EXAFS AND LAXS STRUCTURAL INVESTIGATIONS OF AMORPHOUS ONE-DIMENSIONAL COMPOUNDS (ML3)∞ (M=Mo, Ru ; L=SPh, SePh, PYRAZOLATE)

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EXAFS AND LAXS STRUCTURAL INVESTIGATIONS OF AMORPHOUS ONE-DIMENSIONAL COMPOUNDS $(ML_3)_\infty$ (M=Mo, Ru; L=SPh, SePh, PYRAZOLATE)

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Résumé: Les études conjointes par les techniques EXAFS et LAXS de l'architecture atomique des composés polymériques ML_3 permet de définir l'ordre à courte et moyenne distance, révélant l'existence de distances métal-métal alternativement courtes et longues d'en préciser leur valeur ainsi que les distances interatomiques de leur environnement; ces résultats sont en accord avec leurs propriétés physiques.

Abstract : Short and medium range order has been established for the ML_3 serie of compounds by a joint EXAFS-LAXS techniques. Metal-metal pairs have been evidence and interatomic distances determined; extended models have been built fitting well, up to large r(Å) values the LAXS curves.

Research in the field of inorganic polymers to obtain materials with new and unusual properties has often been inhibited by the micro-crystalline or amorphous nature of these compounds. Hence, structural information is very limited compared to the large number of compounds. Extended X-ray Absorption Fine Structure (EXAFS) and Large Angle X-Ray Scattering (LAXS) provide tools which permit to investigate the short and medium range order of such compounds and to establish structural models that may give further insight into inorganic polymers and their physical properties. The serie of the amorphous polymers $MM'(EDTA)(H_2O)_4.2H_2O$ with M and M' = Ni, Co, Mn, Cu, provides an example of the correlation between local order and magnetic behavior (1).

The aim of this paper is to present for the $(ML_3)_\infty$ with M=Mo, Ru and L=SPh, SePh, pyrazolate, strutural models obtained from joint EXAFS and LAXS experiments.

Experimental Section

Preparation of the compounds. The synthesis and properties of ML_3 compounds have been published elsewhere(2). The amorphous powder were prepared in the usual way, i.e. on slide supports, for EXAFS and were carefully crushed, pressed into pellets at 210 kg/cm^2, and mounted on a goniometric head for LAXS.

Structural Investigation. **EXAFS**-The experiments have been realized on the EXAFS I station at LURE-CNRS, University of Paris-Sud(Orsay), using the Si(400) channel-cut monochromator. The data reduction was performed using the classical single electron single scattering formalism. **LAXS**-The data collection was performed with the LASIP system built up in the Toulouse laboratory(3) using the special ω-θ diffractometer equipped with a position-sensitive detector and the MoKα wavelength. The measurements were carried out at room temperature in the transmission mode. Some 2200 equidistant points were measured in 21.5h with $1.5° < \theta < 66°$. Experimental data were corrected for background, absorption, polarization and multiple scattering according to reference (4).

RESULTS

In a first attempt an effort was developped to understand the LAXS experiments about the two compounds $Mo(SPh)_3$ and $Ru(SPh)_3$. The best fit between theoretical and experimental data (Fig. 1 and 2) was obtained using a chain geometry and the following bond lenghts and angles(Table 1):

Table 1

$Mo(SPh)_3$	Mo-Mo = 3.30 Å; Mo-S = 2.55 Å	S-Mo-S = 99°
	Mo-Mo = 2.70 Å; Mo-S = 2.45 Å	S-Mo-S = 113°
		Mo-S-C = 120°
$Ru(SPh)_3$	Ru-Ru = 3.25 Å; Ru-S = 2.50 Å	S-Ru-S = 98°
	Ru-Ru = 2.65 Å; Ru-S = 2.40 Å	S-Ru-S = 112°
		Ru-S-C = 120°

The geometry is the same as that found in the X-ray structure analysis of the oligomer $Fe_3(SPh)_6(CO)_6$ described in the reference (2)

