Synthesis of clusters containing the OsCoMoS core

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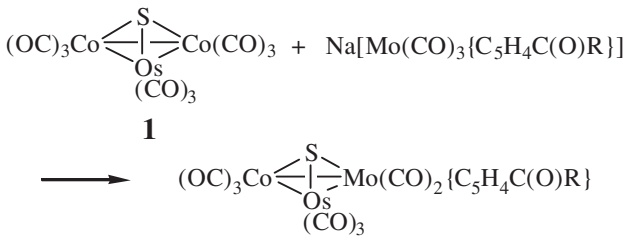
Several new chiral tetrahedral clusters containing the OsCoMoS core were synthesised by the thermal reaction of the precursor [(μ_3-S)$OsCo_2(CO)_9$] with the functionally-substituted metal exchange reagents [$Mo(CO)_3(C_5H_4)R$][(R=CHO, $C(O)CH_3$, $C(O)C_6H_4$-1,4-CO_2Me)]. The structure of cluster [(μ_3-S)$OsCoW(CO)_8C_5H_4C(O)CH_3$] was established by X-ray single crystal diffraction.

Keywords: osmium cluster, chiral tetrahedron, crystal structure

Organo-complexes of the transition elements with metal–metal bonds between the same or different elements have been known for many years,[1] and in recent times new compounds of his class have been reported in rapidly increasing numbers. Although complexes containing an S or Se capping atom are relatively common,[2,3] it is far rarer to find chiral tetrahedral clusters containing an Os atom such as those reported here. The reactivity of many of these species is proving to be particularly interesting. Mixed-metal compounds may be particularly important in this respect since bonds between dissimilar metal atoms could change the reactivity pattern. If this concept is to be tested, new rational syntheses of di-, tri- and poly- heteronuclear metal compounds are required. In recent years the structural and bonding aspects of mixed-metal tetrahedral skeleton clusters have been extensively studied,[4-5] especially the chiral tetrahedral clusters containing four different atoms at the vertices of the tetrahedron because chiral clusters have a potential to induce asymmetric catalysis. Recently we have described the synthesis and structure of chiral clusters containing the cores MoFeCoS and MoRuCoS.[6-7] Here we wish to report the novel chiral clusters $[OsCoMo(CO)_8(\mu_3\text{-}S)\ (\eta^5\text{–}C_5H_4R)]$ [R=CHO, $C(O)CH_3$, $C(O)C_6H_4$–1,4–CO_2Me],which have been obtained from the reaction of $[OsCO_2(CO)_9(\mu_3\text{-}S)]$ with $[Mo(CO)_3(C_5H_4)R]$ in refluxing THF (Scheme 1). The clusters $[OsCoMo(CO)_8(\mu_3\text{-}S)\ (\eta^5\text{–}C_5H_4R)]$ form air-stable black crystals and are soluble in polar solvents. Satisfactory C, H analyses were obtained.

All clusters have been characterised by elemental analysis, IR and ^{1}H-NMR spectra. Their structures, as presented in Fig.1 containing the chiral tetrahedral skeleton SosCoMo, core have been proved by an X-ray structure of **4** as below. All clusters showed a large number of strong terminal carbonyl absorption bands at 2079–1849 cm^{-1} in their IR spectra. The higher absorption bands were attributed to CO coordinating Co and Os atoms and the other S to Co on the Mo atom. The IR spectra of **2**–**4** showed corresponding C=O absorptions at 1694 cm^{-1} in **2**, 1723 cm^{-1} in **3**, 1722cm^{-1} in **4** and the IR spectrumn of **4** has an other absorption band at 1657cm^{-1} attributed to ester C=O. For the ^{1}H NMR assignments of the clusters **2–4**, proton chemical shifts of the substituted cyclopentadienyl groups appeared downfield than the unsubstituted cyclopentadienyl, since formyl, acetyl and ester carbonyl are well known electron-withdrawing groups. All protons in the cyclopentadiedyl groups are non-equivalent, their ^{1}H NMR spectra showed four singlets at 5.70–5.94 for cluster **2**, at 5.61-5.99ppm for cluster **3**, and at 5.66–6.07 for cluster **4**, one part reason may be the chirality of the cluster skeleton. The chemical shift of **2** at 9.70 was attributed to protons in formyl and the singlet at 2.41 in **3** attributed to protons in acetyl. The resonance at 7.85–7.89 and 8.16 was attributed to protons in the benzene ring and at 2.64 was attributed to protons in acetyl in **4**.



