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On the mechanism of the photoinduced magnetism in copper octacyanomolybdates†

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Ab initio calculations show that a possible mechanism for the photomagnetism in copper octacyanomolybdate compounds consists of the initial excitation of the diamagnetic Cu^{II}–Mo^{IV}–CS pair to a Cu^{II}–Mo^{IV-T} state, whose geometry relaxation stabilizes the magnetic doublet and quartet states.

Polycyanometallate compounds are interesting materials because they display highly sought properties like para-magnetism[1–4] and ferroelectricity.[5] For this reason they are used as building blocks of magnetic clusters and networks and are especially important for the development of single molecule magnets.[3,6] Besides, some compounds of this family display photomagnetic behavior,[7–17] which turns them into promising materials, since their magnetic properties can be controlled by external stimuli. Moreover, in some cases the inverse reaction can be induced thermally or by irradiation with light.[7–8,11–14]

Switching of the magnetic state has been explained by a metal to metal electron transfer that changes the electronic state, and hence the spin, on the interacting metallic centers, then giving rise to a high molecular magnetic moment.[4,7,11,18,19] Specifically, for compounds of the type $[Mo(CN)_2(CN–CuL)_6]^{8+}$ (L = 2,2′-bipyridine, tris(2-aminoethyl)amine, N,N'-dimethylethylenediamine), electron transfer in one of the Mo^{IV}–Cu^{II} pairs would lead to a situation with one Mo^{V}–Cu^{I} pair and five Mo^{V}–Cu^{II} magnetic pairs, resulting in a strong ferromagnetic interaction ($J > 100$ cm^{-1}).

Theoretical investigations can contribute to the understanding of the photomagnetic mechanism in these compounds. Here, we present some relevant results to clarify the key aspects of the process. In particular, we show that the metal-to-metal charge transfer (MMCT) state has a very high excitation energy and is probably not involved in the photomagnetic process. In contrast, we propose a mechanism involving an on-site Mo d–d transition followed by important geometrical relaxation effects and eventually evolving to a ferromagnetic interaction between Cu^{II}-3d^9 and Mo^{IV}-4d^2 in its triplet state as the basis of the photoinduced magnetism, see Fig. 1. Recent X-ray magnetic circular dichroism experiments support the possibility of such a mechanism.[20]

To properly study the excited states involved in the photomagnetism, CASSCF and CASPT2 calculations were performed.

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Computational requirements of this methodology constrained us to use model dimers $[Mo(CN)_2(CNH)_5(CN–CuL)]^{3+}$ (L = tris(2-aminoethyl)amine) instead of the full compound. Lack of experimental information about the geometry of the metastable final state made this study particularly challenging and DFT optimizations of the model dimers were carried out, although ONIOM and some DFT calculations on the complete $[Mo(CN)_2(CN–CuL)_6]^{8+}$ molecule were performed to check the reliability of the models. Further details on the computational methodology are given in the ESI†.

First of all, the absorption spectrum for a model dimer was computed. Experimentally two sets of transitions have been measured and assigned: weak metal centered d–d transitions at 680 and 840 nm and strong metal-to-ligand charge transfer (MLCT) transitions at 242 and 270 nm. Additionally, a weak transition at 440 nm was observed and assigned to the inter-valence Mo–Cu MMCT.[7] Since MLCT transitions are not relevant for the photomagnetic process, only metal orbitals were included in the active space. Analysis of the computed spectrum shows that the ground state corresponds to the closed shell Mo^{IV}–Cu^{II} pair (Cu^{II}–Mo^{IV-CS}) and that there is qualitative agreement for the d–d transitions. These transitions in Mo populate two states: a Mo^{IV} triplet (Cu^{II}–Mo^{IV-T}) and a Mo^{IV} open shell singlet (Cu^{II}–Mo^{IV-OS}). Concerning the MMCT transitions, calculations show that these lie much higher in energy (about 11 eV at the CASSCF level), while the relative energies of the d–d Mo centered transitions to a Mo^{IV} triplet excited state and a Mo^{IV} open shell singlet are 2.5 and 2.8 eV, which is about the energy of the irradiation used to trigger the photomagnetic process. This result was consistently obtained at different calculation levels (basis sets, CAS size, CASSCF and CASPT2) and agrees with transition energies for $[Mo(CN)_8]^{4-}$ complexes.[21] To further assess the possibility to populate the MMCT state upon irradiation, the
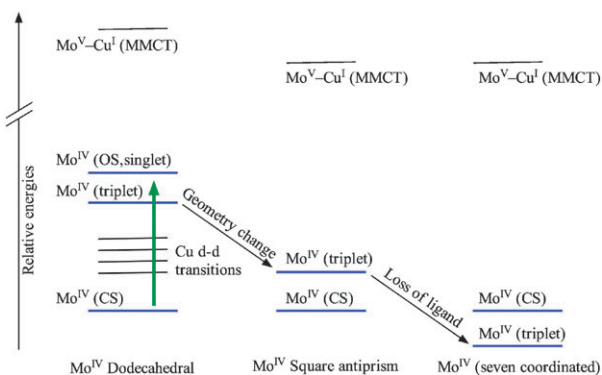

