Rh_4S_7 and Ir_3CuS_6 Clusters with Di- and Trisulfido Ligands Derived from Dinuclear Hydrogensulfido Complexes

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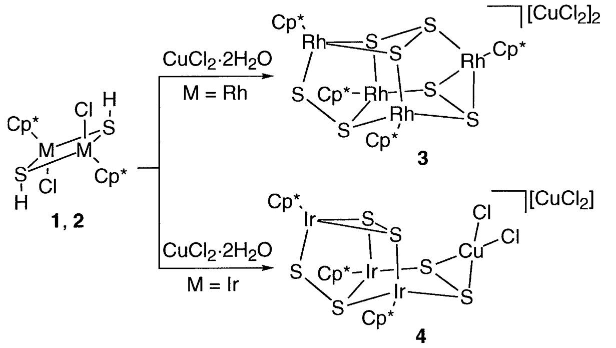
Reactions of the dinuclear hydrogensulfido-bridged complexes $[Cp^*MCl(\mu\text{-}SH)_2MClCp^*]$ (M = Rh, Ir) with $CuCl_2 \cdot 2H_2O$ lead to formation of Rh_4S_7 and Ir_3CuS_6 clusters $[(Cp^*Rh)_4(\mu_3\text{-}S_2)_2(\mu_4\text{-}S_3)][CuCl_2]_2$ and $[(Cp^*Ir)_3(\mu_3\text{-}S_2)_3(CuCl_2)][CuCl_2]$ through the oxidative S–S bond formation, the former of which contains a trisulfido ligand of the unprecedented $\mu_4\text{-}\eta^2{:}\eta^1{:}\eta^1{:}\eta^1$ coordination mode.

Considerable efforts have been devoted to studies on syntheses and properties of transition metal polysulfido complexes because of their outstanding structural diversity[1] as well as their possible relevance to catalytic processes,[2] materials science,[3] and biological systems.[4] We have recently centered our research activity on the chemistry of groups 8–10 noble metal complexes with sulfur-based ligands.[5] In the course of this study, we have synthesized several dinuclear polysulfido complexes of ruthenium[6] and iridium[7] including $[Cp^*Ir(\mu\text{-}SPr^i)_2(\mu\text{-}S_9)IrCp^*]$, which is the first example of the $\mu\text{-}S_9$ complex.[7] Now we have found that novel cationic Rh_4S_7 and Ir_3CuS_6 clusters containing di- and trisulfido ligands are prepared by the Cu(II)-oxidation of the hydrogensulfido-bridged complexes $[Cp^*MCl(\mu\text{-}SH)_2MClCp^*]$ (**1**, M = Rh; **2**, M = Ir).[8]



Scheme 1.

When the dirhodium complex **1** was allowed to react with 3 molar equiv of $CuCl_2 \cdot 2H_2O$ in THF at 50 °C, a dark brown solid was precipitated, whose recrystallization from acetonitrile–ether–hexane gave the cationic cluster $[(Cp^*Rh)_4(\mu_3\text{-}S_2)_2(\mu_4\text{-}S_3)][CuCl_2]_2 \cdot Et_2O$ ($\mathbf{3} \cdot Et_2O$) in 4.6% isolated yield (based on the sulfur atom of **1**) along with $[Cp^*RhCl_2]_2$ (42% yield) (Scheme 1). The discrepancy of the S/Rh atomic ratio in **1** and **3** may be responsible for the low yield of **3**, but attempts to improve the yield of **3** by, for example, conducting the reaction in the presence of S_8 were unsuccessful. This reaction is viewed as oxidative coupling of hydrogensulfido ligands to disulfido and trisulfido ligands by Cu(II) ion, although mechanistic details for the assembly of the rhodium nuclei are unclear. The reaction of **1** with other oxidizing agents such as I_2 and $[Cp_2Fe]PF_6$ failed to give the cluster cation of **3**. It has been reported that certain hydrogensulfido complexes are oxidized electrochemically or by I_2, O_2, or $[Cp_2Fe]PF_6$ to give disulfido complexes.[9] However, application of such reactions to polysulfido cluster synthesis has been poorly investigated,[10] and formation of a trisulfido ligand by the oxidation of hydrogensulfido ligands has not been documented.

