A New Type of Paddle-Wheel Coordination Complex

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Supporting Information

Estimation of Exchange Coupling constant from *M vs H* curve.

In an antiferromagnetic exchange-coupled pair of spins, an applied magnetic field can cancel the exchange coupling. This translates into a so-called S-shaped *M vs H* curve. The inflection point of this curve corresponds to a critical field for which the interaction with the individual spins overcomes the antiferromagnetic interaction between the latter. At this critical field, the energy arising from the coupling of the applied field with the spins thus equals that describing the exchange coupling between these spins. These energies are respectively the Zeeman energy and the intramolecular exchange energy. The Zeeman energy is $g\mu_B HS$ with μ_B being the Bohr magneton. The Heisenberg exchange energy in the case of a pair of isotropic spins is simply the product of the two spin vectors and the exchange integral J ie JS_1S_2.

As a rough approximation the contribution of the anisotropy in this equation is not considered. However, this estimation was done for comparison with the results obtained from fitting of the χT *vs* T data (where the same approximation was made). For the same reason, we also use the value g =2.70. Thus, taking S=3/2, the spin for a HS Co(II) ion, and H_C = 19000 G (1.9 T) as determined from the inflection point in the *M vs H* curve, we obtain a value of –1.15 cm^{-1} for J.

As a reference for the well known expressions for the Zeeman energy and the Heisenberg exchange energy the readers are addressed to A. Herpin, Théorie du magnétisme, Presse Universitaires de France, Paris, 1968, or Van Vleck, J. H. "Electric and Magnetic Susceptibilities, Oxford, Clarendon Press, p. 318 (1932).

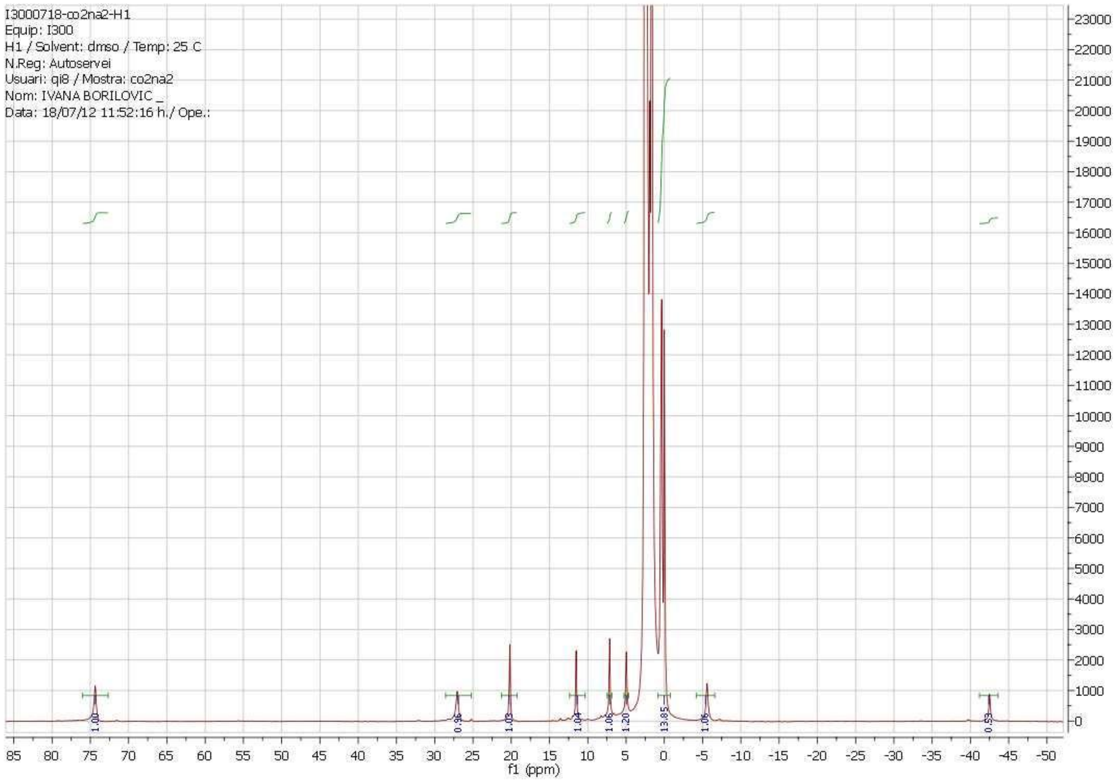
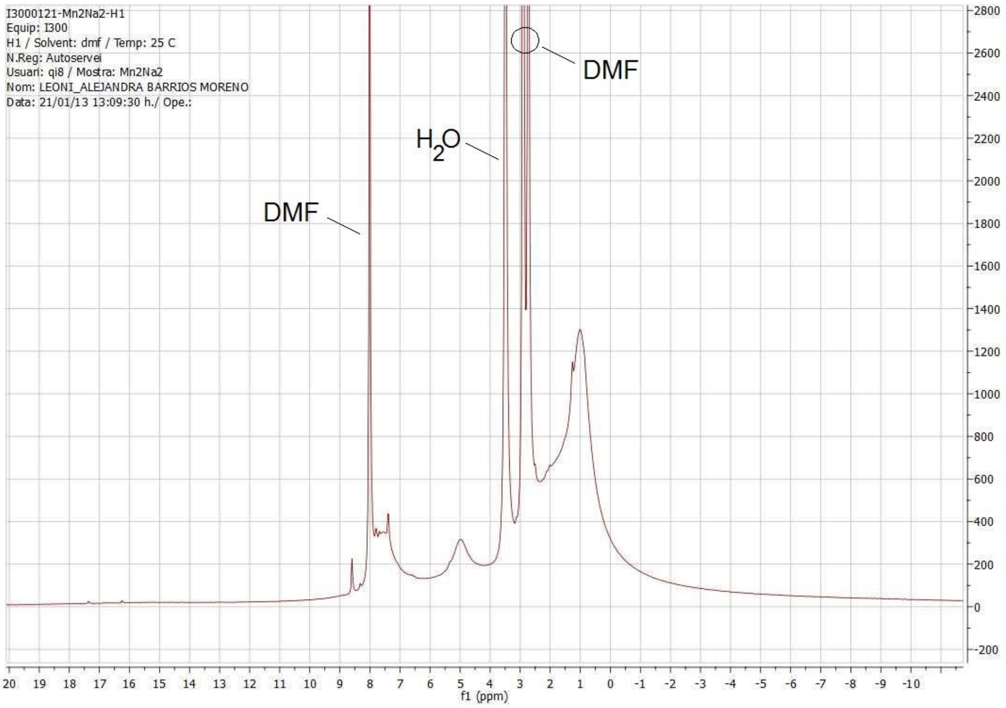