Fig. 1 Schematic representation of the mechanism proposed for the photoinduced magnetism in $Mo^{IV}(CN)_2(CN–CuL)_6$.

level shift technique was applied to compute the energy of the MMCT at the CASPT2 level and its relative energy converged to a value of 5.5–6 eV with increasing level shift. This is significantly higher than the energy used in the experiments to induce the magnetism. On the other hand, CASPT2 calculations with an extended CAS(11,12), which includes all the occupied metal orbitals, show that the MMCT state does not appear at energies lower than 4 eV. Consequently, the MMCT state is probably not populated at the initial stages of the photomagnetic process.

The geometrical changes of the different excited states were studied using small model clusters that allowed us to follow the relaxation of Mo^{IV-T}, Mo^{IV-OS} and the MMCT state. In a first stage, dimers were built by superposition of the $[Cu(CNH)L]^{2+/+}$ and $[Mo(CNH)_6 (CN)_2]^{2+/3+}$ DFT optimized models for the Cu^{II}, Cu^I, Mo^{IV-CS}, $Mo^{IV-T,OS}$ and Mo^V model complexes. A direct optimization of the dimers for all the excited states is highly non-trivial with DFT and computationally unfeasible with CASPT2. The optimized $[Mo^{IV-(T,OS)}(CNH)_6 (CN)_2]^{2+}$ and $[Mo^V(CNH)_6(CN)_2]^{3+}$ units have a similar, square antiprismatic geometry (Mo_{SA}). This means that the Mo coordination sphere undergoes important changes, since the complex initially possess a dodecahedral geometry (Mo_D). On the other hand and as expected, Cu^I loses one of the N ligands with respect to the initial trigonal bipyramid Cu^{II} structure (Cu_{TB}), and displays a tetrahedral geometry (Cu_{TD}). Hence, the MMCT state leads to a Cu_{TD}–Mo_{SA} final state geometry and the $Mo^{IV-(T,OS)}$ state to Cu_{TB}–Mo_{SA} dimers. To determine the feasibility of the two mechanisms, six $[Mo(CN)_2(CNH)_5(CN-CuL)]^{3+}$ dimers were generated, where the $[(CN)CuL]^+$ unit occupies a different position in each of them, to consider all the possible dimers of the real complex.

The Cu_{TD}–Mo_{SA} dimers show a lowering of the MMCT state, which is, however, too insufficient by far to become competitive with the initial state. On the other hand, the $Mo^{IV-(T,OS)}$ states are significantly stabilized in the Cu_{TB}–Mo_{SA} dimers and are now less than 1 eV higher in energy than the initial state. This result practically rules out the possibility of a charge transfer process accompanied by a change in the Cu coordination sphere to stabilize the photoinduced paramagnetic state, and marks the Cu^{II}–Mo^{IV-T} state as a firm candidate to explain the observed ferromagnetism.

