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Using Solution- and Solid-State S K-edge X-ray Absorption Spectroscopy with Density Functional Theory to Evaluate M–S Bonding for MS_4^{2-} (M = Cr, Mo, W) Dianions

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Abstract

Herein, we have evaluated relative changes in M–S electronic structure and orbital mixing in Group 6 MS_4^{2-} dianions using solid- and solution-phase S K-edge X-ray absorption spectroscopy (XAS; M = Mo, W), as well as density functional theory (DFT; M = Cr, Mo, W) and time-dependent density functional theory (TDDFT) calculations. To facilitate comparison with solution measurements (conducted in acetonitrile), theoretical models included gas-phase calculations as well as those that incorporated an acetonitrile dielectric, the latter of which provided better agreement with experiment. Two pre-edge features arising from S 1s $\rightarrow e^*$ and t_2^* electron excitations were observed in the S K-edge XAS spectra and were reasonably assigned as $^1A_1 \rightarrow ^1T_2$ transitions. For MoS_4^{2-} , both solution-phase pre-edge peak intensities were consistent with results from the solid-state spectra. For WS_4^{2-} , solution- and solid-state pre-edge peak intensities for transitions involving e^* were equivalent, while transitions involving the t_2^* orbitals were less intense in solution. Experimental and computational results have been presented in comparison to recent analyses of MO_4^{2-} dianions, which allowed M–S and M–O orbital mixing to be evaluated as the principle quantum number (n) for the metal valence d orbitals increased (3d, 4d, 5d). Overall, the M–E (E = O, S) analyses revealed distinct trends in orbital mixing. For example, as the Group 6 triad was descended, e^* (π^*) orbital mixing remained constant in the M–S bonds, but increased appreciably for M–O interactions. For the t_2^* orbitals ($\sigma^* + \pi^*$), mixing decreased slightly for M–S bonding and increased only slightly for the M–O interactions. These results suggested that the metal and ligand valence orbital energies and radial extensions delicately influenced the orbital compositions for isoelectronic ME_4^{2-} (E = O, S) dianions.

Introduction

Metal chalcogenate (O, S, Se, and Te) materials are of broad interest owing to their versatile properties. These range from materials that have unique thermoelectric behaviors, desirable

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Supporting Information Available. Background subtracted and normalized X-ray absorption data and analyses. This material is available free of charge via the web at <http://pubs.acs.org>.

photoluminescence, fast ion conductivity, selective ion exchange, photocatalytic reactivity, and gas adsorption properties.¹⁻⁷ Among the diverse group of chalcogen materials, those with metal-oxo and metal-sulfide interactions stand out, given that they play key roles in biological/bio-inspired processes, catalysis, and in applications that exploit their magnetic, electronic, and thermal properties.⁸⁻³¹ As expected, M–E (E = O, S) functionality changes significantly with metal identity. Hence, technologies that incorporate metal oxides and sulfides would benefit from increased understanding of how M–E electronic structure and orbital mixing vary as the metal identity changes.

Chalcogen K-edge X-ray absorption spectroscopy (XAS) measurements provide an opportunity to advance understanding of electronic structure and bonding in M–E containing compounds.³¹⁻⁴⁸ In general, chalcogen K-edge XAS probes dipole-allowed bound-state transitions from the chalcogen 1s orbitals to molecular orbitals that contain chalcogen p character resulting from M–E orbital mixing, such that the transition intensity is directly related to the M–E orbital mixing coefficient.^{32-35,49-52} In an effort to evaluate M–S vs. M–O bonding and electronic structure, we contribute here quantitative solid-state and solution-phase analyses of the d⁰ MS₄²⁻ dianions using S K-edge XAS measurements (M = Mo, W) and DFT calculations (M = Cr, Mo, W) (Scheme 1). These highly symmetric Group 6 tetrathiometalates are well suited for establishing trends in M–S orbital mixing with a common S²⁻ ligand. For example, the solid-state S K-edge XAS spectra for the Mo and W members of this series have been previously analyzed and the pre-edge peak intensities qualitatively evaluated.^{50,53,54} Moreover, the metal–ligand bonding within the tetrahedral MS₄²⁻ dianion series is relatively well understood.^{50,55-57} The study presented here offers further insight by providing quantitative analyses of differences in π - and $\sigma + \pi$ -type M–S orbital mixing for metals within Group 6. Results have been presented in the context of previously published O K-edge and DFT analyses of the tetraoxometalate complexes, specifically MO₄²⁻ (M = Cr, Mo, W; Scheme 1)^{58,59}, which provided a unique opportunity to evaluate relative changes in orbital mixing as the principle quantum number for both ligand- (2p vs. 3p) and metal-based (3d, 4d, 5d) valence orbitals increased.

Results and Discussion

S K-edge XAS

The background-subtracted and normalized S K-edge XAS data for the solid- and solution-state samples of (PPh₄)₂MS₄ (M = Mo, W), hereafter referred to as MS₄²⁻, have been provided in Figure 1. The X-ray absorption measurements were obtained using fluorescence yield detection methods, as described in the Experimental Section. Superficially, the solution- and solid-state data appeared to be in good agreement, and a general description of all four spectra follows. For MoS₄²⁻, the solid-state S K-edge XAS spectrum (black trace) was dominated by two pre-edge features near 2470 eV that were well-resolved from the onset of the rising edge (~2473 eV). There also existed a subtle shoulder poorly resolved from the rising edge at approximately 2475 eV. The MoS₄²⁻ edge region (2473–2478 eV) was dominated by a large feature near 2477 eV, while the post-edge region (>2478 eV) contained two prominent features at higher energy (near 2525 and 2630 eV) that were associated with the Mo L_{3/2}-edge absorptions (not shown in Figure 1 but provided in Figure

S1 of the Supporting Information). Unfortunately, the close proximity of these features to the S K-edge complicated accurate modeling of the post-edge region, which made it difficult to objectively normalize the data.

