

ACTIVATION OF Fe-S SYSTEMS FOR CATALYSIS BY HETEROMETAL SUBSTITUTION. G. S. Silu-
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Exploring structure-function relationships in metal-
loenzymes, such as nitrogenase, hydrogenase, carbon
monoxide dehydrogenase/acetyl CoA synthase have
significance in the early earth and evolution of life. In
general Fe-S clusters play limited catalytic role in the
absence of heterometals, such as molybdenum or nick-
el [1-3]. Consequently, understanding how heteromet-
als induce catalytic properties for metalloenzymes can
provide key information for functionalization of Fe-S
systems toward catalysis.

The best structural mimic to date for the Mo-site of
nitrogenase cofactor (FeMo-co, [4]) is the cubane type
MoFe₃S₄ clusters (Chart 1) [5, 6]. We report here our
investigations into the ligand environment effects of
Mo as a function of the reactivity of the MoFe₃S₄ cluster
by multi-edge X-ray absorption spectroscopy
(XAS) at S K-, Mo L_{III}-, Mo L_{II}-, Cl K-, and P K-
edges. The results are further evaluated by electronic
structure calculations using density functional theory.

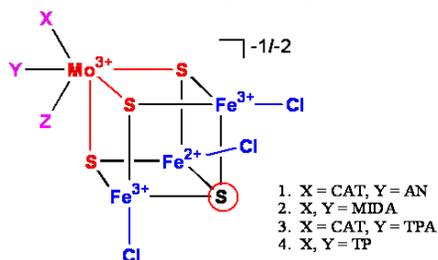


Chart 1: A representation of the complexes 1-4. CAT – tetrachlorocatechol, AN – acetonitrile, MIDA – methyliminodiacetic acid, TPA – 1,3,5-triaza-7-phosphaadamantane, and TP – tris(pyrazolyl)borate.

Multi-edge XAS spectra were measured for a set of
four clusters of composition [MoFe₃S₄(Cl)₃(X)(Y)]^{-1/2}
(Chart 1). These complexes vary only with respect to
the terminal ligands on the molybdenum site and hence
provide a straightforward comparison of the ligand
environment of Mo site.

As a representative example for the data analysis
and information content Figure 1 shows the norma-
lized S K-edge spectra of these complexes. The S K-
edge XAS directly measures the amount of S (ligand)
character in the adjacent metal (Fe²⁺, Fe³⁺ and Mo³⁺)
ions due to orbital mixing, which in turn reflects the
reactivity of the metal sites. The orbital mixing or met-
al-ligand bond covalency is sensitive to the small per-
turbations of the chemical environment around the
metal centers. The splitting and intensity of spectral
features originates from the contributions of various
unoccupied frontier orbitals [7]. S(1s) →
Fe(3dψ*HOMO) peaks showed at lower energy com-

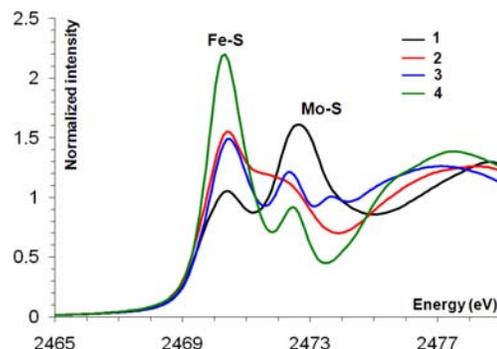


Figure 1: Comparison of the S K-edge XAS of the complexes 1-4.

pared to the S(1s) → Mo(4dψ*HOMO) of molybde-
num owing to the higher effective nuclear charge for
Fe than for Mo, which in turn lowers the energy of its
HOMO. As anticipated, cluster 1 containing a poor e⁻
donor acetonitrile ligand has the most covalent Mo-S
bonds among all. Mo-S covalency of 2 and 3 are simi-
lar. A reverse trend of covalency is seen for the Fe-S
bond. From Chart 1 there are two kinds of Fe-S bonds
in the clusters in 3:1 ratio. Thus the lower energy fea-
ture at 2470 eV can be assigned to the Fe-S bonds ad-
jacent to the Mo site and the feature at 2472 eV is due
to the distal Fe-S bonds. The less well resolved peak at
2473 eV is due to the Mo-S bond. Quantitative analy-
sis of these peaks using Peak Fit will be presented.

Summary: Multi-edge XAS spectra provide com-
plementary structural information that allows for dis-
secting important physico-chemical parameters that
determine the catalytic activity of heterometal deriva-
tized Fe-S systems. Using the example of MoFe₃S₄
cubanes we have started to gain insights into how in
general these parameters can facilitate activation of
small inorganic molecules toward biologically more
relevant organic molecules under early earth condi-
tions. Structural information on these heterometal
substituted iron-sulfur clusters provide synthetic tar-
gets for heterometal deposited iron-sulfur mineral sur-
faces.

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