To obtain more detailed information about the stabilization of the Cu^{II}–Mo^{IV-T} state, DFT geometry optimization of the dimers has been carried out. Since this state is not necessarily the ground state, a total quartet spin state was imposed during the optimization to ensure the Mo^{IV-T} configuration, while doublet and quartet energies were calculated at the final geometries. All the possible dimers were optimized and two different situations were obtained: eight-coordinated Mo complexes similar to the frozen models (Fig. 2, left), and structures in which the Mo has lost one of the (CNH) ligands, which mimics a $[(CN)CuL]^+$ unit (Fig. 2, right). The dissociation takes place in the position *trans* to the CN^- ligands, interacting by hydrogen bonds with the amino ligand of the Cu moiety. This result was corroborated by ONIOM and DFT calculations for the whole molecule (details in the ESI†).
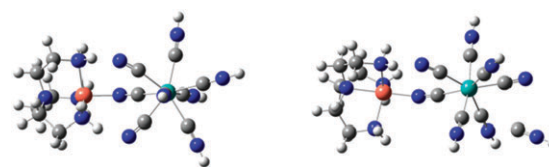
Fig. 2 Cu_{TB}–Mo_{SA} dimers optimized with DFT. On the left, eight-coordinated Mo^{IV}. On the right, after the loss of a ligand.

With respect to the model dimers constructed by superposition of two fragments, there are no large changes in the relative energies in the optimized dimers where the Mo remains octacoordinated. However, important differences are observed for the heptacoordinated Mo dimers. The Cu^{II}–Mo^{IV-CS} doublet state is no longer the ground state. Instead the Cu^{II}–Mo^{IV-T} doublet state is now lower in energy by 0.7 eV (see Table 1), confirming this state as the final state of the photoinduced process.

An estimate of the magnetic coupling strength between the Mo^{IV-T} (S = 1) and Cu^{II} (S = 1/2) centers was calculated by comparing the energy of the doublet state (antiferromagnetic coupling) to the quartet state (ferromagnetic coupling) in the dimer with a heptacoordinated Mo, according to the Heisenberg Hamiltonian $\hat{H} = -J\hat{S_1}\hat{S_2}$

Using a reference wave function that goes beyond the minimal active space, CASPT2 predicts an energy difference of 35 cm^{-1} favoring the quartet state, in agreement with the experimentally observed ferromagnetic behavior. A more accurate estimate of the coupling could possibly be obtained using a configuration interaction scheme. Unfortunately, such calculations are still out of reach at present.

In summary, a possible mechanism for the photomagnetism observed in copper octacyanomolybdate compounds consists of the initial excitation of the diamagnetic Cu^{II}–Mo^{IV-CS} pair to a Cu^{II}–Mo^{IV-T} state, which induces a change in the Mo coordination sphere from dodecahedral to square antiprismatic. Relaxation of the geometry of this excited state can lead to a decoordination of one of the $[(CN)CuL]^+$ units—probably due to formation of one intramolecular hydrogen bond—which stabilizes the magnetic doublet and quartet states. To get back to the initial, non-magnetic structure, the system has to overcome an energetic barrier, since the Mo has

Table 1 CAS(3,3)SCF and CASPT2 relative energies (in eV), and Mulliken spin population on the Mo and Cu atoms for one of the dimers with a seven- or eight-coordinated Mo

State	CASSCF	CASPT2	Spin(Mo)	Spin(Cu)
Heptacoordinated Mo^{IV}(triplet)				
Cu^{II}–Mo^{IV-T}	0.0	0.0	1.1299	−0.2893
Cu^{II}–Mo^{IV-CS}	0.9	0.7	0.0017	0.8703
Cu^{II}–Mo^{IV-OS}	1.0	0.8	0.0016	0.8705
MMCT	11.1	—^{a}	0.8593	0.0010
Octacoordinated Mo^{IV}(triplet)				
Cu^{II}–Mo^{IV-CS}	0.0	0.0	0.0011	0.8684
Cu^{II}–Mo^{IV-T}	0.4	0.6	1.0325	−0.2889
Cu^{II}–Mo^{IV-OS}	1.2	1.3	0.0011	0.8683
MMCT	10.4	—^{a}	0.7171	0.0001

^{a} CASPT2(3,3) calculation for the MMCT state was not successful because of intruder state problems.

to recover its initial geometry, which is consistent with experimental findings.

Additional work is under way to establish a more detailed picture of the photomagnetic process and to provide a mechanism for the reverse reaction. At the same time, we expect these results will prompt experimental studies in order to assess the validity of the proposed mechanism.

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