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S K-edge XAS and DFT Calculations on Square Planar Ni^{II}-thiolate Complexes: Effects of Active and Passive H-bonding

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Abstract

S K-edge XAS for a low-spin Ni^{II}-thiolate complex shows a 0.2 eV shift to higher pre-edge energy but no change in Ni-S bond covalency upon H-bonding. This is different from the H-bonding effect we observed in high spin Fe^{III}-thiolate complexes where there is a significant decrease in Fe-S bond covalency but no change in energy due to H-bonding (Dey, A.; Okamura, T.-A.; Ueyama, N.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **2005**; *127*, 12046-12053.). These differences were analyzed using DFT calculations and the results indicate that two different types of H-bonding interactions are possible in metal-thiolate systems. In the high-spin Fe^{III}-thiolate case, the H-bonding involves a thiolate donor orbital which is also involved in bonding with the metal (active), while in the low-spin Ni^{II}-thiolate the orbital involved in H-bonding is non-bonding with respect to the M-S bonding (passive). The contributions of active and passive H-bonds to the reduction potential and Lewis acid properties of a metal center are evaluated.

Keywords

S K-edge XAS; DFT; H-bonding

Introduction

Hydrogen bonding plays an important role in tuning the reactivity of protein active sites by modulating active-site geometric and electronic structure.^{1,2} The role of these H-bonds has been evaluated using several different experimental and computational techniques.^{3,4} Although there are some significant developments in understanding H-bonding with 2nd row elements (N, O etc), only a few studies have evaluated the effects of H-bonding on the structure and reactivity of inorganic complexes and active sites having sulfur ligands.^{5,6,7,8,9} Metal-sulfur-based active sites are abundant in nature, performing a wide variety of functions, including redox catalysis (e.g., O₂ activation by cytochrome P450), small-molecule activation (e.g., superoxide reductase), Lewis acid catalysis (e.g., nitrile hydratase), and electron transport (e.g., Fe-S and blue copper proteins).^{10,11,12,13} Many of these sites have multiple H-bonding interactions between the sulfur ligands (thiolates or bridging sulfides atoms) and the peptide backbone. These active sites significantly differ in electronic structure relative to geometrically similar inorganic model complexes. H-bonding interactions can affect the M-S bond covalency and thus make a significant contribution to observed large differences in reactivity between

model complexes and protein active sites.¹⁴ However, current knowledge about these relatively weak yet crucial interactions is limited by the fact that conventional spectroscopic techniques are often not very sensitive to the small perturbation of H-bonding.

Ligand K-edge X-ray absorption spectroscopy (XAS) is a powerful physical method that provides a direct experimental estimate of the covalency of metal-ligand bonds.^{15,16} The K-edge XAS of a ligand bound to a transition metal can have an intense *pre-edge* feature. This is assigned to the ligand 1s (L_{1s}) to metal based 3d (M_{3d}) transition. The intensity of this transition is directly proportional to the % ligand np character (in this case % S_{3p}) mixed into unoccupied or half-occupied metal based 3d orbitals of the ground state wavefunction (ψ) of the transition metal complex.

$$\Psi = (1\alpha^2)^{1/2} |M_{3d} + \alpha |L_{np}\rangle \quad (1)$$

where α is the ligand coefficient in the half-occupied or unoccupied orbital. The intensity (I) of the $L_{1s} \rightarrow M_{3d}$ transition is;

$$I(L_{1s} \rightarrow M_{3d}) = \alpha^2 I(L_{1s} \rightarrow L_{np}) \quad (2)$$

where $I(L_{1s} \rightarrow L_{np})$ is the intensity of a purely ligand based $1s \rightarrow np$ transition, which depends primarily on the Z_{eff} of the ligand.¹⁷ The pre-edge intensity thus provides a direct estimate of ligand-metal bond covalency (α^2). Due to the localization of the core hole on the ligand this technique involves minimal final state effects (e.g. core hole interaction with the d^{n+1} final state) and electronic relaxation.¹⁷

