Magnetic Interaction between d^1 [MOR$_4$]$^-$ Units of Molybdenum and Tungsten

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Abstract. Five-coordinate oxo-derivatives [NBu$_4$][MO(C$_6$F$_5$)$_4$] (**1**) have been prepared for the heavier Group 6 elements: **1**-Mo and **1**-W. The magnetic properties of those salts have been studied by a combination of electron paramagnetic resonance (EPR), calorimetric and magnetochemical techniques, pointing out the existence of weak ferromagnetic interactions. These have been correlated with the arrangement of the magnetic units in the crystal.

Introduction

Five-coordinate oxo-molybdenum compounds with formula [MoOX$_4$]$^-$ and d^1 electron configuration are model compounds[1] which have attracted a great deal of attention over the years mainly because of two reasons: 1) they have played a key role in the proper understanding of the chemical bond between the oxo ligand and the metal center [2] and 2) because of their relevance to various Mo-containing enzymatic systems operating as oxotransferases and hydroxylases [3]. In any case, the X ligands under consideration have always been typical (σ+π)-donors, such as halogens or thiolates. The properties of homologous compounds with the MO^{3+} unit being located in a coordination framework of σ-only ligands are virtually unknown [4].

Here we report on the characterization of five-coordinate [MOR$_4$]$^-$ oxo-derivatives for the heavier Group 6 metals with R being the bulky perfluorophenyl group, C$_6$F$_5$, which acts mainly as a σ-donor ligand. The magnetic properties of these open-shell derivatives, **1**-Mo and **1**-W, have been studied by a combination of spectroscopic (EPR), calorimetric and magnetochemical techniques.

Experimental Results

EPR measurements. The room-temperature EPR spectra of fluid solutions of both compounds consist of dominant isotropic lines symmetrically flanked by less-intense, equally spaced signals (six for Mo and two for W) due to hyperfine interaction with magnetic nuclei: ^{95}Mo and ^{97}Mo, both with $I = 5/2$ and 15.9%, 9.6% natural abundance, respectively, and ^{183}W, $I = 1/2$, 14.3% natural abundance. The EPR spectra observed in frozen solutions (Figure 1.a) indicate anisotropic, nearly axial g-tensors with the following principal values: $g_{\parallel} = 2.002(1)$ and $g_{\perp} = 1.974(1)$ for Mo, and $g_{\parallel} = 1.995(3)$ and $g_{\perp} = 1.892(2)$ for W. The pattern in the parallel features denotes hyperfine interaction with $I \neq 0$ nuclei.

In the room-temperature EPR spectra of polycrystalline-powder samples (Figure 1.b) no evidence of hyperfine structure is found. Both spectra show anisotropic electron Zeeman interactions which are clearly resolved in Q-band measurements (not given). Lower g-tensor anisotropy is observed by comparison with the frozen-solution spectra. Moreover, the hyperfine interaction in the bulk

samples, if present, is significantly lower than in the separate molecules. These features strongly suggest the existence of intermolecular interactions that delocalize the spin among neighbor magnetic sites.
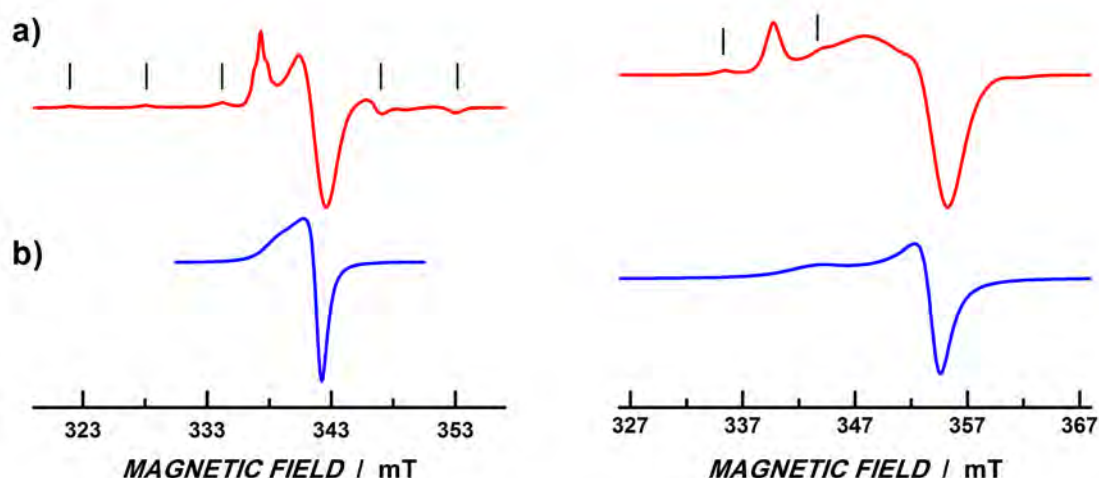

Figure 1. EPR spectra of frozen solutions of [NBu$_4$][MO(C$_6$F$_5$)$_4$] measured at 25 K (a), and of polycrystalline-powder samples measured at RT (b): M = Mo (left) and M = W (right).

