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Synthesis and Crystal Structure of a Novel Octahedral Fe_4Cr_2 Transition Metal Cluster Complex $Cp_2Cr_2Fe_4(CO)_{12}(\mu_6\text{-}O)$†

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Reaction of $Cp(OC)_2Cr{\equiv}S{\equiv}Cr(CO)_2Cp$ with $Fe_3(CO)_{12}$ affords an encapsulated μ_6-O octahedral Fe_4Cr_2 cluster complex $Cp_2Cr_2Fe_4(CO)_{12}(\mu_6\text{-}O)$, whose crystal structure is determined by X-ray diffraction analysis.

Since the 1970s there has been growing interest in transition metal cluster complexes, mainly because of their potential applications such as in catalysis and because of the novelty and versatility of their properties and structures.[1,2] Recently, as part of our project concerning the rational synthesis of mixed transition metal clusters,[3–5] we began a study of the reaction of triply-bonded complex $Cp(OC)_2Cr{\equiv}S{\equiv}Cr(CO)_2Cp$ with $Fe_3(CO)_{12}$ and now report the results obtained.

We found that the complex $Cp(OC)_2Cr{\equiv}S{\equiv}Cr(CO)_2Cp$ reacted with an excess of $Fe_3(CO)_{12}$ in THF at reflux under nitrogen to give, after TLC separation in air, the cluster complex $Cp_2Cr_2Fe_4(CO)_{12}(\mu_6\text{-}O)$. The combustion analysis of **1** is consistent with its constitutional formula and the IR spectrum showed four strong absorption bands in the range 1944–2011 cm^{-1}, characteristic of terminal carbonyls. In addition, the ^1H NMR spectrum displayed a singlet at δ 5.56 characteristic of Cp rings.

In order further to establish its structure, a single-crystal X-ray diffraction analysis was undertaken. Fig. 1 shows the molecular structure and Table 1 lists selected bond lengths and angles. This molecule consists of a closed octahedral Fe_4Cr_2 cluster core with an encapsulated oxygen atom; furthermore each Cr atom of the cluster core is bonded to one Cp ligand, whereas each Fe atom is bonded to three CO ligands. The encapsulated O atom is coplanar with Fe(1)Fe(2)Fe(3)Fe(4) and located in the center of the octahedral cluster core. As seen in Table 1, the distances from O to Cr(1) and Cr(2) are 1.94(1) and 1.97(1) Å, which is close to the O–Cr bond length [average 1.93(1) Å] in the cubane-like cluster $Cp_4Cr_4(\mu_3\text{-}O)_2(\mu_3\text{-}Se)_2$.[6]

Table 1 Selected bond lengths (Å) and angles (°) in complex **1**

Fe(1)–Fe(4)	2.700(3)	Fe(1)–Fe(3)	2.715(3)
Fe(2)–Fe(4)	2.695(3)	Fe(2)–Fe(3)	2.710(3)
Fe(1)–Cr(1)	2.635(3)	Fe(2)–Cr(1)	2.632(3)
Fe(3)–Cr(2)	2.599(3)	Fe(4)–Cr(2)	2.639(3)
Fe(1)–O	1.91(1)	Fe(2)–O	1.92(1)
Fe(3)–O	1.91(1)	Fe(4)–O	1.90(1)
Cr(1)–O	1.94(1)	Cr(2)–O	1.97(1)
Fe(1)–Cr(2)	2.828(3)	Fe(2)–Cr(2)	2.828(3)
Fe(3)-Cr(1)	2.832(3)	Fe(4)–Cr(1)	2.821(3)
Fe(4)–Fe(1)–Fe(3)	88.9(1)	O–Cr(1)–Fe(1)	46.3(3)
Fe(2)–Fe(3)–Fe(1)	89.4(1)	Fe(2)–Cr(1)–Fe(1)	92.9(1)
Fe(4)–Fe(2)–Fe(3)	89.1(1)	O–Cr(2)–Fe(3)	47.0(3)
Fe(2)–Fe(4)– Fe(1)	90.0(1)	Fe(1)–O–Fe(3)	90.6(5)
Fe(1)–O–Fe(2)	172.7(8)	Fe(1)–O–Cr(1)	86.5(5)
Fe(1)–O–Cr(2)	93.8(6)	Fe(3)–Cr(2)–Fe(2)	59.73(8)

