Cluster Compounds

Competing H–H, S–S, and M–M Bond Formation in the "Shape-Shifting" Cluster $[Ru_4S_3(arene)_4]^{2+}$**

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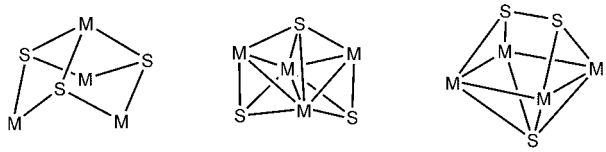
Tetrametallic trisulfido clusters[1] mainly adopt the C_{3v} "Roussin Black salt" structure,[2,3] illustrated by the classical anion $[Fe_4S_3(NO)_7]^-$. This motif has recently attracted interest because M_4S_3-like fragments comprise the FeMo cofactor in nitrogenase.[3–5] The only other M_4S_3 structure is the rare C_{2v} capped-butterfly seen in $[Cp_2Mo_2Co_2S_3(CO)_4]$ ($Cp = C_5H_5$; Scheme 1).[2] Herein we describe the character-



Scheme 1. Structures of M_4S_3 cluster cores; M–M bonding can vary; left: C_{3v} Roussin Black salt structure, middle: C_{2v} capped-butterfly, and right: face-capped trigonal prism (this work).

ization of a third M_4S_3 motif; this new cluster is unusual because of its structural dynamics and catalytic properties. In particular, the new M_4S_3 clusters exhibits a previously unobserved competition between S–S and M–M bonding.

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Studies on this dynamic property revealed that the new clusters catalyze the reduction of protons to H_2.

We have shown that $[\{(cym)RuCl_2\}_2]$ (cym = 4-*i*PrC$_6$H$_4$Me) reacts with $(Me_3Si)_2S$ to produce trigonal bipyramidal $[(cym)_3Ru_3S_2]^{2+}$.[6] We have found that this simple synthesis also affords the previously unrecognized tetrametallic species $[(cym)_4Ru_4S_3]^{2+}$ (**1**$^{2+}$). The distinctive solubility properties of $[(cym)_4Ru_4S_3](PF_6)_2$ (**1**) facilitates its easy isolation in 30% yield [Eq. (1)].

$$2\,[\{(cym)RuCl_2\}_2] \xrightarrow{(Me_3Si)_2S} [(cym)_3Ru_3S_2](PF_6)_2\ (60\%) + [(cym)_4Ru_4S_3](PF_6)_2\ (\mathbf{1},\ 30\%) \quad (1)$$

In MeCN solution, cluster **1**$^{2+}$ is stable at 80 °C in the presence of PPh_3, and it is stable to UV photolysis.[7]

The reaction stoichiometry leading to **1**$^{2+}$ is deceptive: Ru^{II} chlorides are ostensibly converted into the corresponding Ru^{II} sulfides. The ^{1}H NMR data for **1**$^{2+}$ indicate low symmetry, which is incompatible with known M_4S_3 motifs. X-ray crystallographic analysis of **1** revealed that the dication adopts a novel structure, described as a face-capped trigonal prism (Figure 1). An equilateral Ru_4 square (Ru–Ru bond 2.81 ± 0.03 Å) is capped by μ_4-S and μ_4-S_2 ligands. The crystallographic result shows that **1**$^{2+}$ formally arises via an internal reduction of two Ru^{II} to Ru^{I} concomitant with oxidative coupling of two sulfides to persulfide (S_2^{2-}). The 64 electron compound follows the 18 electron rule, although Wade's rules predict a nido cluster (9 electron pair/seven vertex).