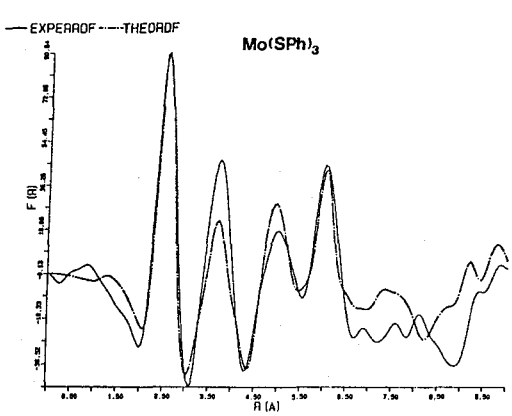

Figure 1

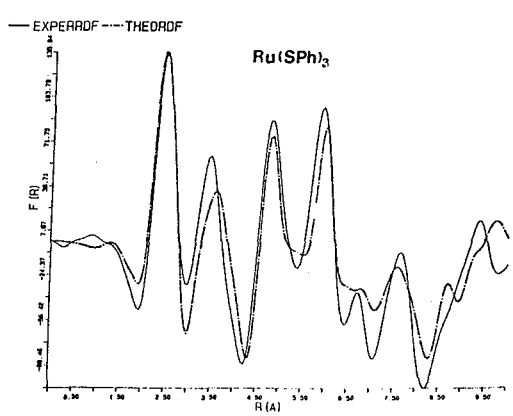

Figure 2

Experimental(full line) and theoretical(dotted line) radial distribution curves F(r) of $Mo(SPh)_3$ and $Ru(SPh)_3$.

The best description of the polymers is obtained on the basis of alternative long and short metal-metal distances leading to a distortion of the octahedral geometry around the metal atoms (Fig. 3). Using an undistorted model with one M-S and M-M distances, it was not possible to obtain a correct broadness of the first peak, which represents the superposition of the first three shells around the metal : two sets of three M-S bonds and one M-M interaction. This observed distortion is in agreement with the vibrational spectrum which shows a splitting of the T_{1u} vibration into two vibrations of the type A_2 and E_u in the vibrational area and the appearance of two deformational vibrations as expected for this type of geometry (2).

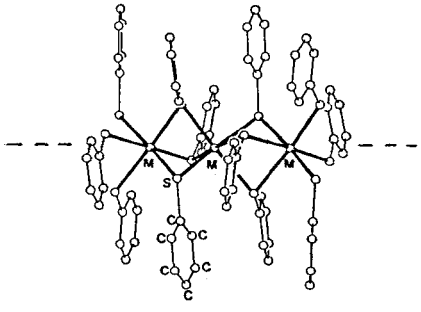

Figure 3 : Partial geometry of the infinite chain $(M(SPh)_3)_\infty$.

It is interesting to note that Cramer et al. (5) propose a similar model for the amorphous MoS_3 (a-MoS_3) evidenced by an EXAFS study indicating a short and long Mo-Mo interaction with 2.75 and 3.15 Å and two different Mo-S distances separated by 0.1 Å. The RDF of a-MoS_3, also, shows the first major peak at 2.45 Å with a spread of 0.7Å.

The encouraging curves fitting obtained for these compounds enable us to enlarge such studies to the selenium derivatives and to combine EXAFS and LAXS experiments. The figures 4 and 5 report Fourier transform of the Mo K-edge Exafs and the corresponding least squares refinements for $Mo(SePh)_3$ and the figures 6 and 7 the corresponding ones for the Se K-edge. The structural informations for $Mo(SePh)_3$ are summarized in the following table II:

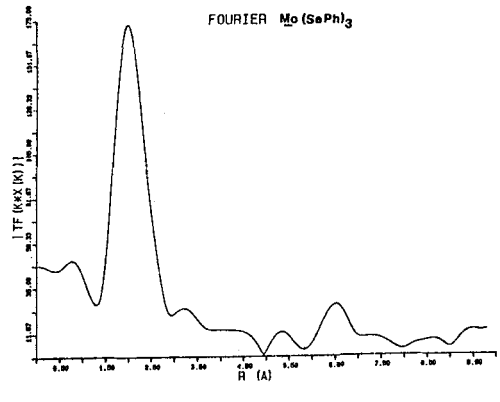

Figure 4 :Fourier transform of Mo K-edge EXAFS of $Mo(SePh)_3$.

