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COMMUNICATION

THE FIRST $Mo_2Fe_2S_2$ CLUSTER COMPOUND WITH FUNCTIONALLY SUBSTITUTED CYCLOPENTADIENYL LIGAND. SYNTHESIS AND CRYSTAL STRUCTURE OF $(\eta^5\text{-}MeO_2CC_5H_4)_2(\mu_3\text{-}CO)_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6$

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Abstract—Reaction of $(\eta^5\text{-}MeO_2CC_5H_4)_2Mo_2(CO)_4$ with $(\mu\text{-}S_2)Fe_2(CO)_6$ in CH_2Cl_2 at room temperature gave the cluster compound $(\eta^5\text{-}MeO_2CC_5H_4)_2(\mu_3\text{-}CO)_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO_6)$, the structure of which was confirmed by X-ray diffraction analysis.

Molybdenum–iron–sulfur (Mo/Fe/S) clusters are of great interest because of their occurrence in nitrogenase[1] and their behaviour as models for catalytic hydrodesulfurization (HDS).[2–3] According to literature reports[4–6] two interesting isomeric $Mo_2Fe_2S_2$ clusters, the butterfly-shaped Mo_2Fe_2 cluster $(\eta^5\text{-}RC_5H_4)_2(CO)_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6$ and the planar Mo_2Fe_2 cluster $(\eta^5\text{-}RC_5H_4)_2(\mu\text{-}CO)_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6$ (R = H, Me) can be prepared from the corresponding metal–metal triply bonded compounds $(\eta^5\text{-}RC_5H_4)_2Mo_2(CO)_4$ and $(\mu\text{-}S_2)Fe_2(CO)_6$. In order to explore the effects of the electron-withdrawing substituents on the cyclopentadienyl ring and to prepare the new type of Mo/Fe/S clusters with functionally substituted cyclopentadienyl ligands, we undertook the study of the reaction between $(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4$ (R = EtO_2C, MeO_2C, MeCO; M = Mo, W) and $(\mu\text{-}S_2)Fe_2(CO)_6$. Herein we report the preliminary results of this kind of reaction, from which a new butterfly Mo_2Fe_2 cluster $(\eta^5\text{-}MeO_2CC_5H_4)_2(CO)_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6$ (**1**) was isolated and structurally determined by X-ray diffraction analysis. The compound is so far the first Mo/Fe/S cluster complex reported with functionally substituted cyclopentadienyl ligands.

Equimolar quantities of $(\eta^5\text{-}MeO_2CC_5H_4)_2Mo_2(CO)_4$ and $(\mu\text{-}S_2)Fe_2(CO)_6$ reacted in degassed CH_2Cl_2 at room temperature for 1 h. After removal of the solvent *in vacuo* the residue was separated by preparative TLC using CH_2Cl_2 as eluent. The first eluted red–brown band was $S_2Fe_3(CO)_9$ and the second red band $(\eta^5\text{-}MeO_2CC_5H_4)_2Mo_2(CO)_6$,[7] which were identified by comparison with authentic samples. The third dark-brown band was the bufferfly cluster **1**.[†] The IR spectrum of **1** shows several carbonyl absorptions, one at 1712.5 cm^{-1} attributed to the methoxycarbonyls, one at 1819.1 cm^{-1} to the carbonyls attached to the molybdenum atoms, the other four between 1958 cm^{-1} and 2049 cm^{-1} to the carbonyls attached to the iron atoms. It should be pointed out that the band at 1819.1 cm^{-1} is slightly higher than the corresponding bands at 1791 cm^{-1} and 1795 cm^{-1} in $(\eta^5\text{-}RC_5H_4)_2(CO)_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6$ (R = H, Me)[4,5] and at 1800 cm^{-1} in $(\eta^5\text{-}RC_5H_4)_2(\mu\text{-}CO)_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6$ (R = Me).[5,6] So, the two carbonyls attached to the molybdenum atoms in **1** are still typical of the bridging carbonyls. The ^1H NMR spectrum exhibits a singlet peak at