The crystallographic analysis reveals that the four isopropyl groups are oriented towards the persulfide-containing face of the Ru_4 square, which is more spacious than the Ru_4S side. A space-filling model indicates steric crowding between the arene substituents, which would lead to restricted rotation about the ruthenium–arene bonds. Indeed, the ^{1}H NMR spectrum for **1**$^{2+}$ is simple at 70 °C but becomes complex at lower temperatures as arene rotation is slowed (Figure 2). At −35 °C, 13 CH_3C$_6$H$_4$*i*Pr signals are resolved (Figure 2b) 14 CH_3C$_6$H$_4$*i*Pr signals would be consistent with seven possible atropisomers: $(up)_4$, $(down)_4$, *trans*-$(up)_2(down)_2$, *cis*-(up-∥)$_2$(down-∥)$_2$, *cis*-(up-⊥)$_2$(down-⊥)$_2$, $(up)_3(down)$, and $(up)(down)_3$, where up and down refer to the orientation relative to the S_2 and S faces of the Ru_4 square (see Scheme 2). The number of isomers implies that rotation of the S_2 ligand is slow on the NMR timescale, such that two *cis*-$(up)_2(down)_2$ isomers are implicated, those where the cisoid Me groups are parallel (∥; Scheme 2) or perpendicular (⊥) to the S_2 unit. Restricted rotation of η^6-arene ligands has rarely been detected in mononuclear complexes[8] and never in a metal cluster. The isomerization barrier could in principle be increased through modifications in the arene ligand.

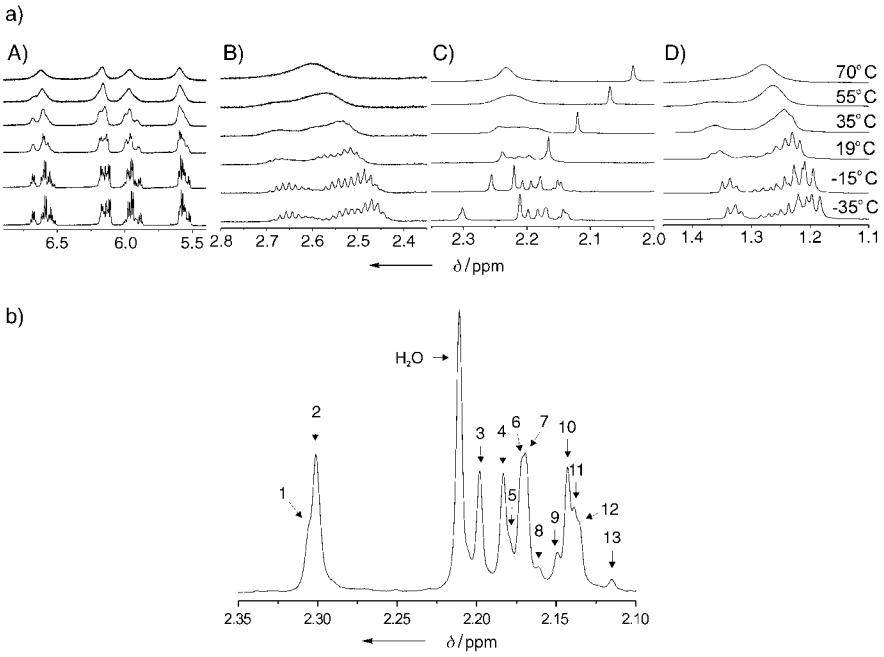


Figure 2. a) Variable temperature ^{1}H NMR spectra ([D$_3$]MeCN) for **1** demonstrating restricted rotation of the cym ligands. A) Aromatic region, B) methyne (isopropyl), C) methyl, and D) methyl (isopropyl) of cym. b) Expansion of the CH_3C$_6$H$_4$*i*Pr region for the −35 °C spectrum, demonstrating the coexistence of several atropisomers.

