An EXAFS study of the molecular structure of heterometallic chalcogenide clusters

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Applicability of EXAFS spectroscopy for determination of the molecular structure of heterometallic chalcogenide clusters in the crystalline state and in solution was examined. The spatial structure of the metal core of the $FeMoW(\mu_3\text{-}Se)(CO)_7(\eta^5\text{-}C_5H_5)$ cluster was determined using EXAFS data obtained at the K absorption edge for Fe, Mo, and Se and at the L_{III}-edge for W. The geometric parameters (the bond lengths and bond angles) obtained from EXAFS data are close to those determined by X-ray analysis. The Mo K-edge EXAFS study of the structurally similar $FeMo_2Te(CO)_7(\eta^5\text{-}C_5H_5)$ cluster both in the crystalline state and in *o*-xylene solution confirmed that the geometry of the metal core of the cluster is retained in solution.

Key words: "multiple-center" EXAFS, structural study, chalcogenide clusters.

The chemistry of organometallic clusters with selenide and telluride bridging ligands is a relatively new and intensively developing area of organometallic chemistry.[1] Potential applications of this class of compounds include their use as bioactive species, catalysts, *etc.* Of particular interest are those cluster compounds whose metal cores comprise atoms of different elements.

The most common methods of structural characterization of clusters in the solid state and in solution are X-ray analysis and multicenter NMR spectroscopy, respectively. Unfortunately, X-ray studies require high-quality single crystals, which are unavailable for some substances. NMR spectroscopy provides only indirect information on the cluster core geometry. Furthermore, interpretation of NMR data is often complicated because of the presence of d-metal atoms with unpaired electrons.

Extended X-ray absorption fine structure (EXAFS) spectroscopy makes it possible to obtain information on the local environment of a particular kind of atoms in samples in any state of aggregation, thus allowing studies of not only crystals and amorphous solids, but also solutions and melts. This method is based on the analysis of the oscillations of the X-ray absorption coefficient near the absorption edge of the element under study. Such oscillations originate from scattering of photoelectrons by the nearest environment of the photoionized atom. A Fourier transform (FT) of EXAFS oscillations gives a radial distribution function (RDF) of atoms, which contains information on the number and types of atoms in the local environment of the central atom (a sphere of radius 5 to 6 Å) as well as on the exact values of the corresponding interatomic distances.

Potentialities of EXAFS spectroscopy and the amount of structural information obtained in EXAFS experiments can be substantially extended in studies of substances containing atoms of different elements with absorption edges in the hard X-ray region. Sometimes, the use of the totality of data on the local environment of each type of atoms allows unambiguous determination of the spatial structure of molecular fragments of the substance under study. This is of particular value in studying ordered molecular fragments in partially disordered or amorphous matrices (heterogeneous samples, intercalates, solutions, *etc.*) where the "classical" structural methods are of limited utility.

Heterometallic chalcogenide clusters containing several types of metal atoms, as well as non-metal (Se, Te) atoms suitable for EXAFS studies, are convenient for use in testing the potentialities and limitations of "multiple-center" EXAFS spectroscopy. In this work, we report the results of EXAFS study of the structure of two heterometallic chalcogenide clusters, $FeMoW(\mu_3\text{-}Se)(CO)_7(\eta^5\text{-}C_5H_5)_2$ (**1**) and $FeMo_2(\mu_3\text{-}Te)(CO)_7(\eta^5\text{-}C_5H_5)_2$ (**2**). Previously, the crystal structures of **1** [2] and **2** [3,4] have been determined by single-crystal X-ray analysis. Preliminary results of this EXAFS study have been reported earlier.[5]

Experimental

Clusters **1** and **2** were synthesized following a known procedure[2,3,6] *via* replacement of one or two $HFe(CO)_3$ groups in the

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initial cluster $H_2Fe_3X(CO)_9$ by the isoelectronic $CpM(CO)_2$ (X = Se, Te; M = Mo, W) fragment.