This technique has previously been used to investigate the effect of H-bonding in active sites of Cu-S and Fe-S electron transfer proteins.^{15, 18} XAS data on the proteins showed significant reductions of M-S bond covalency which qualitatively correlated to the extent of H-bonding interaction in the active site.^{19,20,21} For a quantitative estimate of this effect, S K-edge XAS on a series of heme thiolate model complexes was performed where the H-bonding to the thiolate ligand was systematically increased.²² The data showed dramatic reduction in pre-edge intensity with increasing H-bonding which indicated weakening of Fe-S $d\pi-p\pi$ covalency. The increased H-bonding was calculated to stabilize the reduced site more than the oxidized state, which predicts a positive shift in the reduction potential, as experimentally observed.

In this study we report S K-edge XAS and DFT calculations on square planar Ni^{II} thiolate complexes (Fig. 1) as solids and in H-bonding solvent solutions. The data obtained here show a very different behavior than the experimental results we observed in Ref. 22 for the heme-thiolate system; there is no decrease in Ni-S bond covalency but there is a shift in pre-edge energy due to H-bond. DFT calculations reproduce this behavior and indicate that it is the result of the differences in M-S bonding interactions between a thiolate and a high-spin $d^5 Fe^{III}$ which involves π and σ bonds and a low-spin $d^8 Ni^{II}$ which involves only σ bonds. This reflects two very different types of H-bonding scenarios having similar overall energy but rather different effects on electronic structure.

Experimental Details

Materials and Methods

The complexes $Ni^{II}[N,N'\text{-bis(2-mercaptoethyl)-1,5-diazacyclooctanato}] Ni(DACO)$ and $Ni^{II}[\text{bis-}Ni^{II}[N,N'\text{-bis(2-mercaptoethyl)-1,5-diazacyclooctanato}]]$ ($[Ni(DACO)_2Ni]$) were synthesized as described in Reference 23. Dry acetonitrile (% $H_2O \ll 0.01\%$) was obtained from Acros. For XAS experiments the samples were ground into a fine powder and dispersed as

thinly as possible on sulfur-free Mylar tape. This procedure has been verified to minimize self-absorption effects. The sample was then mounted across the window of an aluminum plate. Fresh solutions of Ni(DACO) and [Ni(DACO)₂Ni] were prepared before the experiments ~ 10 mM in concentration. The solutions were loaded via a syringe into a Pt-plated Al block sample holder sealed in front using a 6.3 μ m polypropylene window and maintained at a constant temperature of 4°C during data collection using a controlled flow of N₂ gas pre-cooled by liq. N₂ passing through an internal channel in the Al block.

Data Collection

XAS data were measured at the Stanford Synchrotron Radiation Laboratory using the 54-pole wiggler beam line 6-2. Details of the experimental configuration for low energy studies have been described previously.²² The energy calibration, data reduction and error analysis follow the methods described in Ref. 16.

Fitting Procedures

Pre-edge features were fit by pseudo-Voigt line shapes (sums of Lorentzian and Gaussian functions) using the EDG_FIT software.²⁴ This line shape is appropriate as the experimental features are expected to be a convolution of a Lorentzian transition envelope and a Gaussian line shape imposed by the beam line optics.^{25, 26} A fixed 1:1 ratio of Lorentzian to Gaussian contribution successfully reproduced the pre-edge features and were kept fixed during the fitting procedure. The rising edges were also fit with the same pseudo-Voigt line shapes. Fitting requirements included reproducing the data and its second derivative, using the minimum number of peaks. The intensity of a pre-edge feature (peak area) was calculated using the expression intensity = $2 \times \text{amplitude} \times \text{full-width-at-half-maximum (fwhm)}$. The fwhm is between 0.45-0.5 for each peak. The reported intensity values for the model complexes are an average of all of the accepted pre-edge fits, typically 5-6 (which differed from each other by less than 3%). The fitted intensities were converted to %S_{3p} character using the pre-edge feature of plastocyanin as a reference (where 1.01 units of intensity, obtained using this program, corresponded to 38% S_{3p} character) as the Z_{eff} on the S atom of the thiolate ligand will not change significantly between the Cu-S active site of plastocyanin and the Ni-S complexes studied here.