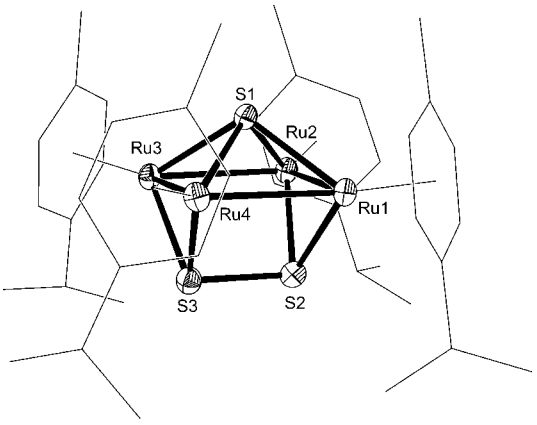
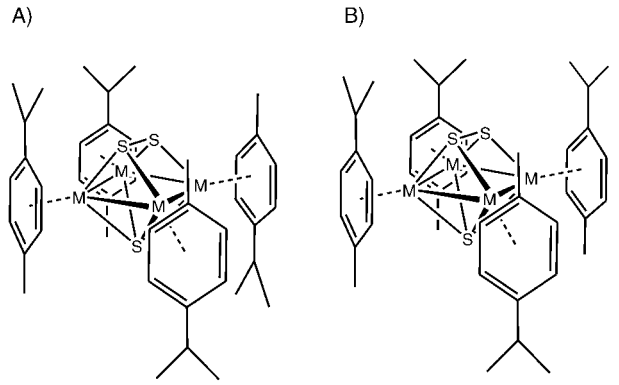


Figure 1. Molecular structure of **1**. Thermal ellipsoids are set at 50% probability. Select bond lengths [Å]: Ru1-Ru2 2.782, Ru1-Ru4 2.827, Ru4-Ru3 2.776, Ru2-Ru3 2.848, S1-Ru2 2.352, S3-S2 2.109, S2-Ru2 2.281.

The cyclic voltammetry (CV) of **1** revealed sequential 1 e$^-$ reductions at −970 and −1270 mV (not shown; all potentials are referenced to the Ag | AgCl couple). A reversible event at 790 mV is assigned to a 2 e$^-$ oxidation. Chemical reduction of **1**$^{2+}$ with two equivalents of $[Cp^*_2Co]$ ($Cp^* = C_5Me_5$; $E° = 1.73$ versus Ag | AgCl) yielded the neutral cluster $[(cym)_4Ru_4S_3]$ (**2**^{0}). The ^{1}H NMR spectroscopy data for this neutral species revealed a 3:1 ratio for the cym signals, which indicates idealized C_{3v} symmetry as expected for the Roussin motif, which was confirmed crystallographically (Figure 3). In contrast to other Roussin-like clusters, the apical metal atom is not connected to the other three metal centers by M–M



Scheme 2. Structures of two atropisomers of **1**, A) the *cis* || isomer and B) the $(up)_3(down)$ isomer.

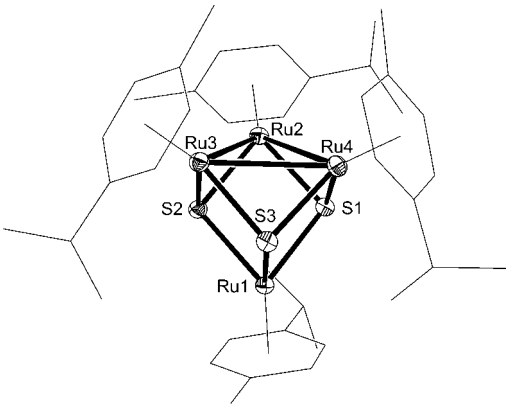


Figure 3. Molecular structure of $\mathbf{2}^0$ with thermal ellipsoids set at 50% probability. Select interatomic distances [Å]: Ru1···Ru2 3.620, Ru3-Ru2 3.079, Ru3-Ru4 3.059, Ru4-Ru2 3.007, Ru1-S2 2.377, Ru2-S2 2.324.

bonds. Two Ru–Ru bonds are expected in a $68\,e^-$ M_4 cluster, thus each of the three comparably elongated Ru–Ru bonds within the Ru_3 basal plane is consistent with a bond order of 2/3. Compound $\mathbf{2}^0$ is formally related to the cubane $[(cym)_4Ru_4S_4]$[9,10] by removal of one sulfur atom and subsequent formation of three Ru–Ru bonds.