The EXAFS data were collected in a transmission mode on the EXAFS station of the VEPP-3 electron storage ring at the Siberian Synchrotron Radiation Center (SSRC, Siberian Branch of the RAS, the Budker Institute of Nuclear Physics, Novosibirsk, Russian Federation) with an electron beam energy of 2 GeV and a maximum stored current of ~100 mA. The edge step ranged from 1.5 to 2 eV. A flat Si [111] channel-cut monochromator was utilized. The intensities of incident (I_0) and transmitted (I_t) X-ray beams were recorded with ion chambers filled with Ar/Kr gas mixtures. For cluster **1**, measurements were carried out at the K absorption edge for Se ($E_0 \approx$ 12.649 keV), Mo ($E_0 \approx$ 20.010 keV), and Fe ($E_0 \approx$ 7.112 keV) and at the L_{III}-edge for W ($E_0 \approx$ 10.212 keV). For cluster **2**, the EXAFS spectra were recorded at the Mo K-edge for both the polycrystalline sample and its solution in *o*-xylene. The concentration of the solution was 0.3 to 0.4 mol L^{-1}.

Standard processing of the EXAFS spectra including polynomial background subtraction, direct and inverse Fourier transformation, and the nonlinear fitting procedure was performed at the Institute of Catalysis (Siberian Branch of the RAS, Novosibirsk, Russian Federation) using UWXAFS software.[7] The theoretical scattering phases and amplitudes were obtained from *ab initio* calculations using FEFF6 software.[8] The Fourier transformations of the normalized k^3-weighted (for Mo, W, Se) or k^2-weighted (for Fe) EXAFS curves multiplied by the Hanning window function with the width parameter dk = 1 $Å^{-1}$ were carried out in the k range from ~2.5 to 14.5 $Å^{-1}$.

Simulation of spectra and nonlinear fitting of structural parameters were performed using the equation[9]

$$\chi(k) = S_0^2 \sum_j N_j F_j(k) e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda_j(k)} \frac{\sin[2kr_j + \delta_{ij}(k)]}{kr_j^2},$$

where $\chi(k)$ is the experimental normalized EXAFS curve, k is the wavenumber of the photoelectron,

$$k = [2m_e(E - E_0)]^{1/2}/\hbar;$$

the summation is performed over all coordination spheres j; S_0 is the scaling coefficient which takes into account the effects of multi-electron excitation (in all cases, S_0 was set equal to 1); λ is the photoelectron attenuation length in the sample; F_j is the scattering amplitude of the photoelectron by atom j; N_j is the coordination number; r_j is the interatomic distance; σ_j^2 is the Debye—Waller parameter; and δ_{ij} are the phase shifts for the corresponding coordination spheres j. Fitting was carried out using the parameters r_j, σ_j^2, and E_0 as independent variables. Multiple scattering effects were ignored. The values of standard R-factors were used as a measure of the quality of the fits.

The accuracy of determination of interatomic distances from EXAFS spectra was 0.01—0.02 Å for the nearest coordination sphere and ~1% for farther spheres.[9]

Results and Discussion

The plots of experimental normalized EXAFS curves $\chi(k)$ obtained for cluster **1** at the Se, Mo, and Fe K-edges and the corresponding FT curves are shown in Fig. 1. Figure 2 shows the $\chi(k)$ and FT curves derived from data obtained for the same sample at the W L_{III}-edge. The attribution of the FT maxima to interatomic distances (with respect to the central atoms) is indicated by dashes. Due to the close values of interatomic distances, the FT maxima are composed of several overlapped contributions. Fitting of EXAFS spectra measured at the Mo K-edge and W L_{III}-edge revealed that the first FT maximum is composed of two contributions originating from scattering by carbon atoms, C and C', lying at different distances from the metal atom. This can be explained by the presence of both carbonyl and cyclopentadienyl ligands in the coordination spheres of the Mo and W atoms. In addition, appreciable contribution from scattering by oxygen atoms (in the M—C—O chain with the M—O distance in the range from 2.9 to 3.2 Å) to the spectral contours for the Mo, W, and Fe atoms were revealed. Such interatomic distances, as well as the intensities of the corresponding FT maxima, imply a "focusing effect"[10] and suggest that all carbonyl ligands in the local environment of Mo, W, and Fe atoms are terminal.

