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Synthesis and characterization of chiral $(\mu_3\text{-S})FeCoM(CO)_8(RCp)$ [M = Mo, W; R = $C_6H_5C(O)$, $CH_3OC(O)C_6H_4C(O)$] clusters and the crystal structures of $(\mu_3\text{-S})FeCoMo(CO)_8[CH_3OC(O)C_6H_4C(O)Cp]$ and $(\mu_3\text{-S})FeCoW(CO)_8[CH_3OC(O)C_6H_4C(O)Cp]$

Er-Run Ding,[a] Sheng-Ming Liu,[a] Yuan-Qi Yin[a]* and Jie Sun[b]

[a] Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, P.R. China

[b] Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai 200032, P.R. China

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Abstract—Several chiral cluster derivatives $[(\mu_3\text{-S})FeCoM(CO)_8(RCp)]$ [M = Mo, R = $C_6H_5C(O)$ (**2**); M = Mo, R = $CH_3OC(O)C_6H_4C(O)$ (**3**); M = W, R = $C_6H_5C(O)$ (**4**), M = W, R = $CH_3OC(O)C_6H_4C(O)$ (**5**)] were synthesized by the thermal reaction of $(\mu_3\text{-S})FeCo_2(CO)_9$ (**1**) with the functionally substituted cyclopentadienyl tricarbonyl metal complex anions $[M(CO)_3RC(O)Cp]^-$ without using benzophenone ketyl to initiate the reaction. The cluster (**2**) reacted with $NaBH_4$ in MeOH gave the secondary alcohol cluster $(\mu_3\text{-S})FeCoMo(CO)_8C_6H_5CH(OH)Cp$. These clusters were characterized by C/H analysis, IR, ^1H NMR, ^{13}C NMR and MS. The results showed that the metal fragment $Co(CO)_3$ in $(\mu_3\text{-S})FeCo_2(CO)_9$ could be exchanged by $M(CO)_2RC(O)Cp$. The structures of $(\mu_3\text{-S})FeCoMo[CH_3O(O)C_6H_4C(O)Cp]$ (**4**) and $(\mu_3\text{-S})FeCoW(CO)_8[CH_3OC(O)C_6H_4C(O)Cp]$ (**5**) were determined by single crystal X-ray diffraction. © 1997 Elsevier Science Ltd

Keywords: crystal structures; iron; cobalt; sulfur; chiralty; cluster complexes.

Since the first transition metal carbonyls were discovered by Schutzenberger [1] and by Mond [2] in the nineteenth century, a great amount of work has been carried out and numerous research papers and reviews are already available in this field of inorganic chemistry [3,4]. Metal cluster compounds can be regarded as intermediate between coordination complexes and bulk metal surface of metals during heterogeneous catalytic processes [5]. Cluster catalysis has become an area of major interest and applies to homogeneous, heterogenized, or heterogeneous processes [6]. A number of tests have been suggested as criteria for catalysis by intact clusters, which was required by the classical question of cluster fragmentation under the catalytic conditions, particularly if high temperatures and pressures are employed. Efforts have thus been made to stabilize cluster framework by using capping ligands (e.g. S, PR). Although there is good indication for catalysis by intact clusters in a few cases, the strongest evidence would be provided by asymmetric catalysis induced by a cluster which contains a chiral metal framework. Considerable efforts have been directed towards the synthesis of chiral tetrahedral clusters consisting of four different atoms at the vertices of the tetrahedron. The first examples of such optically active clusters were provided with $[FeCoM(\mu_3\text{-S})Cp(CO)_8]$ (M = Cr, Mo, W) [7].

