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Spin-Polarization Induced Pre-edge Transitions in the Sulfur K-edge XAS Spectra of Open-Shell Transition-Metal Sulfates: Spectroscopic Validation of σ -Bond Electron Transfer

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Abstract

Sulfur K-edge XAS spectra of the monodentate sulfate complexes $[M^{II}(\text{itao})(\text{SO}_4)(\text{H}_2\text{O})_{0,1}]$ and $[\text{Cu}(\text{Me}_6\text{tren})(\text{SO}_4)]$ exhibit well-defined pre-edge transitions at 2479.4 eV, 2479.9 eV, 2478.4 eV, and 2477.7 eV, respectively ($M = \text{Co}, \text{Ni}, \text{Cu}$), despite having no direct metal-sulfur bond, while the XAS pre-edge of $[\text{Zn}(\text{itao})(\text{SO}_4)]$ is featureless. The sulfur K-edge XAS of $[\text{Cu}(\text{itao})(\text{SO}_4)]$ but not of $[\text{Cu}(\text{Me}_6\text{tren})(\text{SO}_4)]$ uniquely exhibits a weak transition at 2472.1 eV, an extraordinary 8.7 eV below the first inflection of the rising K-edge. Pre-edge transitions also appear in the sulfur K-edge XAS of crystalline $[M^{II}(\text{SO}_4)(\text{H}_2\text{O})]$ ($M = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$, but not Zn) and in sulfates of higher-valent early transition metals. Ground state density functional theory (DFT) and time-dependent DFT (TDDFT) calculations show that charge transfer from coordinated sulfate to paramagnetic late transition metals produces spin polarization that differentially mixes the spin-up (α) and spin-down (β) spin-orbitals of the sulfate ligand, inducing negative spin density at sulfate sulfur. Ground state DFT calculations show that sulfur 3p character then mixes into metal 4s and

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Supporting Information Available: SQUID magnetometry trace of $[\text{Ni}(\text{itao})(\text{SO}_4)(\text{H}_2\text{O})]$; Sulfur K-edge XAS spectra of anhydrous CuSO_4 , $(\text{NH}_4)_2[\text{Cu}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$, and aqueous sulfate; Crystal structure of CuSO_4 and $(\text{NH}_4)_2[\text{Cu}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$; Sulfur K-edge XAS of $[\text{Cu}(\text{itao})(\text{SO}_4)]$ scans; pseudo-Voigt fit sulfur K-edge XAS of $[\text{Co}(\text{itao})\text{SO}_4]$; pseudo-Voigts fit sulfur K-edge XAS of $[\text{Co}(\text{itao})\text{SO}_4]$; pseudo-Voigt fit of sulfur K-edge XAS of $[\text{Ni}(\text{itao})(\text{SO}_4)(\text{H}_2\text{O})]$; pseudo-Voigts fit to the sulfur XAS of $[\text{Ni}(\text{itao})\text{SO}_4(\text{H}_2\text{O})]$; pseudo-Voigt fit to the sulfur XAS of $[\text{Cu}(\text{itao})(\text{SO}_4)]$; pseudo-voigt fit to the sulfur XAS of $[\text{Zn}(\text{itao})(\text{SO}_4)]$; pseudo-Voigt fit to the sulfur XAS of $[\text{Zn}(\text{itao})(\text{SO}_4)]$; pseudo-voigt fit to the sulfur XAS of $[\text{Cu}(\text{Me}_6\text{tren})(\text{SO}_4)]$; Table of pseudo-Voigts used for $[\text{Cu}(\text{Me}_6\text{tren})(\text{SO}_4)]$; Arbitrary pseudo-Voigt Fit to the sulfur XAS of $[\text{Cu}(\text{itao})(\text{SO}_4)]$; Structural Lattice of $[M^{II}(\text{SO}_4)(\text{H}_2\text{O})]$; Sulfur K-edge XAS spectra of $[M^{II}(\text{SO}_4)(\text{H}_2\text{O})]$ complexes; Contour plots of spin-density, spin-polarization, and electron hole distribution for sulfate radical ion and for $[\text{Cu}(\text{Me}_6\text{tren})(\text{SO}_4)]$; Table Summary of Sulfate XAS pre-K-edge Transition Energies; Sulfur K-edge XAS spectrum showing the transition and I_0 intensity at 2472.1 eV; Table: Atomic positional coordinates for $[\text{Zn}(\text{itao})(\text{SO}_4)] \cdot \text{H}_2\text{O}$; Table: Atomic positional coordinates for $[\text{Cu}(\text{itao})(\text{SO}_4)] \cdot \text{H}_2\text{O}$, $S=1/2$; Table: Atomic positional coordinates for $[\text{Ni}(\text{itao})(\text{H}_2\text{O})(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$, $S=1$; Table: Atomic positional coordinates for $[\text{Co}(\text{itao})(\text{SO}_4)] \cdot \text{H}_2\text{O}$, $S=3/2$; Table: Atomic positional coordinates for $[\text{Cu}(\text{Me}_6\text{tren})(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$, $S=1/2$.

4p valence orbitals and various combinations of ligand anti-bonding orbitals, producing measureable sulfur XAS transitions. TDDFT calculations confirm the presence of XAS pre-edge features 0.5 to 2 eV below the sulfur rising K-edge energy. The 2472.1 eV feature arises when orbitals at lower energy than the frontier occupied orbitals with S 3p character mix with the Cu(II) electron hole. Transmission of spin polarization and thus of radical character through several bonds between the S and the electron hole provides a new mechanism for the counter-intuitive appearance of pre-edge transitions in the XAS spectra of transition metal oxoanion ligands in the absence of any direct metal-absorber bond. The 2472.1 eV transition is evidence for further radicalization from Cu(II), which extends across an H-bond bridge between sulfate and the itao ligand and involves orbitals at energies below the frontier set. This electronic structure feature provides direct spectroscopic confirmation of the through-bond electron transfer mechanism of redox-active metalloproteins.

Synopsis

The sulfur K-edge XAS spectra of open-shell 3d transition metal sulfates show multiple pre-edge transitions, including one fully 8.7 eV below the rising K-edge. DFT and TDDFT calculations show these transitions indicate metal-induced ligand radicalization and spin-polarization that mixes sulfur 3p orbitals into metal 4s and 4p valence- and ligand σ -orbitals. Together these results provide the first direct spectroscopic validation of the σ -bond conduction pathway central to biological electron transfer.

Introduction

Covalency in transition metal–ligand bonds is critical to understanding the reactivity of metallo-protein active sites and to design functionally analogous biomimetic compounds.^{1–8} Ligand-metal covalence, as most trivially evidenced in redox non-innocent ligands, is one of the defining traits governing homogeneous catalysis.^{9–13} The coordination of non-innocent ligands to redox inactive metals can result in intramolecular charge transfer and oxidation of the ligand, thus opening new reaction pathways and enabling unexpected ligand-based reactivity.^{14–16}

The covalence of transition metal-ligand bonds can be effectively and directly probed using ligand-centered X-ray absorption spectroscopy (XAS).^{2, 4, 5, 17, 18} Covalent ligand-metal interactions typically involve delocalization of metal d-electron holes into filled ligand p-level valence orbitals (ligand-to-metal electron donation) or mixing of occupied metal d-

orbitals with unoccupied ligand frontier orbitals (metal-to-ligand back-donation). A ligand based $1s \rightarrow np$ valence transitions become possible as formally fully occupied ligand orbitals (np) mix with d-electron holes. Direct overlap between the metal and ligand orbitals is the commonly anticipated origin for the appearance of pre-edge features at the ligand K-edge. Such transitions are indeed observed in the energy region prior to the main rising K-edge within ligand XAS spectra, when the metal and the absorber-ligand centers are formally separated by only one bond. The intensity of these transitions is a quantitative measure of covalence in the ligand-metal bond.^{2, 4, 5}

