

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## COMMUNICATION

# First Evidence of a Light-Induced Spin Transition in Molybdenum(IV)

Cite this: DOI: 10.1039/x0xx00000x

N. Bridonneau,<sup>a</sup> J. Long,<sup>a</sup> J.-L. Cantin,<sup>b</sup> J. von Bardeleben,<sup>b</sup> S. Pillet,<sup>c</sup> E.-E. Bendeif,<sup>c</sup> D. Aravena,<sup>d</sup> E. Ruiz,<sup>d</sup> and V. Marvaud<sup>\*a</sup>

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

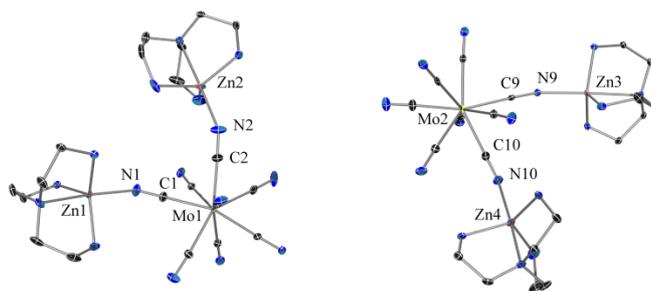
**A photo-induced spin transition in a Molybdenum-Zinc complex has been evidenced and fully characterized by Squid magnetometry and several spectroscopies performed under irradiation (IR, EPR, ...). The phenomenon has been confirmed by X-Ray diffraction and DFT calculations yielding to a Light-Induced Excited Spin State Trapping Effect (LIESST) on a 4d transition metal ion.**

Light is an attractive external trigger for the control of spin transition.<sup>1</sup> The relative LIESST effect (Light Induced Excited Spin State Trapping), firstly demonstrated by Hauser *et al.*, usually concerns octahedral complexes with a central transition metal ion having  $d^4$ - $d^7$  electronic configuration.<sup>2</sup> Most of the examples concern Iron compounds that show reversible bistability between Low Spin (LS) and High Spin (HS) states, when submitted to external perturbation such as light irradiation with an appropriate wavelength (d-d or metal-ligand charge transfer). The optical spin transition usually takes place at low temperature from the  $^1A_1$  low spin state to the  $^5T_2$  high spin state.<sup>3</sup> The relaxation process, back to the LS ground state can be followed by spectroscopic methods as a function of temperature ( $T_{\text{LIESST}}$  is usually below 80 K; it might be above 132 K for the highest relaxation temperature investigated so far).<sup>4</sup> Concerning other metallic ions, light induced spin transition on Nickel species has been evidenced on a square-planar complex Ni(II)-tetrakis(pentafluorophenyl)porphyrin (low spin and diamagnetic) connected to a 3-azopyridine ligand, which can be switched between *cis* and *trans* configurations. When the azopyridine ligand is in the *trans* configuration, it binds well to the axial position of the square-planar nickel-porphyrin complex, switching to an octahedral geometry with a high spin, paramagnetic state ( $S = 1$ ).<sup>5</sup>

For others elements, and especially for 4d transition metal ions, spin transition on Molybdenum(IV) has been suggested in the context of photoswitchable MoCu complexes,<sup>6</sup> by X-Ray Magnetic Circular Dichroism experiments, using a highly energetic synchrotron X-Ray

beam as a source of irradiation. But the effect has only been demonstrated on MoCu complexes, with potential correlation to a photo-induced electron transfer.

In order to better understand the origin of the photomagnetic behaviour on molybdenum-copper complexes,<sup>7</sup> we prepared a series of trinuclear compounds, viewed as reference species,  $[\text{Mo}(\text{CN})_8\text{Zn}_{(2-x)}\text{Cu}_x\{\text{tren}\}_2]$  with ( $x = 0, 0.05, 0.1, 0.2$ ; tren = tris(2-aminoethylamine)), noted  $\text{MoZn}_2$  and  $\text{MoZn}_{(2-x)}\text{Cu}_{(x)}$  respectively. The mixed species,  $\text{MoZn}_{(2-x)}\text{Cu}_{(x)}$  complexes, entirely analysed elsewhere,<sup>8</sup> clearly indicate that, in addition to spin transition, the photo-induced charge transfer mechanism  $\text{Mo}(\text{IV})\text{Cu}(\text{II}) \rightarrow \text{Mo}(\text{V})\text{Cu}(\text{I})$  subsists and is not completely ruled out. The compound  $\text{MoZn}_2$ , fully described in the present communication, exhibits a unique photomagnetic behaviour, attributed to a spin transition from  $\text{Mo}(\text{IV-LS}), S = 0$  to  $\text{Mo}(\text{IV-HS}), S = 1$ , that confirms the possible LIESST effect in a 4d metallic ion and might explain unelucidated photomagnetic behaviours described in the literature.<sup>9</sup>