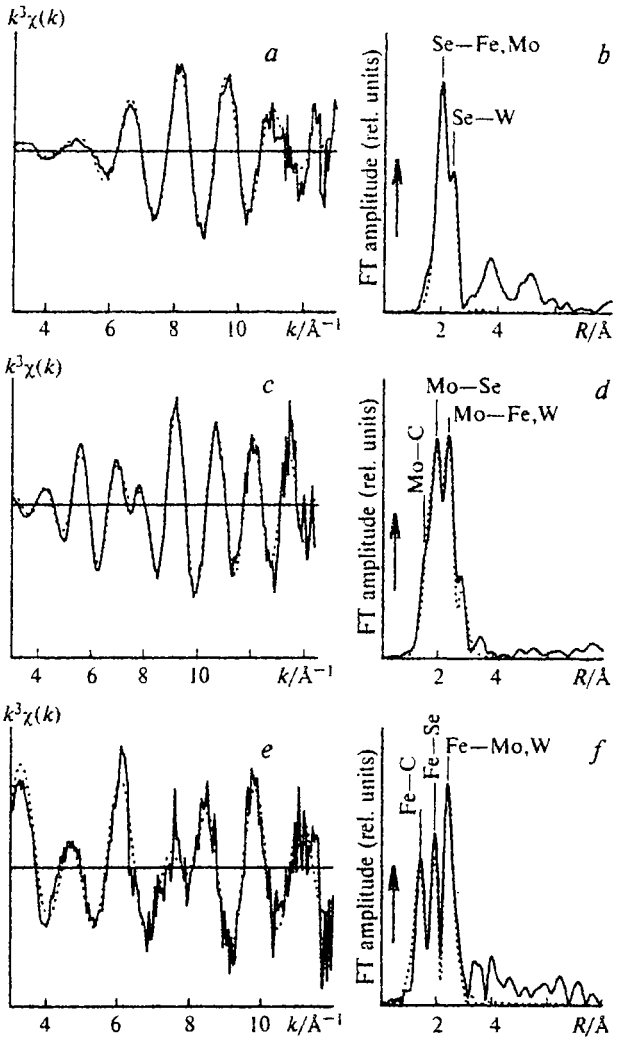

Fig. 1. Normalized $k^3\chi(k)$ EXAFS curves and the corresponding FT curves for cluster **1** obtained at the K absorption edge for Se (*a*, *b*), Mo (*c*, *d*), and Fe (*e*, *f*). Solid lines denote the experimental curves and points denote the best fit results.

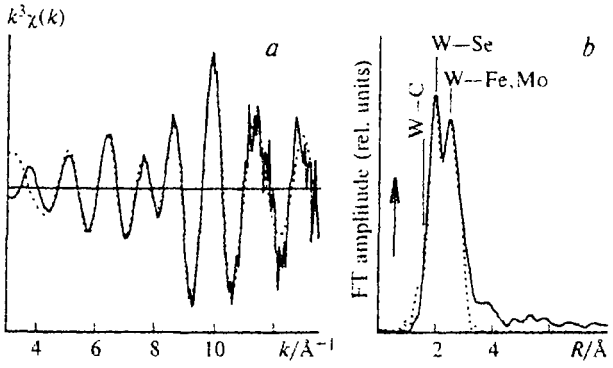

Fig. 2. Normalized $k^3\chi(k)$ EXAFS curve (*a*) obtained at the W L_{III} absorption edge and the corresponding FT curve (*b*) for cluster **1**. Solid lines denote the experimental curves and points denote the best fit results.

