

Synthesis and structure of the cluster $\text{Fe}_2\text{Mo}_2(\mu_3\text{-Se})(\mu_3\text{-AsMe})(\mu_3\text{-CO})(\mu\text{-CO})(\text{CO})_5(\eta^5\text{-Cp})_2$

S. N. Konchenko,* A. V. Virovets, P. A. Petrov, and S. V. Tkachev

Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
 3 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.

Fax: +7 (383 2) 34 4489. E-mail: konch@che.nsk.su

The reaction of $(\text{Et}_4\text{N})_2[\text{Fe}_3(\mu_3\text{-Se})(\text{CO})_9]$ with MeAsI_2 afforded the $[\text{Fe}_3(\mu_3\text{-Se})(\mu_3\text{-AsMe})(\text{CO})_9]$ cluster, which was characterized by ^1H NMR and IR spectroscopy and elemental analysis. The reaction of the resulting compound with the dimeric complex $[\eta^5\text{-CpMo}(\text{CO})_3]_2$ in *m*-xylene upon refluxing gave the heterometallic cluster $\text{Fe}_2\text{Mo}_2(\mu_3\text{-Se})(\mu_3\text{-AsMe})(\mu_3\text{-CO})(\mu\text{-CO})(\text{CO})_5(\eta^5\text{-Cp})_2$, whose structure was established by X-ray diffraction analysis.

Key words: iron, molybdenum, selenium, arsenic, carbonyl clusters, synthesis, ^1H NMR spectra, X-ray diffraction analysis.

The heterometallic clusters $\text{Fe}_2\text{M}_2(\mu_3\text{-X})_2(\text{CO})_7(\eta^5\text{-Cp})_2$ ($\text{M} = \text{Mo}$ or W ; $\text{X} = \text{S}$, Se , or Te) are among the major products of the reactions of $\text{Fe}_2(\mu\text{-X}_2)(\text{CO})_6$ or $\text{Fe}_3(\mu_3\text{-X})_2(\text{CO})_9$ with the dimeric complexes $[\eta^5\text{-CpM}(\text{CO})_3]_2$.^{1–4} Analogous heterometallic clusters containing two different chalcogen atoms were formed in the reactions with the use of mixed-chalcogenide iron complexes as the initial compounds.⁵ In this work, we studied the reaction of the complex $\text{Fe}_3(\mu_3\text{-Se})(\mu_3\text{-AsMe})(\text{CO})_9$ (1) with $[\eta^5\text{-CpMo}(\text{CO})_3]_2$. It was demonstrated that the major reaction product was a heterometallic cluster with an analogous structure containing simultaneously Groups VA and VIA elements.

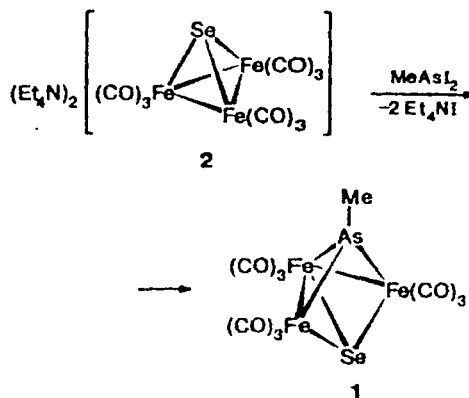
Results and Discussion

Compound 1 was prepared by the reaction of the complex $(\text{Et}_4\text{N})_2[\text{Fe}_3(\mu_3\text{-Se})(\text{CO})_9]$ (2) with MeAsI_2 . This reaction can be formally described as the nucleophilic replacement of the halogen atoms in the MeAsI_2 molecule by a double-charged cluster anion (Scheme 1). The structure of complex 1 was proposed based on the data of elemental analysis as well as on the fact that its spectra (IR and ^1H NMR) are similar to those of the known compound $\text{Fe}_3(\mu_3\text{-S})(\mu_3\text{-AsMe})(\text{CO})_9$.⁶