**Figure 1.** X-ray structure of compound  $\text{MoZn}_2$ -tren (**1**): asymmetric unit (ellipsoid set to 50%), hydrogen atoms have been omitted for clarity.

$\text{MoZn}_2$ -tren (**1**) complex was obtained by slow addition of an aqueous solution of  $\text{K}_4[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$  in a water/acetonitrile mixture of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  and tren ligand. An excess of the zinc complex was required in order to avoid immediate precipitation of

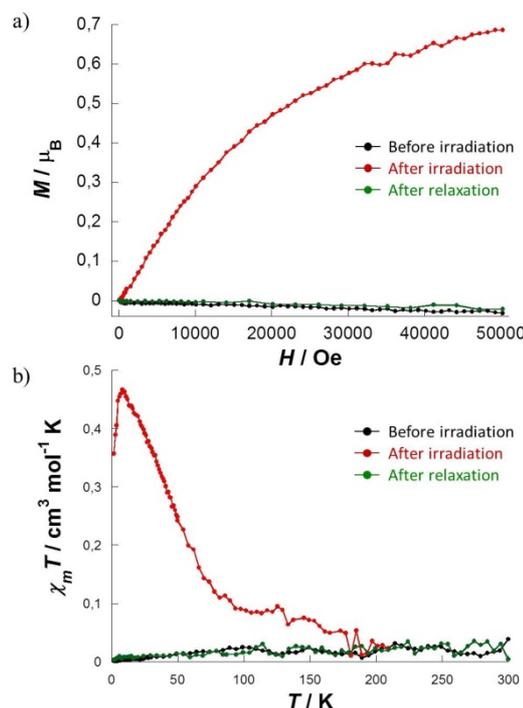
the neutral species. Large yellow crystals (0.6 cm long) were obtained after two weeks of slow evaporation of the mother liquor. Complex **1** crystallizes in an orthorhombic system with the  $Pca_2$  space group; cell parameters are  $a = 14.7778(3)$  Å,  $b = 14.8566(3)$  Å and  $c = 31.0576(7)$  Å with a cell volume of  $V = 6818.6(2)$  Å<sup>3</sup>. Two crystallographically independent trinuclear molecules compose the asymmetric unit. Each assembly is formed by one molybdenum center linked to two zinc fragments through cyanide bridges (Figure 1, Table S1).

Continuous shape measures show that the two octacyanomolybdate complexes have different geometries:<sup>10,11</sup> one of them (Mo1) being pure based square antiprism (BSAP-8), the other (Mo2) adopting a distorted coordination environment between dodecahedron (DD) and BSAP-8 (Table 1). Mo-C distances are slightly longer for Mo2, while C≡N distances are similar from one molybdenum center to the other, the six free cyanide ligands being slightly longer than the bonded ones. The bridging cyanide angles are linear on the molybdenum side ( $175.6(3)^\circ - 178.5(3)^\circ$ ), but very bended on the zinc complex side. Four very different cyanide angles are thus reported, from  $137.1(3)^\circ$  for Zn4-N10≡C10 to  $165.0(3)^\circ$  for Zn3-C9≡N9. The four zinc complexes adopt the same triangular base bipyramidal geometry with similar Zn-N bond lengths. All complexes are well isolated from each other; the shortest intermolecular metal-metal distance reported being 6.424 Å.