The solid-state spectrum for WS_4^{2-} (brown trace) was quite similar to that of MoS_4^{2-} in that two pre-edge features were observed near 2471 eV, as was the shoulder (2475 eV) on the rising edge. While the edge region (2473–2478 eV) of the WS_4^{2-} spectrum was nearly superimposable with MoS_4^{2-} , the pre-edge regions were subtly different. For example, the two WS_4^{2-} pre-edge features shifted to higher energy by approximately 1 eV in comparison to MoS_4^{2-} , which was anticipated given the relative energy differences for the 4d and 5d final states. For the post-edge region (>2478 eV), the only appreciable differences were associated with the expected absence of the Mo L -edge absorbances. Qualitatively, both MoS_4^{2-} and WS_4^{2-} solid-state spectra were similar to those reported previously.^{50,53,54} Notably, the pre-edge peak intensities in the previous spectra appeared smaller than what was observed here, although quantitative intensity values were not included in the original reports. Such differences may be attributed to self-absorption in the previous measurements.⁶⁰

Solution-phase S K-edge XAS experiments^{35,51,53,61-68} were conducted on $(\text{PPh}_4)_2\text{MS}_4$ salts dissolved in acetonitrile. To characterize the influence of self-absorption effects on the peak intensities, samples were analyzed using progressively decreasing analyte concentrations until normalized intensities remained constant. The optimum concentration of sulfur appeared to be 0.06 M. At this concentration, the pre-edge region for the solution-phase MoS_4^{2-} and WS_4^{2-} spectra (red and blue dashed traces, respectively, Figure 1) were similar to the solid-state measurements. For the rising edge and post-edge regions of the spectra, there was more variability between the solution- and solid-state data. For example, in the solution-state measurements the shoulders on the rising edges near 2475 eV decreased in energy while the peak near 2477 eV moved to higher energy. Hence, both features were better resolved in solution. In addition, while MoS_4^{2-} and WS_4^{2-} showed no sign of decomposition during the solid-state S K-edge XAS measurements, a common contaminant easily detected by S K-edge XAS was observed at 2483 eV in solution, specifically SO_4^{2-} .⁶⁹ To better understand the observed MS_4^{2-} decomposition, which appeared to result from radiation damage, solution-phase spectra were repeatedly obtained every 7 min on a sample of WS_4^{2-} dissolved in acetonitrile (0.06 M in sulfur), Figure 2. In these experiments, the SO_4^{2-} feature (2483 eV) increased systematically in intensity, suggesting that for the MS_4^{2-} systems decomposition pathways in solution are more accessible than in the solid state. While spectral normalization can be affected by the presence of SO_4^{2-} , adverse effects on the MoS_4^{2-} and WS_4^{2-} spectral normalizations were likely small given the low intensities of the SO_4^{2-} features.

Models for Experimental Data

The MS_4^{2-} solid- and solution-phase S K-edge XAS spectra were modeled as described in Figure 3 and Table 1 (see Supporting Information for the full curve-fitting models). The pre-edge and edge regions were modeled with two symmetrically-constrained pseudo-Voigt line shapes with fixed 1:1 Lorentzian to Gaussian ratios (see reference 14 for line shape

justification). To model the edge step an additional feature was included, which consisted of a 1:1 ratio of arctangent and error function contributions. An excellent fit was obtained for all spectra, such that the residual data deviated from zero by less than 6% over the region analyzed (see Supporting Information). The analyses indicated that pre-edge peak splittings and energies for MoS_4^{2-} and WS_4^{2-} in the solid state were reproduced exceptionally well in solution, such that solid-state and solution-phase peak positions differed by ~ 0.03 eV.

As apparent in Figures 1 and 3, the nearly identical pre-edge peak heights for the solid- and solution-phase data indicated that the presence of SO_4^{2-} in the post-edge region of the solution-state spectra did not significantly affect spectral normalizations. For both MoS_4^{2-} and WS_4^{2-} , peak areas for the first pre-edge feature in the solid-state data were equivalent to those determined for the solution-phase data. In contrast, comparison of the peak intensities for the second pre-edge feature showed a larger degree of variability. For MoS_4^{2-} , the intensity of the second feature decreased from 1.76(9) to 1.65(8) when moving from solid to solution. However, the change in intensity was a direct result of peak narrowing (decreased full-width half-maximum; FWHM), and was not associated with any appreciable change in peak amplitude. We note that these changes were small and the intensity values were equivalent at 1σ when the 5% estimated error associated with the measurement was considered. Decreased FWHM for the second feature in the WS_4^{2-} solution-phase spectrum was more pronounced, with the 1.62(8) and 1.34(7) values for the respective solid- and solution-state intensities being unique at 1σ and equivalent at 2σ . Potential origins for these differences have been included in the Outlook and Conclusion section.

Ground-State Electronic Structure Calculations

To aid in spectral interpretation, DFT calculations were conducted on CrS_4^{2-} (not experimentally probed), MoS_4^{2-} , and WS_4^{2-} . The theoretical approach initially involved gas-phase DFT. However, because the solution-phase S K-edge XAS experiments were conducted in acetonitrile, calculations were also conducted that incorporated an acetonitrile dielectric. Previous work has shown that the use of solvent dielectrics can improve the calculated energy values for anionic species.^{47,70-72} The computational analyses included here were consistent with expectations from group theory for the $d^0 T_d\text{-MS}_4^{2-}$ dianions. As previously discussed^{11,50,56,57,73} and illustrated in Figure 4, group theory showed that of the twelve symmetry-adapted linear combinations (SALCs) of S 3p atomic orbitals, four SALCs spanned $a_1 + t_2$ symmetries and were σ -symmetric with respect to the M–S bond. The remaining eight S 3p SALCs ($e + t_1 + t_2$) had π symmetry. The metal s, p, and d orbitals of a_1 and t_2 symmetries were allowed by symmetry to mix and form M–S σ interactions, while metal orbitals of t_2 and e symmetries could mix to form π interactions. This left the SALCs of t_1 symmetry as non-bonding sulfur lone pairs.