Recently we have described the syntheses and structures of some clusters containing a chiral tetrahedral core: $(\mu_3\text{-}CC_6H_5)FeCoMo(CO)_8RC(O)Cp$ (R = H, CH_3, C_2H_5O) [8]. Here we report the reaction of the prochiral cluster $(\mu_3\text{-S})FeCo_2(CO)_9$ (**1**) with the new metal exchange reagents $Na[M(CO)_3CpC(O)R]$ [M = Mo, W; R = C_6H_5, $CH_3OC(O)C_6H_4$]. The crystal structures of the clusters $(\mu_3\text{-S})FeCoM(CO)_8$

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* Author to whom correspondence should be addressed.

$CpC(O)C_6H_4C(O)OCH_3$ [M = Mo (**4**), M = W (**5**)] were determined by X-ray diffraction. The cluster (μ_3-S) $FeCoMo(CO)_8CpC(O)C_6H_5$ (**2**) reacted with $NaBH_4$ in MeOH gave the secondary alcohol cluster (**6**).

EXPERIMENTAL

All operations were carried out under nitrogen using standard Schlenck and vacuum line techniques. The solvents were treated by the usual method for preparing anhydrous and deoxygenated solvents. Column chromatography was carried out using 160–200 mesh silica gel. $Mo(CO)_6$, $W(CO)_6$ were purchased from Fluka and Aldrich Chem. Co. $S_2Fe_2(CO)_6$ [10], $Co_2(CO)_8$ [9], RCpNa [R = $C_6H_5C(O)$, $CH_3OC(O)C_6H_4C(O)$] [11] and (μ_3-S)$FeCo_2(CO)_9$ [12] were prepared according to the literature. IR spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer, ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Am 300 MHz spectrometer; C/H analyses and MS determination were performed on a 1106-type analyzer and Finnigan MAT 8430 (FAB) of HP 5988 (EI).

Preparation of cluster (**2**)

In a 50 cm^3 three-neck flask equipped with nitrogen inlet were placed 203 mg (1.0 mmol) $NaCpC(O)C_6H_5$, 264 mg (0.1 mmol) $Mo(CO)_6$ and 20 cm^3 THF. The mixture was refluxed for 12 h, then, the cluster (**1**) 532 mg (1.0 mmol) was added. The mixture was refluxed for 2 h and the residue was extracted by CH_2Cl_2 and chromatographed on a 2.5 × 20 cm silica gel column using CH_2Cl_2/hexane eluent. Products were recrystallized from CH_2Cl_2 at $-18°C$. Yield: 284 mg (44.65%). Found: C, 37.7; H, 1.4. Calc. for $FeCoMoSC_{20}H_9O_9$: C, 37.7; H, 1.4%. IR (KBr disk) ν(CO) 2077vs, 2032vs, 1890m, (cm^{-1}); ν(C=O) 1654m, (cm^{-1}). ^1H NMR ($CDCl_3$) δ 5.30–6.04 (q, 4H, C_5H_4), δ 7.48–7.80 (s, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 93.74, 96.54, 96.82, 97.72 (Cp); δ 129.57, 129.90, 134.11 (C_6H_5); δ 183.02 (C=O); δ 207.55 (*t*-CO).

Preparation of cluster (**3**)

To the flask described above were added 352 mg (1.0 mmol) $W(CO)_6$, 203 mg (1.0 mmol) $NaCpC(O)C_6H_5$ and 20 cm^3 diglyme. The mixture was refluxed for 4 h. After the solvent was evaporated in reduced pressure, 20 cm^3 of THF and 503 mg (1.0 mmol) (μ_3-S)$FeCo_2(CO)_9$ were added. The solution was heated to reflux for 2 h, the solvent was removed and the residue purified by silica gel column by using the mixture of hexane and CH_2Cl_2 (1 : 1) to give the main black product (**3**) 290 mg (40%). Found: C, 33.2; H, 1.2. Calc. for $FeCoWSC_{20}H_9O_9$: C, 33.1; H, 1.2%. IR (KBr disk) ν(CO) 2079vs, 2031vs, 1891s, (cm^{-1}). ν(C=O) 1658m, (cm^{-1}). ^1H NMR ($CDCl_3$): δ 5.26–6.01 (q, 4H, C_5H_4), δ 7.34–7.48 (s, 5H, C_6H_5).

