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Synthesis and Characterization of New $MoFe_4S_6$ Clusters with a Single Fe_4S_4 Core and with Potentially Labile Ligands on the Mo Site

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Reactions of $Mo(CO)_4(nor)$ and $Mo(CO)_2(\pi\text{-allyl})(CH_3CN)_2Br$ with $Fe_4S_6Cp_4$ (nor = norbornadiene, Cp = cyclopentadienyl) in CH_2Cl_2 give $Fe_4S_6Cp_4Mo(CO)_4$ (I) and $Fe_4S_6Cp_4Mo(CO)_2(CH_3CN)Br$ (II). The IR spectral patterns are characteristic of *cis*-$Mo(CO)_4$ and *cis*-$Mo(CO)_2$ moieties and indicative of a structurally unperturbed $Fe_4S_6Cp_4$ cage. Fragmentation of I and II, with use of plasma desorption and fast atom bombardment mass spectroscopies, gives intense peaks at m/z 884 and 772 compatible with $Fe_4S_6Cp_4Mo(CO)_4^+$ and $Fe_4S_6Cp_4Mo^+$ fragments in I and at m/z 869 and 772 compatible with $Fe_4S_6Cp_4Mo(CO)_2(CH_3CN)^+$ and $Fe_4S_6Cp_4Mo^+$ fragments in II. Binding of the Mo moieties to the Fe–S core of $Fe_4S_6Cp_4$ via the two "extracubic" sulfurs is further supported by Mo K-edge EXAFS. The Mo–S distances are 2.57 Å for I and 2.52 Å for II; the Mo–Fe distances are 3.12 Å for I and 3.09 Å for II. These longer distances by comparison to those found in nitrogenase (2.37 Å for Mo–S and 2.70 Å for Mo–Fe) reflect the fact that I and II contain a lower oxidation state Mo than is likely in nitrogenase. Preliminary EPR and Mössbauer studies indicate that coordination of Mo to the Fe_4S_6 core has little influence on the electronic distribution within the Fe–S cage.

Recent developments of the chemistry of model compounds reproducing native clusters present in the FeMo protein and the FeMo cofactor of nitrogenase[1] have led to the design of single-cubane MoFeS clusters, where the Mo has labile terminal ligands for the purpose of binding enzymatic substrates potentially subject to reductive transformation. So far, structurally characterized systems include $[MoFe_4S_4(SC_2H_5)_3(C_6H_4O_2)_3]^{3-}$[2] and $[MoFe_3S_4(L)_3(L')(3,6\text{-}(C_3H_5)_2C_6H_2O_2)]^{2-,3-}$ (L = *p*-$ClC_6H_4S^-$, Cl^-; L′ = *p*-$ClC_6H_4S^-$, solv, PhO^-, CN^-, N_3^-, PR_3).[3] Both types of compounds were obtained by "self-assembly" techniques and contain a cubane-type $MoFe_3S_4$ core made of two interpenetrating, approximate $MoFe_3$ and S_4 tetrahedra. More recently, another cluster with 1Mo/3Fe/4S stoichiometry was reported,[4] $[MoFe_3S_6(CO)_6]^{2-}$, where the metal arrangement results from the adjunction of the two nearly unperturbed starting portions $Fe_2(\mu_2\text{-}S)_2$ and S_2MoS_2Fe.

We have been interested in devising an alternative pathway, in order to obtain a species where the Mo would be bound to an Fe_4S_4 entity, but without participating with the Fe/S cubane core. We concentrated our efforts on a low-oxidation-state Mo site that would also present labile coordination sites. While our work was in progress, a similar strategy was reported[5] to synthesize the $[Fe_6S_6(L)_6(Mo(CO)_3)_2]^{3-,4-}$ (L = Cl^-, *p*-$CH_3C_6H_4O^-$) complex anions, where the $Mo_2Fe_6S_6$ unit is made up by an $Fe_6S_6L_6$ prismane attached by the S atoms of the hexagonal faces to two $Mo(CO)_3$ entities.

Reported here are the synthesis and spectroscopic studies of two mixed-metal clusters of a new structural type, $Fe_4S_6Cp_4Mo(CO)_4$ (I) and $Fe_4S_6Cp_4Mo(CO)_2(CH_3CN)Br$ (II), where a $MoFe_4S_6$ core is present.

Experimental Section

Preparation of Compounds. All operations were carried out under strictly anaerobic conditions, with use of degassed solvents. Both compounds are also somewhat heat- and light-sensitive.