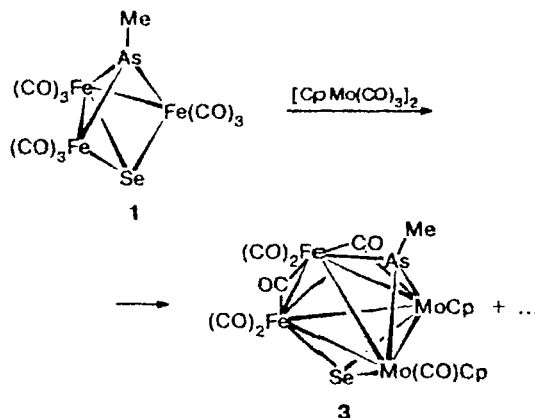
The reaction of cluster 1 with $[\eta^5\text{-CpMo}(\text{CO})_3]_2$ was carried out under conditions of copolyolysis of the initial reagents in *m*-xylene at 140 °C (Scheme 2). As a result, we obtained a mixture of compounds containing cluster 3 as the major product. Of the remaining products only the complex $\text{FeMo}_2(\mu_3\text{-Se})(\text{CO})_7(\eta^5\text{-Cp})_2$ was identified.⁷

The structure of molecule 3 is shown in Fig. 1. The selected bond lengths are given in Table 1. Complex 3 is

Scheme 1



Scheme 2



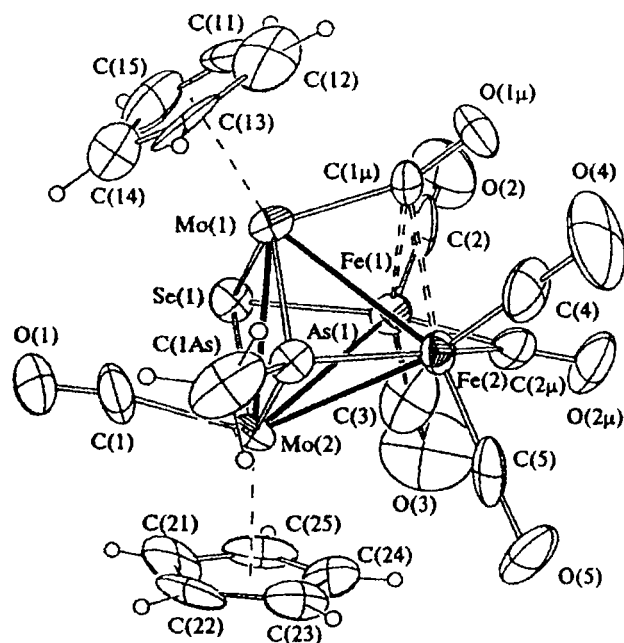


Fig 1. Molecular structure of compound 3 (thermal ellipsoids with the 35% probability).