Preparation of cluster (**4**)

The mixture of $Mo(CO)_6$ 264 mg (1.0 mmol) and 239 mg (1.0 mmol) $NaCpC(O)C_6H_4C(O)OCH_3$ were dissolved in 20 cm^3 THF. The workup was just similar as that of preparation of cluster (**2**). The main product of cluster (**4**) as a red solid was obtained. Found: C, 38.1; H, 1.5. Calc. for $FeCoMoSC_{22}H_{11}O_{11}$: C, 38.0; H, 1.6%. IR (KBr disk) ν(CO) 2083s, 2045vs, 2039s, 2007s, 1982s, 1939m, 1911m, 1860, (cm^{-1}); ν(C=O) 1723s, 1652m (cm^{-1}). ^1H NMR ($CDCl_3$): δ 3.96 (s, 3H, CH_3), δ 5.58–6.04 (q, 4H, C_5H_4), δ 7.82–8.17 (q, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$) 52.61 (CH_3); 91.84, 94.31, 94.77, 95.86, 99.65 (C_5H_4), 128.14, 130.01, 133.84, 141.07(C_6H_4); 166.06, 189.09 (2C=O); 210 (*t*-CO). MS(FAB Mo^{97}) 696 (M^+ + 1), 611 (M^+-3CO), 583 (M^+-4CO), 555 (M^+-5CO), 527 (M^+-6CO), 499 (M^+-7CO), 471 (M^+-8CO).

Preparation of cluster (**5**)

The mixture of $W(CO)_6$ 352 mg (1.0 mmol) and 239 mg (1.0 mmol)$NaCpC(O)C_6H_4C(O)OCH_3$ were dissolved in 20 cm^3 diglyme. The workup was just similar as that of preparation cluster (**3**). The main product of cluster (**5**) as a red solid was obtained. Found: C, 33.6; H, 1.4. Calc. for $FeCoMoSC_{22}H_{11}O_{11}$: C, 33.8; H, 1.4%. IR (KBr disk) ν(CO) 2.79s, 2033vs, 2007vs, 1987s, 1978s, 1932w,m, 1902w,m, 1855m (cm^{-1}); ν(C=O) 1723vs, 1654m (cm^{-1}). ^1H NMR($CDCl_3$) δ 3.90 (s, 3H, CH_3), δ 5.73–5.99 (q, 4H, C_5H_4), δ 7.77–8.12 (q, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$) δ 52.60 (CH_3), δ 88.11, 90.69, 93.79, 94.20, 96.69 (C_5H_4); δ 128.14, 130.14, 134.07, 140.91 (C_6H_4); δ 166.03, 188.30 (2C=O); δ 210.04 (*t*-CO).

Reaction of cluster (**2**) *with* $NaBH_4$

To the flask described above was added 63.8 mg (0.1 mmol) of cluster (**2**), 7.6 mg (0.2 mmol) of $NaBH_4$, and 8 cm^3 MeOH. The mixture was stirred at room temperature for 9 h. Solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2. The extracts were concentrated and subjected to chromatographic separation on silica column. 52 mg (81%) of cluster (**6**) as a brown-red solid was given. Found: C, 37.5; H, 1.7. Calc. for cluster (**6**): C, 37.6; H, 1.7%. IR (KBr disk) ν(OH) 3378w; ν(CO) 2073vs, 2015vs, 1891w,m. ^1H NMR ($CDCl_3$) δ 1.91 (w, 1H, OH), δ 5.29–5.73 (q, 4H, C_5H_4), δ 7.41 (s, 5H, C_6H_5).

