# Novel Reactivity of Thiometallates: Syntheses and Structures of New Transition Metal Sulphide Clusters containing $WRu_2S_6$ and $Ru_2S_2(SR)_2$ Cores

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Reaction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ with an excess of $(NH_4)_2WS_4$ in THF at reflux gave $[(\mu_2\text{-}S_2)\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu_3\text{-}S)(\mu_2\text{-}S)_2WS]$, whereas the analogous treatment of $[(\eta^5\text{-}C_5Me_5)RuCl(\mu\text{-}SPr^i)_2Ru(\eta^5\text{-}C_5Me_5)Cl]$ with $(NH_4)_2MS_4$ (M = W, Mo) resulted in the formation of $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}S_2)(\mu\text{-}SPr^i)_2Ru(\eta^5\text{-}C_5Me_5)]$.

Transition metal–sulphur complexes have received much attention in recent years as possible models for the understanding of a number of biological and catalytic processes. We have been studying the chemistry of ruthenium–sulphur complexes, which may possibly have relevance to the iron–sulphur clusters present in natural metalloproteins and enzymes.[1] Recently we have found that $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ **1** is a potential precursor for the preparation of dinuclear ruthenium complexes with bridging thiolate ligands and the interesting structural diversity of the diruthenium–thiolate complexes produced by the reaction of **1** with various thiolate compounds has been reported in the preceding papers.[2] Here we report the synthesis and X-ray structures of new sulphide clusters with $WRu_2S_6$ and $Ru_2S_2(SR)_2$ cores derived from **1**.

Treatment of **1** with an excess of $(NH_4)_2WS_4$ in tetrahydrofuran (THF) at reflux afforded the diamagnetic mixed metal sulphide cluster with a $WRu_2S_6$ core $[(\mu_2\text{-}S_2)\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu_3\text{-}S)(\mu_2\text{-}S)_2WS]$ **2** as dark green crystals in 13% yield;† see eqn. (1). The X-ray analysis unambiguously disclosed the structure of **2** in detail,‡ which is depicted in Fig. 1 with some selected bond distances and angles.

$$\underset{\mathbf{1}}{[(\eta^5\text{-}C_5Me_5)RuCl_2]_2} + 2(NH_4)_2WS_4 \rightarrow$$

$$\underset{\mathbf{2}}{[(\mu_2\text{-}S_2)\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu_3\text{-}S)(\mu_2\text{-}S)_2WS]} + WS_2 + 4NH_4Cl \qquad (1)$$

$$\underset{\mathbf{3}}{[(\eta^5\text{-}C_5Me_5)RuCl(\mu\text{-}SPr^i)_2Ru(\eta^5\text{-}C_5Me_5)Cl]} + (NH_4)_2MS_4 \rightarrow$$

$$\underset{\mathbf{4}}{[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}S_2)(\mu\text{-}SPr^i)_2Ru(\eta^5\text{-}C_5Me_5)]} + MS_2 + 2NH_4Cl \qquad (2)$$

In **2**, two $(\eta^5\text{-}C_5Me_5)Ru$ units are combined by both a $\mu_2$, $\eta^1\text{-}S_2$ ligand and a $WS_4$ fragment. The latter coordinates to the two Ru atoms by one $\mu_3$-S and two $\mu_2$-S ligands. The long Ru(1)–Ru(2) distance of 3.977(2) Å precludes any metal–metal interaction, whereas the W–Ru(1) and W–Ru(2) distances of 2.864(2) and 2.880(2) Å indicate the presence of a metal–metal bond as observed for $[\{CpRu(MeCN)\}_2WS_4]$ [2.870(2) Å].[3] The configuration of four sulphide ligands around the W atom is a slightly distorted tetrahedron [the S–W–S angles: 106.6(2)–112.1(2)°] and the W–S bond lengths are significantly elongated in the order of W–S(6) < W–S(4) ≈ W–S(5) < W–S(3). It has already been reported that thiometallates such as $WS_4^{2-}$ and $MoS_4^{2-}$ coordinate as bidentate terminal ligands or bridging ligands to give di- or tri-nuclear heterometallic sulphide complexes of the types $(M')S_2MS_2$ and $(M')S_2MS_2(M')$.[4] However, the $\mu$-$WS_4$ ligand