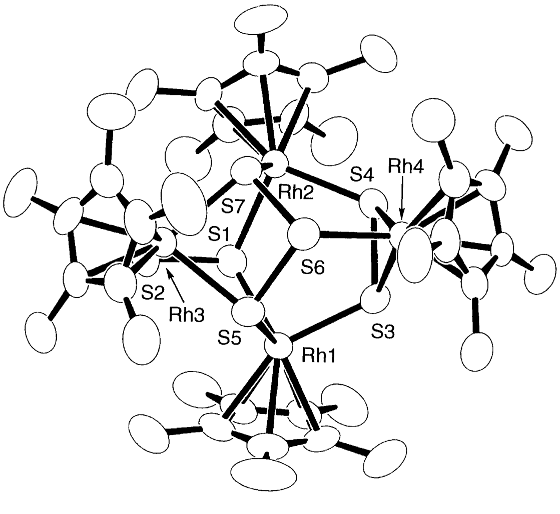


Figure 1. Molecular structure of the cationic part in $\mathbf{3} \cdot Et_2O$. Selected bond distances (Å) and angles (deg): Rh(1)–S(1), 2.337(2); Rh(1)–S(3), 2.316(2); Rh(1)–S(5), 2.314(2); Rh(2)–S(1), 2.332(2); Rh(2)–S(4), 2.316(2); Rh(2)–S(7), 2.319(2); Rh(3)–S(2), 2.332(3); Rh(3)–S(5), 2.397(2); Rh(3)–S(7), 2.399(2); Rh(4)–S(3), 2.343(2); Rh(4)–S(4), 2.334(2); Rh(4)–S(6), 2.266(2); S(5)–S(6)–S(7), 92.5(1).

Cluster **3** is diamagnetic, and the formal oxidation state of each rhodium atom is Rh(III). The ^1H NMR spectrum exhibited three Cp* signals with the relative intensity ratio of 2:1:1 (δ_H 1.75, 1.96, 1.99), which indicates two of the four Cp* ligands are chemically equivalent. The molecular structure of $\mathbf{3} \cdot Et_2O$ was established by X-ray diffraction study.[11] A perspective view of the cluster cation of **3** is shown in Figure 1. The cluster cation is composed of four Cp*Rh units, two disulfido ligands, and one trisulfido ligand, forming a novel $M_4(S_2)_2(S_3)$ polyhedral core. The molecule is almost symmetric with respect to the plane containing the Rh(3), Rh(4), S(1), S(2), and S(6) atoms, as suggested by the ^1H NMR spectrum. For structurally characterized trisulfido complexes, the η^2-, $\mu\text{-}\eta^1{:}\eta^1$-, $\mu\text{-}\eta^2{:}\eta^1$-, and $\mu_3\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-}S_3$ ligands have been observed.[1,12–16] To the best of our knowledge, the μ_4-η^2:η^1:η^1:η^1 coordination mode found for cluster **3** is unprecedented. Furthermore, cluster **3** provides a rare example in which the central sulfur atom of a trisulfido ligand behaves as a donor atom.[12,13] The S–S bond distances in the trisulfido ligand at 2.108(3) and 2.145(3) Å are comparable to those found for $[(Cp^*Ru)_2(\mu\text{-}S_2)(\mu\text{-}S_3)(CO)]$ (2.110(5) Å),[12] $[\{(C_5Me_4Et)Nb\}_3S_4(\mu_3\text{-}S_3)]$ (2.146(6) Å),[14] and $[NH_4][Re_4S_4(\mu\text{-}S_3)_6]$ (2.14(3) Å).[15]

On the other hand, treatment of the diiridium complex **2** with 3 molar equiv of $CuCl_2 \cdot 2H_2O$ in THF at 50 °C gave a dark brown precipitate, whose recrystallization from acetonitrile–ether afforded the cationic Ir–Cu cluster $[(Cp^*Ir)_3(\mu_3\text{-}S_2)_3(CuCl_2)][CuCl_2] \cdot MeCN$ (**4**·MeCN) in 36% yield (Scheme 1). Cluster **4** exhibited two Cp* signals with the relative intensity ratio of 2:1 (δ_H 1.94, 2.18) in the ^1H NMR spectrum. The Cu 2*p* X-ray photoelectron spectrum (XPS) of **4** had no high-binding-energy satellite at around 943 eV, revealing that cluster **4** contains no Cu(II) center.[17] Therefore, the formal oxidation states of the metal atoms in the cluster core are concluded to be Ir(III), Ir(IV), Ir(IV), and Cu(I).