Table 1. Selected bond lengths (*d*) in molecule 3

Bond	<i>d</i> /Å	Bond	<i>d</i> /Å
Mo(1)—Mo(2)	2.878(2)	Fe(1)—C(1μ)	2.35(2)
Mo(1)—Fe(1)	2.765(3)	Fe(1)—C(2μ)	1.90(2)
Mo(1)—Fe(2)	2.836(3)	Fe(1)—C(2)	1.79(2)
Fe(1)—Fe(2)	2.449(4)	Fe(1)—C(3)	1.70(2)
Mo(2)—Fe(1)	2.822(3)	Fe(2)—C(1μ)	2.44(2)
Mo(2)—Fe(2)	2.871(3)	Fe(2)—C(2μ)	1.95(2)
Se(1)—Mo(1)	2.484(2)	Fe(2)—C(4)	1.66(2)
Se(1)—Mo(2)	2.482(2)	Fe(2)—C(5)	1.72(2)
Se(1)—Fe(1)	2.291(3)	C(1μ)—O(1μ)	1.18(2)
As(1)—Mo(1)	2.449(2)	C(2μ)—O(2μ)	1.20(2)
As(1)—Mo(2)	2.446(2)	C(1)—O(1)	1.12(2)
As(1)—Fe(2)	2.241(3)	C(2)—O(2)	1.14(2)
As(1)—C(1As)	1.97(1)	C(3)—O(3)	1.20(2)
Mo(1)—C(1μ)	1.93(2)	C(4)—O(4)	1.21(2)
Mo(1)—C(11)	2.31(2)	C(5)—O(5)	1.20(2)
Mo(1)—C(12)	2.38(2)	C(11)—C(12)	1.35(3)
Mo(1)—C(13)	2.25(2)	C(11)—C(15)	1.29(3)
Mo(1)—C(14)	2.32(2)	C(12)—C(13)	1.39(3)
Mo(1)—C(15)	2.33(2)	C(13)—C(14)	1.38(3)
Mo(2)—C(1)	1.99(2)	C(14)—C(15)	1.32(3)
Mo(2)—C(21)	2.32(2)	C(21)—C(22)	1.36(2)
Mo(2)—C(22)	2.31(2)	C(21)—C(25)	1.40(2)
Mo(2)—C(23)	2.36(2)	C(22)—C(23)	1.40(2)
Mo(2)—C(24)	2.40(2)	C(23)—C(24)	1.38(2)
Mo(2)—C(25)	2.36(2)	C(24)—C(25)	1.34(2)

structurally very similar to the cluster $\text{Fe}_2\text{W}_2(\mu_3\text{-Se})_2(\mu_3\text{-CO})(\mu\text{-CO})(\text{CO})_5\text{Cp}$ ⁸ and its analogs. ¹⁻⁴ Molecule 3 contains the tetrahedral Fe_2Mo_2 metal core, the μ_3 -coordinated Se and AsMe ligands at two FeMo_2 faces, CO at the Fe_2Mo face, and the bridging carbonyl

ligand at the Fe—Fe edge (see Fig. 1). In cluster 3 (as in $\text{Fe}_2\text{W}_2(\mu_3\text{-Se})_2(\mu_3\text{-CO})(\mu\text{-CO})(\text{CO})_5\text{Cp}$), ⁸ the $\mu_3\text{-CO}$ ligand is coordinated unsymmetrically. The Fe—C bonds are noticeably longer than the Mo—C (W—C) bond. The $\mu\text{-CO}$ ligand is coordinated symmetrically. In the crystal of 3, no shortened nonbonded interactions are observed.

Experimental

The IR spectra were recorded on a Bruker IFS85 spectrometer. The ¹H NMR spectra were recorded on a Bruker SXP-4-100 spectrometer (90 MHz) in CDCl_3 relative to Me_4Si .

The solvents used were purified by distillation over the corresponding drying agents. ⁹ The initial compounds $[\eta^5\text{-CpMo}(\text{CO})_3]_2$ ¹⁰ and $(\text{Et}_4\text{N})_2[\text{Fe}_3(\mu_3\text{-Se})(\text{CO})_9]$ ⁷ were prepared according to known procedures. The reactions were carried out under an argon atmosphere. The remaining operations were performed in air.

Synthesis of the complex $\text{Fe}_3(\mu_3\text{-Se})(\mu_3\text{-AsMe})(\text{CO})_9$ (1). THF (15 mL) was recondensed into a flask containing compound 2 (1.37 g, 1.8 mmol) and cooled with liquid nitrogen *in vacuo*. Then MeAsI_2 (0.63 g, 1.8 mmol) was added to the solid mixture and the flask was slowly warmed to room temperature. The resulting red-brown solution was filtered and concentrated to dryness *in vacuo*. The solid residue was extracted with boiling hexane (40 mL). Dark-brown crystals of compound 1 were precipitated upon cooling of this solution to -10°C . The yield was 0.58 g (55%). Found (%): C, 20.4; H, 0.51. $\text{C}_{10}\text{H}_3\text{AsFe}_3\text{O}_9\text{Se}$. Calculated (%): C, 20.4; H, 0.51. IR (*n*-hexane), $\nu(\text{CO})/\text{cm}^{-1}$: 2077 w, 2048 v.s., 2027 s, 2005 m, 1995 m. ¹H NMR, δ : 2.51 (3 H, Me).

