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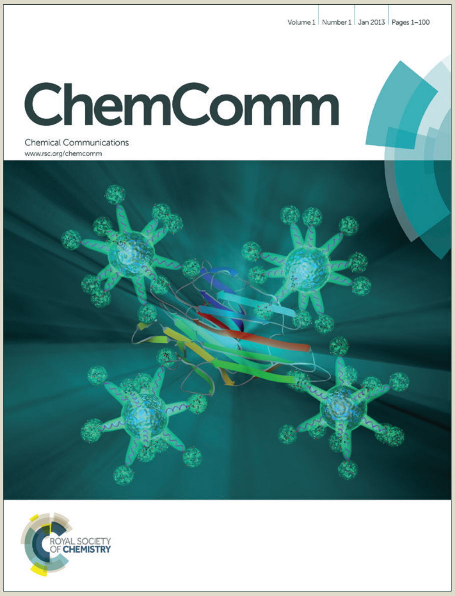

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Relatively strong intramolecular antiferromagnetic coupling in a neutral $Cr^{III}_2Nb^V_2$ heterobimetallic molecular square†

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A relatively large antiferromagnetic interaction between the two chromium(III) ions from the molecular square $[\{Cr(dmso)_3\}_2\{Nb(\mu\text{-}O)_2(C_2O_4)_2\}_2]$ (1) (J = -12.0 cm^{-1}) is mediated by the diamagnetic oxo-Nb(V)-oxo pathway, its nature and magnitude being substantiated by DFT type theoretical calculations.

Niobium is a second-row transition metal with five electrons in its outer valence shell which exhibits a rich redox chemistry through oxidation states ranging from –I to +V. It is used in electronic devices,[1] alloys and steel strengthener mainly for spaceships[2] and automobile industry[3] and more recently in catalysis.[4] Niobium-zirconium alloys have been incorporated in non-toxic, non-immunogenic dental amalgams and bone implants.[5] In a recent study by Carniato *et al.,*[6] the authors took advantage of the highly oxidizing power of Nb^V to decontaminate warfare agents such as the mustard gas. Also NbO-type Metal Organic Frameworks (MOFs) have shown an exceptional high methane adsorption capacity at room temperature under a maximum pressure of 65 bar.[7]

Restricting ourselves to the field of molecular magnetism, the most famous niobium-based building block is the octacyanidoniobate(IV) complex ($[Nb^{IV}(CN)_8]^{4-}$; Nb^{IV} is a $4d^1$ ion) used as a ligand toward fully solvated metal ions or metal complexes whose coordination sphere is unsaturated has provided a wide family of heterobimetallic magnetic systems.[8,9] In this respect, Nb^{IV}-based heterometallic assemblies with T_c as high as 210 K,[10] behaving as magnetic sponges,[11] exhibiting magnetization-induced second harmonic genentation,[12] coexistence of chirality and magnetic ordering[13] and light-induced spin crossover[14] have been reported. The preparative methods of these systems are conditioned by the light sensitivity of the solutions of the Nb^{IV} precursor,[15] a difficulty which is overcome by working in the dark.

Analogous species with oxalate ($[Nb^{IV}(C_2O_4)_4]^{4-}$) has been isolated as an ionic salt using univalent cations as counterions and their crystal structures determined by X-ray diffraction.[16] However, they are susceptible to oxidation and hydrolysis if longer exposed to the air. The corresponding diamagnetic complexes with Nb^V and oxalate have in common the presence of an oxo group and the seven coordination number, the general formula being $[Nb^VO(C_2O_4)_x(H_2O)_y]^{(2x-3)-}$ ($x = y = 2$ or $x = 3$ and $y = 0$).[17,18] Their use as ligands has opened a new gate in the oxalate chemistry of niobium with novel solid state architectures with potential applications as functional materials.[19]

Herein we report the synthesis, and crystal structure of the unprecedented molecular square $[\{Cr(dmso)_3\}2\{Nb(\mu\text{-}O)_2(C_2O_4)_2\}_2]$ (**1**) and the ionic salt $(NH_4)(Hdmphen)_2[NbO(C_2O_4)_3]$ (**2**) (dmphen = 2,9-dimethyl-1-10-phenanthroline) together with the variable-temperature magnetic study of **1.** A relatively large antiferromagnetic coupling between the Cr^{III} ions through the diamagnetic oxo-Nd^V-oxo pathway occurs in **1** which has been substantiated by DFT type calculations.