A prior publication described the unexpected appearance of a weak yet reproducible pre-edge feature in the sulfur K-edge XAS of anhydrous CuSO_4 , despite the separation of copper and sulfur by two bonds.^{19, 20} Ground electronic state DFT calculations were used to assign the appearance of this feature to extensive electron transfer from exclusively oxygen-based valence orbitals of the sulfate ligand into the half-vacant $3d_{x^2-y^2}$ β -spin orbital of Cu(II). This leads to significant deviations in the orbital compositions for the α (spin up or $m_s = +1/2$) and β (spin down or $m_s = -1/2$) electrons. These deviations between the α and β -set of spin orbitals induce spin polarization in ligand molecular orbitals. This intramolecular electron transfer also confers radical character onto the sulfate ligand, causing mixing of sulfur 3p and 4p character into copper 4s/4p unoccupied Rydberg orbitals and providing a new source of sulfur pre-edge XAS transitions without interposition of any direct sulfur-metal bond. Consistent with this interpretation, the sulfur K-edge XAS spectrum of the homologous ZnSO_4 did not show a pre-edge feature.

Extrapolating from these previous results, the present study was extended to molecular first-row transition metal complexes of sulfate to test the generality of oxo-anion radicalization and the emergence of low-energy XAS spectral features. Thus, sulfur K-edge XAS measurements of molecular monodentate sulfate complexes of Co(II), Ni(II), Cu(II), and Zn(II) are reported, and investigated using ground- and excited-state DFT calculations. It is confirmed that X-ray spectroscopy reports metal-ligand covalence for complexes wherein multiple intervening bonds between the metal and the sulfur absorber preclude any direct metal-absorber orbital overlap. The XAS spectra and electronic structure calculations of sulfate complexes reveal mixing of the Cu 3d orbital hole with orbitals below the frontier occupied set. Furthermore, it defines a new and remarkable interaction with distant σ -bonds that, transmitted through H-bonds, can contribute features to sulfur K-edge XAS spectra. These XAS features provide spectroscopic validation of the through-bond mechanism of electron transfer in redox-active metalloproteins.

Materials and Methods

The ligand 2,2',2''-iminotris(acetamidoxime) (itao) and the Co(II), Ni(II), Cu(II), and Zn(II) transition-metal sulfate complexes of this ligand were prepared by the method of Pearse, et al.²¹ Elemental analysis (% C, H, N, calc, found): $[\text{Zn}(\text{itao})(\text{SO}_4)] \cdot \text{H}_2\text{O}$ (FW = 412.691), 17.46, 17.70; 4.15, 4.12; 23.76, 23.87; $[\text{Cu}(\text{itao})(\text{SO}_4)] \cdot \text{H}_2\text{O}$ (FW = 410.767), 17.54, 16.95; 4.17, 3.90; 23.87, 22.64; $[\text{Co}(\text{itao})(\text{SO}_4)] \cdot \text{H}_2\text{O}$ (FW = 406.244), 17.74, 14.65; 4.22, 3.64; 24.14, 20.02; $[\text{Ni}(\text{itao})(\text{SO}_4)(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (FW = 460.047), 15.57, 15.15; 5.04, 4.78; 21.31, 20.76. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Standard of precision for C, H, N analysis is $\pm 0.5\%$. Crystals suitable for diffraction were grown by diffusing methyl alcohol against an equal volume water solution of each of the complexes.

The ligand tris-(2-[N,N-dimethylaminoethyl])amine, (Me₆tren), was prepared according to the method of Ciampolini and Narda.²² The crude product in $\sim 50\text{ cm}^3$ of water was neutralized using solid NaOH. The dark red-orange layer that separated out was extracted with diethyl ether, dried over KOH pellets, decanted, and evaporated to an oil by warming under a stream of air. The oil was distilled under vacuum (60–68 °C at $\sim 30\text{ }\mu\text{torr}$ pressure), yielding the ligand as a clear colorless liquid.

The complex [Cu(Me₆tren)(SO₄)] was prepared by adding 2.3 g (10 mmole) of the ligand to 2.5 g (10 mmole) of CuSO₄·5H₂O dissolved in 10 cm³ of deionized water. The immediate gelatinous blue precipitate re-dissolved on stirring to yield a deep blue solution. The homogeneous blue solution was passed through a 0.45 μm nylon filter, poured into an evaporating dish and allowed to evaporate overnight under a raised cover allowing free circulation of air. The resulting crystalline mass plus mother liquor were transferred to a sintered glass funnel where the solid was collected by filtration, and pressed dry under a latex rubber dam with continued evacuation. The yield was 3.81 g (71%) of waxy blue crystals. Elemental analysis for the octahydrate²³ C₁₂H₄₆N₄O₁₂SCu: Calc. C: 26.98%; H: 8.68%; N: 10.49%. Found C: 26.63%; H: 9.11%; N: 10.37%. Well-faceted crystals of the trihydrate suitable for diffraction were grown by diffusing an equal volume of acetone against a 2-propanol solution of the complex.

Potassium Jarosite, KFe₃(SO₄)₂(OH)₆, was obtained through Prof. Juan Viñales i Olià, Department d'Enginyeria Química i Metallúrgia, University of Barcelona, Spain, as the authentic native mineral originating in the Sierra Madre, Spain. The vanadyl terpy complex [VO(terpy)(SO₄)], was prepared using the method of Pifferi, et al., and deposited from solution as lustrous brown crystals of a greenish cast.²⁴ Elemental analysis for C₁₅H₁₂N₃O₅·0.5H₂O (FW = 405.28), % calc, found: C, 44.45, 44.09; 3.23, 3.15; 10.41, 10.47. The complex *trans*-K₅[V(oxalate)₂(SO₄)₂]·3H₂O was the kind gift of Prof. Kan Kanamori, Department of Chemistry, Toyama University, 3190 Gofuku, Toyama, Japan.

The divalent transition metal sulfate monohydrates [M(II)(SO₄)(H₂O)]; M = Fe, Co, Ni, Cu, and Zn were prepared by dehydration of the heptahydrate or pentahydrate (Cu) sulfate, using literature methods.^{25–30} In a typical procedure, about 1 g of solid metal sulfate polyhydrate was stirred and heated under an argon flow exiting through an external cold trap. Water evolution was monitored and typically ceased after a few minutes at the maximal temperature of: Fe, 140 °C; Zn, 150 °C; Cu, 170 °C; Co, 215 °C, and; Ni, 225 °C. The monohydrates were stored sealed and in a nitrogen-filled glove box to prevent rehydration.

Determination of the crystal structures of [M(itaio)(SO₄)(H₂O)_{0.1}] (M = Co, Ni, Zn) and the re-determination of [Cu(Me₆tren)(SO₄)] were carried out at the Laboratorium fuer Kristallographie, Zurich, Switzerland using an Enraf-Nonius CAD 4 diffractometer, equipped with a fine-focused sealed-tube X-radiation source and a graphite-monochromator. Diffraction for the three itao complexes employed Cu-K α radiation ($\lambda = 1.54178\text{ }\text{\AA}$), while

for [Cu(Me₆tren)(SO₄)], diffraction data were collected using Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97)³¹ and refined using SHELXL-97³². Numerical absorption corrections were applied to all structures (SHELXPREF).

For [Ni(itaio)(SO₄)(H₂O)], magnetization data was recorded on a SQUID magnetometer (Quantum D Design MPMS SQUID VSM System) with an external 1 Tesla magnetic field at the temperature range 1.8 to 300 K. The sample was placed in gel cap sample holder and immobilized in n-eicosane. The susceptibility data were corrected for diamagnetic contributions using Pascal constants.