DFT Calculations

All calculations were performed on dual-CPU Pentium Xeon 2.8 GHz work stations. Geometry optimizations were performed using the BP86^{27, 28} in Gaussian 03 program²⁹ employing a 6-311g* basis set on the Fe, Ni, S and N atoms and a 6-31g* basis set on C and H atoms. Single point calculations were performed using 6-311++g** basis set on all atoms for wavefunction and population analysis. A PCM³⁰ solvation model (acetonitrile as solvent) was used for energy calculations. For calculations of IE's, geometries were optimized for both oxidation states and the energy of a free electron was accounted for (4.43 eV).³¹ The molecular orbitals were plotted using MOLDEN and the Mulliken³² population analyses were performed using the PyMOLyze³³ program.

Results

The S K-edge XAS of Ni(DACO) is shown in Fig. 2A (black). The spectrum has a sharp feature at 2470.8 eV (Table 1, 1st row) which is assigned to the RS_{1s} → Ni_{3d} *pre-edge* transition. The intensity of the pre-edge transition is directly proportional to the S_{3p} mixing in the acceptor Ni_{3d} LUMO (eqn. 2) of this sq. planar Ni^{II} complex; i.e. Ni-S bond covalency. The pre-edge can be fit with a single peak and the intensity obtained is 1.25 units that correspond to 46% S_{3p} character (Table 1, 1st row) in the acceptor Ni_{3d} orbital. Note that the pre-edge feature includes two degenerate transitions one from each sulfur. Thus 46% S_{3p} implies that each

thiolate contributes 23% S_{3p} to the wavefunction. The *rising-edge* at ~ 2472.8 eV (Table 1, 1st row) is assigned to the $RS_{1s} \rightarrow RS_{C-S} \sigma^*$ transition.³⁴ The S K-edge spectra of Ni(DACO) in H_2O solution (Fig. 2A, black, dashed) shows that the pre-edge shifts to 2471.0 eV (Table 1, 2nd row, a ~ 0.2 eV increase) but shows no decrease in intensity. This energy shift could be a result of solvent H-bonding or axial co-ordination of the solvent molecules to the Ni center. The XAS data of Ni(DACO) dissolved in CH_3CN solution (Fig. 2A, red), however, does not show the energy shift observed in the H_2O solution data. This eliminates the possibility of solvent coordination as a cause for the observed pre-edge energy shift and indicates that this is, in fact, a result of solvent H-bonding.³⁵ The lack of intensity change on H-bonding is in contrast to the results obtained for a series of ferric heme thiolate complexes where the pre-edge intensity decreased from 1.3 units to 1.01 units upon introducing two H-bonds to the thiolate (Fig. 2B).²² There was also a 0.5 eV shift in the pre-edge energy which, however, was found to be a result of the electron withdrawing effect of the substituents and not H-bonding.

The S K-edge XAS for the bridged complex $[Ni(DACO)]_2Ni$ (Fig. 2C, green) shows a broad pre-edge at 2471.6 eV.³⁶ The pre-edge in this case represents transitions from four thiolate sulfurs to the three Ni centers. The data do not allow individual resolution of these contributions. The data for the aqueous solution of this complex (Fig. 2C, dashed green) shows no resolvable effect on the energy or the intensity relative to the solid. The lack of any effect of H-bonding in this complex contrasts the behavior of Ni(DACO) (Fig. 2A). This difference originates from the additional Ni-S bonding interactions in $(NiDACO)_2Ni$ considered below.

