Multiple *K*-edge XAS for the structural analysis of thiophenolate bridged heterotrinuclear complexes

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A multiple K-edge X-ray absorption spectroscopic (XAS) approach to determine the structural parameters of an isostructural series of heterotrinuclear thiophenolate-bridged metal-complexes of the general formula [LFeCrFeL]n+ (with n= 1,2,3) is presented. The analysis focuses on the variation of the metal-metal distances and the metal-sulfur distances with the cluster charge n. XAS measurements on the Fe, Cr, and S-K-edges were performed to allow a fit of these distances from these constituent elements. Results show that 3 S atoms and 3 N atoms coordinate each of the terminal Fe atoms, whereas 6 S atoms coordinate the central Cr atom. This symmetry allows extracting structural information with high accuracy especially when the spectra obtained at different edges are refined at the same time. A decrease of the metal-metal distance with increasing cluster charge is also derived from this multiple-edge analysis.

Keywords: bioinorganic chemistry, multiple-edge analysis, EXAFS

1. Introduction

Iron-sulfur proteins are a structural and spectroscopic well studied class of metalloproteins. These proteins contain active sites comprising tetrahedral coordinated Fe^{II} and/or Fe^{III} ions, sulfido and S-bound cysteinato ligands. Mono-, di-, trinuclear core structures have been identified which exist in a variety of oxidation levels. Delocalisation of the „excess" electrons is exhibited by several of these clusters. To analyze the structural changes linked to delocalisation an isostructural series of heterotrinuclear thiophenolate-bridged complexes of the general formula [LFeCrFeL]$^{n+}$ with n=1,2,3 where L^{3-} represents the trianionic form of the ligand 1,4,7-tris(4-tertbutyl-2-mercaptobenzyl)-1,4,7 triazocyclononane has been chosen. These sulfur bridged trinuclear complexes show due to the octahedral coordinated metal atoms only small changes and therefore they

are ideal to show the possibilities of such multiple edge fits. In a forthcoming publication [Glaser et al. (1998)] we focus on the preparation of these complexes, whereas in this contribution we discuss the structural changes upon oxidation of the complexes determined by X-ray absorption spectroscopy.
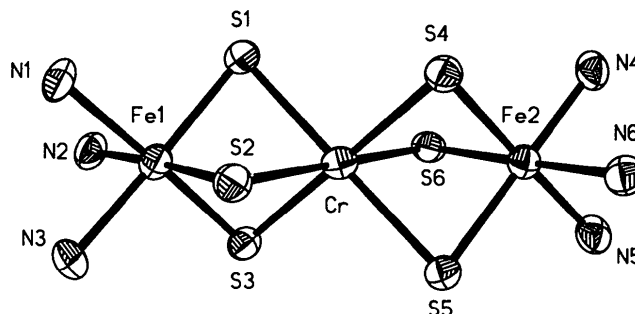
Figure 1
Overall structure of the [LFeCrFeL]$^{n+}$ core.

2. Experimental section

Room temperature Fe and Cr K-edge XAS spectra were recorded at the beam line E4 at HASYLAB (DESY, Hamburg, Germany). This beam line is equipped with three ionization chambers, which allow a calibration of each spectrum according to a reference sample. Monochromatization was achieved by a Si(111)-monochromator. The S-K-edge XAS measurements were performed on the Jumbo beam line at SSRL. Two InSb single crystals served as monochromator. For the energy calibration of the data WINXAS [Ressler (1998)] was used, whereas normalization and data reduction were done with EXPROG [Nolting et al. (1992)] using a Victoreen function below the edge and three cubic splines above the edge. For the EXAFS analysis Feff 6 [Zabinsky et al. (1995)] and Feffit 2.32 [Newville et al. (1995)] were applied.

3. Results and discussion

The terminal Fe ions are coordinated by 3 S and 3 N atoms. Hence, one obtains in the Fourier transform of the Fe-K-edge EXAFS a broad peak at a reduced radius of 1.8 Å compared to the Cr-K-edge, its narrow peak at a reduced radius of 1.9 Å is due to the 6 S atoms at similar distances. The higher Fourier transform peak intensity for Cr reflects the higher degree of order. This higher order it results in a much higher multiple scattering contribution within the first coordination shell around Cr (at about 2.8 Å) compared to the multiple scattering within the first coordination shell around Fe (at about 2.7 Å).