Sulfur K-edge XAS spectra for all the transition metal sulfate complexes were measured at ambient temperature as fluorescence excitation spectra at Stanford Synchrotron Radiation Lightsource wiggler beam line 6-2 (SSRLII) operating in undulator mode at 10.4 kG with ring operating conditions of 3 GeV and 70–100 mA current, and using a nitrogen-filled Lytle detector. Beam line optics included a Si(111) monochromator, and the incident beam intensity was optimized with 0% detuning at 2740 eV.³³ The solids were finely ground in BN mounted on Kapton tape. The spectra are an average of three scans. The raw sulfur K-edge XAS data were processed as described elsewhere.³⁴ Comparison of individual scans revealed no observable radiation damage (Figure S4 in the Supporting Information). Examination of the incident beam trace (I_0) revealed no spikes or glitches that might produce artefactual features in the XAS spectra.

Fits of sulfur K-edge XANES spectra were carried out using pseudo-Voigt lines with Gaussian to Lorentzian ratios of 1:1 within the program EDGFit, which is part of the EXAFSPAK suite of programs.³⁵ Except for the pre-edge features, all the pseudo-Voigt lines included linked half-widths at half-height so that they refined to a common value. At higher energies, this introduces a small error due to uncompensated peak-broadening arising from energy-dependent inelastic scattering.³⁶ Pseudo-Voigt line widths ($p-V_{lw}$) were constrained to be no more than twice the resolution of the Si(111) monochromator ($\Delta E/E \sim 1.3 \times 10^{-4}$) convolved with the ~ 0.6 eV sulfur core hole life time width, i.e.,

$$p-V_{lw} \leq 2 \times \sqrt{(0.6\text{eV})^2 + (0.32\text{eV})^2} = 1.36\text{eV}.$$
³⁷ The energy position of the arctangent function representing the core ionization edge was initially determined by the fit to the sulfur K-edge XAS spectrum of [Cu(Me₆tren)SO₄] to be 2483.8 eV and then fixed at that energy for the fits to the XAS spectra of all the other complexes. An acceptable fit was required to closely reproduce the shape, intensity, and inflections in the energy regions 2476–2480 eV (pre-K-edge), 2480–2481.5 eV (rising K-edge), 2481.7–83 eV (XANES maximum), and 2483.5–2484.5 eV (XANES declining edge) in both the XAS spectrum and its second derivative.

Density functional theory (DFT) calculations were carried out using the Gaussian09 suite of programs.³⁸ Molecular orbital and atomic spin density contours were visualized using ChemCraft³⁹ from the formatted checkpoint files. Ground state molecular orbital compositions were determined by Natural Population Analysis,^{40–42} while excited state calculations were carried out by the time-dependent formalism^{43, 44} for a window of energy range (>2390 eV) corresponding to the excitation from the S 1s (MO 2) orbital. The first 90

excited states had to be calculated due to the large number of frontier virtual orbitals that do not give S 1s excitations with oscillator strength greater than 10^{-5} . The atomic positional coordinates of heavy atoms were taken from the crystal structures, while the positions of the H atom were optimized at the BP86/def2TZVP level of theory.

Density functionals (Becke88 exchange⁴⁵ and Perdew86 correlation⁴⁶) were selected that are known to give an overly covalent electronic structure for late transition metals.^{47, 48} It was necessary to artificially exaggerate the metal-ligand overlap and spin polarization to assign the relevant electronic structure features to spectroscopic transitions, due to the small intensity spectral features considered in this study. Using hybrid DFT functionals that contain HF exchange would result in localization of the electronic structure and reduction of covalent interactions between the metal center and its ligands. However, it is important to highlight that the conceptually correct, saturated basis set⁴⁹ was used to describe the electronic structure, which is able to capture small spin polarization effects and weak covalent interactions.⁵⁰ The optimized structures are provided in Table S7 through Table S11 in the Supporting Information.

The calculated electronic structures were analyzed by the Mulliken,⁵¹ Hirshfeld,⁵² Weinhold,⁵³ natural population analysis in Gaussian09, and Bader's Atoms-in-Molecules methods,⁵⁴ in AIMAll.⁵⁵ The molecular orbitals were deconvoluted using fragment molecular orbitals as implemented in the AOMIX package.^{56, 57}

Results

X-Ray Crystal Structures

The crystal structures of the itao complexes of Ni(II), Co(II), and Zn(II) and the Me₆tren trihydrate complex with Cu(II) determined in this study are shown in Figure 1. The structure of [Cu(itao)(SO₄)] was reported previously.²¹ The structure of [Cu(Me₆tren)(SO₄)] was re-determined for this work and is of higher resolution (R-factor = 4.43%) than the previously published structure (R-factor = 13.2%).²³ The crystallographic parameters are given in Table 1, while Table 2 presents selected bond distances and angles.

XAS Spectroscopy

The sulfur K-edge XAS spectra of the four [M(itao)(SO₄)] complexes are shown in Figure 2a, with the second derivative spectra in Figure 2b. The sulfur K-edge XAS of [Cu(Me₆tren)(SO₄)] was reported previously,²⁰ and is shown in Figure S8 of the Supporting Information. The XANES maxima of all five complexes are near that of neutral aqueous sulfate (2482.5 eV). However unlike the XAS spectrum of uncoordinated sulfate, the second derivative spectra are remarkably structured, with minima that average 0.25 eV lower in energy than that of dissolved sulfate. The Figure 2 insets show the small rising pre-edge features that are the focus of this study. The energy positions of the second derivative pre-edge minima for the itao complexes are: Co, 2479.4 eV; Ni, 2479.9 eV; Cu, 2478.4 eV, and; [Cu(Me₆tren)(SO₄)], 2477.7 eV. Although these energy positions do not follow a particular order, the energy-positions of the intensity weighed pseudo-Voigt fits correlate with the metal effective nuclear charge (see below).

There is no sign of an analogous pre-edge feature in the sulfur XAS of the 3d¹⁰ filled-shell [Zn(itaO)(SO₄)] complex. Likewise, a rising edge feature is visually absent from the sulfur K-edge XAS of dissolved aqueous sulfate, or in that of the Tutton salt (NH₄)₂[Cu(H₂O)₆]SO₄•H₂O (Figure S2 in the Supporting Information). The latter contains an uncoordinated sulfate (Figure S3 in the Supporting Information) H-bonded within the lattice of hexaaquacopper(II) cations. These results correlate the rising K-edge sulfur XAS features with the presence of d-electron holes. However, the frontier occupied sulfate orbitals that covalently bond with the adjacent M(II) ions are exclusively O-based.²⁰ Sulfate sulfur is separated by two bonds from the transition metals, obviating any direct sulfur 3p to metal 3d orbital overlap. Even in the case of monodentate M(II)-O-SO₃ coordination, there is no significant covalent overlap between any metal 3d orbital and any of the S 3p-containing sulfate orbitals (see the electronic structure analysis section below). The metal and the sulfate ions interact via the O-based lone pairs or the symmetry adapted combination of oxygen 2p orbitals. Thus the origin of the sulfate pre-edge features must reside elsewhere than the typically assigned covalent mixing of absorber HOMO and metal LUMO frontier orbitals.^{1, 2} Furthermore, there is an 8–9 eV gap between the HOMO and the LUMO of sulfate (see below), which is considerably greater than the energy gap between the 3d and Rydberg 4s/4p orbitals of a first row transition metal. Any additional ligand-based antibonding orbitals will be lodged between the sulfate O-based HOMO and the S-based LUMO. Thus just from energetic considerations, there is no possibility that the emergence of a pre-edge feature at the S K-edges of transition-metal sulfates derive from a direct S 3p to metal 3d overlap.