The results of multi-sphere fittings of all EXAFS spectra are listed in Table 1. For each pair of atoms (Se—Mo, Se—W, Se—Fe, Mo—W, and W—Fe), the differences between the corresponding best fit interatomic distances obtained from the spectra measured at different absorption edges were at most 0.01 Å. The only exception was the Mo—Fe pair, for which the interatomic distance obtained by fitting the Fe K-edge spectrum was found to be 2.81 Å, whereas fitting of the Mo K-edge spectrum gave a value of 2.87 Å. This discrepancy can likely be due to strong correlations between the

Table 1. Results of multi-sphere fitting of EXAFS data obtained for cluster **1** at the K absorption edge for Se, Mo, and Fe and at the L_{III}-edge for W

Type of spectrum	Interatomic distance	*R*/Å	$\sigma^2 \cdot 10^5/Å^2$
Se K-edge	Se—Fe	2.32	210
(R_f = 0.005)[a]	Se—Mo	2.50	16
	Se—W	2.50	40
Mo K-edge	Mo—C	1.96	640
(R_f = 0.013)[b]	Mo—C′	2.27	780
	Mo—Se	2.50	290
	Mo—Fe	2.87	340
	Mo—W	3.06	340
	Mo...O(CO)	3.15	17
Fe K-edge	Fe—C	1.73	10
(R_f = 0.030)[c]	Fe—Se	2.31	380
	Fe—Mo	2.81	280
	Fe—W	2.84	480
	Fe...O(CO)	2.93	36
W L_{III}-edge	W—C	2.03	380
(R_f = 0.027)[d]	W—C′	2.31	140
	W—Se	2.49	840
	W—Fe	2.84	110
	W—Mo	3.07	270
	W...O	3.24	15

[a] Fitting range in *R* space 1.7—3.1 Å, in *k* space 3.0—13.0 $Å^{-1}$.
[b] Fitting range in *R* space 1.1—3.3 Å, in *k* space 3.0—14.5 $Å^{-1}$.
[c] Fitting range in *R* space 1.0—3.5 Å, in *k* space 3.0—12.0 $Å^{-1}$.
[d] Fitting range in *R* space 1.1—3.5 Å, in *k* space 4.0—14.0 $Å^{-1}$.

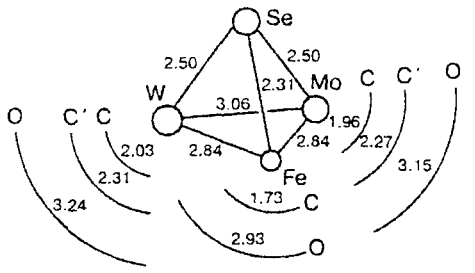

Fig. 3. Three-dimensional model of the geometry of the FeMoW(μ_3-Se) fragment constructed based solely on EXAFS data. The interatomic distances are given in Å.

parameters of the Fe—Mo and Fe...O contacts, which contribute to nearly the same range of distances in the corresponding FT.

This set of interatomic distances corresponds to a unique possible mutual spatial orientation of Se, Mo, W, and Fe atoms in the form of a distorted tetrahedron with the μ_3-Se ligand in one vertex and the metal atoms in other vertices (Fig. 3). In Table 2, the averaged values of interatomic distances, the bond angles in the metal core of cluster **1** calculated from these data, and the metal—carbon distances for the coordinated carbonyl and cyclopentadienyl ligands are compared with the corresponding structural parameters of cluster **1** determined by X-ray analysis.[2] Good agreement between the geometric parameters of the model suggested in this work and the results of X-ray study of cluster **1** [2] confirms the

Table 2. Comparison of bond lengths (*d*) and bond angles (ω) in complex **1** obtained by EXAFS spectroscopy and X-ray analysis

Parameter	EXAFS (this work)	X-ray study[2]
Bond	*d*/Å	
Se—Fe	2.31	2.321(2)
Se—Mo	2.50	2.500(2)
Se—W	2.50	2.497(2)
Mo—C(CO)	1.96	1.92—1.96
Mo—C′(η^5-C_5H_5)	2.27	2.29—2.35
Mo—Fe	2.84	2.820(2)
Mo—W	3.06	3.079(1)
Mo...O	3.15	3.06—3.11
W—C(CO)	2.03	1.94—2.01
W—C′(η^5-C_5H_5)	2.31	2.25—2.37
W—Fe	2.84	2.836(2)
W...O	3.24	3.11—3.13
Fe—C	1.73	1.74—1.77
Fe...O	2.93	2.87—2.91
Angle	ω/deg	
Mo—Se—W	75.5	76.1(3)
Mo—Se—Fe	72.3	71.5(3)
W—Se—Fe	72.3	72.0(3)
Se—Mo—Fe	50.8	51.3(3)
W—Mo—Fe	57.4	57.3(3)
Se—W—Mo	52.2	52.0(3)
Se—W—Fe	50.8	51.1(3)
Mo—Fe—W	65.1	66.0(3)