Photomagnetic measurements were realized on single crystals and homogeneous powder obtained from ground crystals, both samples giving similar results. Before irradiation, the compound shows a purely diamagnetic behaviour (slightly negative magnetization vs field curve,  $\chi T$  value close to zero) expected for Zn<sup>II</sup> ( $3d^{10}$ ,  $S = 0$ ) and Mo<sup>IV</sup> ( $4d^2$ ,  $S = 0$ ) ions. The sample was then irradiated under a 1 kOe field for 4 hours using a 405 nm (blue) laser beam (20 mW power) equipped with a fiber. Irradiation was achieved at a temperature of 18 K in order to avoid thermalization of the sample when switching off the laser.<sup>12</sup> A clear increase of magnetization was immediately observed upon light irradiation and saturation occurred typically after 3 to 4 hours (see Figure S3). After switching off the laser, the temperature was decreased to 2 K to perform the first magnetization curve, then the magnetization data were recorded on the heating mode (2 – 300 K) (Figure 2).

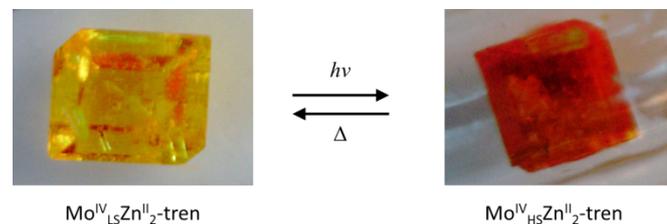
Magnetic susceptibility data, recorded after irradiation showed a drastic change of the magnetic properties:  $\chi T$  reached a maximum value of  $0.47$  cm<sup>3</sup>.mol<sup>-1</sup>.K at 8.5 K (Figure 2b). No evolution of the magnetic susceptibility was detected after a 2 hour period of time, thus demonstrating the stability of the photoinduced state (see SI Figure S4). Relaxation of the process occurred gradually when heating the compound (at about 90 K) and both curves merge around 180 K. Important evolution of the magnetization curve was also recorded after irradiation (Figure 2a), indicating clearly the presence of spin carriers. Saturation of the magnetization was obtained at 50 kOe with a value of  $0.69$  μB. Comparison of this curve with a simulated Brillouin function considering an  $S = 1$  species ( $g = 2.1$ ) allowed extracting a transformation rate of about 50 % of the compound. Note that this rate is in very good accordance with the experimental  $\chi T$  value being close to the theoretical one of  $0.50$  cm<sup>3</sup>.mol<sup>-1</sup>.K expected for an  $S = 1$  moiety (50 %). The sample

was then heated to room temperature for at least two hours to obtain a full relaxation of the system. New magnetization vs field data showed that the compound achieved a complete relaxation (Figure 2a) and that the effect is fully reversible.



**Figure 2.** Evolution of the magnetic data upon light irradiation a) first magnetization curve at 2 K b) temperature dependence of  $\chi T$  under a 1 kOe DC field.

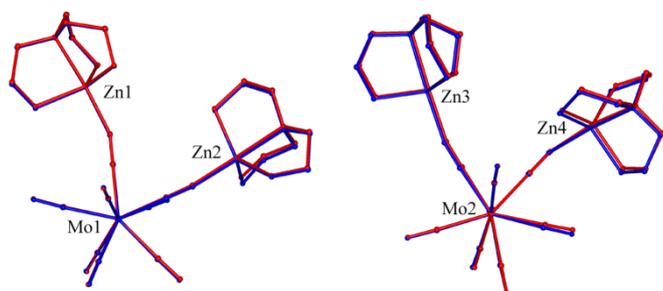
In order to highlight potential crystal modifications upon light irradiation, **1** was introduced in an EPR glass holder and rapidly frozen to 4 K, then irradiated as previously described. The crystal showed no apparent modification of shape and size due to the light irradiation, but a bright red colour was observed instead of the initial yellow one (Figure 3), reflecting photochromic properties of the compound. After approximately two minutes, the crystal recovered its original colour as its temperature increased. A thermochemical effect has not been detected in the range of 300 - 400 K, probably due to partial dehydration of the compound.



**Figure 3.** Colour change of a  $\text{MoZn}_2\text{-tren}$  crystal upon light irradiation.

The photo-magnetic behaviour of **1** has also been investigated by several additional techniques: EPR spectroscopy, XMCD experiments, IR and single crystal XRD. These experiments are fully detailed in the SI.

