

A $[\text{Fe}_8\text{S}_6]^{4+}$ Cluster as Bridging Ligand *via* Sulfur in a Dinuclear Ruthenium Complex

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$[\text{Fe}_6\text{S}_6]_2(\text{PMePh}_2)_4$ **1** reacts with $[\text{RuI}_2(\text{MeCN})_4]$ to afford the novel $[\text{Ru}_2\text{Fe}_8\text{S}_6]^{8+}$ cluster, whose structure, elucidated by a single crystal X-ray crystallographic study, is composed of a $[\text{Fe}_8\text{S}_6]^{4-}$ unit and two $[\text{Ru}(\text{SPMePh}_2)(\text{MeCN})_4]^{2+}$ complex fragments bridged *via* μ_5 -sulfur.

Chemists trying to model active sites of metalloproteins are faced with a number of 'synthetic problems' especially owing to quite uncommon iron coordination in the FeMo-cofactor which has been reported by Kim and Rees¹ in the crystallographic structure of the nitrogenase molybdenum-iron protein from *Azotobacter vinelandii*. Furthermore, the 'P-cluster', although comprising two (possibly disulfide bridged) 4Fe-4S cubes, is unusual, in that in the resting enzyme all the

Fe is in the +2 oxidation state.²⁻⁴ Attempts to prepare stable model compounds containing $[\text{Fe}_4\text{S}_4]^0$ clusters have failed so far.

Very recently it has been shown that reaction of $[\text{Fe}_4\text{S}_4\text{I}_4]^{2-}$ with $[\text{FeI}_2(\text{PMePh}_2)_2]$ gives $[\text{Fe}_8\text{S}_6\text{I}_8]^{4-}$, a complex with Fe exclusively in the +2 state and therefore possibly a useful precursor for a $[\text{Fe}_4\text{S}_4]^0$ cluster.⁵ An intermediate in this reaction is $[\text{Fe}_6\text{S}_6\text{I}_2(\text{PMePh}_2)_4]$ **1**, a so-called 'basket cluster',

which was isolated some years ago with slightly different ligands by Holm and coworkers.^{6†}

A solution of **1** in dichloromethane was treated at ambient temperature with 2 equiv. of $[\text{RuI}_2(\text{MeCN})_4]$ to produce a precipitation of FeS. After filtration black needles of the neutral compound $[(\text{MeCN})_4(\text{Ph}_2\text{MePS})\text{Ru}-\text{Fe}_8\text{S}_6\text{I}_8-$

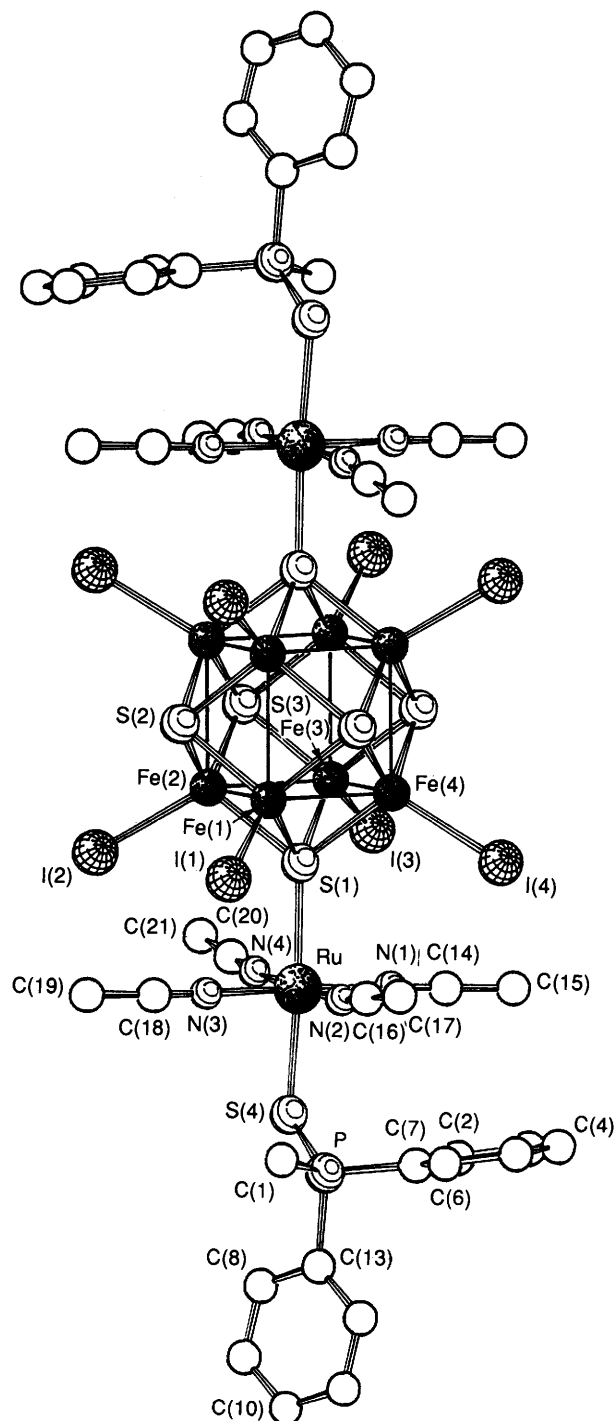
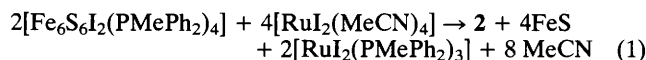