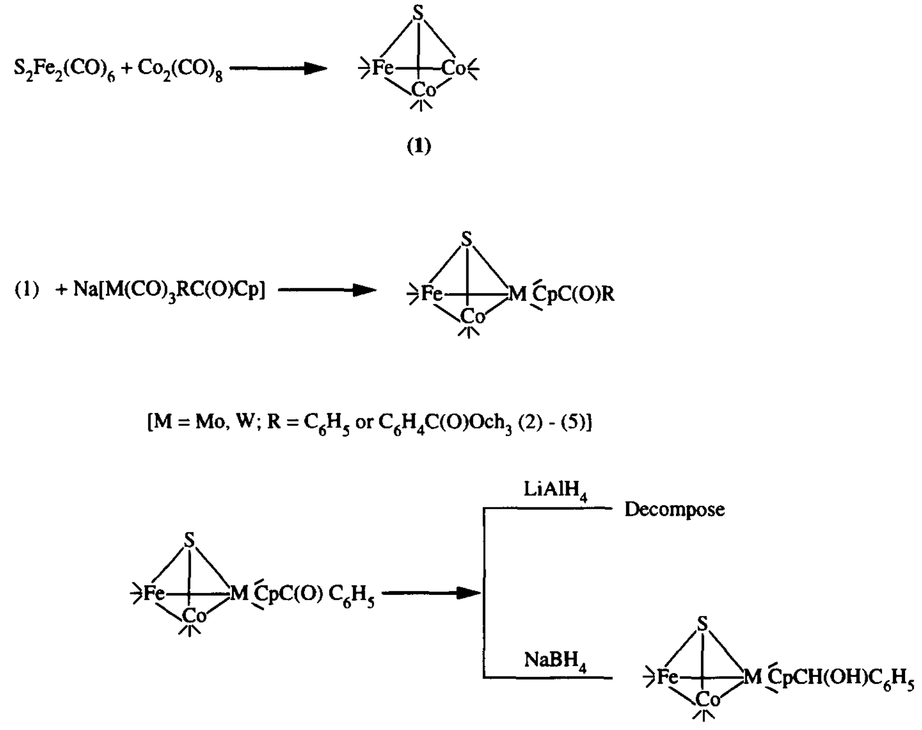
Crystallography of cluster (**4**) *and cluster* (**5**)

A suitable crystal of each compound was chosen and mounted on a glass fibre tip onto a goniometer. Single-crystal X-ray diffraction data were collected on a Rigaku AFC7R diffractometer with graphic monochromatic Mo-K_α (λ = 0.71069 Å) radiation and a 12 kW rotating anode generator. Cell constants and an orientation for data collection obtained from a least-squares refinement using the setting angles of 22 carefully centred reflections in the range $28° < 2\theta < 21°$. The data were collected at a temperature of $2\theta \pm 1$°C using the ω-2θ scan technique.

The structure of each compound was solved by direct methods [13] and expanded using Fourier techniques [14]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber [15]. All calculations were performed using the TEXSAN [16] crystallographic software package of the Molecular Structure Corporation.