Analysis

The S K-edge XAS data of the Ni(DACO) complex show different behavior from those of the high-spin Fe^{III} heme thiolate complex in Ref. 22. While the pre-edge intensity was reduced upon H-bonding in the Fe^{III} case there is no resolvable change in intensity in the Ni^{II} case. The only resolvable change is the shift of the pre-edge to higher energy. DFT calculations were performed to understand this difference.

A. DFT calculations on Ni^{II} -thiolate

The DFT calculations of the Ni(DACO) complex were performed without and with H-bonding. The H-bonding was simulated by adding H_2O molecules in the vicinity of the Ni(DACO).³⁷ The optimized bond distances for Ni(DACO) (Table 2, 1st row) are in reasonable agreement with its reported crystal structure Table 2, 1st row in parenthesis).³⁸ The calculations indicate that both without and with H-bonding the Ni $3d_{x^2-y^2}$ orbital is the LUMO and that it has strong R antibonding interactions with the N_{2p} and the S_{3p} orbitals (Fig. 3; the complete MO diagram is provided in Supplementary Information Fig. S1). The calculated wavefunction has total 38% S_{3p} (19% each) in the acceptor Ni $3d_{x^2-y^2}$ compared to 46% observed experimentally. One possible source of this difference is a final state effect. We have thus calculated the $S_{1s}^1 \dots Ni3d^9$ excited final state. This shows that the valence electron density has redistributed such that the Ni character increased (by 4%) and the character of the S without the 1s hole also increased (by 4%). The effect of this is to redistribute some of the Koopmans' state into the relaxed final state. We have calculated this using the sudden approximation which is appropriate for this high energy region and find that this has the effect of a small decrease ($<20\%$) of pre-edge intensity which gets redistributed into shake-up peaks at energy greater than 4 eV, which will overlap the edge. This electronically relaxed final state slightly increases the deviation of the experimental ground state covalency calculated with DFT.

The calculations on the H-bonded Ni(DACO) complex show that both the Ni-S bond length and the Ni-S covalency were not altered upon H-bonding (Table 2, 2nd row) thus reproducing the experimental data. The calculations also indicate that as a result of the interaction with the water molecules, the S_{1s} orbitals of the H-bonded thiolates, in Ni(DACO) are stabilized by

0.2 eV relative to the S_{1s} orbitals of the non H-bonded thiolates, while no such shift is observed in the acceptor Ni_{3d} orbital. This stabilization of the donor $1s$ orbital relative to the acceptor $Ni\ 3d_{x^2-y^2}$ orbital is consistent with the 0.2 eV upshift of the pre-edge transition. Note that there is a 0.01 Å decrease in the average Ni-N bond length upon H-bonding. However, this decrease does not significantly affect the ground state wavefunction of the Ni complex (Table 2, row 1 and row 2).

The optimized geometry of the H-bonded Ni(DACO) complex (Fig. 4, left) indicates that the water molecules align to interact with the non-bonding π donor orbitals (perpendicular to the S-Ni-S plane) in preference to the σ donor orbitals (in the S-Ni-S plane).³⁷ This model of H-bonding is supported by the lack of a solvent H-bond effect on the S K-edge XAS of the bridged complex $[Ni(DACO)]_2Ni$ (Fig. 2C) where the two available S_{3p} π donor orbitals in Ni(DACO) are coordinated to the bridging Ni^{II} ion (Fig. 1) forming a σ bond.³⁹ Thus there is no lone pair available for H-bonding to H_2O .