The sulfate pre-edge features were extracted using pseudo-Voigt fits to simulate the XANES region of the sulfur K-edge XAS spectra of all five complexes (Table 2). The low-intensity of the pre-edge features makes their extraction and quantitative analysis subject to systematic errors in background removal. Fits that reproduce both XANES spectrum and the inflection regions revealed in the second derivative of the XANES better simulate the underlying spectral structure, producing a more accurate background and reducing systematic errors in background intensity.^{58, 59} The fit to the XAS of [Cu(itaO)(SO₄)] in Figure 3 is representative, while those of the Co(II), Ni(II), and Zn(II) itao complexes and [Cu(Me₆tren)(SO₄)] are shown in Figure S5 through Figure S8 in the Supporting Information. Pseudo-Voigt linewidths, energy positions, and other details of the fits are summarized in Table S1 through Table S5 in the Supporting Information.

In the reported fits, the pseudo-Voigt line-widths were constrained to be no more than twice the sulfur core-hole width convolved with the resolution of the SSRL beamline 6-2 spectrometer (1.36 eV, see the Materials and Methods Section). The second derivative of each final fit was required to reproduce the detailed shape of the second derivative XAS spectra. Fits and fit second derivatives were closely examined over the energy regions 2476–2480 eV (pre-K-edge), 2480–2481.5 eV (rising K-edge), 2481.7–83 eV (XANES maximum), and 2483.5–2484.5 eV (XANES declining edge), as illustrated in Figure S9 of the Supporting Information. These criteria ensured that the intensities and energy positions of the underlying pseudo-Voigts summed correctly to reproduce the inflections hidden within each of the measured XAS spectra.

It should be understood that the pseudo-Voigts used to simulate the main XANES energy region do not represent physically meaningful transitions. They cannot be physically correlated with either calculated ground- or excited-state electronic structure (see below). Rather, they provide the accurate background necessary to quantitatively assess the positions and intensities of the small pre-edge features. Reproduction of the second derivative inflections implies a very good conformance of the fitted line-shape with the physically real spectrum. This in turn implies a good match to the declining XANES background in the energy region of the weak pre-edge features. A good background is critical to accurately resolve these low-intensity features.

In a covalent Cu(II)-sulfur or Cu(II)-halide bond, the single copper 3d hole with β -electron spin produces a single pre-edge transition feature in the ligand rising K-edge XAS,^{1, 6, 60, 61} which can be fit using a single pseudo-Voigt line. However as shown in Figure 3, several pseudo-Voigts were needed to fit the pre-edge feature in the XAS of [Cu(itao)(SO₄)]. This result makes it improbable that the source of this feature is the delocalization of the single hole of 3d⁹ Cu(II) into a filled ligand S 3p valence orbital as in, e.g., Cu(II)-S(thiolate) complexes.^{1, 2, 5, 61} Likewise, several low-intensity pseudo-Voigt lines were required to reproduce the rising K-edge feature of sulfate for every other complex including the sulfate K-edge of [Cu(Me₆tren)(SO₄)], supporting the idea that these features derive from multiple transitions.

The energy positions of the pre-edge absorption features for the complexes were calculated from the intensity-weighted pseudo-Voigts. For the itao complexes of Co(II), Ni(II), Cu(II), and [Cu(Me₆tren)(SO₄)] these are 2480.1 eV, 2480.0 eV, 2479.1 eV, and 2478.2 eV respectively, which follow the periodic trend in metal effective nuclear charge, $Z_{\text{eff}}(\text{M})$. As the $Z_{\text{eff}}(\text{M})$ decreases from Cu to Co, the metal-based sulfur pre-edge feature moves under the XAS rising K-edge. Despite their dissimilar electronic origin, the pre-edge features of Cl and S K-edge spectra of chloro and thiolato complexes of first row transition metals exhibit a similar dependence on Z_{eff} .^{1, 62} This is an unambiguous indication that these low energy sulfate pre-edge features are correlated with the progressively higher-energy electron holes in the transition metal 3d-manifolds from Cu(II) to Co(II) and the diminishing capacity of the sequentially lighter transition metals to radicalize the oxoanion.²⁰

Remarkably, the sulfate XAS of [Cu(itao)(SO₄)] also included a weak but distinct absorption feature at a uniquely low energy of 2472.1 eV (Figure 3, inset), an extraordinary 8.7 eV below the energy of the first inflection on the rising K-edge (2480.8 eV). This 8.7 eV separation is far too great for the transition to arise from one of the sulfur 3p-based LUMOs that normally produce the white-line of the sulfate S K-edge spectrum. None of the XAS spectra of the other complexes, including the structurally similar [Cu(Me₆tren)(SO₄)], included a visually perceptible feature at such low energy. This low-energy feature must then originate from the conjoint interaction of Cu(II) and the itao ligand, with the monodentate sulfate anion. The origin of this distant pre-edge feature must undoubtedly lay outside the frontier orbital energy range, as discussed below.

Extension of the Sulfate Pre-edge Assignments to Other Complexes

The generality of sulfate radicalization can be evidenced by the appearance of analogous pre-edge features in the sulfur K-edge XAS of divalent 3d transition metal sulfate monohydrates, $[M(II)(SO_4)(H_2O)]$, ($M(II) = Fe, Co, Ni, Cu, \text{ and } Zn$), as shown in Figure S10 in the Supporting Information.

The structures are isomorphous, with every sulfate engaged in four $M(II)-O-SO_3$ bonds (Figure S11 in the Supporting Information). In this series, the trend in sulfur XAS pre-edge energy follows the electron affinity of the transition metals, as also observed for the itao complexes. For the $Fe(II)$ complex, the sulfate radicalization is present, but the corresponding XAS features move under the rising K-edge (Figure S10) due to the reduced iron Z_{eff} relative to the later transition metals. The decreasing electron affinities of earlier divalent 3d transition metals is expected to reduce the intensity of such features below the detection limit.⁶³ However, pre-edge features of even greater intensity are observable for $Fe(III)$ or higher-valent early transition metals (Figure 4), as illustrated in the sulfur K-edge XAS spectra of potassium Jarosite, $K[Fe_3(OH)_6(SO_4)_2]$, of *trans*- $K_5[V(ox)_2(SO_4)_2] \cdot 3H_2O$, and of $[VO(terpy)(SO_4)]$.

In the former every sulfate engages three $Fe(III)-O-SO_3$ bonds, in the $V(III)$ complex the sulfates are monodentate, while in the vanadyl terpy complex sulfate is bidentate $V(O_2SO_2)$ with both equatorial and axial V-O bonds.^{24, 64, 65} Thus, the pre-edge features close to the rising-edge energy can be unambiguously related to the direct radicalization effect of the paramagnetic transition metal center.

Electronic structure analysis

In order to substantiate the origin of pre-edge and rising-edge spectral features, ground state electronic structural analysis was carried out by calculating the orbital compositions of the frontier unoccupied molecular orbitals, up to 15 eV above the HOMO. The extent of spin polarization for, or radicalization of, the free sulfate anion in the $Cu(II)$ complex was then evaluated, and the simulated core-level sulfur 1s excited state spectra were compared.