Investigation by single crystal X-ray diffraction, at low temperature, under irradiation, indicates clearly a modification of the cell parameters, as well as a progressive amorphization of the crystal, which prevents a crystallographic analysis to be performed at completeness of the photo-transformation. A structural analysis after 30 min illumination at 10 K (laser beam 405 nm, P = 70 mW), which corresponds to a very incomplete photo-transformation with a yet limited amorphization progress, has been undertaken. The corresponding derived crystal structure is less accurate than the ground state crystal structure, but nevertheless sufficiently good to allow the trend of some structural reorganization to be derived. 76836 reflections were measured up to a maximum resolution of  $\theta_{max} = 31.51^\circ$ , and merged to 21900 unique reflections ( $R_{int} = 0.0759$ ). The new parameters are  $a = 14.8514(3)\text{\AA}$ ,  $b = 14.9939(3)\text{\AA}$  and  $c = 31.0699(7)\text{\AA}$  with a cell volume of  $V = 6918.6(3)\text{\AA}^3$ . The analysis indicates modifications localized only on one molecule (Mo2) with an elongation of the Mo-Zn4 distance (Fig. 4). Due to the amorphization process, the crystallographic analysis does not allow going much further.



**Figure 4.** Superposition of the structural models of the ground state (in blue) and average photo-irradiated state (in red) of **1**

If we compare the molecular structure of the ground state to the photo-irradiated state (corresponding to the average structure), we can draw the same conclusion. For the first molecule (Figure 4, left), no significant structural distortion may be detected, while for the second molecule (Figure 4, right), a displacement of the Zn4 atom with respect to the Mo2 centre is evident.

Electronic structure calculations have been carried out to analyze the energetics of the excited states for the coordination of the molybdenum centers (see Computational Details in Experimental Section); CASSCF/CASPT2 and DFT calculations were performed on the  $[\text{Mo}(\text{CN})_8]^{4-}$  fragments (Table 1). Both methods clearly show that the photo-induced Mo2' coordination gives a relatively lower singlet-triplet excitation energy.

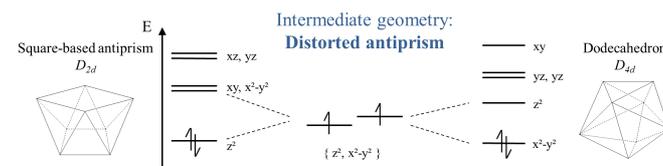
The Mo1 and photo-induced Mo1' centers have approximately the same geometry showing that such centers remain almost unchanged after the irradiation while significant structural changes and also of the electronic structure are detected between the Mo2 and Mo2' centers. This fact is in agreement

with a transformation rate around 50% because only one of the two molecules has the appropriate structure to undergo the spin transition.

	S(SAPR)	S(TDD)	$E_{S \rightarrow T}$ ( $\text{cm}^{-1}$ )		
			B3LYP	CASSCF	CASPT2
Mo1	0.196	2.535	22147	18898	24103
Mo2	0.455	1.681	21888	18130	24313
Mo1'	0.243	2.467	22277	19027	23777
Mo2'	1.048	1.732	13634	8786	14681

**Table 1.** Continuous symmetry measurements values<sup>[10,11]</sup> (S for octa-coordinate models: square antiprism SAPR and dodecahedron DD) for the two molecules of the ground state (Mo1 and Mo2) and the corresponding molecules after the irradiation (Mo1' and Mo2') including as well as the calculated singlet-triplet energy differences calculated at B3LYP and CASSCF(CASPT2)+RASSI level using  $[\text{Mo}(\text{CN})_8]^{4-}$  fragments.

The analysis of the coordination mode of the Mo2 centers shows that the complexation of molybdenum with  $[\text{Zn}(\text{tren})]^{2+}$  complexes enabled to get an intermediate geometry of the Mo2' coordination polyhedron. But the main changes in the coordination sphere between Mo2 and Mo2' centers are an elongation of one of the Mo-C bond distances (0.2 Å involved in a Mo-C-N-Zn bond sequence) and the corresponding C-N-Zn angle (from  $137.9^\circ$  in Mo2 to  $114.8^\circ$  in Mo2'). The increase of the Mo-C bond distance that is almost aligned with the y axis causes an stabilization of the empty  $d_{x^2-y^2}$  molecular orbital (for the square antiprism low-spin  $S = 0$  Mo(IV) cation) reducing the energy difference with the doubly-occupied  $d_{z^2}$  orbital. This distortion can be responsible for reducing the energy gap between the two lowest 4d orbitals and to promote the relative stabilization of the triplet state for the Mo2' centers (Figure 5).