R=H **2**, CH_3 **3**, $C_6H_4C(O)OCH_3$ **4**

Scheme 1 Formation of clusters 2, 3 and 4.

Os(1)–S(1) 2.336(5); Mo(1)–S(1) 2.408(5); Co(1)–S(1) 2.185(6); Os(1)–Co(1) 2.630(3); Os(1)–Mo(1) 866(2); Mo(1)–Co(1) 2.737(3); S(1)–Os(1)–Co(1) 51.80(14); S(1)–Os(1)–Mo(1) 54.01(13); Co(1)–Os(1)–Mo(1) 59.54(7); S(1)–Mo(1)–Co(1) 49.77(14); S(1)–Mo(1)–Os(1) 51.69(11); Co(1)–Mo(1)–Os(1) 55.95(6); S(1)–Co(1)–Os(1) 57.13(14); S(1)–Co(1)–Mo(1) 57.29(15); Os(1)–Co(1)–Mo(1) 64.51(8); Os(1)–S(1)–Mo(1) 74.31(14); Co(1)–S(1)–Mo(1) 72.95(17); Co(1)–S(1)–Os(1) 71.07(15)

Crystals of **4** suitable for diffraction analysis were grown from a solution in CH_2Cl_2/hexane (1:4) solvent mixture at –18°C. The data crystals were mounted on a glass fibre. All measurements were made on a Bruker CCD-APEX diffractormeter with graphite monochromated Mo–Kα (λ = 0.71073 Å) radiation.

All the data were collected at a temperature of 20±1°C using the ω–2θ scan technique. The calculations were performed using the SHELXTL-97 crystallographic software package.

As shown in Fig.1**,** cluster **4** consists of a distorted tetrahedral core MoOsCoS, which carries three carbonyls on the Os atom, three carbonyls on the Co atom and two carbonyls and one cyclopentadienyl ligand attached to the Mo atom. The averaged distance from the Mo atom to the Cp ring center is 2.30(15) Å. The capping S atom is bonded to Os, Co and Mo with bond lengths of 2.336(5)Å, 2.185(6)Å and 2.408(5)Å respectively. The acute angles in the tetrahedral core of cluster **4** about the basal atoms range from 49.86° to 66.19°, and those about the sulfur atom average 72.25°, which deviate considerably from perfect tetrahedral geometry. This is because the metal–metal bonded OsCoMo triangle restricts the angles around the sulfur atom. The angles of C(1)–Os–C(2), C(2)–Os–C(3) and C(1)–Os–C(3) are 93.8(8) °, 91.8(8) ° and 93.1(8) ° respectively, so the carbonyls on the Os atom are vertical with respect to each other.

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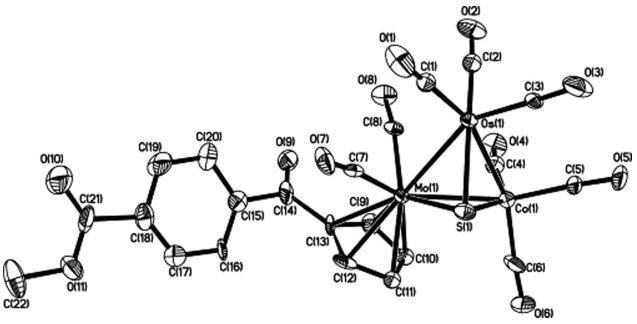

Fig.1 Molecular structure of cluster **4**. Selected bond distances (Å) and angles (°).