Heat capacity measurements. The thermal evolution of the heat capacity of polycrystalline powder samples was measured under various applied magnetic fields, $0 \leq H \leq 25$ kOe. The data for **1**-Mo are given in Figure 2.a. Similar results are found for **1**-W. The magnetic contribution to the heat capacity, C_M/R, is obtained by subtracting the lattice contribution modeled by $C_L/R = aT^3$. In the absence of any applied magnetic field, it increases as the temperature decreases. Although no sign of long-range ordering was detected ($T > 0.35$ K), the observed magnetic heat capacity may be associated to the high-temperature tail due to short-range correlation.
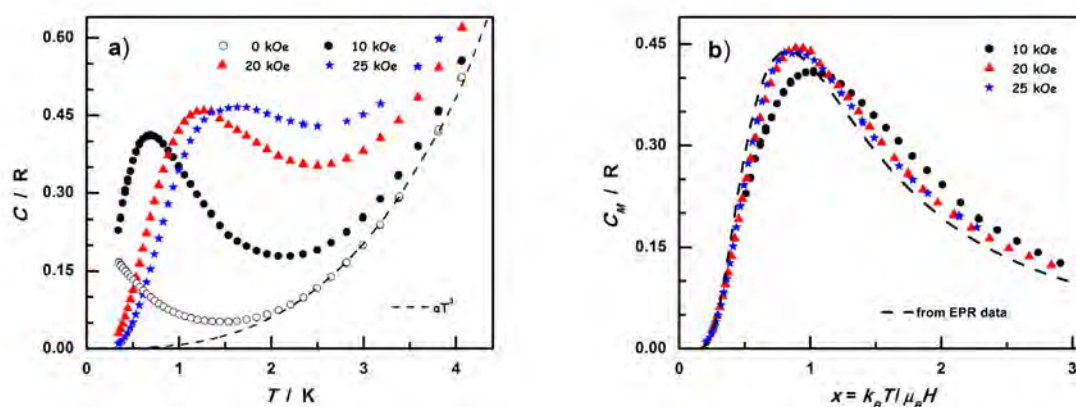

Figure 2. a) Low-temperature heat capacity of a polycrystalline powder sample of **1**-Mo under various applied magnetic fields; the dashed line corresponds to the lattice contribution given by a T^3 dependence. b) Values of C_M/R as a function of $x = k_BT/\mu_BH$ for different values of the applied magnetic field; the predicted evolution calculated from the EPR data and considering non-interacting paramagnetic entities is given by the dashed line.

Under an applied magnetic field, C_M/R shows a Schottky-like anomaly. C_M/R values as a function of the parameter $x = k_BT/\mu_BH$ are given in Figure 2.b. The expected evolution of C_M/R as a function of x calculated with the EPR-derived g-tensor principal values, and assuming non-interacting paramagnetic entities (dashed line), is independent of the magnetic field. The experimentally observed evolution of $C_M(x)$ actually depends on the applied magnetic-field strength. Although the

anomaly is slightly shifted to higher *x*-values in all cases, it tends towards the calculated one as the external magnetic field increases.

Magnetic measurements. The thermal evolution ($1.8 < T < 250$ K) of the magnetic susceptibility in polycrystalline powder samples roughly follows a Curie law, $\chi(T) = C/T + \chi_0$, where *C* is the Curie constant and χ_0 accounts for the temperature–independent (diamagnetic) contribution. A plot of $T \cdot \chi(T)$ against *T* departs at low temperature from the expected straight line (Figure 3.a). A fit of a Curie-Weiss law, $\chi(T) = C/(T - T_C) + \chi_0$, to those data using the EPR-derived *C* value yields $T_C = 0.09(1)$ K for **1**-Mo ($T_C = 0.06(1)$ K for **1**-W).
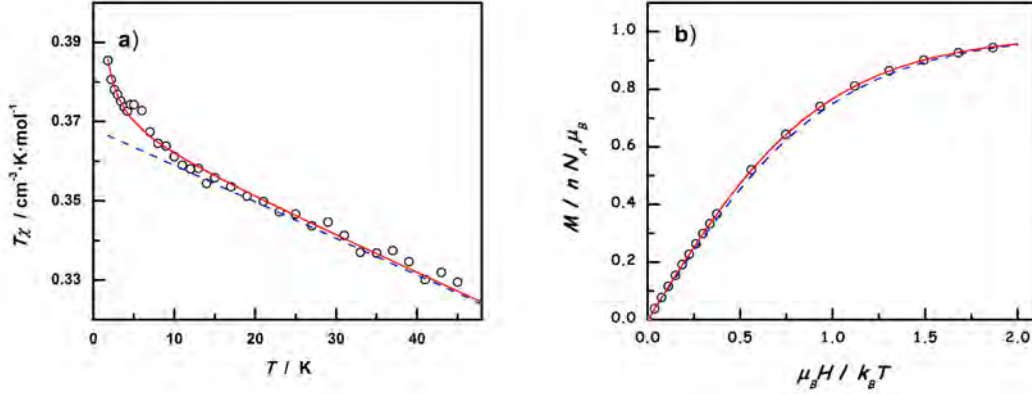

Figure 3. a) Thermal evolution of $T \cdot \chi(T)$ measured (circles) in a polycrystalline powder sample of **1**-Mo together with the predicted values using a Curie law (dashed line) and a Curie-Weiss law with $T_c = 0.09$ K (solid line) and an EPR-derived *C* value (0.368 cm$^3 \cdot$K$\cdot$mol^{-1}). b) Magnetization per formula unit measured (circles) at 1.8 K on polycrystalline samples of **1**-Mo as a function of the reduced field, $\mu_B H/k_B T$, together with the evolution predicted by a standard (dashed line) and a modified (solid line) Brillouin function (see text).