Figure S1. 300MHz ^{1}H NMR in *d*$_6$−DMSO of complex **2**, showing the correct integration of the peaks.



I3000121-Mn2Na2-H1
Equip: I300
H1 / Solvent: dmf / Temp: 25 C
N.Reg: Autoservei
Usuari: qi8 / Mostra: Mn2Na2
Nom: LEONI_ALEJANDRA BARRIOS MORENO
Data: 21/01/13 13:09:30 h./ Ope.:

Figure S2. 300MHz ^{1}H NMR in d_7−DMF of complex **1**, with the peaks labelled, and showing very broad signals from the paramagnetic species.

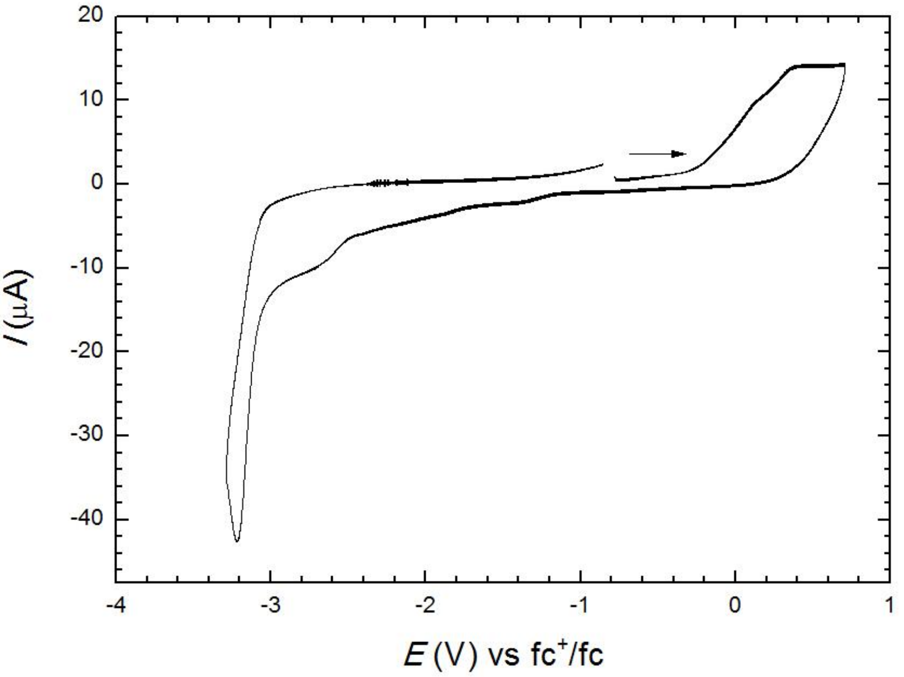


Figure S3. Cyclic voltammogram at 100 mV s^{-1} of $(NBu_4)_3[Mn_2Na_2(H_2L4)_3]$ (**1**) (c = $4{,}46 \bullet 10^{-4}$ M) in DMF on a glassy carbon working electrode, referenced versus the fc$^+$/fc couple and with $NBu^n{}_4PF_6$ (c = 0.1018 M) as a supporting electrolyte.