The scan-rate dependence of the CV of **1** is consistent with a coupled electrochemical–chemical process. The reduction $\mathbf{1}^{2+}\rightarrow\mathbf{1}^{+}$ is fully reversible, but the second reduction is not, hence this event is attributed to the rearrangement to the Roussin-like cluster **2**. At slow scan rates ($20\,mV\,s^{-1}$), the initially generated $\mathbf{2}^{+}$ is fully converted into $\mathbf{1}^{+}$, indicated by the event at -970 mV. At faster scan rates ($500\,mV\,s^{-1}$) separate oxidations are observed for $\mathbf{2}^0\rightarrow\mathbf{2}^{+}$ and $\mathbf{2}^{+}\rightarrow\mathbf{2}^{2+}$. The scan-rate dependence suggests that the rearrangement of $\mathbf{2}^{+}$ into $\mathbf{1}^{+}$ occurs with a half-life of approximately 100 ms. A plausible pathway for rearrangement associated with the oxidation of $\mathbf{2}^0$ is shown in Scheme 3.

Reflecting its electron-rich character and the robustness of the Ru–S ensemble, $\mathbf{2}^0$ reacts efficiently with acids, such as HOTf ($OTf=[CF_3SO_3]^-$), to regenerate $\mathbf{1}^{2+}$. When this reaction is conducted in CH_2Cl_2 solution, $\mathbf{1}^{+}(OTf)_2$ crystallizes in near quantitative yield. Interestingly, this reaction occurs with formation of H_2 (^1H NMR: $\delta=4.6$ ppm in CH_2Cl_2 solution), [Eq. (2)].

$$[(cym)_4Ru_4S_3]+2\,H^+\rightarrow[(cym)_4Ru_4S_3]^{2+}\ (100\,\%)+H_2 \qquad (2)$$

Qualitative experiments suggest that $\mathbf{2}^0$ is a two-electron reductant since the addition of one equivalent of HOTf precipitates an approximately 50% yield of $\mathbf{1}^{+}(OTf)_2$. Thus, the implied monohydride intermediate $\mathbf{2}H^{+}$ is apparently more reactive towards HOTf than $\mathbf{2}^0$. Since $\mathbf{2}^0$ is capable of reducing protons and $\mathbf{1}^{2+}$ undergoes efficient reduction, a catalytic cycle is apparent, but the CV results were unexpected. Indeed with HOTs a catalytic current that correlates with [HOTs] is observed, but not at the expected potential of approximately $i_{cat}=-1$ V. Instead i_{cat} emerges in the range -0.80 to -0.60 V (Figure 4). The two new reduction events

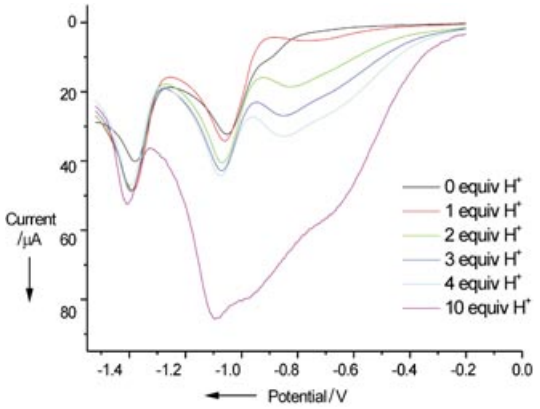
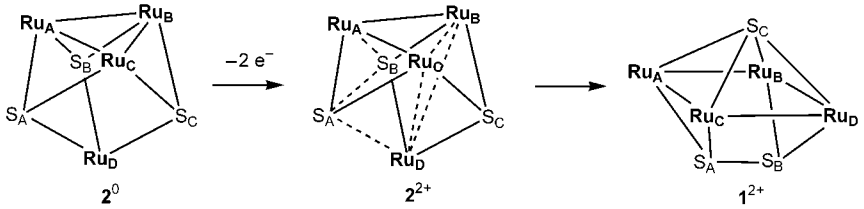


Figure 4. Voltammograms of 10^{-3} M **1** in 0.1 M Bu_4NPF_6 MeCN solution. The reductive current at approximately -800 mV can be seen to correlate with the [*p*-$MeC_6H_4SO_3H$]. Conditions: scan rate $=100\,mV\,s^{-1}$, Pt wire counter electrode, a glassy carbon electrode working electrode, Ag/AgCl reference.