(a) $Fe_4S_6Cp_4Mo(CO)_4$ (I). To a solution of 1 g (1.4 mmol) of $Fe_4S_6Cp_4$ in 300 mL of dichloromethane was added 0.434 g (1.4 mmol) of solid $Mo(CO)_4$ (nor)[7a] (nor = norbornadiene) with stirring at room temperature. The first crystals of complex I appeared after ca. 0.5 h. The solution was then cooled overnight at −20 °C and the product collected by filtration and washed with toluene (30 mL) and then with hexane (20 mL). After the solid was dried in vacuo, 1 g (80% yield based on $Mo(CO)_4(nor)$) of red-black crystalline product was obtained. Anal. Calcd for $C_{24}H_{20}O_4S_6Fe_4Mo\cdot 0.5CH_2Cl_2$: C, 31.7; S, 20.8; Fe, 24.1; Mo, 10.35. Found: C, 31.9; S, 21.1; Fe, 24.0; Mo, 10.5.

(b) $Fe_4S_6Cp_4Mo(CO)_2(CH_3CN)Br$ (II). The preparation is similar to that in (a), but with the Mo starting compound being $Mo(CO)_2(\pi\text{-allyl})(CH_3CN)_2Br$[7b] (0.51 g). One gram of the desired complex was obtained (75% yield based on Mo). Anal. Calcd for $C_{24}H_{23}NO_2BrS_6Fe_4Mo\cdot 0.5CH_2Cl_2$: C, 29.7; Br, 8.1; S, 19.4; Fe, 22.6; Mo, 9.7. Found: C, 30.0; Br, 7.9; S, 19.8; Fe, 22.4; Mo, 9.3.

EXAFS Data Acquisition and Analysis. The spectra were collected in transmission mode on powdered samples at the Daresbury Synchrotron Radiation Source, under dedicated conditions (1.8 GeV, 180 mA). The Mo data were taken on the samples kept under vacuum, at room (for model 1 and complexes I and II) and liquid-N_2 (for models 2 and 3) temperatures, by using a Si(220) monochromator on the EXAFS station of the Wiggler (4.5-T) beam line. The Br data were taken on complex II under vacuum and at liquid-N_2 temperature, on EXAFS station 7.1 using a Si(111) monochromator. Data analysis utilized the single-scattering spherical wave method[8] for calculating the EXAFS spectra and where appropriate, multiple-scattering calculations were included in curve-fitting procedures.[9] Best-fit values for ΔE_0 were 20.25 eV for $Mo(CO)_6$ and 17.05 eV for complexes I and II. Phase shifts were derived from ab initio calculations.[10] Quality of fit and refinement were examined as previously described,[11] by using the program EXCURVE developed by Binsted et al.,[12] which utilizes the fast curved wave approach.

Other Physical Measurements. All measurements were made under strictly anaerobic conditions, by use of an argon-filled glovebox for sample preparations. Infrared spectra of solid KBr pellets and benzonitrile solutions were recorded on a Beckman IR 4240 spectrometer. Plasma desorption mass spectra were obtained on a home-built machine at the Institut Curie, on the basis of a heavy-ion bombardment generated by

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Table I. Summary of EXAFS Results for Mo(CO)$_6$ (Model 1),[25] $[Et_4N]_2[S_2MoS_2Fe(p\text{-}ClC_6H_4S)_2]$ (Model 2),[26] $[Et_4N]_3[(MoS_4)_2Fe]$ (Model 3),[27] $Fe_4S_6Cp_4Mo(CO)_4$ (I), and $Fe_4S_6Cp_4Mo(CO)_2(CH_3CN)Br$ (II)