B. DFT on Fe^{III} -thiolate

Pervious S K-edge results on high-spin Fe^{III} (porphyrinato)thiolates showed significant decrease of pre-edge intensity, i.e. Fe-S bond covalency. There was however a 0.5 eV increase in pre-edge energy on H-bonding. Calculations on a model with an electron withdrawing group (EWG) but not an H-bonding substituent (ester) showed that this shift was not due to H-bonding but a inductive effect of the EWG which shifted charge density from the C-S σ bond.²² Similar results are obtained here in the DFT calculations on a Fe^{III} (porphyrinato)(methylthiolate) ($FePSMe$) complexes. The Fe-S bond elongates by only 0.01 Å and the Fe-S π bond covalency decreases by 5% upon H-bonding (Table 2, rows 3 and 4). These calculations also show that the stabilization of the S_{1s} orbital (due to dipolar interaction with H_2O) is associated with an equal stabilization of the Fe_{3d} orbitals (due to increased Z_{eff} due to decreased covalency) and thus there is no effect on the pre-edge energy upon H-bonding in this case. The calculated behavior of the high-spin Fe^{III} thiolate complex is different from the results obtained for the low-spin Ni thiolate complex, where upon H-bonding there is no change in Ni-S bond covalency but a shift to higher energy.

Discussion

H-bonding effects on M-S bond covalency are different in high-spin Fe^{III} relative to sq. planar Ni^{II} -thiolate systems. Although in both cases the H-bonds are oriented along the π donor orbitals, in case of Fe^{III} , this orbital is involved in bonding to the half-occupied Fe_{3d} orbitals, while in the case of Ni^{II} the thiolate π orbital is non-bonding as the d- π orbitals are filled. Therefore H-bonding to the π donor orbital of a thiolate weakens the π bonding in Fe^{III} but has no effect on the σ bonding in Ni^{II} .

The orientations of the H_2O molecules suggest that the π donor orbitals are better H-bond acceptors than the σ donor orbitals.⁴⁰ This preferential H-bonding reflects the higher electron density in the π donor orbitals. The σ orbital of the thiolate has better overlap due to its orientation and covalently donates more charge to the metal orbitals. The π orbital thus retains more residual electron density for H-bonding.⁴¹ This predominantly π -based H-bonding interaction in M-S systems is “active” in the Fe^{III} -thiolate system as it weakens the Fe-S π bond. However, in the case of the low spin Ni^{II} -thiolate, the H-bonding is “passive” as this interaction with the nonbonding π donor orbitals does not affect the Ni-S bond covalency.

In the active system, H-bonding lowers the thiolate donation to the metal. This shifts the reduction potential more positive and increases its Lewis acidity. The calculated ionization energies (solvent corrected and free energy of electron subtracted) for the $Fe^{III/II}PSMe$ complex indicate that one active H-bond shifts the $Fe^{III/II}$ potential in $FePSMe$ by +163 mV (Table 3).

This effect can be expected to be smaller in a passive system. Similar calculations on Ni(DACO) indicate that even two passive H-bonds shift the $\text{Ni}^{\text{II/I}}$ potential by only +15 mV (Table 3). The Lewis acidity is estimated from the NPA (natural population analysis) charge on the metal center without and with H-bonding. In the case of passive H-bonding there is an 0.01 e change in the charge of the metal,⁴² while there is an increase of 0.02 e in the active case (Table 3). This change of Lewis acidity is reflected in the enhanced F^- binding energy (calculated to be 10 kcal/mol for FePSMe and 2 kcal/mol for Ni(DACO) in the gas phase, Table 3) to the vacant axial position of the complex with an active H-bond.