The gas-phase DFT calculations agreed in many ways with the calculations that incorporated an acetonitrile dielectric. For example, both sets of calculations were in agreement with the molecular orbital picture described above and showed the MS_4^{2-} dianions' highest occupied molecular orbitals (HOMOs) as a triply degenerate set of S 3p orbitals that had $1t_1$ symmetry (Figure 4, Figure 5, and Table 2). At higher energy were the molecular orbitals of $2e^*$ symmetry (π^* ; LUMO) that resulted from appreciable metal nd

and sulfur 3p mixing. The two sets of calculations also provide equivalent results regarding the calculated HOMO/LUMO gaps, which increased from 2.6 to 3.4 to 3.9 eV for Cr, Mo, and W (Table 2). These computational values were in good agreement with the 2.7 (Mo) and 3.2 (W) eV HOMO/LUMO gap determined experimentally by electronic absorption spectroscopy.⁵⁵ The gas- and solution-phase DFT calculations also revealed the expected set of higher lying orbitals of $4t_2^*$ symmetry ($\sigma^* + \pi^*$; LUMO + 1).

While the gas- and solution-phase DFT calculations showed similar orbital compositions for the $2e^*$ orbitals (Table 2), appreciable differences associated with the compositions for the higher-lying $4t_2^*$ orbitals were observed. For example, the gas-phase Mulliken population analyses showed significant amounts of metal $(n+1)p$ character while the solution-phase calculation indicated less metal $(n+1)p$ and metal nd hybridization. Hence, in the solution-phase DFT calculations the $4t_2^*$ orbitals are reasonably described as resulting from primarily metal nd and S 3p mixing. Because the solution-phase molecular orbital picture agreed better with previous theoretical models used to evaluate MS_4^{2-} , MO_4^{2-} , and MCl_4 ligand K-edge XAS spectra,^{58,59,73-77} and in light of the gas- vs. solution-phase TDDFT results (*vide infra*), the solution-phase DFT data appeared to provide a more relevant model than the gas-phase calculations. Consistently, others have observed that including solvent dielectrics improves DFT agreement with XAS experimental data for anionic species.^{47,70,71,78} Future efforts are underway to better model the degree of metal $(n+1)p$ and metal nd hybridization by incorporating spin-orbit coupling into these calculations, which (as suggested in previous reports)^{74,79,80} will likely enhance metal $(n+1)p$ and metal nd mixing in the orbitals of t_2^* symmetry.

Spectral Interpretations

To support interpretation of the S K-edge XAS spectra, time-dependent density functional theory (TDDFT) calculations were conducted to simulate the experimental data (Figure 6).^{41,47,59,70,71,77,81-88} The computed spectra were carried out using linear response theory, based on density functional theory. This formalism is commonly referred in the community as TDDFT as it is from the time-dependent perturbation theory to DFT. The results from the gas-phase TDDFT calculations have been compared with calculations that incorporated a uniform acetonitrile dielectric environment (Table 1 and Figure 6). This medium acts upon and reacts to the electronic structure of the molecule, but does not interact chemically, i.e. forming bonds or reducing/oxidizing the molecule. Including the effect of the environment can yield an improved model with respect to calculations in the “gas phase.” For example, including a dielectric can provide extra stabilization of polarized states via interaction with the polarizable medium surrounding the molecule. Both sets of calculations (solution and gas phase) were consistent with expectations based on group theory analyses, and showed the spin- and dipole-allowed transitions between $^1A \rightarrow ^1T_2$ electronic states. To account for omission of electronic relaxation, relativistic stabilization, and errors associated with the functional,^{89,90} spectra were shifted so that the first calculated transition (+56.6 to 56.7 eV) matched the maxima of the first experimental pre-edge peak, which provided good agreement between the TDDFT and experimental data (Figure 6). Consistent with the molecular orbital picture in Figure 4, the calculations showed a single transition at low energy from the S 1s orbitals of $1t_2$ symmetry to molecular orbitals of $2e^*$ symmetry, which

was reasonably assigned to the first pre-edge feature in each MS_4^{2-} experimental spectrum. At intermediate energy the calculations showed a pair of excitations from S 1s ($1a_1$ and $1t_2$) orbitals to molecular orbitals of $4t_2^*$ symmetry.

Further comparison between the gas- and solution-phase TDDFT calculations revealed that the solution-phase TDDFT-derived intensities for the two pre-edge features were in excellent agreement with the experimental MS_4^{2-} S K-edge XAS spectra, while the gas-phase calculations slightly underestimated the intensities of transitions to the $4t_2^*$ orbitals (Figure 6). However, we note that there are concerns when analyzing the TDDFT intensities. For example, as described previously, the non-Coulombic asymptotic form of the potential associated with the employed functional may cause inaccuracies in the computed oscillator strengths.⁸⁷ These issues will be the focus of future efforts, but given the approximate agreement with the experimental intensities noted earlier, we utilized the TDDFT intensities bearing the caveats above in mind.