Experimental

All reactions were carried out under a highly pure dinitrogen atmosphere using standard Schlenk and vacuum techniques. Petroleum ether was distilled over sodium-benzophenone while CH_2Cl_2 was distilled over CaH_2. Column chromatography was carried out using 160–200 mesh silica gel. [$Mo(CO)_6$] was purchased from Fluka Chem.Co. IR spectra were recorded on a Nicolet FT-IR 10 DX spectrometer; ^{1}H NMR spectra on a Bruker AM-400 MHz spectrometer; analyses(C, H) were performed on an 1106-type analyzer

Preparation of cluster **2**: $Mo(CO)_6$ 0.11g (0.44mmol) was added to a solution of sodium formylcyclopentadienyl (0.13g, 1.1mmol) in THF (30ml). The mixture was refluxed for 14h and cooled to room temperature. Then cluster **1** 0.25g (0.42mmol) was added and then the mixture was stirred at 60°C for 4h. The solvent was removed under vacuum, the residue was extracted with the minimum amount of CH_2Cl_2 and the products were chromatographed on a 2.5×40cm silica gel column using CH_2Cl_2/hexane (2:1) as eluent. The purple-red band was the main product, the rest were unreacted material and slight by-product (uncharacterised). After solvent was removed under vacuum, the black solid cluster **2** was obtained (0.14g, yield 48.5%). Anal. calcd for **2** $C_{14}H_5O_9OsCoMoS$: C, 24.08; H, 0.72%. Found: C, 24.23; H, 0.75%. IR (KBr disk):(υCO) 2078s, 2039s 1989s, 1973s, 1896mcm^{-1}; (CHO) 1692 s cm^{-1}. ^{1}H NMR (TMS, $CDCl_3$) δ5.69, 5.79, 5.83, 5.94 (q, 4H, C_5H_4); δ9.68 (s, 1H, CHO).

Preparation of cluster **3**: The workup for **3** was similar to that of the preparation of cluster **2**. 0.14g (1.1mmol) $NaCpC(O)CH_3$ was used. The cluster **3** was obtained (0.16g, yield 52.3%). Anal. calcd for **3** $C_{15}H_7O_9OsCoMoS$: C, 25.29H,0.99%. Found: C, 24.35%; H, 1.11%. IR (KBr disk): (υCO) 2082s, 2042s, 1998scm^{-1}; (C=O) 1684cm^{-1}. ^{1}H NMR (TMS, $CDCl_3$) δ5.60, 5.64, 5.85, 5.99 (q, 4H, C_5H_4); 2.41 (s, 3H, CH_3).

Preparation of cluster **4**: The workup for **4** was similar to that of the preparation of cluster **2**. 0.28g (1.1mmol) $NaCpC(O)C_6H_4C(O)OCH_3$ was used. The cluster **4** was obtained (0.15g, yield 42.8%). Anal. calcd for **4** $C_{22}H_{11}O_{11}OsCoMoS$: C, 31.74%; H, 1.33%. Found: C, 31.85%; H, 1.38%. IR(KBr disk): (υCO)2083, 2042, 1996cm^{-1}; (C=O) 1684, 1722cm^{-1}; (C_6H_4) 2952w, 2924w, 2851w cm^{-1}. ^{1}H NMR (TMS, $CDCl_3$) δ5.66, 5.73, 5.96, 6.07 (q, 4H, C_5H_4); 2.64 (s, 3H, CH_3); δ7.85, 7.89, 8.16(t, 4H C_6H_4).

Crystal data for **4**: Empirical formula: C_{22} H_{11} Co Mo O_{11} Os S M r = 828.44 Crystal size 0.25 × 0.20 x 0.20 mm; Crystal system Triclinic; space group P-1; a=8.014(6) (Å), α=88.584(11) (°); b= 8.108(6) (Å), β= 87.213(12) (°). c=19.370(14) (Å) γ=71.253(12) (°). V=1190.4(15) A^3 ; Z=2; Dc= 2.311 g/cm^3; μ=6.680 mm^{-1}; F(000) = 784.

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References

1 H. Vahrenkamp, *Adv. Organomet. Chem.,* 1983 **22** 169.
2 F.G.A. Stone, *Angew. Chem. Int. Engl.,* 1984 **23** 89.
3 M.L. Ziegler, H.P. Neumann, *Chem. Ber*., 1989 **112** 115.
4 T. Albiez, H. Bantel, H. Vahrenkamp, *Chem. Ber*., 1990, **123**, 1805.
5 R.C. Lin, Y. Chi, S.M. Peng, G.H. Li, *Inorg. Chem*., 1992, **31**, 3818.
6 E.R.Ding, S.L.Wu, C.G.Xia, Y.Q.Yin, *J.Organomet.Chem.,* 1998 **568**, 157.
7 E.R.Ding, Q.S.Li, Y.Q.Yin and J.S, *J.Chem.Res*., 1998, 624.