In summary, H-bonds to a thiolate ligand can be considered active or passive based on the involvement of the H-bond acceptor orbital in thiolate-metal bonding (Fig. 5). In the active case the H-bond (Fig. 5, left) acceptor orbital is involved in M-S O bonding and H-bonding significantly alters the electronic structure and reactivity of the metal center. However, if the H-bond acceptor orbital is not a thiolate donor orbital (i.e. there is no π bonding) then it is passive in nature (Fig. 5, right) and does not affect MS covalency or tune reactivity.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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35. This is also supported by ¹H NMR (data not shown) on this complex in CD₃CN and D₂O solvents.
36. Note that this pre-edge has contributions from three Ni^{II} center and four thiolates.
37. Both the two and four H₂O water molecules were added near the complex and gave the same electronic structure description. Also two different starting structures were used for these optimizations, one where the water molecules were above the S-Ni-S plane and another where they were in the plane. Both starting structures optimized to the same final geometry presented in the text. Restricting the water molecules to stay in the S-Ni-S plane resulted in a structure that was 2.5 Kcal/mol higher in energy.
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39. Geometry optimized DFT calculations were performed on Ni-[Ni(DACO)]₂ with and without H-bonding from H₂O. The results show that the average S-O distance is 3.5 Å and the average S---H-O angle is 100° in Ni-[Ni(DACO)]₂ + 4H₂O relative to 3.3 Å and 175° in Ni(DACO) + 2H₂O. This indicates that the H-bonding in Ni-[Ni(DACO)]₂ is weak consistent with experimental results.
40. This is also indicated in the calculated H-bonding energy which is -2.6 kcal/mol and -1.9 kcal/mol for π and σ orientations, respectively.
41. The total donation from the thiolate σ donor orbital into Fe_{4p} and Fe_{4s} orbital in FePSMe is calculated to be 13% in addition to 22% donation to the Fe_{3d} orbital. The π donor orbital only donates 20% to the Fe_{3d} orbital. Thus the total donation from the σ donor orbital is higher.
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Figure 1.
Schematic representation of Ni(DACO) and [Ni(DACO)]₂Ni complexes used in this study.

Figure 2.

S K-edge XAS of A) [Ni(DACO)] as solid (black), aqueous solution (dotted black) and acetonitrile solution (red); of B) Fe(porp)SPh (blue) and Fe(porp)SL2 (dashed blue, SL2 refers to 2,6-bis(trifluoroacetamide)-thiophenol as shown in inset) adapted from Ref. 22; and of C) [Ni(DACO)]₂Ni as solid (green) and in aqueous solution (dashed green).

Figure 3.
Contour of the Ni 3d_{x²-y²} acceptor LUMO in Ni(DACO).

Figure 4.
Optimized geometries of the H-bonded Ni(DACO) (left) and FePSMe (right).

Figure 5.
Schematic representation of active (left) and passive (right) H-bonds.

Table 1

XAS Results

Complex	Pre-edge Intensity	%S _{3p}	Pre-edge energy	Rising-edge energy
Ni(DACO)	1.25±0.01	46±1%	2470.8±0.1	2472.8±0.1
Ni(DACO)+H ₂ O	1.25±0.01	46±1%	2471.0±0.1	2473.0±0.1

Table 2

DFT calculated geometry and wavefunction

Model	Geometric Parameters (average)			Wavefunction (summed over all unoccupied M_{3d} orbitals)		
	M-S ^a	M-N ^a	S...O ^d	S-H-O ^b	%M _{3d}	%N _{2p}
Ni(DACO)	2.17 (2.17)	2.00 (1.98)			47	11
Ni(DACO) + 2H ₂ O	2.18	1.99	3.33	165	47	12
FePSMe	2.30	2.09			359	59
FePSMe + H ₂ O	2.31	2.09	3.36	151	361	60

^a Units in Å.

^b Units in degrees.

Table 3Calculated ionization energies and F⁻ binding energies

Model	IE (Volts) ^a	Q _M ^b (NPA)	ΔBE _{M-F} ^c (kcal/mol)
Ni (DACO)	-2.050	0.50	0
Ni(DACO) + 2H ₂ O	-2.035	0.51	-2
FePSMe	-0.936	1.33	0
FePSMe + H ₂ O	-0.773	1.35	-10

^a IE refers to Ionization Energy,^b Q_M refers to the natural charge on metal,^c ΔBE_{M-F} refers to the metal-fluoride bonding energy