Another indication that the solution-phase TDDFT calculations were more representative of the experimental data was associated with the high energy of pre-edge transitions to Rydberg-type orbitals that were composed primarily of metal ($n+1$)p character, but also contained some S 3p contributions. In the gas-phase TDDFT, a one-to-one agreement with experiment was not observed (Figure 6), and these transitions were calculated to occur in the valley between the $4t_2^*$ feature and the onset of the rising edge (near 2471, 2472, and 2472.5 eV for Cr, Mo, and W, respectively). In contrast, the solution-phase TDDFT showed these transitions shifted to higher energy (near 2472.5, 2473, and 2473 eV for Cr, Mo, and W, respectively), such that they fell under the shoulder on the rising edge in the experimental spectra. Overall, these analyses are in agreement with previous findings, suggesting that more reasonable transition energies can be obtained for anionic species when an appropriate dielectric is included in the TDDFT analyses.^{47,70,71,78} Given that the incorporation of an acetonitrile dielectric in the ground-state DFT and excited-state TDDFT calculations provided better agreement with the experimental S K-edge XAS data, only the solution-phase calculations have been included in the orbital mixing discussion that follows.

Evaluation of Trends in M–S Orbital Mixing

Because S K-edge XAS probes bound-state dipole-allowed transitions, and because the pre-edge features are associated with transitions from S 1s orbitals to molecular orbitals that contain S 3p character, the intensities for the pre-edge features shown in Figure 3 are directly related to the M–S orbital mixing coefficient.³² Hence, the experimental pre-edge intensities could be used to quantitatively evaluate trends in M–S orbital mixing as the Group 6 triad was descended. For example, as shown in Figure 7 and Table 1, the $1s \rightarrow 2e^*$ transition intensities in the solid-state experimental S K-edge XAS spectra increased from 1.32(7) to 1.50(8) when comparing Mo to W. When the 5% error in these intensities was considered, this modest 14% increase is difficult to resolve by S K-edge XAS. The problem was further magnified by the difficulties in normalization for the MS_4^{2-} data, caused by the proximity between the Mo $L_{3/2}$ and S 3p edges.⁹¹ Confidence in these experimental values was obtained from the solution-phase DFT calculations, which also showed only small changes in S 3p character when moving from MoS_4^{2-} to WS_4^{2-} (47.6 to 46.4%,

respectively). Additionally, the solution-phase TDDFT-derived oscillator strengths (also related to the mixing coefficient) for the transitions involving the $2e^*$ orbitals remained constant at 0.0036. For the $1s \rightarrow 4t_2^*$ transitions, a subtle increase in S 3p character was calculated by solution-phase DFT (Table 2) when moving from Mo to W and an 18% decrease in oscillator strength was determined by TDDFT. For the solid-state experimental S K-edge XAS measurements, changes in peak intensity between Mo and W for the $1s \rightarrow 4t_2^*$ transitions were bracketed by the DFT and TDDFT extremes, showing an 8% decrease.

Because the S K-edge XAS spectrum for the CrS_4^{2-} dianion was not measured, the experimental data precluded a comparison of π and $\sigma + \pi(2e^*$ and $4t_2^*)$ M–S orbital mixing for the Cr, Mo, and W tetrathiometalate salts. However, we can compare the calculated values for the 3d, 4d, and 5d MS_4^{2-} dianions with the Mo and W results described above. Overall, as shown in Figure 7 and Table 1, the magnitude for the changes in Cr–S, Mo–S, and W–S orbital mixing observed by solution-phase DFT and TDDFT as well as solid-state S K-edge XAS provided a unified bonding picture best described as having no change to mild increases in orbital mixing for interactions involving π orbitals of e^* symmetry and modest decreases in $\sigma + \pi$ orbital mixing for orbitals of t_2^* symmetry (concomitant calculated compositions of metal d and p character are provided in Table 2). For MoS_4^{2-} and WS_4^{2-} , the trends in orbital mixing described above held true once the compounds were dissolved in acetonitrile and examined experimentally. For example, the solution-phase S K-edge XAS spectra showed a 2% increase in the intensity for the $1s \rightarrow 2e^*$ transitions when moving from Mo to W, which agreed well with the data described above. Similarly, the solution-phase peak intensities for the $1s \rightarrow 4t_2^*$ features showed an appreciable decrease of 19%, which is also in good agreement with the trend observed by solid-state XAS and TDDFT.

Experimental peak splittings were determined based on the energy differences between the $1s \rightarrow 2e^*$ and $1s \rightarrow 4t_2^*$ pre-edge peak maxima. Both the solid- and solution-phase experimental data showed a splitting increase of 0.1 eV when moving from MoS_4^{2-} to WS_4^{2-} . This marginal increase in peak splitting is similar to the 0.1 eV increase observed by solution-phase TDDFT. Peak splitting differences calculated by solution-phase ground-state DFT increased by 0.29 eV from CrS_4^{2-} to MoS_4^{2-} and only slightly decreased by 0.12 eV as Group 6 was further descended to WS_4^{2-} .

Outlook and Conclusion

The comparative analysis of the MS_4^{2-} solid-state and solution-phase S K-edge XAS data provided a platform for determining if conclusions derived from evaluation of compounds fixed in solid-state matrices were relevant after the analytes were dissolved in solution. In MoS_4^{2-} , effects from the crystal environment were found to be very similar to those in the solution environment, both yielding similar spectra. In WS_4^{2-} , the intensity of the $4t_2^*$ pre-edge peak was smaller in solution than in the solid state, but at 2σ the solid- and solution-state $4t_2^*$ intensities for WS_4^{2-} were equivalent. There existed several possibilities that could account for the intensity differences. For instance, variation between the solid- and solution-phase spectra may have resulted from self-absorption in the solid-state measurement;⁹² however, we would expect peak heights and widths for all of the features to systemically

vary in that case, which they did not. It is also possible that an unforeseen dynamic process available to the MS_4^{2-} analytes occurring on the S K-edge XAS time scale affected the observed spectrum. Additionally, the differences might have occurred from stronger polarization and charge migration to the ligand in solution. Hence, future efforts are focused on better characterizing the influence from self-absorption, dynamic processes, and polarization on solution phase S K-edge XAS.