As a starting point for the discussion, Figure 4a and 4b compare the ground state orbital compositions for the free, uncoordinated sulfate dianion and its 1-electron oxidized radical mono-anionic form. The latter would be the situation for sulfate coordinated to a paramagnetic metal center in the ionic limit of maximal ligand-to-metal donation, where a full electron is transferred. The energy gap of about 9 eV between the HOMO and the LUMO of sulfate anion is notable. The HOMO donor orbital to metals with an unfilled d-manifold contains exclusively O 2p contributions in a non-bonding combination. The LUMO (contour, left side inset in Figure 5a), which is one of the σ^* orbital for S-O bonds, is the total symmetric, antibonding combination of S 3s and O 2p orbitals. The remaining LUMO+1...LUMO+3 σ^* -orbitals have dominantly S 3p contributions with minor S 4p. The next three LUMOs are dominantly S 4p based as can be seen in the orbital contours inset in Figure 5a.

The ground state electronic structure description of the $Zn(II)$, $Cu(II)$, $Ni(II)$, and $Co(II)$ complexes are shown in Figure 5c-5f, respectively. A common feature of the orbital

composition is the lack of any sizeable S 3p or S 4p contributions for the first 6 eV for all complexes. The lower energy region of the LUMOs contains antibonding orbitals related to the itao ligand, crystal waters and their admixture with the valence metal 4s and 4p orbitals. In other words, the HOMO/LUMO gap for the sulfate ligand is filled with unoccupied frontier orbitals from the itao ligand and the Rydberg metal orbitals. For the Cu complex, two orbitals are observed with significant S character, well resolved from the main group of orbitals with large S 3p and 4p contributions. These orbitals are S-containing antibonding sulfate orbitals that split off from the main group above 9 eV. The latter set of orbitals gives rise to sharp and intense white line at the S K-edge. Similar small, but significant S contributions appear at the lower energy side of the block of orbitals with dominant S contributions for both Ni and Co complexes. The Ni features (7.5–8 eV) are about 1 eV lower than the corresponding Co features (8–9 eV). It is also notable how the magnitude of S 4p mixing, or the redistribution of S 4p character into lower energy orbitals, changes along the Cu(II), Ni(II), and Co(II) series of itao complexes. The Zn(II) complex shows a clustering of the S 3p/4p features in a narrow energy range, which contributes to the appearance of a narrow, intense spectral feature forming the white-line excitation of the sulfate S K-edge spectrum. In addition, as the number of electron holes increases, the S 4p contributions move to lower energies and increase (0–38%), while the S 3p contributions remain practically constant (8–13%).

As presented in detail in the previous study of extended solids,²⁰ the redistribution of S character from higher to lower energy orbitals can be attributed to the radicalization of the sulfate anion ligand, which results in a spin polarization effect that differentially mixes the spin-up (α) and spin-down (β) spin orbitals. Spin polarization is known to follow ligand-to-metal electron transfer in paramagnetic 3d transition metal complexes.⁶¹

Figure 6 graphically demonstrates the extent of spin polarization. In Figure 6a is shown the spin density contour for the 1-electron oxidized sulfate mono-anion. The spin polarization of the entire set of valence molecular orbitals put positive spin density on the peripheral O centers and a large negative spin density on the S center. Figure 6b shows that the single electron hole for the $(\text{SO}_4)^{\cdot -}$ radical anion completely lacks any sulfur contribution. Figure 6c–6e shows the analogous spin density distribution for the $[\text{Cu}(\text{itao})(\text{SO}_4)]$ complex with a formally 3d⁹ electron configuration.

As can be seen only negative spin density (green lobe) is observed around the S center of the sulfate anion (the yellow sphere), which means that the sulfur has less spin-up (α) than spin-down (β) density in comparison with the peripheral O centers where the positive spin density (orange lobes) dominates. Due to only partial sulfate-to-Cu(II) charge transfer, the magnitude of spin polarization is considerably less in Figure 6c than for the sulfate radical anion in Figure 6a. However, remixing of the sulfate orbitals and also the Cu 4s and 4p valence orbitals will occur, as indicated by the green lobes around the Cu center that show the effect of directional 4p orbitals versus a spherical 4s.

The extent of difference between the entire set of α - and β -spin orbitals is well demonstrated by the residual spin density plot in Figure 6d, after occupying the Cu 3d-based β LUMO spin-orbital with an electron, but not allowing the electronic structure to relax (initial guess

analysis only). The alternating orange and green lobes corresponding to positive and negative spin densities that show the extent of difference between the occupied α - and β -spin orbitals for the occupied set of valence orbitals.

It is notable that the S contribution in Figure 6d is comparable to any other C, N, or O centers on the ligand. From molecular orbital theory, the occupied bonding orbitals have corresponding counterparts in the unoccupied orbital set (even though this is now applied for Kohn-Sham DFT orbitals). Thus, the visualized electron spin densities from the occupied orbitals have a counterpart for the virtual orbitals in terms of electron-hole densities. Their corresponding excited states are experimentally revealed in the K-edge XAS spectra as pre-edge and rising-edge features.

Restricted open-shell calculations (ROBP86) with $2S+1=2$ spin multiplicity were carried out to separate the effect of spin polarization and localize the effect of ligand radicalization into a single electron hole. Accordingly, these calculations show the complete absence of any green lobes in the spin density distribution because the ROBP86 formalism does not allow for spin polarization. The electron hole in Figure 6e is due to the incomplete occupation of the β -set of spin orbitals of the $\text{Cu}(3d^9)$ metal center. It shows contributions from the N 2s/2p ligand orbitals in the axial and equatorial plane, the singly unoccupied Cu $3d_{z^2}$ orbital, and one of the symmetry adapted linear combinations of the O 2p orbitals (or lone pairs). Interestingly, there is a slight polarization of the O 2p orbital/lone pair on the O center that covalently links the sulfate anion ligand to the Cu center. However, this appears to be an electrostatic effect, without significant covalent sulfur contribution, because the total S 3s/3p/3d character in the β LUMO is non-significant, as discussed below for the origin of the low-energy feature in the $[\text{Cu}(\text{itao})(\text{SO}_4)]$ complex.

The causal connection between core-level excited state XAS features and the ground state description was described in the Introduction. Nevertheless, it is important to show that excited-state-based simulation of XAS spectra from TDDFT theory can reproduce the differences in spectral features. It is also noteworthy that the simulations discussed here are at the limit of TDDFT calculations because the targeted excited states are 8–10 eV above the LUMO and involve Rydberg orbitals from both the metal center and the ligands. Thus, it is acknowledged that an exact reproduction of the energy positions and intensities of the spectral features is not currently attainable using the single-reference MO-based formalism.

The TDDFT spectrum of the sulfate anion in Figure 7a shows two well-defined peaks that in the experimental spectrum merge to form the intense, white line of the S K-edge spectrum. The approximately 2.4 eV splitting between the 3p- and 4p-based excitations overestimates the 1 eV splitting experimentally observed in the second derivative spectra (Figures 2b and 3b). This S 1s, core level, excited state spectrum matches well the discussed ground state description in Figure 5a. Similar to Figure 5b, upon creation of an electron hole in the sulfate HOMO, the lowest energy unoccupied frontier orbitals of the sulfate anion radical split and spin polarization emerges. There is a considerable redistribution of intensity between the two features, even in the absence of metal 4s/4p and ligand σ^*/π^* orbitals.

The [Zn(itaO)(SO₄)] complex shows the expected sharp white line feature and a featureless rising-edge (Figure 7c). As seen for the ground state orbital composition analysis in Figure 5, there are no appreciable S contributions in the first 60 excited states, because these are composed of itao ligand, water, and metal 4s/4p contributions. The electron hole in the 3d manifold in [Cu(itaO)(SO₄)] results in the appearance of weak pre-edge features and shoulders close to the rising K-edge. These features can be correlated with the experimentally detected pre-edge features near 2478 eV. The overly covalent pure density functional with gradient corrected exchange and correlation functions (BP86) could not explain the appearance of the weak but discernable pre-edge feature at 2472.1 eV (Figure 3), which is present in [Cu(itaO)(SO₄)], but absent in [Cu(Me₆tren)(SO₄)] (discussed further below). However, in traversing the Cu(II) (Figure 7d), Ni(II) (Figure 7e), and Co(II) (Figure 7f) complexes, the low energy pre-edge features appear to move closer to the intense rising-edge as observed experimentally (Figure 2). The difference between the coordination environments manifest in the different structures of the rising-edge features as the Cu and Co complexes show more distributed low-energy excitations before the white line, while excitations from the Ni complex are grouped due to the more symmetrical, pseudo-octahedral coordination environment.