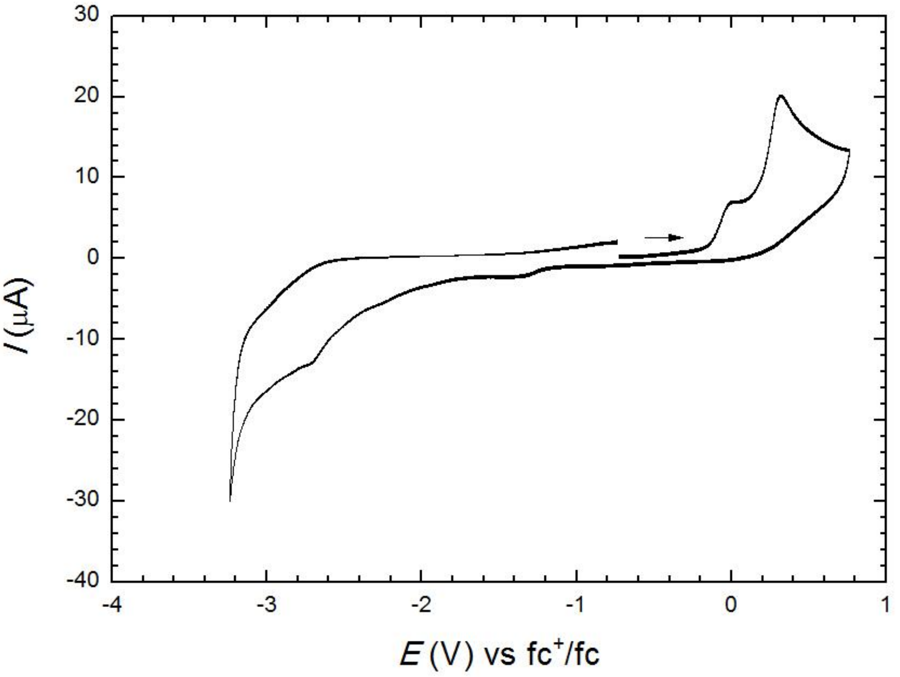


Figure S4. Cyclic voltammogram of $(NBu_4)_3[Co_2Na_2(H_2L4)_3]$ (**1**) in the same conditions as for complex **1** (Fig S3).

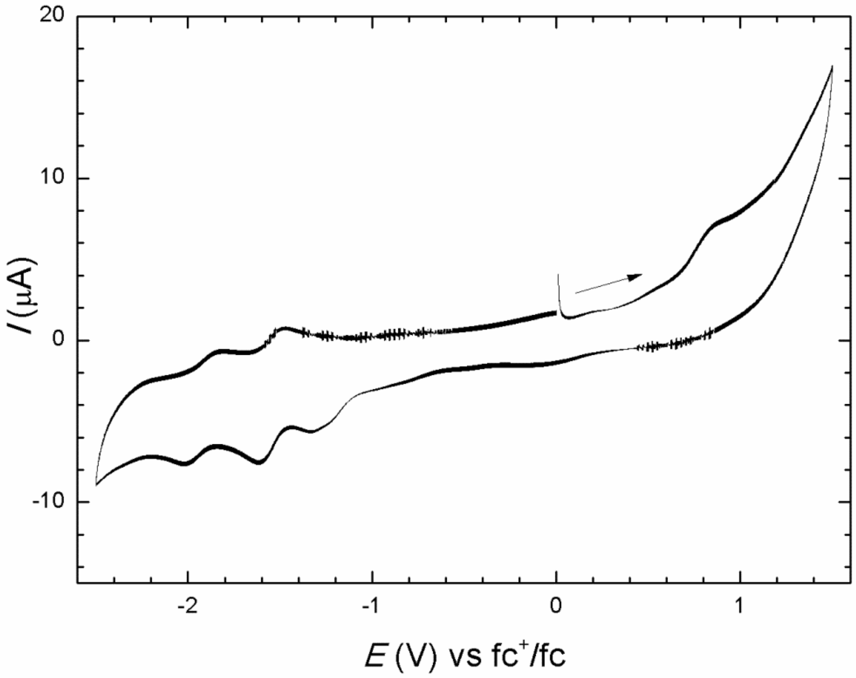


Figure S5. Cyclic voltammogram of H_5L4 in the same conditions as for complex **1** (Fig S3).