Comparing the MS_4^{2-} dianion S K-edge XAS ($M = \text{Mo}, \text{W}$) and DFT analyses ($M = \text{Cr}, \text{Mo}, \text{W}$) reported here with previously reported O K-edge studies on MO_4^{2-} ($M = \text{Cr}, \text{Mo}, \text{W}$) offers a unique opportunity to evaluate M–S vs. M–O electronic structure and orbital mixing in a series of structurally similar and isoelectronic compounds. Before discussing the data, it is instructive to consider first-order perturbation theory as a platform to rationalize the observations. In a simplified perturbation model, the orbital mixing is directly proportional to the Hamiltonian matrix element between the metal and ligand valence atomic orbitals and inversely proportional to their energy separation.⁹³ Furthermore, the Hamiltonian matrix element is proportional to the overlap between the orbitals. Our calculations on the free Cr, Mo, W, O and S ions gave support to this simplified interpretation for evaluating the influence of frontier atomic orbital energy and radial extension for the elements involved in the M–S and M–O bonds. For instance, our calculations indicated that the radial extension ($r^2\psi^2$) for the Cr, Mo, and W d-atomic orbitals increased from 0.764 (3d) to 1.033 (4d), and 1.128 Å (5d), respectively, while the nd ($n = 3, 4, 5$) atomic orbital energies remained relatively constant near -5 eV (Figure 8). Hence, as the Group 6 triad was descended for the MS_4^{2-} dianions, contributions to covalent M–S bonding associated with the metal-ligand energy separation became slightly more favorable from Cr to Mo and then slightly less favorable from Mo to W. These changes were quite small in comparison to the large variation in radial extension for the Cr, Mo, and W nd atomic orbitals, which likely promoted orbital mixing for the heavier Group 6 transition metals based on spatial overlap considerations.^{85,94}

The data provided herein also enabled the evaluation of orbital mixing as a function of ligand identity, e.g. M–O vs. M–S. For the MO_4^{2-} compounds, appreciable increases in O 2p character were observed previously for the orbitals of $2e^*$ symmetry as the Group 6 triad was descended.^{58,59} The increased M–O orbital mixing likely resulted from improved spatial overlap between the O 2p and metal 4d vs. 5d atomic orbitals, which outweighed the negative effect on orbital mixing resulting from the increased orbital energy separation (Figure 8). In contrast, MS_4^{2-} orbitals of $2e^*$ symmetry showed virtually no change in S 3p character for MoS_4^{2-} (4d) vs. WS_4^{2-} (5d). Overall, these results suggest that the radial extension for second and third row transition metal atomic orbitals had a more profound influence on orbital mixing when interacting with small O 2p ligand orbitals ($r^2\psi^2 = 0.72$ Å) than with the more diffuse S 3p orbitals ($r^2\psi^2 = 1.19$ Å).

Direct comparisons between the MO_4^{2-} and MS_4^{2-} $\sigma + \pi$ orbitals of t_2^* symmetry also suggested that increasing radial extension of the metal atomic orbitals (when moving from Mo to W) played a more important role in M–O than M–S bonding than the energy separation term. For example, the ligand character in the $4t_2^*$ orbitals increased slightly for MO_4^{2-} , but decreased slightly for MS_4^{2-} . Future efforts are focused on better characterizing

the complex effects of spatial overlap and energy separation on covalency in bonding. We anticipate that these results may aid in the advancement of technologies that incorporate metal oxides and sulfides. This is especially true if future studies validate the generality of the conclusions described here on how M–E electronic structure and orbital mixing vary as the metal identity changes. Hence, our efforts will continue to focus on evaluating M–O vs. M–S bonding in both the solution- and solid-state for even heavier metals, namely lanthanide and actinide elements,^{41,58,59,83,85,87} where f- and d-orbital contributions to covalency are anticipated.

Experimental Section

General Experimental Considerations

The PPh_4Br (Acros), $(\text{NH}_4)_2\text{MoS}_4$ (Strem) and $(\text{NH}_4)_2\text{WS}_4$ (Strem) reagents were used as received. Diethyl ether (anhydrous, Acros) was dried over K and benzophenone, degassed with three freeze-pump-thaw cycles, and vacuum distilled prior to use. Unless otherwise indicated, acetonitrile (anhydrous, Acros) was dried over CaH_2 , degassed with three freeze-pump-thaw cycles, and vacuum distilled prior to use. Using a Thermo-Scientific Barnstead Nanopure water purification system, H_2O was purified to 18.2 MW-cm resistivity. Single crystals of $(\text{PPh}_4)_2\text{MoS}_4$ and $(\text{PPh}_4)_2\text{WS}_4$ were mounted in a nylon cryoloop with Paratone-N oil. Crystallographic data were collected on a Bruker D8 diffractometer, with an APEX II charge-coupled-device (CCD) detector, and cooled to 120(1) K using an American Cryoindustries low temperature device. The instrument was equipped with graphite monochromatized Mo K α X-ray source ($\lambda = 0.71073 \text{ \AA}$) and a 0.5 mm monocapillary. A hemisphere of data was collected using ω scans, with 10–30 s frame exposures and 0.5° frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software.⁹⁵ Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.⁹⁶ The data were corrected for absorption using redundant reflections and the SADABS program.⁹⁷ Decay of reflection intensity was not observed as monitored via analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution and refinement were performed using SHELXTL.⁹⁸