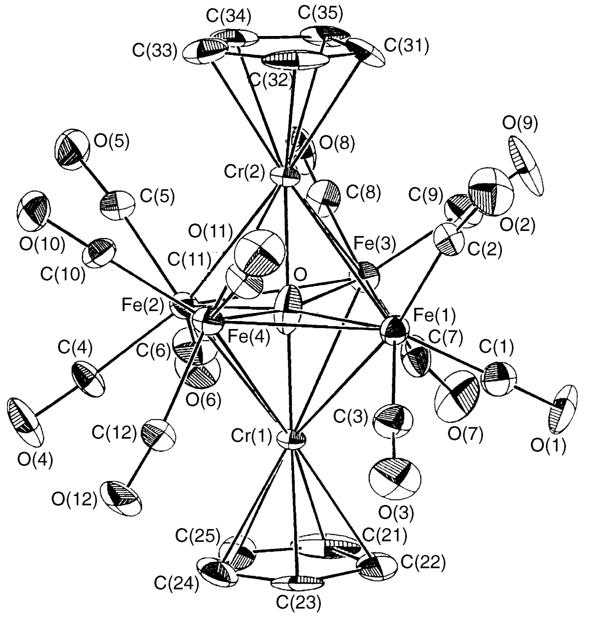

Fig. 1 Structure of compound **1**

The bond lengths O–Fe(1) 1.91(1), O–Fe(2) 1.92(1), O–Fe(3) 1.91(1) and O–Fe(4) 1.90(1) Å are almost the same, and similar with that 1.936(3) Å in $MeO_2CC_5H_4(OC)_2MoFe_2(\mu_3\text{-}O)(\mu\text{-}Bu^tS)Fe_2(CO)_6$.[7] The distances from Cr(1) to Fe(1) and Fe(2), 2.635(3) and 2.632(3) Å, and from Cr(2) to Fe(3) and Fe(4), 2.599(3) and 2.639(3) Å, are obviously shorter than that [2.901(1) Å] in $Cp(OC)_3CrFe(CO)_2Cp$,[8] but those from Cr(1) to Fe(3) and Fe(4), 2.832(3) and 2.821(3) Å and from Cr(2) to Fe(1) and Fe(2), 2.828(3) and 2.828(3) Å, are close to that in $Cp(OC)_3CrFe(CO)_2Cp$.[8] In addition, the average Cr–Fe bond distance of 2.727(3) Å in complex **1** is more close to that {2.762(3) Å in $Cp_2Cr_2Fe_2(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2(CO)_6$ prepared from $Fe_2(CO)_6S_2$ and $[(CpCr(CO)_3]_2]$}.[9] It is also can be seen that the distances Fe(1)–Fe(3), Fe(2)–Fe(3), Fe(2)–Fe(4) and Fe(1)–Fe(4) are between 2.695(3) and 2.715(3) Å, which is much longer than those of Fe–Fe [2.576(4), 2.566(4) Å] in $[(\mu\text{-}EtS)Fe_2(CO)_6]_2(\mu_4\text{-}Se)$.[10] In the four-membered ring Fe(1)Fe(2)Fe(3)Fe(4) the four internal angles are all close to 90°, so it is almost square. In addition, since the dihedral angles between, Fe(1)-through-Fe(4) and C(21)-through-C(25), between Fe(1)-through-Fe(4) and C(31)-through-C(35) and between C(21)-through-C(25) and C(31)-through-C(35) are 0.64, 2.56 and 1.95° respectively; these three planes are approximately parallel to each other.

Finally, it is worth noting that (i) this octahedral Fe_4Cr_2 cluster core with an encapsulated oxygen atom, to our knowledge, is unprecedented. (ii) The encapsulated oxygen atom coordinated to six transition metals in a μ_6 high

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coordination mode is very rare. So far, to our knowledge, only one such case is known, in which the encapsulated μ_6-O is coordinated to six Mo atoms in a complex anion.[11] (iii) The μ_6-O atom in cluster **1** is probably derived from air during the course of TLC separation. However, the mechanism for production of **1** requires further study.

Experimental

The reaction was carried out under nitrogen. $Cp(CO)_2Cr{\equiv}S{\equiv}Cr(CO)_2Cp$[12] and $Fe_3(CO)_{12}$[13] were prepared according to literature methods. IR and ^{1}H NMR spectra were recorded on a Nicolet FT-IR 5DX and a JEOL FX 90Q spectrometer. Elemental analyses and the melting point were determined using a Yanaco CHN MT-3 analyzer and Yanako MP-500 instrument, respectively.

Preparation of Complex **1**.—A 100 ml three-necked flask fitted with a magnetic stir-bar, a rubber septum, and a reflux condenser topped with a nitrogen inlet tube was charged with $Cp(CO)_2Cr{\equiv}S{\equiv}Cr(CO)_2Cp$ (0.5 g, 1.32 mmol), $Fe_3(CO)_{12}$ (1.78 g, 3.52 mmol) and THF (40 ml). The mixture was stirred for 5 h. Solvent was removed at reduced pressure and the residue extracted with CH_2Cl_2. The extracts were subjected to TLC separation using light petroleum as eluent to give complex **1** as a black solid, yield 5.4%, mp 132°C (decomp.), $\tilde{\nu}_{max}/cm^{-1}$ 2011, 1984, 1954, 1944 ($C{\equiv}O$). $\delta_H(CDCl_3)$ 5.56 (s, 10 H, $2C_5H_5$) (Found: C, 32.54; H, 1.42. $C_{22}H_{10}Cr_2Fe_4O_{13}$ requires C, 32.64; H, 1.24%).

Crystal Structure Analysis of Complex **1**.— The single crystals of **1** were obtained by slow evaporation of its CH_2Cl_2–hexane solution at −20 °C. A single crystal suitable for X-ray diffraction analysis was mounted on an Enraf Nonius CAD4 diffractometer equipped with a graphite monochromator and Mo-Kα (λ 0.71069 Å) radiation. A total of 5631 independent reflections were collected at 23 °C by the ω–2θ scan mode, of which 3190 with $I \geq 4\sigma(I)$ were considered observed and used in subsequent refinement. The structure was solved by a direct phase determination method (MULTAN 82). The final refinement was accomplished by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms. All calculations were performed on a MICRO-VAX II computer using the TEXSAN program system.

Crystal Data.—$C_{22}H_{14}Cr_2Fe_4O_{15}$, $M = 845.72$, monoclinic, space group, $P2_1/c$ (no. 14), $\alpha = 11,253(4)$, $b = 15.179(3)$, $c = 17.942(5)$ Å, $\beta = 92.70(2)°$, $V = 3061(1)$ Å^3, $Z = 4$, $D_c = 1.835$ Mg m^{-3}), $\mu = 2.581$ mm^{-1}, $F(001) = 1672$, $T = 296$ K, $R = 0.089$, measured reflections 5993, independent reflections 5631, $R_{int} = 0.022$. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research (S)*, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 423/22.

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