Synthesis of the complex $\text{Fe}_2\text{Mo}_2(\mu_3\text{-Se})(\mu_3\text{-AsMe})(\mu_3\text{-CO})(\mu\text{-CO})(\text{CO})_5(\eta^5\text{-Cp})_2$ (3). A mixture of complex 1 (200 mg, 0.34 mmol) and $[\eta^5\text{-CpMo}(\text{CO})_3]_2$ (336 mg, 0.69 mmol) in *m*-xylene (5 mL) was refluxed for 2.5 h and then concentrated *in vacuo* with a small amount of silica gel.

Table 2. Crystallographic data for compound 3

Parameter	Conditions and X-ray diffraction data
Molecular formula	$\text{C}_{18}\text{H}_{13}\text{AsFe}_2\text{Mo}_2\text{O}_7\text{Se}$
Molecular weight	798.74
System	Orthorhombic
<i>a</i> /Å	16.178(2)
<i>b</i> /Å	18.295(2)
<i>c</i> /Å	15.328(2)
<i>V</i> /Å ³	4537(1)
Space group	<i>Pbcn</i>
<i>Z</i>	8
<i>d</i> _{calc} /g cm ⁻³	2.339
Diffraction	Enraf-Nonius CAD-4
Radiation (λ /Å)	Mo-K α (0.7107)
Crystal dimensions/mm	0.08×0.12×0.24
μ/mm^{-1}	5.423
Number of measured reflections	2119 ($2\theta_{\text{max}} = 46^\circ$)
<i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	
for 830 $F_{hkl} \geq 4\sigma(F_{hkl})$	0.0318, 0.0373
<i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	
for all reflections	0.0983, 0.0482
$\sigma^2(F_{\text{obs}}^2)$	

Table 3. Coordinates of nonhydrogen atoms ($\times 10^4$) and equivalent isotropic thermal parameters ($U_{eq} \times 10^3$)* in the structure of 3

Atom	x	y	z	$U_{eq}/\text{\AA}^2$
Mo(1)	2952(1)	1087(1)	10484(1)	50(1)
Mo(2)	1664(1)	992(1)	9194(1)	47(1)
As(1)	2968(1)	1657(1)	9039(1)	46(1)
Se(1)	1649(1)	382(1)	10641(1)	59(1)
Fe(1)	1384(2)	1598(1)	10861(2)	56(1)
Fe(2)	2180(2)	2381(1)	9875(2)	49(1)
C(1As)	3819(10)	1670(9)	8121(10)	98(7)
C(1 μ)	2746(12)	1912(10)	11241(12)	86(7)
O(1 μ)	2861(9)	2354(7)	11783(8)	104(5)
C(2 μ)	1289(12)	2621(10)	10679(11)	65(6)
O(2 μ)	898(9)	3144(7)	10903(9)	120(6)
C(1)	2446(14)	193(11)	8891(13)	91(8)
O(1)	2847(10)	-249(9)	8608(9)	150(7)
C(2)	1279(15)	1566(10)	12023(13)	100(8)
O(2)	1195(13)	1535(10)	12758(9)	175(9)
C(3)	347(15)	1578(13)	10701(16)	128(10)
O(3)	-389(9)	1605(14)	10625(13)	233(12)
C(4)	2758(12)	3089(10)	10162(14)	94(8)
O(4)	3162(9)	3604(8)	10411(15)	195(9)
C(5)	1624(12)	2849(9)	9102(13)	78(7)
O(5)	1265(10)	3207(7)	8571(8)	107(6)
C(11)	3842(18)	710(20)	11574(18)	118(13)
C(12)	4286(16)	1205(15)	11120(30)	149(18)
C(13)	4306(14)	820(20)	10341(18)	93(9)
C(14)	3914(18)	154(19)	10320(20)	123(11)
C(15)	3665(19)	127(17)	11150(30)	123(12)
C(21)	750(15)	326(12)	8336(19)	101(9)
C(22)	1185(13)	776(18)	7795(12)	94(8)
C(23)	999(16)	1508(13)	7970(15)	82(8)
C(24)	400(12)	1474(14)	8609(15)	73(7)
C(25)	261(13)	780(18)	8857(13)	97(9)