RESULTS AND DISCUSSION

The reaction described in this work is summarized in Scheme 1. As described previously [13], $S_2Fe_2(CO)_6$ reacted with $Co_2(CO)_8$ in THF at room temperature gave the cluster (**1**) $FeCo_2S(CO)_9$ in 90% yield without irradiation. The new reagents NaCpC(O)R [R = C_6H_5, $C_6H_4C(O)OCH_3$] have been used as starting materials for the preparation of functionally substituted cyclopentadienyl tricarbonyl complexes of molybdenum and tungsten, which reacted with cluster (**1**) gave the title compounds (**2**)–(**5**). The cluster (**2**) was reduced by $NaBH_4$ in MeOH at room temperature in high yield. The clusters (**2**)–(**4**) also can be prepared at ambient temperature but in low yield. The results showed that the metal fragment $Co(CO)_3$ in cluster (**1**) could be exchanged by the new metal exchange reagents $^{-}M(CO)_2[CpC(O)R]$ [R = C_6H_5, $C_6H_4C(O)OCH_3$; M = Mo, W]. The IR spectra of all clusters exhibited a large number of absorption bands between 1860–2083 cm^{-1}, which were assigned to terminal carbonyl peaks. The spectra of the cluster (**6**) revealed OH absorption peaks at 3382 cm^{-1}. These results are consistent with the reduction of $NaBH_4$. The absorptions of C=O in clusters (**2**)–(**5**) appeared at 1654–1655 cm^{-1}, which were very much lower than that of the normal C=O. This was due to the conjugative effect (+M) of the π-system of the CpC(O)R [R = C_6H_5, $C_6H_4C(O)OCH_3$]. For ^1H NMR assignment of the clusters, chemical shifts of the substituted cyclopentadienyl in the clusters (**2**)–(**5**) appeared at lower fields than that of the unsubstituted cyclopentadienyl in known clusters [17], because of their electron-withdrawing groups. It is interesting that the ^1H NMR spectra of the cyclopentadienyl protons of these clusters show an A_2BB' pattern instead of A_2B_2 pattern. This is maybe due to a chiral tetrahedral core FeCoMoS in these clusters [18]. Proton chemical shifts on the cyclopentadienyl in cluster (**6**) appeared at higher field than that in cluster (**2**), because the shielding of substituent —CH(OH)— to the protons of cyclopentadienyl is larger than that of —C=O—. The chemical shift of the OH in cluster **6** appears at 1.91 ppm.



Scheme 1.

Single crystal X-ray analysis of cluster (**4**) *and cluster* (**5**)

The molecular structure of compound (**4**) has been established by single crystal X-ray diffraction shown in Fig. 1. Crystal data are collected in Table 1, and Table 2 gives the selected bond lengths and angles. The tetrahedral skeleton of the cluster (**4**) is composed of the four different atoms S, Fe, Co, Mo. The Fe and Co atoms are coordinated by three carbonyl ligands,