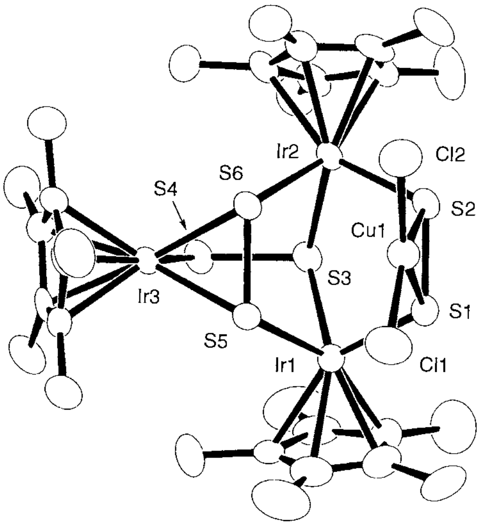


Figure 2. Molecular structure of the cationic part in **4**·MeCN. Selected bond distances (Å): Ir(1)–S(1), 2.255(2); Ir(1)–S(3), 2.357(3); Ir(1)–S(5), 2.354(3); Ir(2)–S(2), 2.254(3); Ir(2)–S(3), 2.367(2); Ir(2)–S(6), 2.372(2); Ir(3)–S(4), 2.331(3); Ir(3)–S(5), 2.379(3); Ir(3)–S(6), 2.407(2); Cu(1)–S(1), 2.265(3); Cu(1)–S(2), 2.244(3).

The molecular structure of **4** determined by X-ray diffraction study is depicted in Figure 2.[18] In contrast to the structure of **3**, the cluster core of **4** is consisted of three iridium atoms, one copper atom, and three disulfido ligands. Two of the three disulfido ligands bridge the three iridium centres, while the third disulfido ligand is coordinated by two of the iridium atoms and the $CuCl_2$ unit. In agreement with the ^1H NMR spectrum, the cluster cation possesses approximate *Cs* symmetry with the mirror plane through the Ir(3), Cu(1), S(3), and S(4) atoms. The $Cu(S_2)Cl_2$ moiety is essentially planar. No metal–metal bonding interaction is observed (Ir···Ir > 3.8447(6) Å, Ir···Cu > 3.761(1) Å), but the diamagnetic nature of **4** may be accounted for by spin coupling through the disulfido ligands.[6]

The above reactions demonstrate that the oxidative conversion of hydrogensulfido complexes by Cu(II) provides a unique synthetic method for polysulfido clusters. Further application of this method to polysulfido cluster synthesis as well as studies on reactivities of clusters **3** and **4** are now in progress.

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11 Crystallographic data for **3**·Et_2O: $C_{44}H_{70}Cl_4Cu_2ORh_4S_7$: M = 1519.98, monoclinic, space group $P2_1/n$, a = 12.603(2), b = 22.038(3), c = 20.873(2) Å, β = 92.77(1)°, V = 5790(1) Å^3, Z = 4, T = 294 K, $\mu(MoK_\alpha)$ = 23.00 cm^{-1}, R = 0.044 and R_w = 0.032 for 560 variables and 6125 unique reflections [$I > 3.0\sigma(I)$].

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18 Crystallographic data for **4**·MeCN: $C_{32}H_{48}Cl_4Cu_2Ir_3NS_6$, M = 1484.66, monoclinic, space group $P2_1/c$, a = 13.412(2), b = 23.317(2), c = 14.858(2) Å, β = 107.92(1)°, U = 4420(1) Å^3, Z = 4, T = 294 K, $\mu(MoK_\alpha)$ = 105.19 cm^{-1}, R = 0.041 and R_w = 0.030 for 431 variables and 6866 unique reflections [$I > 3.0\sigma(I)$].