One of the systems under study here, e.g. [LFeCrFeL]$^{3+}$, was successfully crystallized, thus providing an X-ray structure, which was used as a basis for the detailed multiple scattering EXAFS analysis of all complexes. To avoid the problem of parameter correlation we have applied the simplest model possible. For the Cr-K-edge this procedure includes the contributions from six sulfur atoms in the first shell, the backscattering from the neighboring iron atoms, the very important multiple scattering contributions for the Cr-S-Fe-Cr

paths and, even more important, the multiple scattering contribution within the first shell up to 4th order.
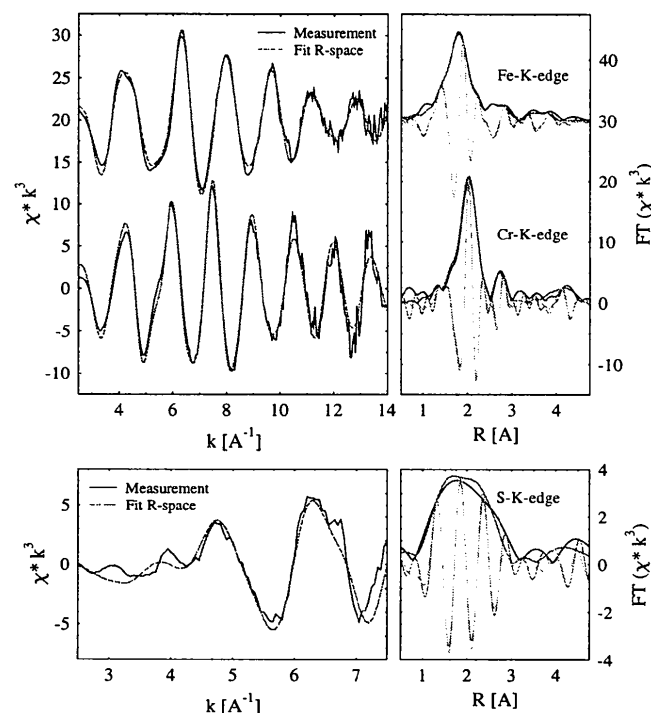
Figure 2
XAS results for [LFeCrFeL]$^{1+}$. All fits were performed in R space.

The local environment of the terminal iron atoms is not symmetric. Therefore, more parameters had to be included in the refinement. The first coordination sphere consists of sulfur and nitrogen atoms. The multiple scattering contributions within this shell are much smaller due to the lower symmetry. The shorter bond length for the nitrogen atoms at the terminal metal atom compared to the sulfur atoms around the central Cr atom result in lower reduced radii of the multiple scattering contribution within the first shell of Fe compared to Cr. The peak at 4.2 Å for the Cr-K-edge and at 3.7 Å for the Fe-K-edge is mainly attributed to this effect. The lower intensity of this peak in the Fe-Fourier transform represents the lower symmetry in its first shell. The fit of these peaks is not perfect because additional contributions from single scattering of several carbon atoms at distances ≥ 4 Å were not included in the refinement. In contrast carbon atoms of the macrocyclic ligand at about 3 Å had been considered to obtain correct metal-metal distances.

The measurements on the terminal and central metal atoms contain the same information about the metal-metal distances and its disorder. Hence, this information can be extracted with much higher accuracy when applying a multiple edge fit, which implies for the coordination of the three absorption atoms the use of the same parameters for the Fe-Cr distance, the metal-S distances and their Debye-Waller parameters, respectively. The high accuracy obtained with this approach allows analyzing whether the two terminal Fe atoms in the mixed valent sample [LFeCrFeL]$^{2+}$ have different distances to the central Cr atom or not.

During the refinement the sum of the χ^2 of the three single measurements has been minimized. This implies to use the same k-weighting for all spectra. Due to the shorter k range for the S-measurement, its weighting in the refinement is lower compared to the others.