On the origin and relevance of the 2472.1 eV XAS feature of [Cu(itaO)(SO₄)]

The very low-intensity yet distinct 2472.1 eV feature in the XAS spectrum of [Cu(itaO)(SO₄)] deserves further discussion, in part because it did not appear in the XAS of the [Cu(Me₆tren)(SO₄)] complex despite the similarity in overall structure and bonding. This feature is also puzzling because it was not visible in the ground- and excited-state calculations. The raw data showed the incident beam intensity (*I*₀) to be smooth and without glitches in this energy region (Figure S13 in the Supporting Information). This removes the likelihood that the 2472.1 eV feature is an artifact. The lack of an analogous feature in the XAS of the [Cu(Me₆tren)(SO₄)] complex suggests that its origin rests in the electronic and geometric structure of the itao ligand, because the Cu(II) and the sulfate dianion are common to both complexes. That is, if mixing of Cu(II)- and sulfate-based orbitals were solely responsible for the 2472.1 eV feature, then the structural similarity of the two complexes implies this transition should appear in both the [Cu(itaO)(SO₄)] and the [Cu(Me₆tren)(SO₄)] XAS spectra. However, this low energy pre-edge feature was observed only in the former, 8.7 eV below the first inflection point of the rising sulfur K-edge.

From both the ground state orbital plots (Figure 5) and excited state spectra (Figure 7) this 8.7 eV energy excites to the first few LUMOs with considerable metal contribution. The fraction of S 3p character (α^2) in this transition can be estimated using the transition dipole equation,^{2, 47, 66, 67}

$$\alpha^2 = 3D_0N/hI, \quad [1]$$

where *D*₀ is the integrated normalized intensity of the transition, *N* is the number of absorbers, *h* is the number of electron holes (here taken as 1) and *I* is the sulfate transition dipole moment integral for S K XAS (S 1s→3p) pre-edge excitations. The value of *I* can be

estimated from the energy difference between the first inflection point along the rising K-edge XAS of Na₂S (2471.7 eV) and that of sulfate (2480.8 eV for [Cu(itaO)(SO₄)]) and a slope parameter, yielding $I = 35$ eV.^{47, 67} The integrated intensity of the 2472.1 eV feature is 0.03 normalized units, thus Eq. 1 yields $\alpha^2 = 0.3\%$ S 3p character in an orbital responsible for the 2472.1 eV transition. This small fraction of sulfur 3p contribution is far below the fidelity of any population analysis derived from density functional or wave function-based electronic structure calculations. However, from either the ground- (Figure 5d) or the excited-state (Figure 7d) calculation, candidates for this orbital must exclude any ligand anti-bonding orbitals of [Cu(itaO)(SO₄)].

The similarity and differences in the atomic spin density distributions in the [Cu(itaO)(SO₄)] and the [Cu(Me₆tren)(SO₄)] complexes were evaluated using a comprehensive series of population analysis methods. Table 3 summarizes the Cu and S atomic spin densities, the magnitudes of the spin polarization upon occupation of the β LUMO, and the β LUMO composition leading to the 2472.1 eV transition. Despite the presence of the low-energy feature in the former complex, the ground state bonding description indicates a more covalent picture for the [Cu(Me₆tren)(SO₄)] complex. Independently, from the population analysis method, the Cu spin density is smaller in the Me₆tren complex than in the itao complex. The more covalent bonding can also be seen in the shorter Cu-L distances for the [Cu(Me₆tren)(SO₄)] complex, shown in Table 2. Although indirect, these observations nevertheless support the conjecture that the origin of the low-energy feature differs from the traditional description based on direct metal-ligand overlap. The S atomic contribution to any of the electronic structural features in Table 3 shows a small, but significant range in comparison to the experimental estimate of 0.3% character. However, the Hirshfeld population analysis (HPA) grossly overestimates this value. The Mulliken and Bader analyses produce similar values, though still greater than the experimental estimate. The Weinhold Natural Population Analysis method, although slightly underestimating, nevertheless gives similarly small values for both the [Cu(itaO)(SO₄)] and [Cu(Me₆tren)(SO₄)] complexes. Thus, the ground state frontier unoccupied orbital compositions and atomic spin densities cannot unambiguously explain either the presence or the absence of spectral features that might distinguish the two Cu complexes.

Following this exploration, the fragment orbital analysis as implemented in AOMIX package was employed for more detailed analysis of the orbital compositions. As a first step, the binding energies of the Cu(II) and sulfate ions, plus Me₆tren or itao ligands can be demarcated as 34.4 or 36.4 eV, without a correction for basis set superposition error. The energy difference of about 2 eV indicates stronger M-L interactions in the formally less covalent itao complex due to stronger ionic interactions, indicated in the Cu spin densities in Table 3. The greater M-L binding is further supported by the Mayer bond orders,⁶⁸ which are lower in the Me₆tren complex (Cu-sulfate: 0.82, Cu-Me₆tren: 1.66) than in the itao complex (Cu-sulfate: 0.83, Cu-Me₆tren: 2.17). The direct bond orders between the (SO₄)²⁻ and the itao or Me₆tren ligands can also be derived, which are 0.70 and 0.44 for [Cu(itaO)(SO₄)] and the [Cu(Me₆tren)(SO₄)], respectively. The larger bond order in the itao complex can be correlated with the presence of the stronger O-H $\cdots$ OSO₃ H-bonding interactions compared to the C-H $\cdots$ OSO₃ in Me₆tren.

A detailed look at the composition of the β LUMO orbital with respect to fragment molecular orbitals revealed no indication of any sulfate-based unoccupied orbital contribution to the formally d-electron hole on the Cu(II) ion. The first S 3p-containing sulfate fragment unoccupied orbitals do not appear until 6–7 eV above the LUMO of the complex, which is in agreement with the ground electronic state orbital plots in Figure 5d. In contrast, great differences can be observed in the contribution of the occupied sulfate orbitals to the electron hole on the Cu(II) ion, which reaches below the frontier occupied O-based sulfate orbitals.

The [Cu(itao)(SO₄)] complex has only 31% fragment orbital contribution from the sulfate in the β LUMO, while the fragment orbital contribution is 45% for the [Cu(Me₆tren)(SO₄)] complex. An additional major difference is that the latter is practically localized (44%) to the HOMO of the sulfate, which is the symmetry adapted combinations of O 2p (lone pairs) orbitals with less than 2% S 3p contribution (see also Figure 6b). In the itao complex, the HOMO and HOMO-1 orbitals together contribute 28%, while 3% originates from lower lying orbitals (sulfate HOMO-3, HOMO-5, HOMO-6, HOMO-8) with considerably higher (11–26%) S 3p contributions. The overall S 3p contribution on the basis of fragment orbitals is 0.5%, which is now in good agreement with the experimental estimate for the S 3p character of the low-energy 2472.1 eV feature.