**Figure 5.** The intermediate geometry of molybdenum Mo2' centers could stabilize the triplet state of the  $\text{Mo}^{\text{IV}}$  system.

Taking into account all these results, we can suggest that **1** exhibits a light induced excited spin state trapping (LIESST) effect, as already observed mainly in Iron(II) complexes. The compound can be switched upon light irradiation from the low spin state ( $S = 0$ ) to the high spin state ( $S = 1$ ), leading to drastic changes in the magnetic properties. Only one of the two molecules present in the unit cell is active towards spin-transition, explaining why despite all our attempts we never

succeeded in reaching more than 50% of transformation rate. As confirmed by electronic structure calculations, the specific geometry of the coordination polyhedron (distorted antiprism) might justify the stabilization of the triplet state (Figure 5).

## Conclusions

The results presented here show a photo-induced spin transition, achievable on a Molybdenum(IV) center, evolving from  $\text{Mo}^{\text{IV}}_{\text{LS}} (S = 0)$  to  $\text{Mo}^{\text{IV}}_{\text{HS}} (S = 1)$ . This study puts forward that such phenomenon could be induced on a 4d transition metal ion, as already suggested in the literature. Work is in progress to analyse the photophysical process of the LIESST effect and specifically the relaxation process by spectroscopic methods as a function of temperature. The observed phenomenon is explained by a specific coordination environment of molybdenum and offers an additional point of view on photo-magnetism based on octacyanomolybdate compounds. It demonstrates as well that spin crossover phenomenon might occur in a new class of coordination compounds. The switching properties make such material potential candidate for practical applications in sensors as well as optical devices.

## Acknowledgments

The research has been supported by the CNRS – UMR 8232, UPMC, Labex Michem, the French Ministry of Research, ANR Switch (2010-Blan-712) and ANR E-storic (14-CE05-0002), Spanish *Ministerio de Economía y Competitividad* (CTQ2011-23862-C02-01) and the regional *Generalitat de Catalunya* authority (2009SGR-1459). The authors thank Marie-Anne Arrio, Laurent Lisnard and Katharina Ollefs for XMCD experiments.

## Notes and references

[\*] Dr. Valérie Marvaud, IPCM-CNRS-UMR-8232, UPMC-Univ. Paris 6, cc 42, 4 place Jussieu, 75252 Paris Cedex 05, FRANCE. Fax: +33 (0)1 44 27 38 41, Tel: +33 (0)1 44 27 32 77; \* E-mail : [valerie.marvaud@upmc.fr](mailto:valerie.marvaud@upmc.fr)

- a) IPCM-CNRS-UMR-8232, UPMC-Univ. Paris 6, cc 42, 4 place Jussieu, 75252 Paris Cedex 05, FRANCE.  
 b) INSP - CNRS UMR-7588, UPMC- Univ. Paris 6, 4 place Jussieu, 75252 Paris cedex 05, FRANCE  
 c) CRM2, UMR CNRS 7036, Institut Jean Barriol, Université de Lorraine, 54506 Vandoeuvre-les-Nancy, FRANCE  
 d) Departament de Química Inorgànica and Institut de Recerca de Química Teòrica i Computacional, Universitat de Barcelona, Diagonal 645, E-08028 Barcelona, Spain

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201xxxxx>. CCDC 1009240 (for compounds 1) contains the supplementary crystallographic data for this paper.