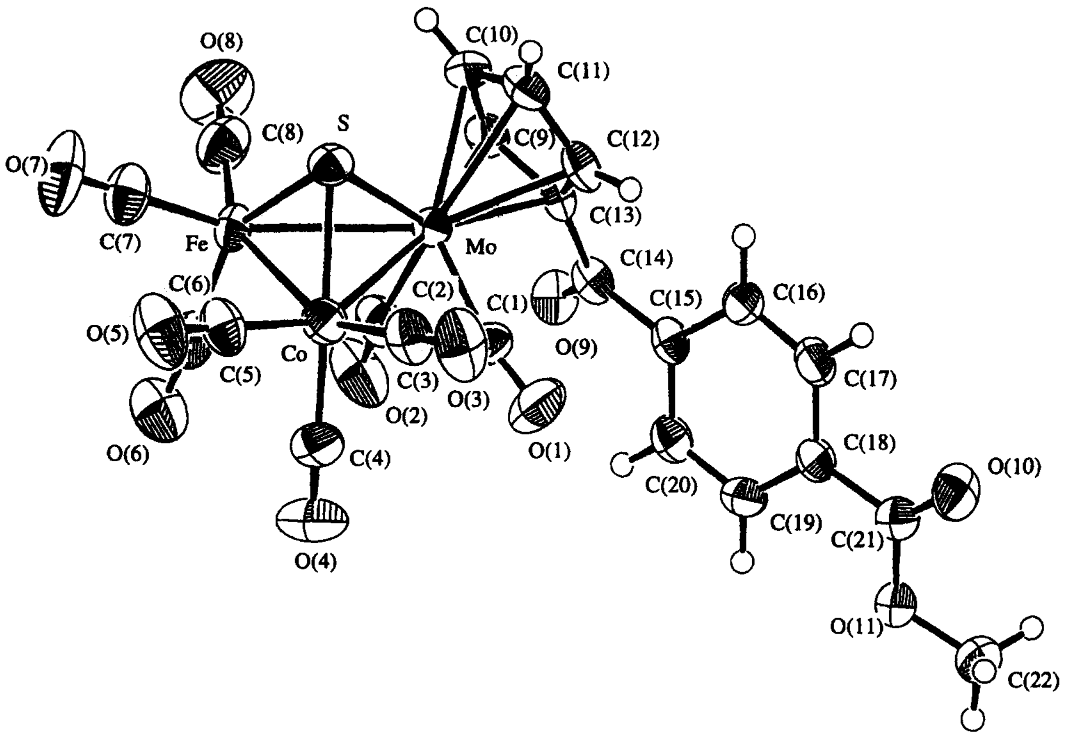


Fig. 1. Molecular structure of cluster (4).

Table 1. Summary of crystal and intensity data for the clusters (4) and (5)

	4	**5**
Formula	$C_{22}H_{11}O_{11}SFeCoMo$	$C_{22}H_{11}O_{11}SFeCoW$
fw	694.10	782.01
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$
a (Å)	16.362(4)	16.298(3)
b (Å)	7.823(3)	7.831(3)
c (Å)	19.423(6)	19.376(4)
β (°)	100.63(2)	100.69(2)
V (Å^3)	2443(1)	2430(1)
Z	4	4
D_{cal} (g/cm^3)	1.887	2.137
F(000)	1368.00	1496.00
μ(Mo-K_α) (cm^{-1})	19.06	61.37
Radiation (Mo-K_α) (Å)	0.71069	0.71069
Temp. (°C)	20.0	20.0
Scan type	ω-2θ	ω-2θ
$2\theta_{max}$ (°)	45.0	50.0
No. of reflections	Total: 3357	Total: 4791
Measured	Unique: 3216 (R_{int} = 0.048)	Unique: 4619 (R_{int} = 0.029)
No. observations [$I > 3.00\ \sigma(I)$]	2415	3358
No. variables	334	334
Residuals: R^a, Rw^a	0.041; 0.057	0.029; 0.034

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$

Table 2. Selected bond lengths (Å) and bond angles (°) for cluster (**4**)

Mo—Co	2.803(1)	Mo—Fe	2.782(1)	Mo—S	2.351(2)
Mo—C(1)	1.960(8)	Mo—C(2)	1.993(9)	Co—Fe	2.576(2)
Co—S	2.158(3)	Co—C(3)	1.796(9)	Co—C(4)	1.804(9)
Co—C(5)	1.783(9)	Fe—S	2.185(2)	Fe—C(6)	1.788(10)
Fe—C(7)	1.809(10)	Fe—C(8)	1.80(1)	C(13)—C(14)	1.482(10)
C(14)—C(15)	1.48(1)	C(18)—C(21)	1.51(1)	C(Cp)—C(Cp)	1.38–1.44
C(ph)—C(ph)	1.38–1.39	O(9)—C(14)	1.217(8)	O(10)—C(21)	1.188(9)
C—O(t-CO)	1.141av	Mo—Cp	1.996		
Co—Mo—Fe	54.93(4)	Co—Mo—S	48.54(6)	Co—Mo—C(1)	64.1(2)
Co—Mo—C(2)	91.0(2)	Fe—Mo—S	49.52(5)	Fe—Mo—C(1)	113.3(2)
Fe—Mo—C(2)	71.8(2)	S—Mo—C(1)	105.0(2)	S—Mo—C(2)	120.1(2)
Mo—Co—S	54.71(6)	Mo—Co—Fe	62.11(4)	Mo—Co—C(3)	104.1(2)
Mo—Co—C(4)	100.6(2)	Mo—Co—C(5)	150.6(3)	Fe—Co—S	54.11(7)
Fe—Co—C(3)	156.7(3)	Fe—Co—C(4)	100.3(3)	Fe—Co—C(5)	92.6(3)
S—Co—C(3)	102.7(3)	S—Co—C(4)	149.4(3)	S—Co—C(5)	99.1(3)
Mo—Fe—Co	62.96(4)	Mo—Fe—S	54.92(6)	Mo—Fe—C(6)	106.8(3)
Mo—Fe—C(7)	147.9(3)	Mo—Fe—C(8)	91.8(3)	Co—Fe—S	53.15(7)
Co—Fe—C(6)	92.2(3)	Co—Fe—C(7)	99.5(3)	Co—Fe—C(8)	154.3(3)
S—Fe—C(6)	144.7(3)	S—Fe—C(7)	92.9(3)	S—Fe—C(8)	109.2(3)
Mo—S—Co	76.74(7)	Mo—S—Fe	75.56(7)	Co—S—Fe	72.74(7)