X-ray quality green plates (**1**) and colorless prisms (**2**) were obtained by slow diffusion of $[Cr(H_2O)_6](ClO_4)_3$ and $(NH_4)_3[NbO(C_2O_4)_3]\cdot 6H_2O$ in a dmso-MeOH mixed solvent in presence of dmphen (see experimental procedure in ESI). The structure of **1** consists of centrosymmetric neutral $Cr^{III}_2Nb^V_2$ molecular squares (Fig. 1) and free dmso molecules whereas that of **2** contains discrete $[NbO(C_2O_4)_3]^{3-}$ anions and NH_4^+ and $Hdmphen^+$ cations (Fig. 2).

Alternating *cis*-$[Nb(\mu\text{-}O)_2(ox)_2]^{3-}$ and $[Cr(dmso)_4]^{3+}$ units in the vertexes of a centrosymmetric square with an oxo group in the middle point of each edge occur in **1**. Surprisingly, the starting $[Nb^VO(ox)_3]^{3-}$ species turned into the *cis*-di(oxo)bis(oxalate)niobate(V) fragment, $[NbO_2(ox)_2]^{3-}$, by releasing one oxalate and taking an oxo group, the resulting species being unknown up to day. Each Nb^V ion is six-coordinate with two *cis*-positioned oxo groups and four oxygen atoms from two didentate oxalate ligands building a distorted octahedral environment. The short bite of the chelating oxalate ligands [O3-Nb1-O6 = 73.82(14) Å and O7-Nb1-O10 = 73.92(14) Å] together with the shortening of the Nb-O_{oxo} bond lengths [1.786(3) and 1.783(3) for Nb1-O1 and Nb1-O2, respectively] are the main factors for this distortion. Each chromium(III) ion is six-coordinate with two oxo groups in *cis* position and four dmso ligands building a distorted octahedral surrounding. The two Cr-O_{oxo} bond distances are shorter [1.912(3)

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† Electronic Supplementary Information (ESI) available: physical characterization data, computational details, Figures of the crystal packing (Figs. S1 and S2) and crystallographic refinement details for **1** and **2**. CCDC 1402553 (**1**) and 1402554 (**2**). For ESI and crystallographic data in CIF or other crystallographic electronic format see DOI: 10.1039/x0xx00000x

and 1.909(3) for Cr1-O1 and Cr1-O2^{i}, respectively] than the Cr-O$_{dmso}$ bonds [values in the range 1.960(4)-2.002(3) Å], as expected. The edges of the square are quasi linear [Nb-O-Cr = 173.0(2) and 170.9(2)^{o}] and the values of the Nb···Cr separation along them are 3.6851(9) and 3.6873(9) Å. The intramolecular Cr1···Cr1^{i} distance is 5.439(1) Å, a value much shorter than the shortest intermolecular one [11.43(5) Å for Cr1···Cr1^{ii}; (ii) = 1+*x*, *y*, *z*], the molecular squares being well isolated from each other (see Fig. S1)

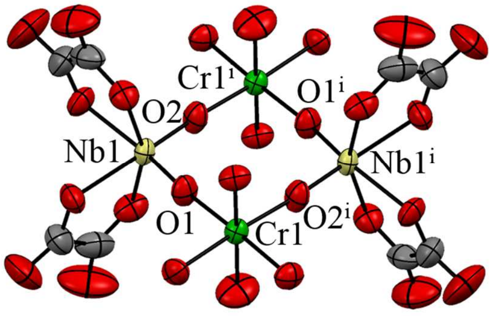

Fig. 1 Perspective view of the Cr$^{III}_2$Nb$^{V}_2$ molecular square in **1** showing the atom numbering of the metal ions and oxo groups. The molecules of crystallization and the methyl groups of the dmso ligands are omitted for clarity. Thermal parameters are drawn at the 50% probability level. Carbon, oxygen and sulphur atoms are represented in grey, red and yellow colours, respectively [Symmetry code: (i) = -*x*, -*y*, -*z*].

