

Sulfur K-Edge X-Ray Absorption Spectra for Dimethyl Sulfoxide in the Solvated Thallium(III), Indium(III), Gallium(III) and Aluminum(III) Ions

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Abstract

The sulfur K-edge X-ray absorption near edge spectra (XANES) of the hexakis(dimethyl sulfoxide) solvated trivalent group 13 ions, Al, Ga, In and Tl, in the solid state show larger splitting and different intensity distribution of the main sulfur 1s electronic excitations than for the uncoordinated dimethyl sulfoxide molecule. The transitions have been interpreted by density functional calculations, and the increased splitting is shown to be an effect of metal-oxygen orbital interactions in the bonds to the oxygen coordinated dimethyl sulfoxide ligand.

1. Introduction

The hexakis(dimethyl sulfoxide) solvates of the group 13 metal ions aluminium(III), gallium(III), indium(III) and thallium(III), were previously structurally characterized in the solid state as iodides or perchlorates by crystallography, EXAFS and vibrational spectroscopy (Table I) [1–3]. In the present study, sulfur K-edge XANES spectra are presented for dimethyl sulfoxide, free or as ligand to the group 13 metal ions. Dipole-allowed excitations of the sulfur 1s electron to unoccupied molecular orbitals with some p-character in bound states, dominate the absorption features in the near-edge region, and provide sensitive probes of the bonding because of the relatively narrow line widths and wide energy range. We found significant changes in the sulfur K-edge spectra of dimethyl sulfoxide even for coordination *via* the oxygen atom by the group 13 metal ions (Figure 1).

2. Experimental

Sulfur K-edge XANES spectra were recorded in fluorescence mode on beam line 6-2 of Stanford Synchrotron Radiation Laboratory (SSRL), under dedicated conditions (3 GeV and 75–100 mA). The beam path and sample were kept in helium of atmospheric pressure. A Lytle detector without filter and Soller slit was used for detection of the fluorescence signal from the sample. The X-ray energy was varied using a fully tuned Si(111) double monochromator with the energy scale calibrated by setting the lowest energy peak of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) to 2469.2 eV [4]. Higher order harmonics were rejected by means of a nickel-coated mirror. The instrumental broadening of the spectral features is about 0.5 eV. Finely ground metal salts, prepared as described elsewhere [2, 3], were dispersed as a thin layer on a sulfur-free Mylar adhesive tape. A cell with 5 μm sulfur-free polypropylene film windows was used for a 50 mM solution of DMSO in acetonitrile. The data were analyzed using the EXAFSPAK suite of computer programs [5], and normalized intensity spectra are presented in Figure 2.

Table I. Bond lengths (\AA), angles ($^\circ$) and force constants (Ncm^{-1}) for $\text{M}(\text{dms})_6^{3+}$ complexes in the solid state (Refs. [2, 3]).

Atom	Al(III)	Ga(III)	In(III)	Tl(III)	DMSO
M-O	1.894(4)	1.974(4)	2.145(3)	2.224(3)	
O-S	1.540(5)	1.539(5)	1.541(3)	1.544(4)	1.495(4)
M-O-S	127.1(3)	124.1(3)	123.1(2)	120.7(2)	
$K(\text{MO})$	1.76	1.62	1.32	1.30	
$K(\text{OS})$	4.60	4.17	4.27	4.28	5.06

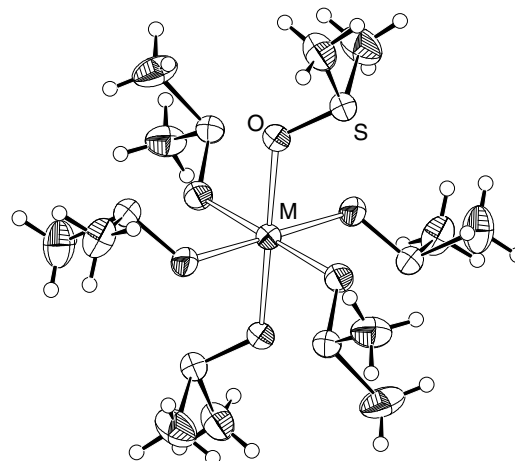


Fig. 1. The hexakis(dimethylsulfoxide)indium(III) ionic complex with six equivalent oxygen-coordinated DMSO ligands in the crystal structure of $[\text{In}(\text{dms})_6]\text{I}_3$ (295 K, 50% probability ellipsoids).