	Mo–C			Mo–S			Mo–S′			Mo–Fe			Mo–O(CO)		
compd	N^a	R,^{b} Å	σ^2,^{c} Å^2	N	R, Å	σ^2, Å^2	N	R, Å	σ^2, Å^2	N	R, Å	σ^2, Å^2	N	R, Å	σ^2, Å^2
model 1	6	2.06 (±0.02) [2.057]	0.0025^d										6	3.16 (±0.03) [3.185]	0.0050^d
model 2				2	2.15 (±0.02) [2.153]	0.0015 (±0.0001)	2	2.24 (±0.02) [2.255]	0.0010 (±0.0002)	1	2.75 (±0.04) [2.756]	0.0030 (±0.0006)			
model 3				2	2.19 (±0.02) [2.171]	0.0035 (±0.0003)	2	2.24 (±0.02) [2.256]	0.0125 (±0.0025)	1	2.71 (±0.04) [2.75]	0.0060 (±0.0012)			
I	4	2.02 (±0.02)	0.0050^d	2	2.57 (±0.02)	0.0060 (±0.0005)	2	3.10 (±0.08)	0.0040 (±0.0008)	2	3.12 (±0.08)	0.0080 (±0.0009)	4	3.14 (±0.08)	0.0050^d
II	2	1.94 (±0.02)	0.0015^d	2	2.52 (±0.02)	0.0085 (±0.0006)	2	3.06 (±0.08)	0.0045 (±0.0008)	2	3.09 (±0.08)	0.0105 (±0.0010)	2	3.04 (±0.08)	0.0015^d

[a] Coordination number kept fixed at all times. [b] Interatomic distance [diffraction value]. [c] σ is the Debye–Waller disorder term. [d] Kept constant because of multiple-scattering treatment.

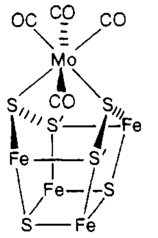
spontaneous fission of ^{252}Cf. The compounds were deposited on the target by evaporation of an acetonitrile solution containing approximately 1 μg of material. Fast atom bombardment mass spectra were obtained on a Kratos MS 50 spectrometer, and nitrobenzyl alcohol was used as a support matrix for the samples. X-Band EPR spectra were recorded with a Varian E 109 spectrometer equipped with an Oxford Instruments ESR 900 helium-flow cryostat. The Mössbauer equipment has been described before.[13] Isomer shifts are quoted relative to the centroid of the spectrum of iron metal with the ^{57}Co source and the iron foil at room temperature.

Results and Discussion

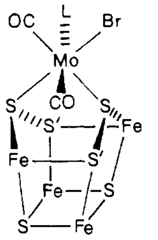
Disulfur ligands present in metal cluster compounds have been known to exhibit two different types of reactivity: either by use of the nonbonded pairs of electrons present on the sulfurs to coordinate additional metal atoms[14a] or by nucleophilic cleavage of the S–S bond (in the presence of suitable metal hydrides or chlorides)[14b] followed by S-bonding to the latter metal atoms or by extrusion of sulfur.

It has been shown previously that when the initial cluster $Fe_4S_6Cp_4$ reacts with high-oxidation-state Mo complexes, one or two S atoms are expelled and $[Fe_4S_5Cp_4]^+$ or $Fe_4S_4Cp_4$ is obtained.[15]

Here it has been found that, in the presence of low-valent Mo(0 or I) the μ_3-S_2 groups will bind coordinatively to give the neutral[16] complexes I and II (in the drawings, the iron-bonded π-cyclopentadienyles are omitted for clarity).



I



II

Complex I displays four strong absorptions in its IR spectrum, attributed to the ν(CO) vibrations, at 2000, 1901, 1860, and 1832 cm^{-1}. Their number and intensity pattern are characteristic of *cis*-Mo(CO)$_4$ fragments;[17,18] also, the replacement of norbornadiene by the two persulfide-type sulfurs of $Fe_4S_6Cp_4$ induces the observed shift to lower frequencies, because of increased electron density at the Mo. The IR spectrum of complex II displays two strong absorptions, assignable as ν(CO), at 1915 and 1815 cm^{-1} in good agreement with previously reported values for similar *cis*-Mo(CO)$_2$ entities.[17,19] Bands due to the π-allyl have disappeared and only one band due to CH_3CN is left, at 2333 cm^{-1}. The perpendicular C–H bending vibrations of the Cp ring, which appear as most diagnostic of structural and oxidation-state variations,[20] remain unchanged at 810–850 cm^{-1} and one can assume therefore that the structural integrity of the $Fe_4Cp_4S_6$ moiety is maintained. The Fe–(μ_3-S) stretching band moves slightly from 442 to 450 cm^{-1} with the same intensity, whereas the S–S stretching bands (at 498 and 507 cm^{-1} in $Fe_4S_6Cp_4$) have disappeared, thus indicating that the Mo will bind to the Fe_4S_6 cage through the S–S group rather than the μ_3-S group. These assumptions are further supported by the fact that, when I and II are redissolved in CH_2Cl_2 and the solutions are allowed to stand at −20 °C for 1 week, the starting compound $Fe_4S_6Cp_4$ was obtained as monocrystals and identified by solving the X-ray structure.[21]