Synthesis

The $(\text{PPh}_4)_2\text{MoS}_4$ compound was prepared using a procedure reported by Tatsumi.⁹⁹ Specifically, PPh_4Br (1.04 g, 2.47 mmol) and $(\text{NH}_4)_2\text{MoS}_4$ (203 mg, 0.779 mmol) were combined in H_2O to yield $(\text{PPh}_4)_2\text{MoS}_4$ (599 mg, 0.663 mmol, 85%) as a bright red solid. Red crystals (80 mg, 0.089 mmol, 11%) suitable for single crystal X-ray analysis were obtained by diffusion of Et_2O into a solution of $(\text{PPh}_4)_2\text{MoS}_4$ in acetonitrile. Analysis by single crystal X-ray diffraction confirmed the identity of the $(\text{PPh}_4)_2\text{MoS}_4$ analyte.

Similarly, $(\text{PPh}_4)_2\text{WS}_4$ was prepared using a procedure reported by Tatsumi. Again, PPh_4Br (830 mg, 1.98 mmol) and $(\text{NH}_4)_2\text{WS}_4$ (345 mg, 0.991 mmol) were combined in H_2O to yield $(\text{PPh}_4)_2\text{WS}_4$ (724 mg, 0.731 mmol, 74%) as a yellow solid. Small yellow blocks (231 mg, 0.233 mmol, 24%) suitable for single crystal X-ray analysis were obtained by diffusion

of Et₂O into a solution of (PPh₄)₂WS₄ in acetonitrile. Analysis by single crystal X-ray diffraction confirmed the identity of the (PPh₄)₂WS₄ analyte.¹⁰⁰

Sulfur K-edge XAS Measurements

All solid-state S K-edge XAS data were either collected at the Stanford Synchrotron Radiation Lightsource (SSRL; beam lines 4-3 and 6-2) or the INE beam line for Actinide Research at Angstroemquelle Karlsruhe (ANKA), Karlsruhe Institute of Technology (KIT) Campus. Solution-phase measurements were made at the SSRL beam line 4-3. At SSRL, dedicated operating conditions of 3.0 GeV and 300–500 mA were used at beam line 4-3. This beam line was equipped with a 20-pole, 2.0-Tesla wiggler and utilized a liquid nitrogen-cooled double crystal Si(111) monochromator. Bent vertically collimating mirrors (FWHM beam spot sizes of 3 x 16 mm are achievable) were employed to reject harmonics, thus experiments at SSRL were conducted with the crystals fully tuned. At the ANKA-INE beam line, operating conditions of 2.5 GeV and 120 mA were used. The beam line was equipped with a 1.5 Tesla bending magnet and a water-cooled Si(111) double crystal monochromator. The crystals were de-tuned by 30% from the rocking curve maximum to reject harmonics and preferentially select for first-order beam.¹⁰¹ Two mirrors were utilized, the first mirror vertically collimating and the second mirror vertically and horizontally focusing. All XAS data were obtained at room temperature under an atmosphere of continually flowing helium using the sample chamber provided at each respective beam line. The chambers consisted of a helium-flushed sample compartment that was separated from the beam pipe by either a 3525 Ultralene window (4μm, SPEX CertiPrep) or a Kapton window (25μm). An additional 3525 Ultralene window (4μm) separated the sample from a Vortex Si fluorescence detector that was positioned sufficiently far from the sample to ensure dead times that were less than 3%. Sample fluorescence was monitored using a solid-state Vortex detector against the incident radiation (I₀), which was monitored using an ionization chamber through which He was continually flowed. Energy calibrations for all S K-edge XAS spectra were conducted between each sample scan, and based on the maximum of the first pre-edge feature (2472.02 eV) in the S K-edge X-ray absorption spectrum of the Na₂S₂O₃ standard.³² We note that the maximum for the first pre-edge feature of Na₂S₂O₃ varies as the substance becomes hydrated, and differences of up to 0.1 eV have been reported.¹⁰²

Solid-state XAS samples were prepared in an Ar- or He-filled glovebox and mounted in an aluminum sample holder, which is best described as a simple aluminum plate with 5 x 20 x 1 mm wells. Double-sided tape with matching 5 x 20 x 1 mm wells was applied to the front side of the holder. Single-sided tape (40μm) that had been confirmed by S K-edge XAS to contain very low concentrations of sulfur was fixed to the back side of the holder. The analyte was prepared by finely grinding the sample (~10 mg) for 2 min in polystyrene canisters with Teflon pestles using a Wig-L-Bug mixer. The sample canisters and pestles showed no detectable S by X-ray fluorescence analysis. The finely divided powder was then uniformly dispersed onto the single-sided tape using a Winsor & Newton paintbrush, which did not contain significant amounts of S as determined by independent S K-edge XAS analysis. A series of samples were prepared of varying thicknesses to characterize contributions to the spectra from self-absorption. All samples were sealed in Mylar bags,

removed from the glovebox, and shipped. Once unpackaged, the samples were immediately introduced into a He-flushed sample chamber.

In general, spectra were obtained using step sizes of 1.00, 0.08 and 1.50 eV over the pre-edge (2400–2465 eV), edge (2465–2490 eV), and post-edge (2490–2690 eV) regions, respectively. The beam was constrained by horizontal and vertical slit sizes of 4–10 mm and 1 mm, respectively. Spectra were collected in triplicate with a count time of 1.0–3.0 s. Unique samples of $(\text{PPh}_4)_2\text{MoS}_4$ and $(\text{PPh}_4)_2\text{WS}_4$ were analyzed during 4 different synchrotron scheduling periods to establish reproducibility and evaluate error associated with the measurements. Solution-phase measurements were collected using a freshly prepared solution of $(\text{PPh}_4)_2\text{MS}_4$ in acetonitrile (0.06 M in sulfur; Acros, used as received). The solution cell consisted of an aluminum sample well fitted with Viton gasket and an 8 μm polypropylene window.