3. Computational details

Theoretical sulfur K-edge transitions were calculated for dimethyl sulfoxide molecules, free and with different types of simulated coordination (Table II), to assign the transitions observed in the experimental spectra. The computations were performed by means of the deMon StoBe density functional theory (DFT) program, using non-local gradient-corrected functionals throughout [6].

The overall spectrum was first generated by the transition potential DFT method [7], where the potential used to determine the excited states is by exciting half an electron from the 1s orbital. The differential relaxation effects on each excited state were computed separately by Kohn-Sham's excited state (ΔKS) DFT calculation method [8]. The relativistic effect was calculated to shift the ionization potential 7.4 eV for the sulfur K-edge, and was applied as an overall shift of the spectrum. Absolute energies corrected in this way in previous computations show satisfactory agreement with the experimental calibration used (see above) [8].

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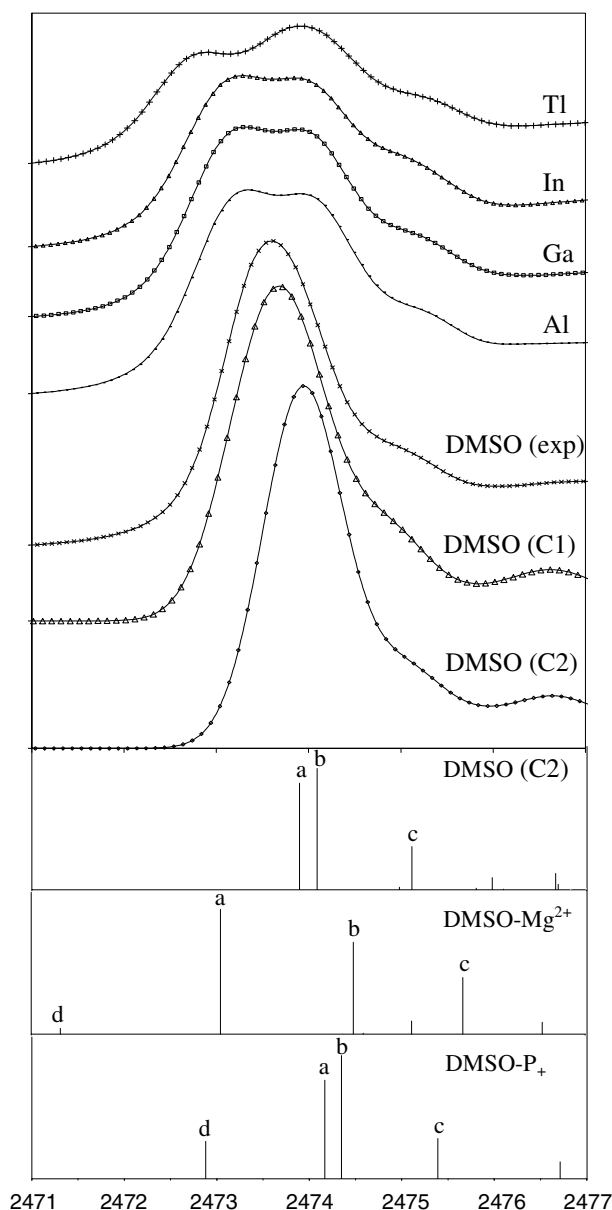


Fig. 2. Experimental sulfur K-edge XANES spectra (normalized intensities) of the hexakis(dimethyl sulfoxide)-M(III) solvates of the group 13 metal ions (from the top $M = \text{Tl, In, Ga and Al}$), and of 50mM DMSO in acetonitrile. Below calculated spectra for free DMSO, C1 with the S-O distance 1.595 Å, and C2 with 1.495 Å (*cf.* Table II). The rows vertical bars represent the calculated energies and cross-sections for the X-ray induced excitations of the sulfur 1s electron for free DMSO (C2), for DMSO connected to an Mg^{2+} ion, and to a +1 point charge P_+ , respectively.

Table II. Interatomic distances (Å) and angles (°) used in the computation of spectra for free (C1 & C2) and coordinated ($M = \text{Mg}^{2+}$ or P_+) DMSO. P_+ represents a point charge +1.

	Free	Coordinated
O-S	1.495 & 1.595	1.544
S-C	1.773	1.773
O-S-C	105.7	105.7
M-O	—	2.0
M-O-S	—	125

However, another calibration scheme with the thiosulfate peak set to 2472.02 eV, i.e. +2.8 eV, is also in use [9].