and Mo atom is coordinated by two carbonyl ligands and one substituted cyclopentadienyl ligand. The acute angles in the tetrahedral geometry of cluster (**4**) about the basal atoms range from 54.93° to 62.96°, and those about the sulfur atom average 75.02°, which deviates considerably from perfect tetrahedral geometry. This results because the metal–metal bond Fe CoMo triangle restricts the angles around the sulfur atom. The distances from the sulfur atom to the three metal atoms [S—Mo = 2.351 Å, S—Co = 2.158 Å, S—Fe = 2.185 Å] are very similar to those of the reported complex SFeCoMo$(CO)_8[C_2H_5OC(O)Cp]$ [19] [S—Mo = 2.371 Å, S—Co = 2.200 Å, S—Fe = 2.187 Å]. Since the π-system of the benzene derivative —$C(O)C_6H_4C(O)$— would be quite well conjugat with that of Cp ring, the bond lengths of C(13)—C(14) (1.482 Å), C(14)—C(15) (1.48 Å) and C(18)—C(21) (1.51 Å) became shorter than that of a normal C—C single bond (1.54 Å), but longer than that of C=C double bond (1.34 Å). Cluster (**4**) contains total of 48 electrons and is electronically saturated.

The red prismatic crystal of cluster (**5**) suitable for structure determination was obtained from the solution of CH_2Cl_2, and single crystal diffraction study was performed. The molecular structure is shown in Fig. 2. Crystal data are collected in Table 1. The

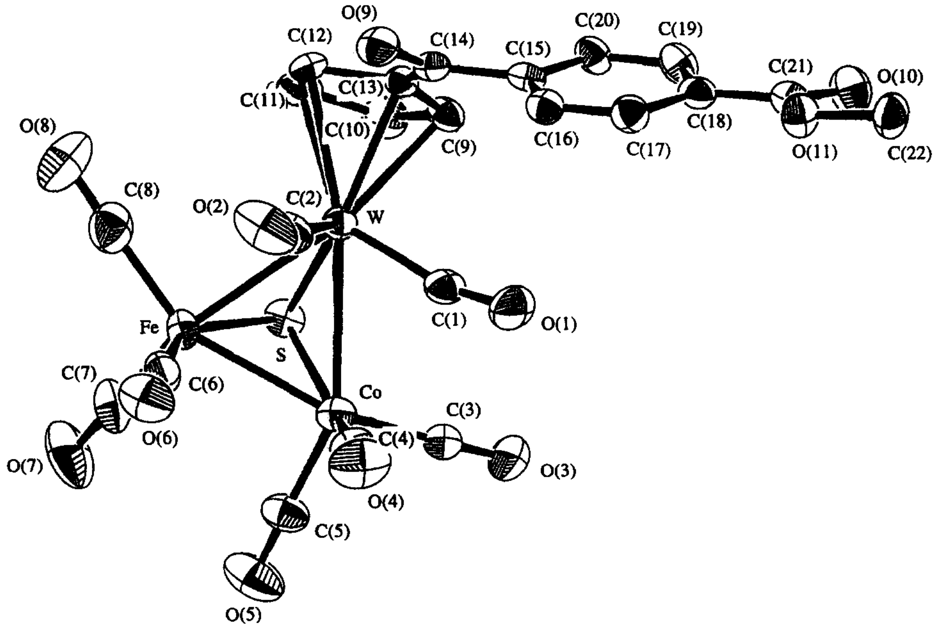


Fig. 2. Molecular structure of cluster (5).