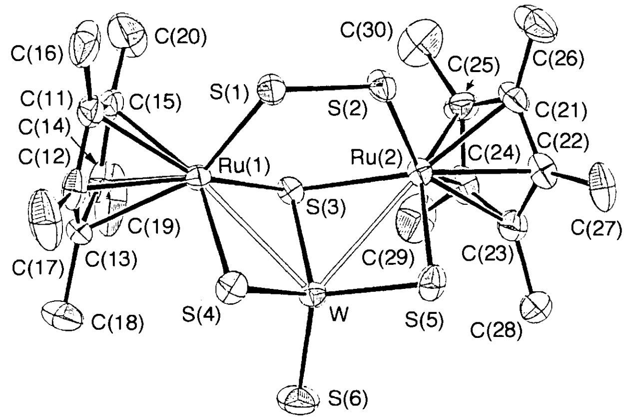

**Fig. 1** An ORTEP drawing of **2**. Selected bond distances (Å) and angles (°): W–S(3) 2.257(4), W–S(4) 2.210(5), W–S(5) 2.214(5), W–S(6) 2.147(6), Ru(1)–S(1) 2.224(5), Ru(2)–S(2) 2.216(5), Ru(1)–S(3) 2.366(5), Ru(2)–S(3) 2.373(5), Ru(1)–S(4) 2.357(5), Ru(2)–S(5) 2.359(6), S(1)–S(2) 1.991(7); Ru(1)–S(1)–S(2) 116.3(3), Ru(2)–S(2)–S(1) 116.8(3), W–S(3)–Ru(1) 76.5(1), W–S(3)–Ru(2) 76.9(1), Ru(1)–S(3)–Ru(2) 114.1(2), W–S(4)–Ru(1) 77.6(2), W–S(5)–Ru(2) 78.0(2).

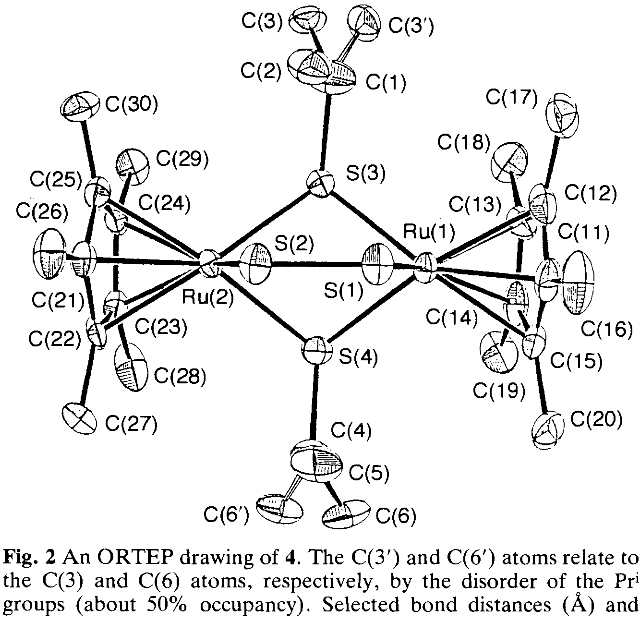

**Fig. 2** An ORTEP drawing of **4**. The C(3′) and C(6′) atoms relate to the C(3) and C(6) atoms, respectively, by the disorder of the Pr$^i$ groups (about 50% occupancy). Selected bond distances (Å) and angles (°): Ru(1)–S(1) 2.215(4), Ru(2)–S(2) 2.209(5), Ru(1)–S(3) 2.417(4), Ru(1)–S(4) 2.430(4), Ru(2)–S(3) 2.423(4), Ru(2)–S(4) 2.424(4), S(1)–S(2) 2.008(6); Ru(1)–S(1)–S(2) 111.2(2), Ru(2)–S(2)–S(1) 110.8(2), Ru(1)–S(3)–Ru(2) 95.8(1), Ru(1)–S(4)–Ru(2) 95.4(2).

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† $^1H$ NMR ($CDCl_3$) **2**: δ 1.93 (s, 30H, $\eta^5\text{-}C_5Me_5$); **4**: 1.80 (s, 30H, $\eta^5\text{-}C_5Me_5$), 0.34 (d, 12H, $SCHMe_2$), 1.05 (m, 2H, $SCHMe_2$); **5**: 1.56 (s, 30H, $\eta^5\text{-}C_5Me_5$), 2.21 (s, 4H, $SCH_2$), 6.84–7.10 (m, 10H, Ph); **6**: 1.74 (s, 30H, $\eta^5\text{-}C_5Me_5$), 0.39 (s, 18H, Bu$^t$).