The greater spread of the sulfate orbitals that contribute to the Cu-based β LUMO orbitals, and hence the appearance of the low-energy feature in the [Cu(itao)(SO₄)] complex can be correlated with the strong H-bonding interactions between the hydroxylamine groups and the sulfate ligand. The H-bonding reduces the nucleophilicity of the sulfate O-atoms, thus decreasing the bond polarity and ionic character of the S-O bond. This allows for greater mixing of the S 3p and O 2p atomic orbitals compared to the more polarized, and more ionic S-O bonding in the [Cu(Me₆tren)(SO₄)] complex. Furthermore, there is a greater extent of spin-polarization in [Cu(itao)(SO₄)] than in [Cu(Me₆tren)(SO₄)] or the other itao complexes. This in turn has increased the role of S 3p-based orbitals in the electronic structure of the molecule, resulting in the appearance of a uniquely low energy pre-edge feature.

These considerations further imply that analogous low-intensity features are not observed in the sulfur K-edge XAS of the [Ni(II)(itao)(SO₄)(H₂O)] and [Co(II)(itao)(SO₄)] complexes, because their lower Z_{eff} induces less intramolecular electron transfer from sulfate and the itao ligand. Radicalization of sulfate is therefore limited, making the transmission of spin polarization into the itao ligand orbitals experimentally undetectable.

The involvement of lower-energy occupied orbitals rather than the directly interacting ligand HOMO or HOMO-1 is a sign of the importance of σ -bond electron-transfer mediated by H-bonding. Intramolecular H-bonds between the sulfate and the hydroxylamine groups of the itao ligand stabilize the position of the pendant sulfate with respect to the central metal, as the smaller thermal ellipsoids indicate relative to sulfate in the Me₆tren complex (Figure 1). In addition, the small but non-negligible covalent nature of the H-bond creates a pathway through the ligand for further radicalization of the sulfate indirectly from Cu(II). That is, the itao ligand is partially oxidized as the result of the itao N→Cu(II) donation (Figure 6e), and thus can transmit radical character through the H-bond to sulfate.

The observed trends in the kinetics of electron transfer through the amino acid backbone of ruthenated metalloproteins have demonstrated the importance of through σ -bond electron transfer.^{69–73} H-bonds provide an efficient bridge between chains and across β -sheets for electron or hole propagation between the metal active site centers.^{70, 71, 73, 74} The σ -bond pathway includes coupling through localized bonding and anti-bonding orbitals.^{69, 72} The unique 2472.1 eV XAS pre-edge feature is direct spectroscopic evidence for this mechanism. Transmission of hole character across H-bonds and through σ^* bonds is thus now spectroscopically verified here and experimentally and theoretically justified elsewhere.^{69, 70, 72} Transmission of this radical character into a chain of otherwise filled-shell diamagnetic bonds opens a low-energy electron transfer pathway.

Discussion

This study has reiterated that the pre-edge features observed in the sulfur K-edge spectra of anhydrous CuSO_4 ,²⁰ arise from radicalization of the sulfate anion followed by spin-polarization and a redistribution of sulfur 3p-based unoccupied orbitals to lower energy. These features are now known to generalize to molecular first-row transition metal sulfate complexes.

Extensive electronic structure calculations found that the sulfur XAS pre-edge features of the paramagnetic molecular complexes likewise emerged as a result of the spin polarization and radicalization of the sulfate anion. This state is induced by the paramagnetic center via intramolecular non-integer electron transfer from the oxygen frontier orbitals, producing spin-polarization and electron density differences in the spin-up and spin-down orbitals. Sulfur-based contributions to the white line excitation then spread over a wide energy range, resulting in the new low-intensity pre-edge transitions and mixing further into metal 4s/4p Rydberg or ligand-based orbitals. The energy position of the pre-edge features along the rising-edge correlate with the magnitude of the metal effective nuclear charge, Z_{eff} . The pre-edge feature intensity is weak for the Co(II) complex, but stronger and well-resolved in the Ni(II) or Cu(II) complexes. From the comparison of the latter two complexes, it is concluded that the spread of the S-based excitation is independent of a six-fold (Ni) or five-fold (Co, Cu) sulfate coordination environment.

On the basis of these findings, it is proposed that polyoxoanions other than sulfate can be involved in covalent bonding and can become radicalized when coordinated to a paramagnetic central ion. Analytical views of the oxo-ions should be modified to include that small but significant and experimentally detectable covalent interactions affect their structure and reactivity.

Combined XAS and electronic structure calculations further show that the remarkable 2472.1 eV transition is direct spectroscopic evidence that intramolecular H-bonds can transmit spin polarization, and thus radical character from a Cu(II) center into an otherwise saturated diamagnetic σ -bond framework. The fact that one of the ligands here included sulfate anion allowed the opportune mixing of S 3p character into the ligand orbitals, permitting the appearance of this sulfur-based XAS transition.

These considerations further imply that analogous low-intensity features are not observed in the sulfur K-edge XAS of the Ni(II) and Co(II) itao complexes because their lower Z_{eff} induces less intramolecular electron transfer. The consequently smaller sulfate and itao ligand radicalization makes the transmission of spin polarization so minor as to be undetectable. This finding has prospective implications for the relative efficiency of paramagnetic M(II) ions in biological electron transfer, and for the evolutionary winnowing of metals toward a biological redox role.

Finally, the 2472.1 eV transition represents spectroscopic evidence of radical character and spin polarization transmitted across an H-bond and over several Å into otherwise diamagnetic saturated ligand-based σ -orbitals of second-row elements. The low-energy sulfate transitions are the spectroscopic signature of this electron transfer. The orbitals lower-lying than the commonly considered frontier occupied levels are involved in forming the 2472.1 eV spectroscopic feature. The contribution of these orbitals is generally difficult to detect experimentally. However, despite their small (<1%) contribution, they are essential in forming the electron transfer coupling elements within the σ -bond pathway. The results overall expressly validate the through-bond electron transfer mechanism directly inferred from the definitive kinetic studies of ruthenated metalloproteins.^{75–77} This study thus reports the first direct spectroscopic confirmation of the theory of σ -bond conduction pathways critically central to electron transfer in metalloproteins and enzymes.^{69, 72, 76, 77}

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Crystal structural diagrams of the complexes; showing 50% ellipsoids.

Figure 2.

a. Sulfur K-edge XAS spectra of the $[M(II)(\text{itao})(\text{SO}_4)(\text{H}_2\text{O})_{0,1}]$ complexes. M is: (black), Co(II); (blue), Ni(II); (red) Cu(II); (green), Zn(II); while (dotted) is sulfate dissolved in pH 6.3 solution scaled for comparison. Inset: close-up of the pre-edge energy region. b. Second derivatives of the same spectra. Lines and colors have the same meaning. Inset: close-up of the pre-edge energy region.

Figure 3.

a. (**blue dots**), the sulfur K-edge XAS spectrum of $[\text{Cu}(\text{itao})(\text{SO}_4)]$ and; (**red**), the fit with constituent pseudo-Voigts (light colored lines). Insets: bottom, the fit to the rising edge energy feature, with (**green**), the rising K-edge background; top, (**blue**) the fit to the very low-intensity feature found at 2472.1 eV. b. (**blue dots**), the second derivative of the XAS spectrum, and; (**red**), of the fit, and; (light colored lines), the constituent pseudo-Voigts. Insets: bottom, the fit to the second derivative of, (**red**), the rising edge feature, and; top, (**blue**), the 2472.1 eV feature.

Figure 4. Sulfur K-edge XAS spectra of: a. (blue), potassium Jarosite; (green), *trans*-K₅[V(ox)₂(SO₄)₂]·3H₂O, and; (red), [VO(terpy)(SO₄)]; b. the second derivatives of the same XAS spectra. Arrows point to sulfate pre-edge features due to sulfate radicalization, with the less intense features more readily visible in the second derivative XAS. The dashed line indicates the nearly identical energy of the V(III,IV) pre-edge features.

Figure 5.