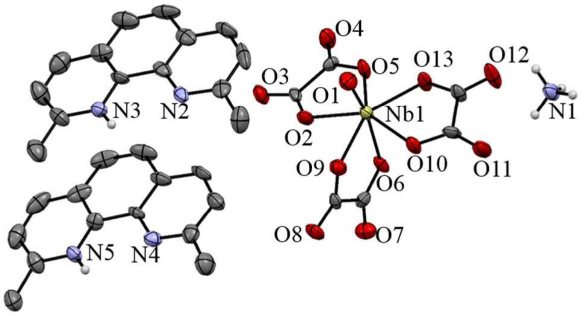

Fig. 2 Perspective view of the structure of **2** showing the atom numbering of the non-carbon atoms. All hydrogen atoms, except those of the N-H groups, were omitted for clarity. Thermal parameters of the non-hydrogen atom are drawn at the 50% probability level. Carbon, oxygen and nitrogen atoms are represented in grey, red and sky blue colours, respectively.

The conformation and the bond distances and angles of the discrete [NbO(C$_2$O$_4$)$_3$]$^{3-}$ anions present in **2** agree with those previously for this entity in the compounds (NH$_4$)$_3$[NbO(C$_2$O$_4$)$_3$] · H$_2$O,[18a] (Cs)$_3$[NbO(C$_2$O$_4$)$_3$] · 2H$_2$O[18b] and [M(bpy)$_3$][NbO(C$_2$O$_4$)$_3$]Cl · nH$_2$O (M = Fe, Co, Ni, Cu and Zn).[18c] The crystal packing of **2** shows the occurrence of a tree-dimensional supramolecular network where the [NbO(C$_2$O$_4$)$_3$]$^{3-}$ anions and the NH$_4^+$ and Hdmphen$^+$ cations are interlinked by electrostatic forces, hydrogen bonds and π-π type interactions (see Fig. S2).

The magnetic properties of **1** under the form of both χ_M and $\chi_M T$ against *T* plots [χ_M is the magnetic susceptibility per two Cr(III) ions] are shown in Figure 3. At 300 K, the $\chi_M T$ value is 3.65 cm^3 mol^{-1} K as expected for one uncoupled pair of Cr^{III} ions. The decrease of $\chi_M T$ from room temperature upon cooling down tending to vanish at very low temperatures together with the maximum of the magnetic susceptibility at 28 K unambiguously support the occurrence of a relatively strong antiferromagnetic interaction between the Cr^{III} ions. Keeping in mind the diamagnetic nature of the Nb^{V} ions and the good magnetic isolation of the neutral Cr$^{III}_2$Nb$^{V}_2$ molecular squares, the magnetic properties of **1** were analyzed through the spin Hamiltonian $\boldsymbol{H} = -J\boldsymbol{S}_{Cr1} \cdot \boldsymbol{S}_{Cr1i} + \beta H(g_{Cr1}\boldsymbol{S}_{Cr1} + g_{Cr1i}\boldsymbol{S}_{Cr1i})$, *J* being the exchange coupling parameter and $g_{Cr1} = g_{Cr1i} = g$ (average Landé factor). Least-squares best-fit parameters are: J = -12.0 cm^{-1}, *g* = 2.0 and *R* = 1.1 x 10^{-5} {*R* is the agreement factor defined as $\sum_i[(\chi_M)_i^{obs}-(\chi_M)_i^{calc}]^2/[(\chi_M)_i^{obs}]^2$}. The calculated curve matches well the experimental data in all the temperature range investigated. A comparison if this value with that obtained in the oxalate-bridged dichromium(III) complex (*J* = -6.2 cm^{-1} with a Cr···Cr separation of 5.313(4) Å , reveals for the first time the remarkable efficiency of the diamagnetic -O-Nb^{V}-O- pathway to mediate electronic effects between the paramagnetic Cr^{III} ions in **1**.

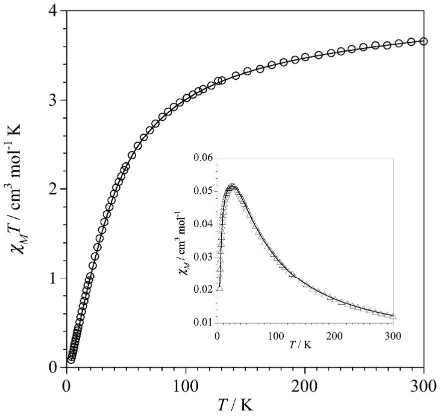

Fig. 3 $\chi_M T$ (o) and χ_M (Δ) *vs.* *T* plots for **1**. The solid line is the best least-squares fit to the experimental data using the parameters given in the text.