The magnetization per formula unit, in Bohr magnetons, of a polycrystalline sample of **1**-Mo measured at 1.8 K as a function of the reduced magnetic field, $\mu_B H/k_B T$ (Figure 3.b), shows a saturation trend corresponding to an $S = \frac{1}{2}$ paramagnetic entity in keeping with a mononuclear d^1 system. Considering the low anisotropy of the *g*-tensor, a simple Brillouin function can be safely used to describe the isothermal evolution of the magnetization of non-interacting paramagnetic entities against the applied magnetic field [5]. However, the predicted evolution calculated in this way (dashed line in Figure 3.b) lies slightly under the experimental values, which denotes the existence of a weak ferromagnetic interaction between the paramagnetic entities. In such a case, the magnetization dependence on the magnetic field is given by:

$$\frac{M}{nN_A\mu_B} = gS \cdot B_S^{(1)}\left(\frac{T_C}{T}, gS \cdot \frac{\mu_B H}{k_B T}\right). \tag{1}$$

where a modified Brillouin function is defined as:

$$B_S^{(1)}(a,x) = \frac{B_S(x)}{1 - a\left(\dfrac{3S}{S+1}\right)B_S'(x)}. \tag{2}$$

B'_S being the derivative of the Brillouin function, B_S. A detailed derivation is given in reference [5].

Solid line in Figure 3.b shows the calculated evolution of the magnetization using equation (1) with the parameters derived from the analysis of the thermal dependence of the magnetic susceptibility (Figure 3.a). It gives a satisfactory fitting to the experimental data.

Structural characterization. Crystals of the [NBu$_4$][MO(C$_6$F$_5$)$_4$] salts of the heavier Group 6 metals, **1**-Mo and **1**-W, are isomorphic and isostructural with those of the lighter metal, **1**-Cr [5]. In all cases, the crystal lattice is formed by alternating layers of cations and anions. The metal centers are located in regular square-pyramidal coordination environments with the oxo ligand occupying the axial position. Thus, the paramagnetic (d^1) MO^{3+} units are placed within an organic framework of near tetragonal symmetry defined by the four basal *C*-donor atoms of the C$_6$F$_5$ groups, which are hard ligands of mainly σ-donor character.

The square-pyramidal [MO(C$_6$F$_5$)$_4$]$^-$ anions show weak intermolecular contacts between *meta*- and *para*-C atoms of neighboring and roughly parallel C$_6$F$_5$ rings (interplanar angle ~10°). We consider these weak π–π interactions as the most likely path to explain the interactions between individual magnetic centers that become noticeable at very low temperatures.

Discussion.

The five-coordinate oxo-derivatives [NBu$_4$][MO(C$_6$F$_5$)$_4$] (**1**) have been prepared for the heavier Group 6 elements: **1**-Mo and **1**-W. The structural and magnetic properties of these open-shell organometallic species have been thoroughly studied both in solution and in the solid state. In the crystal, the [MO(C$_6$F$_5$)$_4$]$^-$ anions exhibit square-pyramidal structures with the oxide ligand in the apical position, as established by single-crystal X-ray diffraction methods. Thus, the MO^{3+} unit is located in a nearly tetragonal environment of organic σ-donor ligands. These discrete units show the behaviour expected for separate, single-spin ($S = \frac{1}{2}$) paramagnetic entities both in fluid and in frozen solution (EPR). The loss of hyperfine coupling with the metal nuclei with non-zero nuclear spin in the condensed phase (Figure 1b) denotes the existence of magnetic interaction between the individual units. The bulk magnetic properties (Figure 3) indicate its ferromagnetic character and provide an estimation of its magnitude. We suggest that the weak π–π interactions between C$_6$F$_5$ rings of neighbour [MO(C$_6$F$_5$)$_4$]$^-$ units in the crystal are responsible for these magnetic interactions between the paramagnetic centres.

Summary

The electron-withdrawing C$_6$F$_5$ group is able to stabilize the MO^{3+} unit in the [MO(C$_6$F$_5$)$_4$]$^-$ anions for all Group 6 metals (M = Cr [5], Mo, W). The bulkiness of the perfluorophenyl group provides efficient shielding to the MO^{3+} unit —both chemical and magnetic. Only at very low temperatures it is possible to detect the existence of weak magnetic interactions between the individual paramagnetic centres. The strength of these interactions is observed to decrease down the Group: Cr > Mo > W.

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