 2.04. Found: C, 22.96; H, 3.22; N, 2.14.

11 All measurements were performed on a Rigaku AFC7R diffractometer with Mo K$\alpha$ source. Structures were solved by Patterson methods (PATTY), expanded by Fourier synthesis (DIRDIF 94), and refined by full-matrix least-squares techniques by using teXsan program package. Crystallographic data for **5a**·2DMF: monoclinic, $P2_1/a$ (No. 14), $a = 16.896(1)$, $b = 11.687(2)$, $c = 21.798(2)$ Å, $\beta = 90.831(8)^\circ$, $V = 4303.8(10)$ Å$^3$, $Z = 4$, $D_\mathrm{calc} = 1.956$ g cm$^{-3}$, $\mu(\mathrm{Mo\ K}\alpha) = 33.92$ cm$^{-1}$, $R = 0.040$ and $R_\mathrm{w} = 0.041$ for 5664 unique reflections ($I > 3\sigma(I)$) and 434 variable parameters. Crystallographic data for **5b**·DMF: orthorhombic, $Pbca$ (No. 61), $a = 16.695(1)$, $b = 15.680(3)$, $c = 29.489(3)$ Å, $V = 7719(3)$ Å$^3$, $Z = 8$, $D_\mathrm{calc} = 2.362$ g cm$^{-3}$, $\mu(\mathrm{Mo\ K}\alpha) = 98.28$ cm$^{-1}$, $R = 0.040$ and $R_\mathrm{w} = 0.042$ for 4704 unique reflections ($I > 3\sigma(I)$) and 389 variable parameters.