Sulfur K-edge XAS Data Analysis

Data were analyzed using methods similar to those described previously.³² The data were fit with a first-order polynomial in the pre-edge region (ca. 2401–2456 eV), which was then subtracted from the experimental spectrum to eliminate the background contribution. For MoS_4^{2-} , normalization was achieved by fitting a second-order polynomial to the region of the spectrum after the S K-edge and before the Mo $\text{L}_{3/2}$ -edge (ca. 2488–2512 eV). For WS_4^{2-} , the data were normalized by fitting a second-order polynomial to the entire post-edge region of the spectrum (ca. 2520–2689 eV). For all data, the edge jump was set to an intensity of 1.0 at 2490 eV. Detector dead times were evaluated by obtaining a response curve for the single channel analyzer (SCR) vs. the incoming count rate (ICR) of the detector. The SCA to ICR relationship was modeled assuming that $r = kr_1e^{-rt}$ where t is the dead time, r is the SCA count rate, r_1 is the ICR total count rate, and k is a constant of proportionality. These analyses showed dead time contributions of less than 3%. A deconvoluted model for the sulfur K-edge XAS data was obtained using a modified version of EDG_FIT¹⁰³ in IGOR 6.22A. Approximate peak positions were determined by using first- and second-derivatives of each spectrum. Pseudo-Voigt line shapes and a step function were used to model the pre-edge and rising edge features, with a fixed 1:1 ratio of Lorentzian and Gaussian contributions for the pre- and post-edge features and a 1:1 ratio of arctangent and error function contributions for the step function, which were not allowed to vary during the fitting routine.

Ground-State DFT Calculations

Ground-state electronic structure calculations for all species were performed using restricted DFT in the Gaussian 09 code.¹⁰⁴ The hybrid B3LYP functional employed used Becke's three-parameter exchange functional (B3)¹⁰⁵ along with the correlation functional of Lee, Yang, and Parr (LYP).¹⁰⁶ Sulfur atoms were modeled using an all-electron Pople-style double- ζ 6-31G(d',p') basis set with polarization functions optimized for heavy atoms,¹⁰⁷ while Cr, Mo, and W were modeled with the effective core potential (ecp) and accompanying basis set by Hay and Wadt (LANL2DZ).¹⁰⁸ This ecp and basis set were augmented with the addition of f-polarization functions on the metals (exponents = 1.941, 1.043 and 0.823 for Cr, Mo, and W, respectively).¹⁰⁹ Implicit solvent effects were

calculated using the polarizable continuum model (PCM)¹¹⁰ with radii and nonelectrostatic terms from Truhlar and co-workers' SMD solvation model and the geometries were reoptimized in the solution phase.¹¹¹ The parameter $\epsilon = 35.688$ was used for acetonitrile. The relative contributions of the sulfur 3p and metal *nd* and (*n*+1)p orbitals in each compound were obtained by Mulliken population analysis of individual MOs.

TDDFT Calculations

The sulfur K-edge XAS spectra were simulated using TDDFT. These calculations were conducted as previously described,^{41,81-85,87,112} and involved evaluating core electron excitations by exploiting the small amount of mixing between the core orbitals and the high-lying unoccupied virtual orbitals. Specifically, this analysis involved a linear response calculation to extract the probability amplitudes from the transition densities and dipole moments between the calculated excited states and the ground states.¹¹³ The excitations originating from all of the intermediate states between the sulfur 1s orbitals and the HOMO were excluded so that only excitations from the core levels to virtual MOs could be analyzed. This allowed the virtual orbitals to mix with one another to reflect, at least to first order, the presence of the core hole on sulfur. Relaxations in the occupied orbitals other than the sulfur 1s orbitals were not included. Although excluding orbital relaxations in the occupied orbitals affects the absolute transition energies, the relative excitation energies are more reliable. In fact, previous calculations on transition-metal compounds have provided very good agreement with experimental measurements.^{41,81-85,87,112} For comparison with experiment, the first calculated TDDFT transition was shifted to match the maxima of the first experimental pre-edge peak, such that the MoS₄²⁻ and WS₄²⁻ TDDFT results were shifted by +56.6 eV and +56.7 eV, respectively. Because there was no experimental data for CrS₄²⁻, the Cr TDDFT shift was determined by averaging the Mo and W values (+56.65 eV). A constant scaling factor was applied to the TDDFT intensities for comparison with experimental data.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Scheme 1.
Tetrathiometalate and tetraoxometalate dianions.

Fig. 1.

A comparison of the solid-state and solution-phase S K-edge X-ray absorption spectra for $(\text{PPh}_4)_2\text{MoS}_4$ (solid black and dashed red traces, respectively) and $(\text{PPh}_4)_2\text{WS}_4$ (solid brown and dashed blue traces, respectively).

Fig. 2. Sulfur K-edge XAS solution-phase measurements made on $(\text{PPh}_4)_2\text{WS}_4$ (0.06 M in sulfur) in acetonitrile as a function of time. Spectra were obtained sequentially with acquisition times of 7 min and are displayed with time increasing from top to bottom.

Fig. 3.

S K-edge X-ray absorption data (●) for $(\text{PPh}_4)_2\text{MS}_4$ (M = Mo solid, *top left*; Mo solution, *top right*; W solid, *bottom left*; W solution, *bottom right*). The model for the data (red trace), pre-edge functions (blue and green traces), and post-edge residuals (dashed gray trace) are also provided. Fully deconvoluted spectra are provided in the Supporting Information.