Due to the overlap of metal-metal signal with the carbon atom backscattering at about the same distance the errors for the Fe-Cr distances and Debye-Waller factors are relatively large. For higher metal-metal distance the two contribution can be better resolved. The main parameters arising from the three fits are given in Table 1. Totally 16 parameters have been refined. Its final values are listed in the supplementary material.

As an example the fit of [LFeCrFeL]$^{1+}$ is shown in Figure 2. It is obvious that the fits obtained for the Fe- and Cr-K-edges are of high quality. Even the multiple scattering contributions at about 3.5 Å for the Fe-N-Fe-S-Fe path and at 4 Å for the Cr-S-Cr-S-Cr, respectively, can be identified although light backscatterers at such a distance have not been considered. The interpretation of the S-K-edge lacks for a wider k-range. This limitation results in moderately resolved peaks in its Fourier transform. Also a small mismatch in the interpretation of the peak at about 4.5Å arising from the S-Cr-S-Cr-S multiple scattering could only be explained on such a basis. Nevertheless the S K-edge EXAFS proves the consistency of the results obtained from the other measurements and supplies information about the S-C distances. We note that the imaginary part of the Fourier transform in all three graphs perfectly matches the refined curve.

	1+	2+	3+
d(Fe-Cr)	3.07 (1)	3.00 (1)	2.95 (2)
σ^2(Fe-Cr)	0.008 (1)	0.009 (2)	0.009 (2)
d(Fe-S)	2.265 (4)	2.248 (7)	2.254 (4)
σ^2(Fe-S)	0.0029 (3)	0.0027 (5)	0.0024 (3)
d(Fe-N)	2.045 (9)	2.06 (2)	2.050 (9)
σ^2(Fe-N)	0.0040 (7)	0.005 (2)	0.0023 (7)
d(Cr-S)	2.414 (4)	2.400 (4)	2.398 (6)
σ^2(Cr-S)	0.0040 (2)	0.0040 (2)	0.0035 (3)
d(S-C)	1.78 (2)	1.79 (5)	1.77 (8)
σ^2(S-C)	0.004 (3)	0.002 (6)	0.001 (9)
ΔE_0 (Fe)	3.2 (8)	4 (2)	4.2 (9)
ΔE_0 (Cr)	3.1 (7)	2.5 (8)	3 (1)
ΔE_0 (S)	10 (1)	10 (3)	9 (4)
Red χ^2	18.8	33.1	14.1

Table 1
XAS results for the three different complex oxidation states (1+, 2+ and 3+). The first metal and sulfur coordination shell as obtained from a multiple-edge analysis are given; all distances (d) in Å; all Debye-Waller factors (σ^2) in Å^2.

The data summarized in Table 1 show how the structural parameters of the complex change with its overall oxidation state. Mainly the metal-metal distances reflect this change. The higher the overall oxidation state the smaller the metal-metal distances is. For the Cr-S distance we found a similar but less pronounced behavior. Surprisingly the shortest Fe-S distance has been found for the 2+ state with its delocalized excess electron. The S-C bond length could only be extracted with relatively large error margins due to the short k-range and the signal overlap with the

backscattering from iron- and chromium- ions. The attempt to refine the delocalized state with two different iron-chromium distances, which would reflect one localized Fe^{II} and one Fe^{III} ion results in two practically identical distances.

4. Conclusions

In this study we have shown that $[LFeCrFeL]^{n+}$ contains a linear array of two terminal iron atoms and a central CrS_6 unit; the charge of this complex can be varied between 1+ and 3+ without changing the gross overall structure. By multiple K-edge XAS analysis we were able to show the changes in the metal-metal distances occurring upon changes of the cluster charge n, i.e. 2.95Å, 3.00Å and 3.07Å for n = 3+, 2+ and 1+. For the chromium-sulfur distances a similar but much weaker tendency has been found, whereas the iron-sulfur distances have a minimum for the delocalized $[LFeCrFeL]^{2+}$ state.

Furthermore, we showed that a consistent fit of EXAFS measurements on three different K-edges is possible. For further investigations a longer k-range for the S-K-edge should be aimed at.

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