To simulate the interaction between a metal ion and a dimethyl sulfoxide ligand, we have computed the spectra of models with a point charge +1 (P_+) or an Mg^{2+} ion located at a possible coordination site relative to the oxygen atom of the DMSO molecule (Table II). In all calculations, C_s symmetry was assumed. For sulfur the iglo basis of Kutzelnigg was used in order to describe relaxation effects upon core-excitation [10]; this was extended with a very large, diffuse additional basis set for the evaluation of the spectra in a double-basis set approach. The basis sets used were for oxygen and carbon TZVP ((6311/311/1)), for hydrogen (311/1) and for the magnesium ion DZVP (6321/411*/1). The auxiliary bases (5,4;5,4) were introduced for sulfur and magnesium, (5,3;5,3) for oxygen and carbon, and (4,2;4,2) for hydrogen, where the nomenclature (($N_{\text{C}}(\text{s})$, $N_{\text{C}}(\text{spd})$; $N_{\text{XC}}(\text{s})$, $N_{\text{XC}}(\text{spd})$) indicates the number of s and spd-type functions that were used to fit and expand the Coulomb and exchange-correlation potentials, respectively.

4. Results and discussion

The sulfur K-edge XANES spectrum of dimethyl sulfoxide in solution shows an asymmetric peak at about 2473.5 eV with a shoulder at 2475 eV. These features are well explained by the three main calculated transitions (*a*, *b*, *c* in Fig. 2). By applying a Gaussian 1.0 eV broadening of the calculated features up to the computed ionisation potential, followed by a linear increase up to 8 eV over a 10 eV interval from the edge, the calculated curves C1 and C2 result, with a similar shape as the experimental (Figure 2). The calculated (gas phase) spectrum C2 is shifted 0.5 eV relative to the experimental solution spectrum. This shift may be caused by uncertainties in the calculated energy or the experimental calibration [4, 9]. Also, dipole-dipole interactions between the DMSO molecules in the acetonitrile solution may influence the shift, even though a large increase in the S–O bond length (0.1 Å, *cf.* Table II) would be needed to eliminate this shift (C1 in Fig. 2).

The shapes of the excited state molecular orbitals (MO) show, for the strongest *b* transition (of A'' symmetry species in the C_s point group, *cf.* Fig. 3) excitation of the sulfur 1s electron to an antibonding MO of p character, and for the *a* and *c* transitions (of A' symmetry) charge transfer from sulfur to the carbon and oxygen atoms.

The site symmetry of the crystalline $[\text{M}(\text{dms})_6]^{3+}$ solvates implies all six oxygen-bonded dimethyl sulfoxide ligands to be equivalent (Fig. 1). The sulfur K-edge XANES spectra for the Al, Ga and In solvates are similar with a slight increase in the splitting between the two main peaks from about 0.7 to 0.8 eV. For the Tl(III) solvate the split increases to 1.5 eV (Fig. 2). To simulate the effect on a coordinated DMSO ligand an Mg^{2+} ion was placed 2.0 Å from the oxygen atom in a similar position as the metal ions in the hexasolvates (Table II). The distance is chosen, based on previous DFT calculations [11], to give a reasonable balance between the electrostatic attraction and the Pauli repulsion effects between the orbitals in the M–O bond.

The Mg^{2+} ion shifts the transition *a* about 1.5 eV to lower energy, and increases its probability to slightly higher than that of *b* (Fig. 2). The orbital character of *a* becomes clearly antibonding with increased charge on the oxygen atom (Fig. 3). The *b* and *c* transitions increase only slightly in energy, and satisfactorily explain the features at 2474 and 2475.3 eV,

