Photoinduced magnetization on Mo ion in copper octacyanomolybdate: an XMCD investigation

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Abstract: Recently synthesized copper octacyanomolybdate molecules present interesting photomagnetic properties. Before irradiation, the complexes behave as paramagnetic species while after irradiation (410 nm) they behave as high spin molecules. The hypothesis for these magnetic properties is the photoinduced charge transfer from Mo^{IV} (S=0) to Cu^{II} (S=1/2) leading to the formation of Mo^{V} (S=1/2) and Cu^{I} (S=0) with strong ferromagnetic coupling between the residual spin carriers. This paper presents X-ray magnetic circular dichroism measurements at the Molybdenum $L_{2,3}$ edges. Two molecules have been investigated: $MoCu_6$–tren and $MoCu_2$-Meen. In both cases, before irradiation the XMCD signal is null as expected for diamagnetic Mo^{IV} (S = 0). After irradiation a XMCD signal appears which directly demonstrates the formation of spin density on the Mo ion. After reaching room temperature, the signal disappears, indicating clearly the reversibility of the photoinduced process. The XMCD experiments allow to evidence of an unsuspected X-ray photoinduced excited state based on high spin Mo^{IV} (S = 1). The application of the sum rules to the isotropic spectra shows that there is no variation of the molybdenum oxidation state. From the Mo $L_{2,3}$ XMCD signal of the X-ray photoexcited $MoCu_2$-Meen, we obtain an orbital magnetic moment equals to 0.13 μ_B and a spin magnetic moment equal to 1.22 μ_B. These results show that the Mo ion in the X-ray photoinduced metastable state of Mo-Cu complexes is high spin Mo^{IV} (S = 1). Some insight is given into the photoinduced mechanism of the excited and metastable states of MoCu complexes.

KEYWORDS. Photomagnetism, high spin molecules, XMCD, X-ray absorption, X-ray magnetic circular dichroism, Mo $L_{2,3}$ edges.