Fig. 1 Molecular structure of **2** with atom numbering scheme (hydrogen atoms omitted for clarity). The complex exhibits C_2 symmetry. Selected bond lengths (Å) and angles (°): Fe(1)–Fe(2) 2.656(4), Fe(2)–Fe(3) 2.672(4), Fe(3)–Fe(4) 2.683(4), Fe(4)–Fe(1) 2.674(4), Fe(1)–Fe(3') 2.812(5), Fe(2)–Fe(4') 2.826(4), S(1)–Fe(1) 2.354(6), S(1)–Fe(2) 2.342(6), S(1)–Fe(3) 2.343(7), S(1)–Fe(4) 2.370(6), S(1)–Ru 2.393(6), S(4)–Ru 2.472(7), [S(2)–Fe and S(3)–Fe between 2.299 and 2.318, mean 2.307; angles Fe–Fe–Fe 89.3–90.7].

† We modified the synthesis of the basket cluster by starting from $[\text{Fe}_4\text{S}_4\text{I}_4]^{2-}$ and $[\text{FeI}_2(\text{PMePh}_2)_2]$.

$\text{Ru}(\text{SPMePh}_2)(\text{MeCN})_4$ **2** crystallised within 3 days in 78% yield as dichloromethane solvate $2 \cdot 2\text{CH}_2\text{Cl}_2$ according to eqn. (1) to which the yield was related. (The obtained analysis was



in good agreement with the formula $2 \cdot \text{CH}_2\text{Cl}_2$, suggesting the loss of one dichloromethane. The correct formula $2 \cdot 2\text{CH}_2\text{Cl}_2$ was established by X-ray structure analysis.) The structure of **2** was determined from single crystal X-ray data.‡ The most striking feature is the formation of the novel $[\text{Ru}_2\text{Fe}_8\text{S}_6]^{8+}$ cluster, which may be described in another way as a $[\text{Fe}_8\text{S}_6\text{I}_8]^{4-}$ complex with additional coordination of two $[\text{Ru}(\text{SPMePh}_2)(\text{MeCN})_4]^{2+}$ fragments *via* sulfur (Fig. 1). Owing to Ru^{II} coordination the rhombododecahedral $[\text{Fe}_8\text{S}_6]^{4+}$ core exhibits a tetragonal distortion, *i.e.* an elongation of the Fe_8 cube parallel to the Ru–Ru axis. The mean values of the Fe–Fe distances parallel and perpendicular to this axis are 2.819 and 2.671 Å, respectively.

The coordinated SPMePh_2 clearly indicates that the cluster conversion $[\text{6Fe6S}] \rightarrow [\text{8Fe6S}]$ proceeds *via* the redox reaction $2\text{Fe}^{3+} + \text{S}^{2-} \rightarrow 2\text{Fe}^{2+} + \text{S}$ and subsequent phosphane oxidation by sulfur. The first step of the reaction is possibly an iodide/phosphane ligand exchange between iron and ruthenium which leads to a destabilisation of the anionic Fe–S cluster. By using appropriate metal complexes this new synthetic pathway to $[\text{M}_8\text{S}_6]$ clusters opens up the possibility to incorporate these metals into the cluster. Analogous reactions with nickel (see also ref. 9), copper and molybdenum are under way. Furthermore sulfide and disulfide possibly react with the $[\text{Fe}_8\text{S}_6]$ core to give model complexes of the P-cluster.

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‡ Crystal data for $2 \cdot 2\text{CH}_2\text{Cl}_2$ ($\text{C}_{44}\text{H}_{54}\text{Cl}_4\text{Fe}_8\text{I}_8\text{N}_8\text{P}_2\text{Ru}_2\text{S}_8$): $M = 2819.39$, triclinic, space group $P1$, $a = 11.914(2)$, $b = 12.645(3)$, $c = 14.750(3)$ Å, $\alpha = 85.67(2)$, $\beta = 72.57(2)$, $\gamma = 87.44(1)^\circ$, $V = 2113.47$ Å³, ($T = 295$ K), $Z = 1$, $D_c = 2.215$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 4.95$ mm⁻¹. A thin needle-like crystal was mounted on a AED2 Siemens four-circle diffractometer. Data collection using Mo-K α radiation ($\lambda = 0.71073$ Å) and ω - 2θ scans gave 6637 independent reflections ($2\theta_{\text{max}} 48^\circ$), of which 2999 with $I \geq 2\sigma(I)$ were used in all calculations. The structure was solved by direct methods⁷ and the solution developed using full-matrix least-squares refinement and difference Fourier syntheses. Anisotropic thermal parameters were refined for non-H atoms, except for disordered C atoms (8)–(13) (two positions with occupancy factors 0.5), phenyl groups refined with fixed geometry, H atoms were included in fixed calculated positions.⁸ At convergence, $R = 0.067$, $R_w = 0.051$, GOF = 1.453 for 320 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.