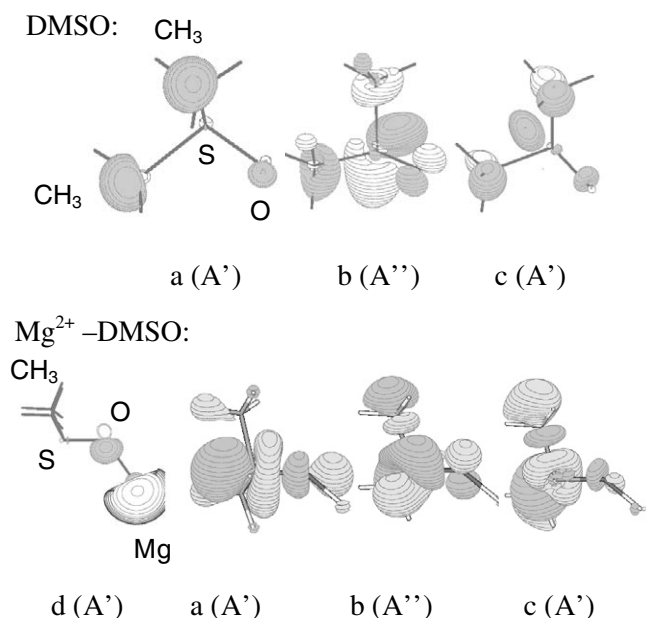


Fig. 3. Electron density contours for MO:s (different gray tones indicate different phase) corresponding to the one-particle excitations in Figure 2 of the sulfur 1s electron in: (top) free DMSO; (bottom) DMSO coordinated to an Mg²⁺ ion at a distance of 2.0 Å (*cf.* Table II).

respectively, which are found throughout the experimental spectra. A new weak transition (*d*) that appears at low energy (2471 eV), corresponds to charge transfer from sulfur to the magnesium ion, as shown by the orbital shapes in Figure 3.

To assess the importance of interatomic orbital interactions versus pure electrostatic effects the Mg²⁺ ion was replaced with a point charge (+1). The main effect is that the charge transfer transition *d* is less shifted but gains intensity, while the transitions *a*, *b* and *c* remain similar in energy and intensity to those in the free DMSO molecule (Figure 2). Thus, the orbital interactions induced by the M-O bond seem to cause the observed splitting in the spectra. The gradual increase in covalency from Al to In is only reflected in a small increase in the split between the main transitions, with the Tl(III) sulfur XANES spectrum clearly deviating from that trend. Thus, the large split in the Tl(III) spectrum indicates a substantial increase in the orbital interaction. Even though the Tl-O bond is the longest of the group 13 M-O bonds, it is the most covalent [3]. This is indicated by e.g. the trends of the vibrational force constants, the M-O-S angles and

the S-O bond length (Table I). For the thallium(III) solvate the disorder parameters indicate vibronic mixing in the M-O bonds of the 5d_{z²} and 6s orbitals, which are close in energy [2]. It seems probable that the isoelectronic hexakis(dimethyl sulfoxide) mercury(II) solvate, which is affected by vibronic mixing (or pseudo Jahn-Teller effect) to a higher extent [2], would show an even larger split in its sulfur spectrum (not studied yet).

5. Conclusions

The orbital interactions in the M-O bonds are the reason for the increase in the splitting observed between the main electronic transitions in the sulfur K-edge spectra of DMSO as oxygen coordinated ligand to a metal ion. The large splitting in the hexakis(dimethyl sulfoxide) thallium(III) solvate is probably connected to the close energy levels causing vibronic mixing between valence shell atomic orbitals in the Tl-O bonds.

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References

1. Harrowfield, M. J., Skelton, B. W. and White, A. H., *Aust. J. Chem.* **43**, 759 (1990).
2. Ma, G. *et al.*, *Inorg. Chem.* **40**, 6432 (2001).
3. Molla-Abbassi, A. *et al.*, *J. Chem. Soc., Dalton Trans.* 1746 (2003).
4. Sekiyama, H., Kosugi, N., Kuroda, H. and Ohta, T., *Bull. Chem. Soc. Jpn.* **59**, 575 (1986).
5. George, G. N. and Pickering, I. J., EXAFSPAK; A Suite of Computer Programs for Analysis of X-ray Absorption Spectra, SSRL, Stanford University, CA., USA (1993).
6. deMon-KS StoBe version 1.0, Casida M. E. *et al.*, deMon Software (2001).
7. Stöhr, J., *NEXAFS spectroscopy*, (Springer-Verlag, Berlin, Heidelberg 23, 1992).
8. Kolczewski, C. *et al.*, *J. Chem. Phys.* **115**, 6426 (2001).
9. Hedman, B. *et al.*, *Nucl. Instr. Meth.* **A246**, 797 (1986).
10. Kutzelnigg, W., Fleischer, U. and Schindler, M., "NMR-Basic Principles and Progress" (Springer Verlag, Heidelberg, 1990).
11. Pavlov, M., Siegbahn, P. E. M. and Sandström, M., *J. Phys. Chem.* **102**, 219 (1998).