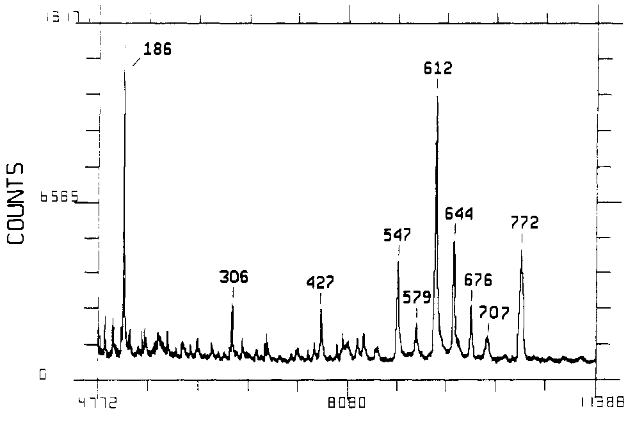


Figure 1. PDMS fragmentation pattern for complex I.

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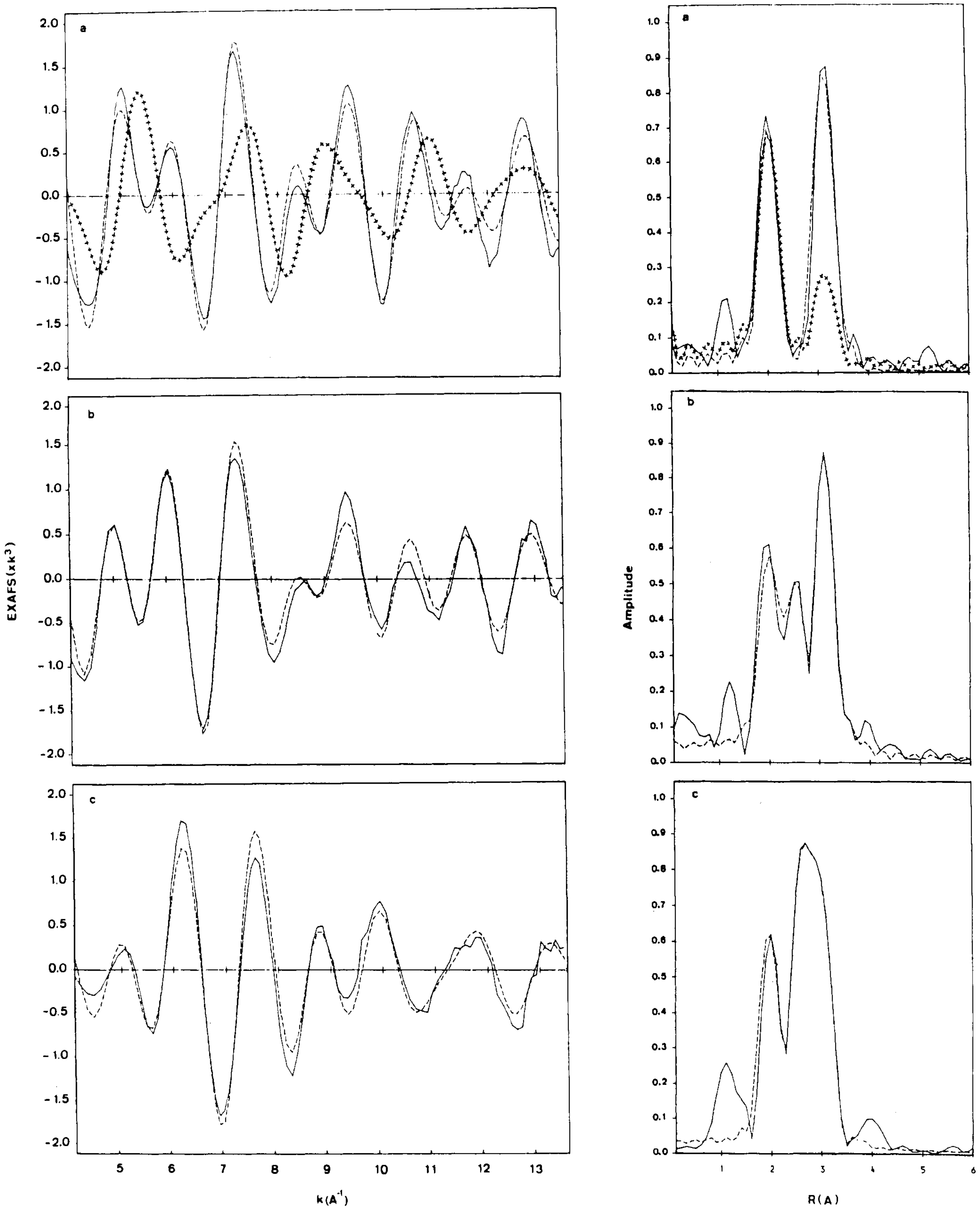