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[†] *Characterization data for* **1**: Yield 44.6%. M.p. 260°C(decomp.). ^1H NMR [$CDCl_3$, TMS, δ(ppm)]: 3.92 [s, 6H, 2(CH_3)]; 5.08 [t, 4H, 2(H_3, H_4)]; 6.04 [t, 4H, 2(H_2, H_5)]. IR (KBr): $\nu(C{=}O)$, 1712.5 s; $\nu(C{\equiv}O)$, 1819.1 s, 1958.6 s, 1983.2 s, 2032.4 s, 2048.8 s, cm^{-1}. Anal. Found: C, 31.6; H, 1.6. Calc. for $C_{22}H_{14}Fe_2Mo_2O_{12}S_2$: C, 31.5; H, 1.7%. EIMS: *m/z* (^{98}Mo) 400 [$S_2Fe_2Mo_2(CO)$, 0.9%].

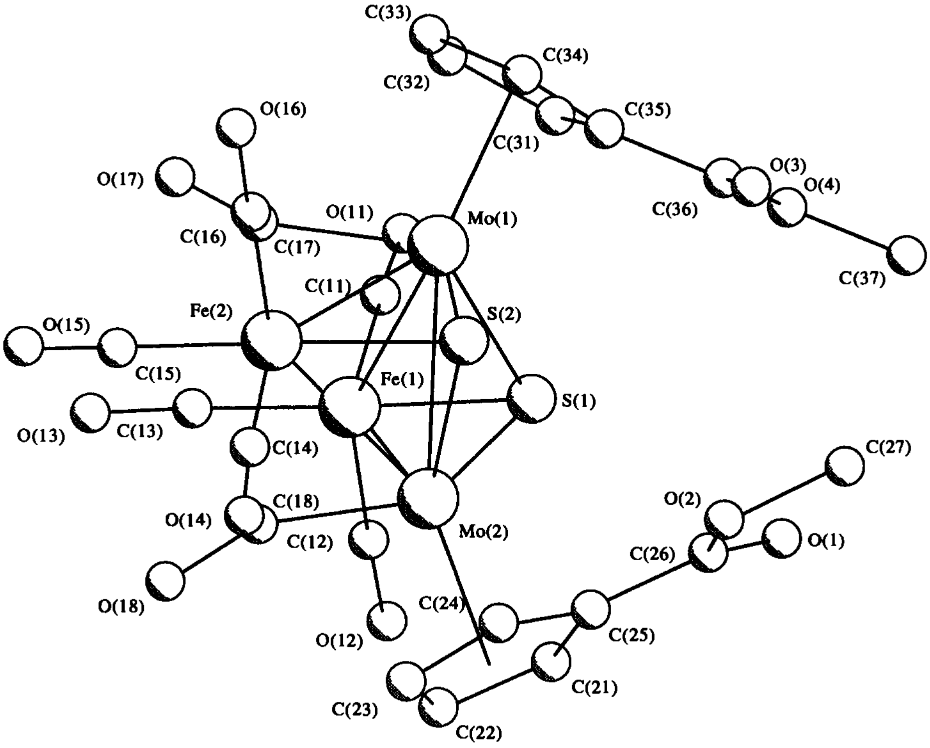

Fig. 1. The molecular structure of **1**. Selected bond lengths (Å) and angles (°): Mo(1)—Mo(2), 2.8615(7); Mo(1)—Fe(1), 2.811(1); Mo(1)—Fe(2), 2.814(1); Mo(1)—S(1), 2.344(2); Mo(2)—S(1), 2.337(2); Fe(1)—S(1), 2.183(3); Mo(1)—C(17), 2.01(1); Mo(2)—C(18), 1.98(1); C(17)···Fe(1), 2.699; C(17)···Fe(2), 2.642; C(18)···Fe(1), 2.612; C(18)···Fe(2), 2.658; Fe(1)···Fe(2), 3.931; Fe(1)—Mo(1)-Mo(2), 59.51(3); Fe(1)—Mo(2)—Mo(1), 59.35(3); Mo(1)—Fe(1)—Mo(2), 61.15(3); Fe(1)—Mo(1)—Fe(2), 88.70(3); Fe(1)—Mo(2)—Fe(2), 88.73(3); Mo(1)—C(17)—O(17), 158.6(9); Mo(2)—C(18)—O(18), 156.2(9).

