Electronic supplementary Information for:

Identification of a spin-coupled Mo(III) in the Nitrogenase Iron-Molybdenum Cofactor

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Experimental details

A set of four different model complexes containing both molybdenum and iron, and with known oxidation states were selected to be part of the present study. The models (1-4) were synthesized according to known literature procedures^{1,2}. MoFe protein was expressed and purified using a previously published technique³. The schematic representation of the model compounds is shown in Figure S1.



Figure S1. Structures of the model compounds measured.

Sample preparation

Solid samples for the XAS measurements were finely ground and mixed with boron nitride such that the absorbance peaks at approximately 1. The samples were then compacted into PEEK sample holders of 2 mm path length and sealed with Kapton tape of 38 μ m thickness. All the sample manipulations were performed in a dry nitrogen atmosphere.

The liquid MoFe nitrogenase sample was concentrated to approximately 3.25 mM. Solutions were then loaded into a non-standard sample holder designed to maximize the x-ray path in the sample while minimizing the volume, which was also sealed with Kapton tape of $38 \mu \text{m}$ thickness. (Figure S2).

Mo K-edge HERFD-XAS measurements

High-energy resolution fluorescence detection XAS data of intact nitrogenase MoFe protein and FeMo model complexes were obtained at the ID26 beamline at the European Synchrotron Radiation Facility (ESRF). The storage ring operated at 6.04 GeV, in the 7/8 + 1 filling mode and 200 mA current. A double-crystal monochromator with Si(311) crystals was used to select the incoming x-ray energy with intrinsic resolution ($\Delta E/E$) of 0.3×10^{-4} . At the Mo Kedge this translates into approximately 3.5 eV. The x-ray beam size was 200 x 700 µm² (V x H) at the sample position. A closed-cycle liquid helium cryostat was maintained at approximately 10 K in order to prevent radiation damage and to preserve them in an inert atmosphere. Prior to the measurements each sample was checked for signs of radiation damage by performing fast XANES scans. These tests showed that the model complexes and the MoFe protein were stable under x-ray irradiation for >120 seconds. A more detailed description of the damage studies can be found below. Regular XAS data was also collected in transmission (Transm.) and total fluorescence yield (TFY) modes concomitant with the high-resolution (HERFD-XAS) measurements.

The energy calibration of the incoming x-rays was performed by recording the transmission K-edge XAS spectrum of a Mo foil and assigning the energy of the maximum of the white line to 20016.4 eV. A multi-crystal Johann-type x-ray spectrometer was used to select the energy of the emitted x-rays and record HERFD-XAS data. It was equipped with five curved Ge(111) crystals, posed at a Bragg angle of approximately 77.74°, which focused Mo K α_1 emission at ~ 17.4 keV, (corresponding to the [999] reflection) onto the detector.

Basic XAS data processing, *i.e.*, background subtraction and normalization were performed using the ATHENA package⁴ following standard protocols for x-ray absorption spectroscopy. The number of peaks present in the pre-edge region and their respective energies were estimated by inspection of the second derivative. The quantitative determination of the energy positions and areas of the pre-edge features were determined by fitting the peaks using the Blueprint XAS software^{5,6}. The number of peaks in the pre-edge region were estimated by inspection of the second derivative. A set of pseudo-Voigt functions seemed to properly account for features in the pre-edge and the XANES region of the spectrum. The absorption edge was accounted for by an arctangent function with a step size of one.

Sample holder for the liquid protein

The limited available quantities of protein sample and the large penetration power of the x-rays at 20 keV required the design of a special sample holder for the experiments reported here. An illustration of this sample holder (connected to the rod used to insert it in the cryostat) is shown in Figure S2. Each sample holder fit approximately 100 μ l of protein solution.



Figure S2. Illustration of the sample holder used in the HERFD-XAS experiments of MoFe nitrogenase. The directions of the incoming, transmitted and fluorescence x-rays are indicated by blue arrows *(left)*. View from the propagation direction showing the alignment hole, sample volume in red and several irradiated spots used in consecutive measurements to prevent radiation damage *(right)*.