In order to substantiate the nature and magnitude of the magnetic coupling in **1**, we have carried out DFT type calculations on the real structure (see Computational Details in ESI). The computed spin density distribution for the square of **1** is shown in Figure 4. Most of the spin density is localized on the chromium(III) ions with weak polarization onto the oxo-Nb^{V}-oxo exchange pathway for the magnetic communication in this complex.

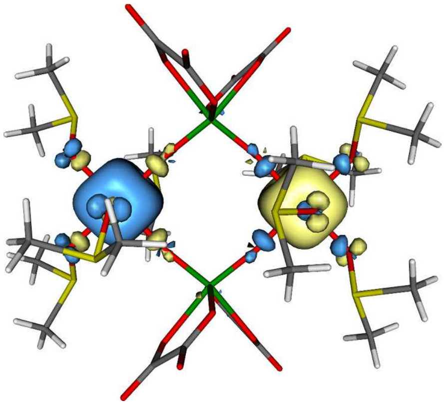

Fig. 4 Spin density distribution in the molecular square [Cr$^{III}_2$Nb$^{V}_2$] of **1**. Blue and yellow colors represent positive and negative isodensity surfaces with a cut-off value of 0.003 e bohr^{-3}.

The SOMOs (single occupied molecular orbitals) resulting from the calculations which are depicted in Figure 5, reveal small energy gaps (Δ) for the d(yz) and d(xz) pairs whereas a big Δ value is computed for the d(x^2-y^2) pair due to the better orbital overlap for this last couple. Given that the antiferromagnetic contribution to *J* is proportional to Δ^2,[21] this pair of SOMOs are the main contributors to the calculated value of *J* which is -12.9 cm^{-1}. The fact that this computed value is very close to that obtained by the fit of the magnetic data gives additional support to the efficiency of the triatomic oxo-Nb^V-oxo bridge as a new mediator of exchange interactions between paramagnetic metal ions.

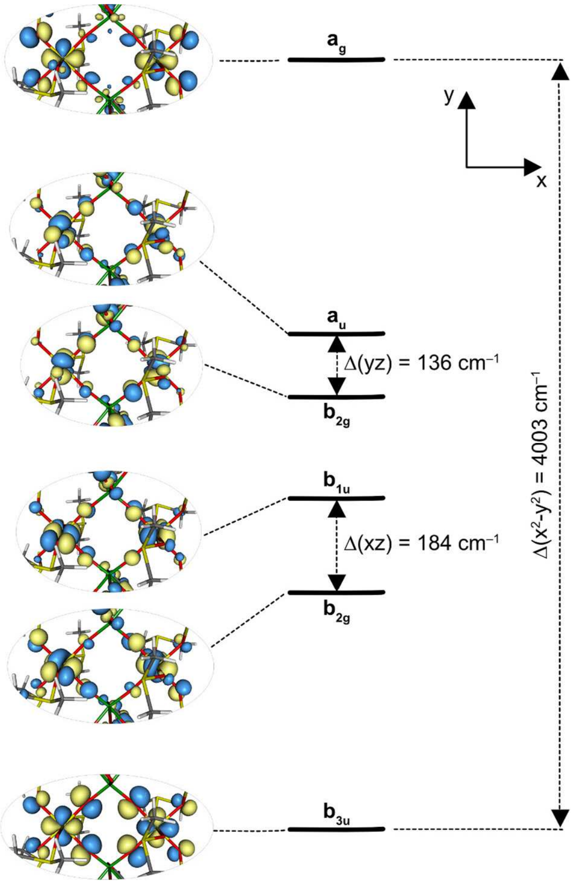

Fig. 5 Calculated SOMOs in the molecular square $[Cr^{III}_2Nb^V_2]$ of **1**. *Δ* is the energy gap between the symmetric and antisymmetric combination of the magnetic orbitals on the Cr^{III} ions and it is directly related to the antiferromagnetic contributions (see text).

In summary, we have reported the structure and magnetic properties of a new heterobimetallic $Cr^{III}_2Nb^V_2$ molecular square containing the unprecedented *cis*-dioxobis(oxalate)niobate(V) as ligand and demonstrated from experimental and theoretical points of view the remarkable ability of the diamagnetic –O-Nb^V-O- spacer to transmit relatively large magnetic interactions between the paramagnetic linked by it.

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