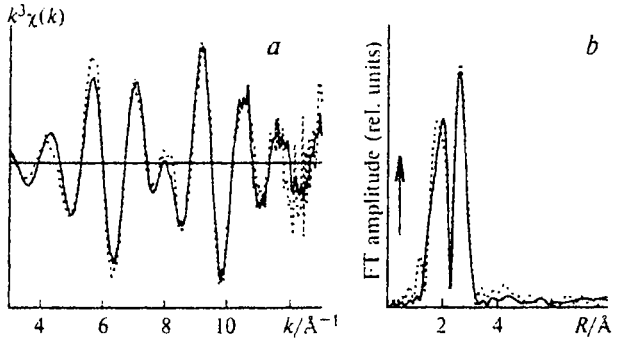

Fig. 4. Normalized $k^3\chi(k)$ EXAFS curve (*a*) obtained at the Mo K-edge and the corresponding FT curve (*b*) for cluster **2** in the crystalline state (solid lines) and in *o*-xylene solution (points).

correctness of the model and demonstrates the high accuracy of determination of the structural parameters obtained from EXAFS spectra. The differences between the results of the X-ray and EXAFS studies lie within the limits of experimental error.

An attempt to determine the mutual orientation of the ligands based on the analysis of distant FT maxima followed by their attribution to nonbonded intramolecular contacts failed because of the low intensities of the corresponding FT maxima and a large number of contributions from various scattering paths contributing to this region. According to the data of single-crystal X-ray study,[2] four spatial isomers differing in the mutual orientation of the ligands coexist in the unit cell of $FeMoW(\mu_3\text{-}Se)(CO)_7(\eta^5\text{-}C_5H_5)$ crystals. This also precludes attribution of the distant FT maxima to particular intramolecular contacts. A more reliable and comprehensive description of the spatial structure based solely on "multiple-center" EXAFS data can be obtained using simultaneous fitting of all experimental curves because of the smaller number of independent variables and correct consideration of mutual correlations between the values of structural parameters.

According to the data of X-ray studies,[3,4] clusters **1** and **2** are structurally similar. The plots of normalized EXAFS curves $\chi(k)$ obtained for polycrystalline **2** and its *o*-xylene solution (**2a**) at the Mo K-edge and the corresponding FT curves are shown in Fig. 4. Both FT curves for the spectra of **2** and **2a** look very similar. The largest differences are observed for the shape of the first FT maximum, which is composed of the Mo—C contributions due to scattering by the carbon atoms of the CO and Cp ligands. This can be explained by a higher lability of the nearest ligand environment of the Mo atoms in solution. The second maxima resulting from the superposition of the Mo—Te, Mo—Fe, and Mo—W contributions have virtually identical shapes and positions. This suggests that for cluster **2** the molecular fragment geometry typical of the crystalline state is also retained in solution.

Thus, we succeeded in determining the spatial structure of the metal core of cluster **1** using EXAFS spectra. The metal—metal and metal—selenium bond lengths, as well as the corresponding bond angles in the tetrahedral fragment $FeMoW(\mu_3\text{-}Se)$, were found. The average metal—ligand bond lengths were determined. The absence of bridging carbonyl groups was revealed. The structural parameters (bond lengths and bond angles) obtained in this work coincide within the limits of experimental error with the known results of X-ray study.[2] It was confirmed that the geometry of the metal core of the cluster $FeMo_2(\mu_3\text{-}Te)(CO)_7(\eta^5\text{-}C_5H_5)$ remains essentially the same on going from the crystalline state to solution.

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