Tests for radiation damage

Each sample was carefully checked for signs of damage induced by exposure to an intense x-ray beam, as the one from ESRF ID26. The procedure consisted of performing a series of fast XAS scans around the edge region, lasting from 15-20 seconds in the case of the solid model complexes, and 60 seconds in the case of the liquid MoFe sample. Up to 15 scans were accumulated in each sample spot, allowing the separation of the signal for different (increasing) x-ray doses. In the case of the model complexes (solid samples) it was found that the XANES signal (HERFD and TFY) did not show measureable changes after 360 seconds of irradiation. The actual data acquisition was performed by collecting a series of 3 scans of 120 seconds, or alternatively 2 scans of 180 seconds, which were then averaged to compose the HERFD-XAS signal. The same procedure was followed for the liquid MoFe protein sample. It was found that the HERFD-XAS signal after 240 seconds of irradiation was identical to the one after 60 seconds of x-rays exposure. An illustration of the assessment of x-ray damage in the MoFe protein sample is shown in Figure S3. Therefore, the actual data acquisition for the MoFe protein was performed by collecting a series of 4 scans lasting 60 seconds at each sample spot, then moving to a new one and repeating the procedure. The protein data reported here is composed by an average of 410 individual scans.



Figure S3. Radiation damage assessment of the MoFe nitrogenase sample using the HERFD-XAS data. Each curve is composed by an average of at least 40 individual scans taken on fresh sample spots

and varying the x-ray exposure time. The signals are identical within the noise level.

Fits of the pre-edge features

Result from the fits of the pre-edge features of the HERFD-XAS spectra of compounds 1-4 and the MoFe nitrogenase (figures S4-S8).



Figure S4. Results of the peak fitting procedure for the HERFD-XAS data of compound 1.



Figure S5. Results of the peak fitting procedure for the HERFD-XAS data of compound 2.



Figure S6. Results of the peak fitting procedure for the HERFD-XAS data of compound 3.



Figure S7. Results of the peak fitting procedure the HERFD-XAS data of compound 4.



Figure S8. Results of the peak fitting procedure for the HERFD-XAS data of MoFe nitrogenase.



Figure S9. Correlation plots showing calculated vs. experimental preedge intensities (top) and energies (bottom) for Mo-only models (see Lima et al.⁷) and the Fe-Mo-S models in Figure S1. All 3 possible charges of FeMoco are considered.

Computational details

All DFT computations were carried out using the ORCA program⁸. The nitrogenase FeMoco was approximated as a large 225 atom cluster as shown in Figure S10. This computational model includes part of the protein environment and crystallographically resolved water molecules from the 2011 X-ray structure by Einsle et al. and was calculated in the 3 charge states ([MoFe₇S₉C]ⁿ n=-3,-1,+1), currently proposed in the literature. Broken-symmetry solutions of MoFe₃S₄ clusters and FeMoco were found by first converging to high-spin SCF solutions and then performing spin flips on selected atoms and converging to broken-symmetry states of a particular M_S value. Lowest energy broken-symmetry surface using appropriate constraints (all non-covalently bound protein residues were fixed at X-ray crystal structure positions except for hydrogen atoms, in FeMoco calculations). Geometries were optimized at the TPSSh⁹ level using the RIJCOSX^{10,11,12} approximation and the relativistic ZORA approximation^{13,14} and relativistically recontracted versions of the Karlsruhe def2-TZVP basis sets^{15,16}. The Mo 1s core-level excited state spectra were calculated by time-dependent density functional theory following previously established protocols^{7,17} from the

 M_s =3/2 broken-symmetry solutions using DFT-optimized geometries. The TDDFT computations were carried out using the Tamm-Dancoff approximation¹⁸ as implemented in ORCA using the B3LYP hybrid functional^{19,20} and the RIJCOSX approximation. Relativistic effects were incorporated using the ZORA approximation and relativistically recontracted def2-TZVP basis sets were used. A dielectric field was introduced using the COSMO approximation²¹ in order to account for environmental effects. Only transitions from Mo 1s donor orbitals were calculated and intensities include electric dipole, magnetic dipole and quadrupole contributions. Localized orbitals were calculated using the Pipek-Mezey scheme.²²



Figure S10. The 225 atom FeMoco model used in calculations.

Computations of $[MoFe_7S_9C]^{3-}$ and $[MoFe_7S_9C]^{1+}$ FeMoco charge models

The main article emphasises $[MoFe_7S_9C]^{1-}$ results. In order to demonstrate that the Mo(III) assignment applies also to the more reduced model ($[MoFe_7S_9C]^{3-}$) and the more oxidized model ($[MoFe_7S_9C]^{1+}$), we show here the localized orbital analysis of these models in Figure S11 and the TDDFT computed Mo XAS 1s \rightarrow 4d t_{2g} transitions in Figure S12.



Figure S11. Localized orbitals of $[MoFe_7S_9C]^{3-}$, $[MoFe_7S_9C]^{1+}$ and $[MoFe_7S_9C]^{1-}$.