Table 3. Selected bond lengths (Å) and bond angles (°) for cluster (**5**)

W—Co	2.797(1)	W—Fe	2.777(1)	W—S	2.342(2)
W—C(1)	1.953(7)	W—C(2)	1.981(8)	Co—Fe	2.573(1)
Co—S	2.171(2)	Co—C(3)	1.787(8)	Co—C(4)	1.804(8)
Co—C(5)	1.785(8)	Fe—S	2.191(2)	Fe—C(6)	1.782(8)
Fe—C(7)	1.810(8)	Fe—C(8)	1.797(9)	O(9)—C(14)	1.219(7)
O(10)—C(21)	1.204(8)	C(13)—C(14)	1.489(9)	C(14)—C(15)	1.507(9)
C(18)—C(21)	1.490(9)	C(Cp)—C(Cp)	1.398(10)–1.453(9)	C(ph)—C(ph)	1.388(9)–1.397(9)
C—O(*t*-CO)	1.141av	W—Cp	1.990		
Co—W—Fe	54.99(3)	Co—W—S	49.01(5)	Co—W—C(1)	65.3(2)
Co—W—C(2)	90.2(2)	Fe—W—S	49.81(5)	Fe—W—C(1)	115.1(2)
Fe—W—C(2)	71.9(2)	S—W—C(1)	105.7(2)	S—W—C(2)	120.4(2)
W—Co—Fe	62.10(3)	W—Co—S	54.49(5)	W—Co—C(3)	104.3(2)
W—Co—C(4)	100.5(2)	W—Co—C(5)	151.3(3)	Fe—Co—S	54.21(6)
Fe—Co—C(3)	156.3(2)	Fe—Co—C(4)	101.2(2)	Fe—Co—C(5)	93.5(3)
S—Co—C(3)	102.1(3)	S—Co—C(4)	149.8(2)	S—Co—C(5)	99.8(3)
W—Fe—Co	62.91(3)	W—Fe—S	54.73(5)	W—Fe—C(6)	107.3(2)
W—Fe—C(7)	147.4(2)	W—Fe—C(8)	91.9(3)	Co—Fe—S	53.50(6)
Co—Fe—C(6)	91.1(2)	Co—Fe—C(7)	99.5(3)	Co—Fe—C(8)	154.4(3)
S—Fe—C(6)	144.1(2)	S—Fe—C(7)	92.7(2)	S—Fe—C(8)	109.3(3)
W—S—Co	76.50(6)	W—S—Fe	75.47(6)	Co—S—Fe	72.30(6)

atomic coordinates and relevant bond lengths and angles of cluster (**5**) are summarized in Table 3. The tetrahedral core in the cluster (**5**) is composed of four different atoms S, Fe, Co and W. It contains a slightly distanced triangular FeCoW capped by a sulfido ligand with Fe—Co = 2.573 Å, W—Co = 2.797 Å and Fe—W = 2.777 Å. Six of the CO ligands bond terminally to the Fe and Co atoms, while the remaining CO ligands on the tungsten are slightly nonlinear. The bond lengths of the C(13)—C(14) (1.489 Å), C(14)—C(15) (1.507 Å), C(18)—C(21) (1.490 Å) are much shorter than that of a normal C—C single bond (1.54 Å), but longer than that of C=C double bond (1.34 Å), which are due to the conjugative effect of the π-system as the discussion above.

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