Comparison of orbital compositions for the first 15 eV energy range above the HOMO for: a, the free $[\text{SO}_4]^{2-}$; b, its 1-electron oxidized form $(\text{SO}_4)^-$, and; the $[\text{M}(\text{II})(\text{itao})(\text{SO}_4)(\text{H}_2\text{O})_{0,1}]$ complexes, where M is c, Zn; d, Cu; e, Ni, and; f, Co, all calculated at BP86/def2TZVP level of theory.

Figure 6.

Comparison of contour plots of spin-density distribution for: a, the 1-electron oxidized sulphate mono-anion; b, the $(\text{SO}_4)^-$ β LUMO electron hole; c, the $S=1/2$ $[\text{Cu}(\text{itao})(\text{SO}_4)]$ complex. The green or orange lobes correspond to net negative or positive spin density distributions, respectively, which were obtained after subtracting away all the fully occupied spin-up and spin-down orbitals; d, $[\text{Cu}(\text{itao})(\text{SO}_4)]$ residual spin polarization with β LUMO occupied and formally d^{10} copper electron configuration without relaxed electronic structure; e, the singly occupied molecular orbital corresponding to the 3d electron hole. The same DFT calculations for $[\text{Cu}(\text{Me}_6\text{tren})(\text{SO}_4)]$, shown in Figure S12 of the Supporting Information, reveal different distributions of spin density and polarization.

Figure 7.

Simulated TDDFT core-level excitation spectra calculated at BP86/def2TZVP level for: a, the sulfate; b, 1-electron oxidized sulfate, and; the $[M(II)(itao)(SO_4)]$ complexes, c, Zn; d, Cu; e, Ni, and; f, Co. Color-coding of spectra matches those in Figure 2. Pseudo-Voigt line-widths of 1.1 eV were used to plot the envelope of transitions.

Table 1Summary of crystallographic data for complexes **1–4**

	1: Co(itaO)SO₄	2: Ni(itaO)(SO₄)H₂O	3: Zn(itaO)SO₄	4: Cu(Me₆tren)SO₄
Empirical Formula	C ₆ H ₁₅ N ₇ O ₇ SCo·0.5H ₂ O	C ₆ H ₁₇ N ₇ O ₈ SNi·3H ₂ O	C ₆ H ₁₅ N ₇ O ₇ SZn·0.5H ₂ O	C ₁₂ H ₃₀ N ₄ O ₄ SCu·3H ₂ O
fw	397.25	460.08	403.69	444.05
crystal size, mm	0.11×0.09×0.07	0.10×0.10×0.07	0.11×0.09×0.08	0.10×0.10×0.09
crystal syst.	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P2₁/n</i>
a, Å	12.519(9)	8.340(3)	12.541(10)	9.4770(19)
b, Å	12.816(10)	13.219(4)	12.878(12)	15.661(3)
c, Å	10.043(6)	16.197(5)	10.055(7)	13.741(3)
α, deg.	90.00	90.00	90.00	90.00
β, deg.	113.60(5)	100.21(3)	113.72(3)	91.00(3)
γ, deg.	90.00	90.00	90.00	90.00
V, Å ³	1476.6(18)	1757.4(10)	1487(2)	2039.1(7)
Z	4	4	4	4
D, calc	1.787	1.739	1.804	1.446
μ (Cu-Kα), mm ⁻¹	10.947	3.378	4.117	1.212 (Mo-Kα)
F(000)	816	960	848	948
range, deg.	3.85–66.97	4.34–66.50	3.85–67.00	3.24–26.03
no. of reflns coll	2560	4614	2652	4402
no. of indep reflns	2559	3088	2650	3999
<i>R</i> _{int}	0.0603	0.0377	0.0464	0.0517
no. of reflns <i>I</i> > 2σ(<i>I</i>)	1616	1917	1353	3406
no. of refined params	226	259	217	250
goodness-of-fit (<i>F</i> ²)	0.910	1.042	0.967	1.010
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.0495	0.0344	0.0412	0.0420
<i>wR</i> 2	0.1253	0.0744	0.1109	0.1070
Residuals, e/Å ³	1.032, –0.587	0.758, –0.261	0.841, –0.492	0.812, –0.680

Table 2

Selected Crystallographic Distances (Å) and Angles (°) of the Complexes

	Co(itaio)SO ₄	Ni(itaio)SO ₄ H ₂ O	Cu(itaio)SO ₄ ^a	Zn(itaio)SO ₄	Cu(Me ₆ tren)SO ₄
M ^a -N ₁	2.219(4)	2.127(2)	2.053(5)	2.291(4)	2.0261(8)
M-N ₂	2.014(4)	2.057(2)	2.069(5)	2.014(4)	2.1564(9)
M-N ₃	2.001(4)	2.062(2)	2.013(5)	2.001(4)	2.1333(9)
M-N ₄	1.992(4)	2.049(2)	2.010(5)	2.205(4)	2.1597(9)
M-O ₁	2.009(3)	2.027(2)	1.941(4)	1.984(3)	1.903(3)
Ni-OH ₂	---	2.162(2)	---	---	---
S-O ₁	1.502(3)	1.471(2)	1.505(5)	1.500(3)	1.473(3)
S-O ₂	1.460(4)	1.460(3)	1.467(4)	1.459(3)	1.449(1)
S-O ₃	1.444(4)	1.427(2)	1.468(5)	1.459(3)	1.462(3)
S-O ₄	1.454(4)	1.448(2)	1.462(6)	1.436(3)	1.427(1)
∠N ₁ MN ₂	77.61(14)	80.82(8)	79.72	76.20(13)	84.53(3)
∠N ₂ MN ₃	114.04(16)	93.20(7)	120.33	115.94(15)	120.00(4)
∠N ₃ MN ₄	116.28(15)	157.46(8)	116.17	114.91(15)	118.61(3)
∠N ₁ NiO ₈	---	95.39(8)	---	---	---
∠MO ₁ S	125.58(19)	136.40(10)	127.0(2)	126.28(15)	146.53(20)

^aReference 21. The atoms of [Cu(itaio)(SO₄)] have been renumbered to match the others presented here.

Table 3

Atomic spin densities (in electrons), spin polarizations (in electrons) with formally closed shell electron configuration, and β LUMO compositions (in percent) for copper and sulfur centers in the [Cu(itaio)(SO₄)] and [Cu(Me6tren)(SO₄)] complexes using the Mulliken (MPA), Hirshfeld (HPA), Weinhold Natural Orbital (NPA), or Bader Atoms-in-Molecule (AIM) population analysis method.^a

		Cu(itaio)(SO ₄)				Cu(Me6tren)(SO ₄)			
		spin density	polarization	spin composition	β LUMO composition	spin density	polarization	spin composition	β LUMO composition
MPA	Cu	0.46	0.00	0.00	46.8%	0.36	-0.01	-0.01	37.7%
	S	-0.02	-0.03	-0.03	0.6%	-0.03	-0.04	-0.04	0.8%
HPA	Cu	0.49	0.01	0.01	47.8%	0.39	0.00	0.00	38.2%
	S	0.01	-0.02	-0.02	2.1%	0.01	-0.02	-0.02	3.2%
NPA	Cu	0.44	-0.01	-0.01	44.5%	0.35	-0.01	-0.01	35.6%
	S	-0.01	-0.01	-0.01	0.1%	-0.02	-0.02	-0.02	0.1%
AIM	Cu	n/a	n/a	n/a	49.3%	n/a	n/a	n/a	39.4%
	S	n/a	n/a	n/a	0.6%	n/a	n/a	n/a	0.9%

^aCorresponding spin density contour plots are shown in Figure 6 and Figure S12 in the supporting information for the itao and tren complexes, respectively.