Figure 2. Experimental (—) Mo K-edge EXAFS, $k^3[\chi(k)]$ vs k, spectra and Fourier transforms and theoretical simulations with single (+++) and multiple (- - -) scattering included for $Mo(CO)_6$ (a), complex I (b), and complex II (c).

Mass spectra were obtained by using californium-252 plasma desorption mass spectrometry (PDMS). This new soft ionization method, originally introduced by MacFarlane et al.,[22a] has shown some success in characterizing fragile and non-volatile molecules (and is now available in a few laboratories[22,23]). The PDMS spectrum of the I positive ion (Figure 1) exhibits a quite intense

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peak at *m/z* 772, attributed to the $\mathrm{Fe_4S_6Cp_4Mo^+}$ fragment (as confirmed by the theoretical simulations utilizing the Mo isotopes). At lower masses, loss of Mo produces $\mathrm{Fe_4S_6Cp_4^+}$ at *m/z* 676, which in turn loses sulfur to form $\mathrm{Fe_4S_5Cp_4^+}$ (*m/z* 644) and then $\mathrm{Fe_4S_4Cp_4^+}$ (*m/z* 612) as the most stable structure.[24] Observation of these peaks also argues for a retention of the $\mathrm{Fe_4S_6}$ original structure. Since no CO could be clearly seen, $\mathrm{FAB^+}$ mass spectroscopy was also used, and conclusive evidence was obtained. Indeed, the highest mass peak appears at *m/z* 884 in I, which corresponds to the $\mathrm{Fe_4S_6Cp_4Mo(CO)_4^+}$ fragment, and at *m/z* 869 in II, which is compatible with a $\mathrm{Fe_4S_6Cp_4Mo(CO)_2(CH_3CN)^+}$ fragment. At lower masses the same fragmentation pattern as with PDMS is obtained.

Further support of the Mo local environment proposed in the scheme above was provided by X-ray absorption spectra at the molybdenum and bromine K edges. Phase shifts and calculation procedures were checked against model compounds of known crystal structures (see Table I).[28] Agreement between the crystallographic distances and the best EXAFS fits is good for all three models, giving us confidence in the refinement procedure and in transferring the calculated phase shifts to I and II. In EXAFS spectra collected on systems where central and first- and second-shell atoms are collinear, the contribution of the last atom is greatly affected by the forward scattering of the photoelectron from the atom in front of it.[9] This feature is present in model 1 and complexes I and II, the $\mathrm{Mo{-}C{\equiv}O}$ bond angle being close to 180°. Multiple-scattering pathways must therefore be included in the data fitting, and model 1 provides a check on the calculation procedure. In Figure 2a the theoretical spectra, with and without multiple scattering included, and their Fourier transforms are compared to the experimental data of $\mathrm{Mo(CO)_6}$. Alternatively, it is also possible to improve the single-scattering fit by adding an extra degree of freedom, obtained when the coordination numbers are allowed to float. However, the final parameters then become less realistic: 6.5 carbons at 2.02 Å ($\sigma^2 = 0.0035$ Å^2) and 13.1 oxygens at 2.25 Å ($\sigma^2 = 0.002$ Å^2), with the second shell being approximately twice its true value, the shell radii differing from the crystallographic values by up to 0.06 Å, and E_0 being rather high (30.1 eV).

The Mo K-edge EXAFS spectra and Fourier transforms for I and their best fits appear in Figure 2b. Table I lists the parameters required for the simulation, which includes the multiple-scattering calculation for $\mathrm{Mo{-}C{\equiv}O}$, this bond angle being kept at 180°. It should be noted that the outer three shells, due to Mo–S′, Mo–Fe, and Mo–O(CO) contributions, are at very similar distances and were therefore strongly correlated during the fitting procedure. When one shell is varied, there is a compensation effect by the other two shells, which produces a shallow minimum, and the error bars are then quite large. Thus, the bond distances and Debye–Waller factors for these shells are not totally reliable, although they do give a good indication of the O, S′, and Fe distances to Mo.