- 1 a) P. Gütlich, A. B. Gaspar and Y. Garcia, *Beilstein J. Org. Chem.* 2013, **9**, 342; b) M.A. Halcrow, *Coord. Chem. Rev.*, 2009, **253**, 2493; c) J. Olguín, S. Brooker, *Coord. Chem. Rev.*, 2011, **255**, 203; d) S. Hayami, Y. Komatsu, T. Shimizu, H. Kamihata, Y. H. Lee, *Coord. Chem. Rev.*, 2011, **255**, 1981; e) J. Tao, H. Maruyama, O. Sato, *J. Am. Chem. Soc.*, 2006, **128**(6), 1790.  
 2 a) S. Decurtins, P. Gutlich, C. P. Kohler, H. Spiering, A. Hauser, *Chem. Phys. Lett.* 1984, **105**, 1; b) P. Gütlich, A. Hauser, *Coord. Chem. Rev.* 1990, **97**, 1; c) P. Gutlich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed.* 1994, **106**, 2109; d) A. Hauser, *Chem. Phys. Lett.* 1983, **124**, 543; e) P. Gutlich, A. Hauser, Spiering, H., *Angew. Chem. Int. Ed.* 1994, **33**, 2024.  
 3 P. Gütlich, A. Hauser, *Coord. Chem. Rev.* 1990, **97**, 1.  
 4 a) S. Hayami, Z.-Z. Gu, Y. Einaga, Y. Kobayashi, Y. Ishikawa, Y. Yamada, A. Fujishima and O. Sato, *Inorg. Chem.*, 2001, **40**, 3240; b) J.-F. Létard, *J. Mater. Chem.*, 2006, **16**, 2550.  
 5 S. Thies, H. Sell, C. Schütt, C. Bornholdt, C. Näther, F. Tuczek, R. Herges, *J. Am. Chem. Soc.*, 2011, **133**, 16243.  
 6 a) M.-A. Arrio, J. Long, C. Cartier dit Moulin, A. Bachschmidt, V. Marvaud, A. Rogalev, C. Mathoniere, F. Wilhelm, P. Saintavitt, *Jour. of Phys. Chem. C*, 2010, **114**, 593; b) S. Brossard, F. Volatron, L. Lisnard, M.-A. Arrio, L. Catala, C. Mathoniere, T. Mallah, C. Cartier dit Moulin, A. Rogalev, A. Smekhova, P. Saintavitt, *J. Am. Chem. Soc.*, 2012, **134**, 222.  
 7 a) T. Hozumi, K. Hashimoto, S.-I. Ohkoshi, *J. Am. Chem. Soc.*, 2005, **127**, 3864; b) Y. Arimoto, S.-I. Ohkoshi, Z. J. Zhong, H. Seino, Y. Mizobe, K. Hashimoto, *J. Am. Chem. Soc.*, 2003, **125**, 9240; c) G. Rombaut, M. Verelst, S. Golhen, L. Ouahab, C. Mathoniere, O. Kahn; *Inorg. Chem.* 2001, **40**, 1151; d) A. Bleuzen, V. Marvaud, C. Mathoniere, B. Sieklucka, M. Verdagner, *Inorg. Chem.* 2009, **48**, 3453; e) J. M. Herrera, V. Marvaud, M. Verdagner, J. Marrot, M. Kalisz, C. Mathoniere; *Angew. Chem. Int. Ed.*, 2004, **43**, 5468.  
 8 N. Bridonneau, *PhD thesis UPMC*, Paris 6, France, 2013.  
 9 a) C. Mathoniere, R. Podgajny, P. Guionneau, C. Labrugere, B. Sieklucka, *Chem. Mater.* 2005, **17**, 442; b) T. Korzeniak, C. Mathoniere, A. Kaiba, P. Guionneau, M. Koziel, B. Sieklucka, *Inorg. Chim. Acta*, 2008, **361**, 3500-3504.  
 10 a) S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell, D. Avnir, *Coord. Chem. Rev.*, 2005, **249**, 1693; b) D. Casanova, J. Cirera, M. Llunell, P. Alemany, D. Avnir, S. Alvarez, *J. Am. Chem. Soc.*, 2004, **126**, 1755; c) J. Cirera, E. Ruiz, S. Alvarez, *Organometallics* 2005, **24**, 1556.  
 11 Shape 2.0 M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, 2010, Program for the Stereochemical Analysis of Molecular Fragments by Means of Continuous Shape Measures and Associated Tools.  
 12 Y. Zhang, D. Li, R. Clérac, M. Kalisz, C. Mathoniere and S. M. Holmes, *Angew. Chem., Int. Ed.* 2010, **49**, 3752.