[**MoFe₇S₉C]**¹⁻ <u>M_s=3/2</u> Mo spin pop: -0.59



 $[MoFe_7S_9C]^{1+}$.

Computation of Mössbauer parameters

Mössbauer parameters (isomers shifts and quadrupole couplings) were calculated at the non-relativistic B3LYP level using the CP(PPP)TZVP basis set. The isomer shift computations were calibrated using a combined test set of complexes from Römelt et al.²³ and the iron-sulfur non-nitrosyl subset by Sandala et al.²⁴ The correlation of experimental isomer shifts δ_{exp} and B3LYP/CP(PPP)/TZVP calculated ρ values in Figure S13 is used to derive a linear relation that is used to calculate the reported isomer shifts.



Figure S13. Calibration of the B3LYP/CP(PPP)/TZVP method for calculation of isomer shifts. RI-BP86-ZORA/def2-TZVP optimized geometries were used.

Orbital and Mo spin population analysis of $[MoFe_7S_9C]^{1-}$ calculated with different functionals

Figure S14 shows localized occupied orbitals of Mo calculated with 3 different functionals (BLYP, PBE and B3LYP), orbital contributions and Mulliken Mo spin populations. These results reveal that the electronic structure of the $[MoFe_7S_9C]^{1-}$ remains qualitatively the same when using a different density functional and that a smaller Mo spin population which is obtained with pure GGA functionals like BLYP and PBE (than with the hybrid functional B3LYP) is not indicative of a spin-paired closed-shell Mo(IV) but rather due to a different degree of delocalization between Mo and Fe.

A spin density plot of $[MoFe_7S_9C]^{1-}$ calculated at the B3LYP level is also shown in Figure S15.



Figure S14. Occupied localized t_{2g} orbitals of $[MoFe_7S_9C]^{1-}$ calculated on the lowest $M_s=3/2$ brokensymmetry state with DFT methods: BLYP, PBE and B3LYP. Orbital contributions and Mulliken Mo spin populations are also shown.



Figure S15. Spin density plot (isovalue 0.08) of $[MoFe_7S_9C]^{1-}$ calculated at the B3LYP level using full 225 atom FeMoco model (only metal-cluster shown). α density is shown in blue and β density in red.

Fe	10.114690	-7.703790	55.997150
Fe	12 592775	-8 339455	55 593136
Fe	11 356470	-7 022600	53 763435
Fe	11 989671	-5 848783	55 995784
Fe	1/ 8/2328	7 594401	54 593006
Fo	12 612667	6 211558	52 817252
Fo	14.224005	-0.211338	54 099650
ге	14.234093	-5.150527	52 244560
C	10.077071	-3.033493	54 625040
C	13.102/40	-0./09030	57.520924
5	11.80/082	-/.458315	57.529824
5	16.1/1063	-6.063151	55.523514
S	9.960555	-5./06635	54.999953
S	13.080692	-4.002049	56.434792
S	14.474498	-9.492158	55.653370
S	14.345906	-4.097768	53.045264
S	10.859698	-9.137724	54.335204
S	15.240920	-7.632743	52.391762
S	11.782288	-6.521044	51.634265
S	8.472275	-8.499543	57.326499
С	13.316384	-2.413022	49.965591
Ν	12.425824	-3.225190	50.780743
С	11.214124	-2.866263	51.225022
Ν	10.617098	-1.750139	50.745069
Ν	10.601417	-3.600968	52.165990
С	15.063349	-1.104757	59.472637
С	16.188172	-0.874018	58.459017
Ċ	17.508370	-1.552718	58.851301
Õ	17 846567	-1 662403	60 041149
Ň	18 260644	-1 971887	57 810564
C	8 309011	-1 265150	60 668388
C	9 374563	-2.061132	59 971486
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С	5.372065	-9.531258	57.863129
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Ň	20 044831	-7 265925	53 720731
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C	17 113047	-1 730929	52 686509
C	17 733656	3 116261	52.000507
C	10 27/227	2 020528	52 305364
C	19.274227	-3.030338	51 428700
C	19.830300	-4.143129	51.456790
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0	17.251489	-3.161760	50.073394
0	17.404062	-3.972800	53.533269
0	15.606667	-5.093831	47.074467
0	20.552808	-3.046822	45.680199
0	20.972620	-2.045375	56.442518
0	14.512807	-5.469426	49.697130
0	21.343511	-7.627457	49.656651
0	20.916164	-4.711191	48.061396
0	18 255575	-4 325647	47 685024
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Н	22.888649	-6.825622	54.914125
Н	22.782379	-8.370279	55.048978

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