3.92 ppm for methyl groups in the substituents and two triplets at 5.08 and 6.04 ppm which are assigned to $H_{3,4}$ and $H_{2,5}$ of the rings[7] respectively.

A dark-brown crystal of **1** suitable for X-ray diffraction was obtained from its THF solution at room temperature after one week. The X-ray diffraction analysis revealed that **1** has the structure shown in Fig. 1.* The four metal atoms Mo_2Fe_2 of this molecule are arranged as a butterfly-shaped skeleton with two molybdenum atoms in the hinge position. The butterfly angle and the Fe(1)—Fe(2) nonbonding distance are 108.61° and 3.931 Å, respectively. These values are slightly larger than 104.1° and 3.833(5) Å in $(\eta^5\text{-}RC_5H_4)_2(CO)_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6$ (R = H).[4] So the two $FeMo_2$ wings of **1** are more open. The two sulfur atoms are four-electron donors which are μ_3-bonded on each $FeMo_2$ wing. The two substituted cyclopentadienyls and two carbonyls coordinated to molybdenum atoms are *cis* with respect to the Mo—Mo bond. Since the distances of C(17)—Fe(1) (d_2), C(17)—Fe(2) (d_2) and C(17)—Mo(1) (d_1) are 2.699, 2.642 and 2.01(1) Å, respectively, the asymmetric parameters[8] α

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* *Crystal data for* **1**: $C_{22}H_{14}Fe_2Mo_2O_{12}S_2$; $M = 838.05$; crystal dimensions 0.2 × 0.3 × 0.2 mm, monoclinic, space group *Cc*, $a = 12.014(2)$, $b = 15.735(2)$, $c = 15.456(3)$ Å, $\beta = 112.87(1)°$, $V = 2692(2)$ Å^3, $Z = 4$, $D_x = 2.07$ g cm^{-3}. Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å), μ(Mo-$K\alpha$) = 21.56 cm^{-1}, $F(000) = 1640$. A total of 2033 independent reflections were collected in the range $2 \leqslant \theta \leqslant 23°$ with Mo-$K\alpha$ radiation by the $\omega - 2\theta$ scan mode, of which 1805 reflections were considered to be observed with $I \geqslant 3\sigma(I)$ and used in structure solution and refinement. The structure was solved by direct method and refined to $R = 0.036$ and $Rw = 0.042$. Atomic coordinates, thermal parameters and structure factor tables have been deposited at the Cambridge Crystallographic Data Centre.

($\alpha = (d_2 - d_1)/d_1$) of the bridging carbonyl C(17)—O(17) are 0.34 and 0.31. These parameters are smaller than the corresponding 0.38 and 0.39 in $(\eta^5\text{-RC}_5\text{H}_4)_2(\text{CO})_2\text{Mo}_2\text{Fe}_2(\mu_3\text{-S})_2(\text{CO})_6$ (R = H).[4] The other carbonyl C(18)—O(18) is similar to C(17)—O(17). Hence, the two carbonyls attached to the molybdenum atoms are reasonably assigned to be μ_3-coordinated. So, the formula of this molecule may be written as $(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)_2(\mu_3\text{-CO})_2\text{Mo}_2\text{Fe}_2(\mu_3\text{-S})_2(\text{CO})_6$.

The electron-withdrawing group on the cyclopentadienyl ring appears to influence the reaction of the Mo≡Mo compound with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$. Thus, although the butterfly Mo_2Fe_2 cluster was formed and its structural data are little changed, the isomeric planar Mo_2Fe_2 cluster was not found. The detailed influence of the electron-withdrawing group towards the reaction and the functional transformation of the methoxycarbonyl group are under investigation.

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