For confirmation that the S′ and Fe atoms are indeed present in the third shell, three additional and separate fits were performed in the case of complex I: one with no S′ present, one with no Fe present, and one with neither S′ nor Fe present. The three fit indices thus obtained (respectively 7.391, 8.156, and 3.521) are clearly worse than the one obtained with both elements present (1.59). The same occurs with complex II, where the fit index climbs from 1.309 to 1.791 (no S′ and no Fe), to 2.488 (no Fe), and to 3.076 (no S′). Thus, the fits are clearly improved when both S′ and Fe are included in the last shell.

The Mo K-edge EXAFS spectra and Fourier transforms for II and their best fits appear in Figure 2c. The best-fit Mo–X distances are listed in Table I. The same fitting method was employed, but it was very difficult to place the Br atom. We therefore collected the Br K-edge EXAFS spectrum, and its Fourier transform (see supplementary material, Figure 3) contained one major peak, which was fitted with 1 Mo at 2.70 Å (±0.02 Å, $\sigma^2 = 0.0045 \pm 0.0008$ Å^2). The fitting procedure for II was then modified by keeping the Br distance and Debye–Waller factor fixed at all times. The best simulation was achieved when the $\mathrm{Mo{-}C{\equiv}O}$ bond angle was fixed at 170°. The deviation from the collinear $\mathrm{Mo{-}C{\equiv}O}$ arrangement may be due to the presence of the large bromine atom causing a distortion in the geometrical arrangement. Also, the Br induces a shortening of all distances when compared to the case for I.

The Mo–S distances are within the range found for similar Mo–S(thioether) averaged bonds, 2.52 Å in $\mathrm{(ttcn)_3Mo(CO)_3}$[29a] and 2.56 Å in $\mathrm{(ttn)_3Mo(CO)_3}$[29b] (ttcn = trithiacyclononane; ttn = trithianonane). They are slightly shorter than those found in $\mathrm{[Fe_6S_6(Mo(CO)_3)_2]}$[4,5b] by 0.04 Å in I and 0.09 Å in II, whereas the Mo–Fe distances are somewhat longer, by 0.13 and 0.09 Å, respectively. The longer Mo–S and Mo–Fe distances by comparison to those in nitrogenase (2.37 and 2.7 Å) reflect the fact that I and II contain a lower oxidation state Mo than is likely in nitrogenase. The Mo–Br distance in II, when compared to the evolution of Mo–Br bond distances with the metal oxidation state (2.584 Å for $\mathrm{Mo^{III}}$–Br and 2.686 Å for $\mathrm{Mo^{II}}$–Br[30]), is also indicative of a low oxidation state. No EPR signals were detected from $\mathrm{C_6H_5CN}$ frozen solutions at 11 K of I and II, suggesting that no half-integer spin density is present.

This is supported by the fact that Mössbauer spectra at 4 K show for I a doublet with an isomer shift (IS) of 0.43 mm s^{-1} vs Fe and a quadrupole splitting (ΔE_Q) of 1.07 mm s^{-1} and similar values for II (0.44 mm s^{-1} for IS and 1.11 mm s^{-1} for ΔE_Q). These values are near those that we obtain for the "parent" $\mathrm{Fe_4S_6Cp_4}$, 0.45 mm s^{-1} for IS and 1.15 mm s^{-1} for ΔE_Q. It thus appears that coordination of the $\mathrm{Mo(CO)_4}$ or $\mathrm{Mo(CO)_2(CH_3CN)Br}$ unit to the $\mathrm{Fe_4S_6}$ core has little influence on the electronic distribution within the Fe–S cage. Preliminary electrochemical studies by cyclic voltammetry reveal a reversible 1e oxidation and 1e reduction in benzonitrile solution. Further work on the redox properties of both complexes, as well as on their chemical reactivity vs that of unsaturated substrates, is currently in progress.

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Registry No. I, 115338-20-0; II, 115321-76-1; $\mathrm{Fe_4S_6Cp_4}$, 72256-41-8; $\mathrm{Mo(CO)_4(nor)}$, 12146-37-1; $\mathrm{Mo(CO)_2(\pi\text{-}allyl)(CH_3CN)_2Br}$, 33221-76-0.

Supplementary Material Available: Figure 3, giving Br K-edge EXAFS and Fourier transform spectra of complex II (1 page). Ordering information is given on any current masthead page.

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