observed in presence of H^+ suggest that $\mathbf{1}^{2+}$ forms an electroactive protonated derivative, although we were unable to spectroscopically detect such a species. The two new reduction events not only increase in current with increasing $[H^+]$, but shift to a more negative potential with increasing $[H^+]$, as seen in catalytic systems.[11,12]

In summary, new M_4S_3 clusters have been shown to exhibit "shape-shifting", involving redox- and proton-induced conversions between C_{3v} and trigonal-prismatic structures. The parent cationic cluster is further unusual in that its arene



Scheme 3. Pathway for the oxidation of $\mathbf{2}^0$.

ligands exhibit restricted rotation owing to steric compression. The work underscores the promise of metal sulfide ensembles for hydrogen processing.

Experimental Section

1: A stirred suspension of (4.160 g, 6.8 mmol) of $[\{(cym)RuCl_2\}_2]$[13] in warm THF (150 mL) was treated with (2.14 mL, 10.2 mmol) of $(Me_3Si)_2S$. The solid slowly dissolved followed by formation of a brown precipitate. The slurry was stirred at 50 °C for 1 h. The solid was collected by filtration and washed with THF (20 mL). The dried brown powder was extracted into H_2O (100 mL) this solution was treated with KPF_6 (2.50 g 13.3 mmol) to precipitated a mixture of $[(cym)_3Ru_3S_2](PF_6)_2$ and **1**. After washing this solid with CH_2Cl_2 to remove $[(cym)_3Ru_3S_2](PF_6)_2$, the residue was extracted into acetone, and this solution was concentrated to 5 mL. Addition of Et_2O (80 mL) precipitated a brown powder. Yield: 1.34 g (30 %). ^{1}H NMR (500 MHz, [D$_3$]MeCN): 1.28 (m, 6H), 2.22 (m, 3H), 2.61 (m, 1H), 6.61 (m, 1H), 6.14 (m, 1H), 5.96 (m, 1H), 5.59 ppm (m, 1H). ESI-MS: *m*/*z* 519 ([M^{2+}]). Elemental analysis (%) calcd for $C_{40}H_{56}F_{12}P_2Ru_4S_3$: C 36.19, H 4.25, N 0; found: C 35.74, H 4.15, N 0.28.

2^0: A solution of [Cp*$_2$Co] (424 mg, 1.29 mmol) in THF (40 mL) was added to a stirred solution of **1** (814 mg 0.61 mmol) in MeCN (130 mL). After 1 h, the solvent was removed in vacuo, and the resulting red powder was extracted with hexane (50 mL). Dark red crystals were obtained upon concentrating and cooling the solution. Yield: 464 mg (65 %). ^{1}H NMR (500 MHz, [D$_8$]THF): 1.22 (d, J = 7 Hz, 6H), 1.37 (d, J = 7 Hz, 18H), 1.78 (s, 3H), 2.34 (s, 9H) 2.58 (sept, J = 7 Hz, 1H) 2.78 (sept, J = 7 Hz, 3H) 4.13 (d, J = 6 Hz, 2H) 4.47 (d, J = 6 Hz, 2H) 4.80 (d, J = 6 Hz, 6H) 4.97 ppm (d, J = 6 Hz, 6H). Elemental analysis (%) calcd for $C_{40}H_{56}Ru_4S_3$: C 46.31, H 5.44, N 0; found: C 46.48, H 5.45, N 0.17.

Crystallography: Data was collected at −78 °C on a Siemens Platform/CCD automated diffractometer. Data processing was performed with SAINT PLUS version 6.22. Structures were solved using direct methods and refined using full-matrix least-squares on F^2 using Bruker SHELXTL version 6.10. Hydrogen atoms were fixed in idealized positions with thermal parameters 1.5 × those of the attached carbon atoms. The data were corrected for absorption on the basis of Ψ-scans. CCDC-244393 and CCDC-244394 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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