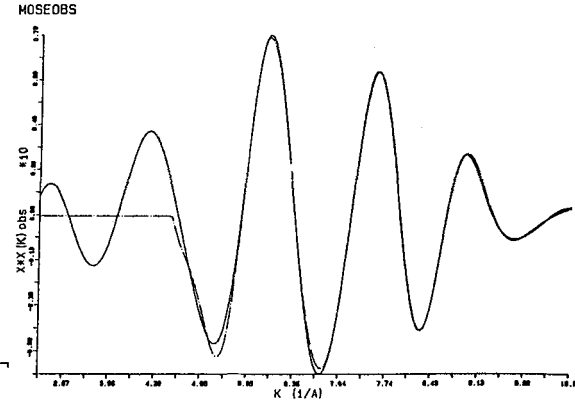

Figure 5 : Least squares refinements of EXAFS function parameters: experimental (full line) and theoretical values (dotted line)for $Mo(SePh)_3$ at the Mo K-edge.

Mo K-edge

	N	R(Å)	σ
Mo-Se	6	2.48 ± 0.03	0.118 ± 0.004
Mo-Mo	1	2.88 ± 0.04	0.084 ± 0.02
Mo-Mo	1	3.37 ± 0.01	0.099 ± 0.03
Se K-edge			
Se-Mo	2	2.52 ± 0.02	0.087 ± 0.005
Se-Se	2	3.19 ± 0.19	0.087 ± 0.01
Se-C	1	1.93 ± 0.12	0.105 ± 0.07

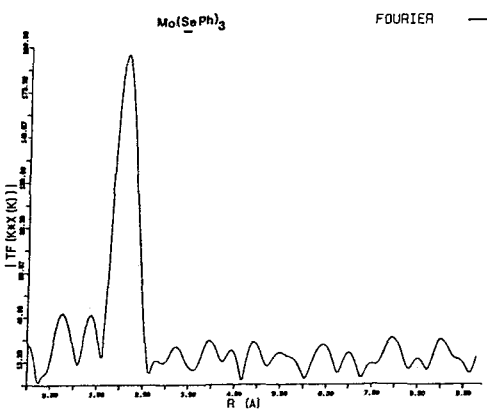

Figure 6 :Fourier transform of Se K-edge EXAFS of $Mo(SePh)_3$.

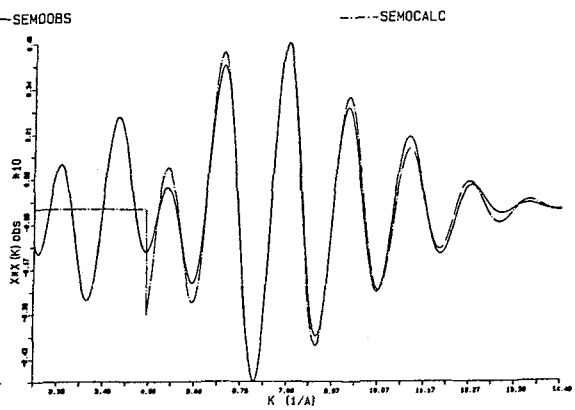

Figure 7 : Least squares refinements of EXAFS function parameters: experimental (full line) and theoretical values (dotted line)for $Mo(SePh)_3$ at the Se K-edge.

Based on this results an extended model was built up and its theoretical radial distribution function compared with the experimental one(Figure 8).

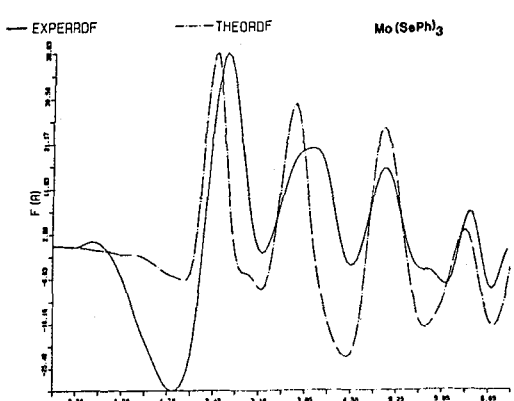

Figure 8 :Experimental radial distribution function of $Mo(SePh)_3$ compared with the theoretical RDF calculated on a model derived from EXAFS experiments.

Small discrepancies between LAXS and EXAFS are mainly due to difficulties in obtaining sufficiently good spectra at the Mo K-edge.

The related compound, with L= pyrazolate, has also been entirely investigated; the results are under publication (VOGT et al. (6)).

In conclusion, we like to emphasize for the future, the need for systematic investigations combining these two complementary techniques, LAXS and EXAFS; they give, carefully handled, a tremendous insigth in the knowledge of the short and middle range order, very often, directly connected with the physical properties of the material.

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