‡ *Crystal data for* **2**: $M$ = 848.8, monoclinic, space group $P2_1/c$ (No. 14), $a$ = 16.460(2), $b$ = 10.009(3), $c$ = 16.582(2) Å, $\beta$ = 93.68(1)° $V$ = 2726 Å$^3$, $Z$ = 4, $D_c$ = 2.068 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 58.26 cm$^{-1}$, $R$ = 0.053 and $R_w$ = 0.065 for 3060 reflections ($|F_0| > 3\sigma|F_0|$). **4**: $M$ = 687.0, tetragonal, space group $P4_12_12$ (No. 92), $a = b$ = 15.368(5), $c$ = 25.863(8) Å, $V$ = 6108 Å$^3$, $Z$ = 8, $D_c$ = 1.494 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 12.46 cm$^{-1}$, $R$ = 0.055 and $R_w$ = 0.066 for 2582 reflections ($|F_0| > 3\sigma|F_0|$). 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.

in **2** described here demonstrates a unique $\mu_3$ bridging coordination mode of this ligand, leading to the formation of a novel trimetallic sulphide cluster with a bent Ru–W–Ru array.

Another interesting feature observed in the structure of **2** is the presence of a $\mu_2$, $\eta^1$-$S_2$ ligand that bridges two Ru atoms. Although the detailed mechanism for the formation of this $S_2$ ligand from $WS_4^{2-}$ is not clear, it presumably results from the degradation of the Ru–S–$WS_2$–S–Ru moiety initially formed. Such a conversion of the coordinating $MS_4$ into the $S_2$ ligand is not yet a well demonstrated pathway for the preparation of disulphide complexes.[5] We have also found that the dinuclear $Ru^{III}$ complex with bridging thiolate ligands $[(\eta^5\text{-}C_5Me_5)RuCl(\mu\text{-}SPr^i)_2Ru(\eta^5\text{-}C_5Me_5)Cl]$ **3**, prepared from **1** and $Me_3SiSPr^i$,[6] reacts with an excess of $(NH_4)_2MS_4$ (M = W, Mo) in THF at reflux to give the disulphide complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}S_2)(\mu\text{-}SPr^i)_2Ru(\eta^5\text{-}C_5Me_5)]$ **4** in 8–12% yields;† see eqn. (2). The structure of **4** was also determined by X-ray crystallography (Fig. 2),‡ which has clearly shown the presence of the bridging $S_2$ ligand as in **2** together with two bridging thiolate ligands. The long Ru(1)–Ru(2) distance of 3.590(2) Å suggests the absence of a Ru–Ru bond. Despite the presence of two formal $Ru^{III}$ centres without any bonding interaction, **4** is essentially diamagnetic. This is indicative of the presence of the spin coupling through the $S_2$ ligand, as suggested by the substantially short Ru(1)–S(1) and Ru(2)–S(2) distances in **4**. Analogous ligand-based coupling mechanism involving S–Fe p$\pi$-d$\pi$ bonding in the $S_2$ ligand has been proposed previously for the relating $S_2$ complexes such as $[cpFe(\mu\text{-}S_2)(\mu\text{-}SEt)_2Fecp]$[7] and $[cpFe(\mu,\eta^2\text{-}S_2)(\mu,\eta^1\text{-}S_2)Fecp]$.[8]

Complex **4** can be prepared more readily by the reaction of **3** with an excess of $Li_2S_2$ in toluene at room temperature in 25% yield. By this procedure, the diruthenium complexes $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}S_2)(\mu\text{-}SR)_2Ru(\eta^5\text{-}C_5Me_5)]$ (**5**: R = $CH_2Ph$, **6**: $Bu^t$) were prepared analogously and characterised spectroscopically† as well as by X-ray analysis (for R = $CH_2Ph$). Details of the electrochemical properties and reactivities of the new sulphide clusters consisting of the $WRu_2S_6$ and $Ru_2S_2(SR)_2$ cores, as well as the X-ray data for **5**, obtained here will be reported in a subsequent paper.

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