Protein-Assisted Formation of Molybdenum Heterometallic Clusters:
Evidence for the Formation of $S_2MoS_2-M-S_2MoS_2$ Clusters with $M = Fe, Co, Ni, Cu or Cd$ within the Orange Protein

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SUPPORTING INFORMATION

INDEX

S1. Mo/Cu-ORP (Figure S1) pag. S2
S2. Mo/Fe-ORP (Figures S2-S4) pag. S3
S3. Mo/Co-ORP (Figure S5) pag. S6
S4. Mo/Ni-ORP (Figure S6) pag. S7
S5. Mo/Cd-ORP (Figure S7) pag. S8
References (S1 to S3) pag. S9
**S1. Mo/Cu-ORP**

*Figure S1.* UV-visible spectrum of the inorganic Mo/Cu complex(es) (100 µM Mo, 50 µM Cu) formed in 50 mM Tris-HCl, pH 7.6, in the absence of protein, as described in "Materials and Methods" (black line). For comparative purposes, the spectra of (NH₄)₂MoS₄ (100 µM) is also shown (gray line).

The MoS₄²⁻ also reacts with Cu²⁺ in an aqueous buffer system, in the absence of the apo-ORP, but to form different heterometallic complexes, depending on the Mo:Cu ratio used.¹²,⁵¹,⁵² For a Mo:Cu ratio of 2:1, in 50 mM Tris-HCl, pH 7.6, the complex(es) formed has(have) a visible spectrum distinctly different from the one of the Mo/Cu-ORP (Figure 3), with absorption maxima at 316 and 468 nm and shoulders at 360 and 520 nm (Figure S1, black line; Table 1). The features at 360 and 520 nm indicate the formation of Mo/Cu complex(es) with a higher copper content (because the molybdenum charge transfer bands shifted to higher wavelength values⁵³), while the features at 316 and 468 nm suggest the presence of "free" MoS₄²⁻ units (if each MoS₄²⁻ unit binds more than one copper ion, then "free" MoS₄²⁻ units are expected; Figure S1, gray line).
**S2. Mo/Fe-ORP**

![UV-visible spectrum of the inorganic Mo/Fe complex(es)](image)

**Figure S2.** UV-visible spectrum of the inorganic Mo/Fe complex(es) (100µM Mo, 50µM Fe) formed in 50 mM HEPES, pH 7.5, in the absence of protein, as described in "Materials and Methods".

As with copper (section S1), MoS$_4^{2−}$ also reacts with Fe$^{II}$ in an aqueous buffer system (50mM HEPES pH 7.5), in the absence of the apo-ORP, to yield Mo/Fe complex(es). The visible spectrum of that(those) complex(es) is distinct from the one of the Mo/Fe-ORP (Figure 4), with absorption maxima at 282, 319, 346, 470, 505 and 568nm (Figure S2; Table 1).
Figure S3. - X-band EPR spectra of the Mo/Fe-ORP (800µM), in 50 mM HEPES, pH 7.5, at 4 to 40K (as indicated). The low field area of the spectra at 10, 20 and 40K were multiplied by 2.5, 5.0 and 5.0, respectively (as indicated). The values marked with *, ● and ♦ are interpreted as arising from $S = 3/2$ species, from a sulfur radical-containing species and from an amino acid radical-containing species, respectively.
Figure S4. - X-band EPR spectra of the inorganic Mo/Fe complex(es) (1mM) synthesized in 50mM HEPES, pH 7.5 (as described in "Materials and Methods"), at 4, 10 and 20K (as indicated). The spectra at 10 and 20K were multiplied by 2.5, and 5.0, respectively. The values marked with * and with ♦ are interpreted as arising from $S = 3/2$ species and from a sulfur radical-containing species, respectively.
**S3. Mo/Co-ORP**

![UV-visible spectrum](image)

**Figure S5.** UV-visible spectrum of the inorganic Mo/Co complex(es) (100 µM Mo, 50 µM Co) formed in 50 mM HEPES, pH 7.5, in the absence of protein, as described in "Materials and Methods".

MoS$_4^{2-}$ reacts with Co$^{2+}$ in an aqueous buffer system (50 mM HEPES pH 7.5), in the absence of the apo-ORP, to yield uncharacterized complex(es), whose spectrum (315 and 466 nm features; Figure S5; Table 1) is dominated by the contributions of the MoS$_4^{2-}$ units (Figure S1, gray line).
MoS₄²⁻ reacts with Ni²⁺ in an aqueous buffer system (50mM HEPES pH 7.5), in the absence of the apo-ORP, to yield uncharacterized complex(es), whose spectrum (315 and 468nm features; Figure S6; Table 1) is dominated by the contributions of the MoS₄²⁻ units (Figure S1, gray line).
Figure S7. UV-visible spectrum of the inorganic Mo/Cd complex(es) (100µM Mo, 50µM Cd) formed in 50 mM HEPES, pH 7.5, in the absence of protein, as described in "Materials and Methods".
REFERENCES