Fig. 4. Qualitative molecular orbital diagram for the MS_4^{2-} dianions.

Fig 5.

Quantitative molecular orbital diagrams for MS_4^{2-} ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) derived from DFT calculations that included CH_3CN dielectric media. Only the $\text{S } 1s$ ($1a_1$; black), $1t_1$ HOMO (black), $2e^*$ LUMO (green), and $4t_2^*$ antibonding orbitals (red) have been shown. Molecular orbital energies were shifted by setting the $\text{S } 1s$ orbital energy for each anion to match that of CrS_4^{2-} at -2415.70 eV.

Fig 6.

A comparison of the gas-phase TDDFT-calculated spectra (red traces) with the TDDFT-calculated spectra with a CH_3CN dielectric medium (blue traces) for MS_4^{2-} ($\text{M} = \text{Cr}$, left; Mo , middle; W , right). The calculated transitions are represented as red or blue bars whose height signifies the calculated oscillator strengths. The experimental solid-state sulfur K-edge XAS spectra (**O**, top row) have been overlaid with the gas-phase TDDFT-calculated spectra, while the solution-phase S K-edge XAS spectra (**O**, bottom row) have been overlaid with the solution-phase TDDFT-calculated spectra.

Fig 7.

A comparison of the trends in solid-phase XAS intensities (red), solution-phase XAS intensities (black), gas-phase TDDFT-calculated intensities (green), and TDDFT-calculated intensities that employed a CH₃CN dielectric medium (blue) for the $1s \rightarrow 4t_2^*$ (top) and $1s \rightarrow 2e^*$ (bottom) transitions for MS_4^{2-} (M = Cr, Mo, W).

Fig 8.

A comparison of the DFT-calculated free-ion energies for Cr, Mo, W, O, and S. For consistency, all single ion calculations were carried out with all electrons, with the Universal Gaussian Basis Set, using the B3LYP functional and 2nd order Douglas-Kroll-Hess scalar relativistic corrections.

Table 1

Comparison of experimental and calculated S K-edge pre-edge peak energies (eV),^a normalized intensities (Int),^b and TDDFT-calculated oscillator strengths (*f*)^c for MS₄²⁻ (M = Cr, Mo, W).

Assignment	Experimental (Solid)		Experimental (Solution)		TDDFT ^a (Gas-phase)		TDDFT ^a (CH ₃ CN)	
	Energy (eV)	Int ^b	Energy (eV)	Int ^b	Energy (eV)	<i>f</i> ^c	Energy (eV)	<i>f</i> ^c
CrS₄²⁻								
S 1s → 4t ₂ *	n/a	n/a	n/a	n/a	2469.8	0.0031	2469.9	0.0044
S 1s → 2e*	n/a	n/a	n/a	n/a	2469.2	0.0035	2469.1	0.0034
MOS₄²⁻								
S 1s → 4t ₂ *	2470.7	1.76(9)	2470.7	1.65(8)	2470.7	0.0031	2470.8	0.0039
S 1s → 2e*	2469.6	1.32(7)	2469.6	1.46(7)	2469.6	0.0036	2469.6	0.0036
WS₄²⁻								
S 1s → 4t ₂ *	2471.3	1.62(8)	2471.3	1.34(7)	2471.3	0.0025	2471.3	0.0032
S 1s → 2e*	2470.1	1.50(8)	2470.1	1.49(7)	2470.2	0.0036	2470.2	0.0036

^a Calculated values were taken from the TDDFT-simulated spectra (see Figure 6).

^b Experimental intensities were derived from the area under pseudo-Voigt functions used to generate the curve fit, and have an estimated error of approximately 5%.

^c The 1s → 4t₂* transition peak positions were determined using a weighted average of the oscillator strengths for each 4t₂* peak. Oscillator strengths for each 1s → 4t₂* transition are reported as a sum of the calculated transitions.

Table 2

Calculated energies^a and compositions^b of selected valence molecular orbitals (MOs) for MS₄²⁻ (M = Cr, Mo, W).

MO	% Orbital Composition (Gas-phase)				% Orbital Composition (CH ₃ CN)			
	Energy (eV) ^c	S 3p	M d	M p	Energy (eV) ^c	S 3p	M d	M p
CrS₄²⁻								
4t ₂ *	5.98	14.0	23.3	60.0	-1.02	45.6	39.0	13.3
2e*	5.56	43.6	55.6	0.0	-1.86	42.8	56.3	0.0
1t ₁ (HOMO)	3.01	100.0	0.0	0.0	-4.47	100.0	0.0	0.0
MoS₄²⁻								
4t ₂ *	6.96	21.6	31.6	45.3	-0.36	42.8	40.8	14.0
2e*	6.05	47.6	50.9	0.0	-1.49	47.6	51.0	0.0
1t ₁ (HOMO)	2.70	100.0	0.0	0.0	-4.91	100.0	0.0	0.0
WS₄²⁻								
4t ₂ *	7.34	30.0	36.7	33.7	0.06	43.2	43.4	10.9
2e*	6.47	46.4	51.8	0.0	-0.95	46.4	51.9	0.0
1t ₁ (HOMO)	2.59	100.0	0.0	0.0	-4.90	100.0	0.0	0.0

^a Alpha spin-orbital energies are reported.

^b The use of a non-orthogonal basis set can cause Mulliken analysis to have non-physical results such as compositions > 100% or < 0.¹¹³

^c Energies have been normalized by setting the S 1s orbital energy for each anion to match that of CrS₄²⁻ at -2408.25 eV and -2415.70 eV for gas-phase and CH₃CN calculations, respectively.