* U_{eq} was determined as 1/3 of the trace of the normalized U_{ij} tensor.

The residue was transferred to a column (2 \times 20 cm) with silica gel and chromatographed (benzene as the eluent). Two fractions were collected, namely, a red-brown fraction containing a mixture of small amounts of $[\eta^5\text{-CpMo(CO)}_3]_2$,⁶ $\text{FeMo}_2(\mu_3\text{-Se})(\text{CO})_7(\eta^5\text{-Cp})_2$,⁷ and an unidentified compound that decomposed in air* and a brown fraction containing complex 3.

* The components of the mixture were separated by TLC (Silufol plates, hexane-benzene, 1 : 1).

Crystals of complex 3 were obtained by slow diffusion of hexane into a solution of 3 in toluene at -10°C . The yield was 0.027 g (10%). IR (CHCl_3), $\nu(\text{CO})/\text{cm}^{-1}$: 2012 s, 1985 s, 1949 s, 1828 w sh, 1734 w sh. ^1H NMR, δ : 3.22 (3 H, CH_3); 5.01 (5 H, C_5H_5); 5.26 (5 H, C_5H_5).

X-ray diffraction study of compound 3. The crystallographic data and characteristics of X-ray diffraction study (at 20°C) are given in Table 2. Absorption corrections were applied taking into account two azimuth scanning curves. The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms using the SHELX-97 program package.¹¹ The positions of the hydrogen atoms were calculated geometrically and included in the refinement in the rigid-body approximation. The coordinates of the nonhydrogen atoms are given in Table 3. Selected bond lengths are listed in Table 1.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-33320).

References

1. L. E. Bogan, Jr., T. B. Rauchfuss, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1985, **107**, 3843.
2. X. Yang, J. Huang, and J. Huang, *Chinese J. Struct. Chem. (Jiegou Huaxue)*, 1985, **4**, 50.
3. X. Yang, J. Huang, and J. Huang, *Chinese J. Struct. Chem. (Jiegou Huaxue)*, 1987, **6**, 257.
4. P. Mathur, M. M. Hossain, and A. L. Rheingold, *Organometallics*, 1994, **13**, 3909.
5. P. Mathur, M. M. Hossain, S. B. Umbarkar, C. V. V. Satyanarayana, A. L. Rheingold, L. M. Liable-Sands, and G. P. A. Yap, *Organometallics*, 1996, **15**, 1898.
6. K. Fisher, W. Deck, M. Schwarz, and H. Vahrenkamp, *Chem. Ber.*, 1985, **118**, 4946.
7. S. N. Konchenko, A. V. Virovets, V. A. Varnek, S. V. Tkachev, N. V. Podberezskaya, and V. A. Maksakov, *Zh. Strukt. Khim.*, 1996, **37**, 337 [*Russ. J. Struct. Chem.*, 1996, **37** (Engl. Transl.)].
8. S. N. Konchenko, A. V. Virovets, and N. V. Podberezskaya, *Polyhedron*, 1997, **16**, 1689.
9. A. J. Gordon and R. A. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, J. Wiley and Sons, New York-London, 1972.
10. R. Birdwhistle, P. Hackett, and A. R. Manning, *J. Organomet. Chem.*, 1978, **157**, 239.
11. G. M. Sheldrick, *SHELX-97, Release 97-2*, University of Göttingen, Göttingen (Germany), 1998.

Received December 18, 1998