Electronic Supplementary Information

Relatively strong intramolecular antiferromagnetic coupling in a neutral Cr^{III}₂Nb^V₂ heterobimetallic molecular square

Willian X. C. Oliveira,^a Cynthia L. M. Pereira^a, Carlos B. Pinheiro,^b Joan Cano,^{c,d} Francesc Lloret,^c Miguel Julve^{c*}

- ^a Departamento de Química, Instituto de Ciências Exatas
 Universidade Federal de Minas Gerais
 Av. Antônio Carlos, 6627, Pampulha, BH, MG, 31270-901 (Brazil)
 E-mail: <u>cynthialopes@ufmg.br</u>
- ^b Departamento de Física, Instituto de Ciências Exatas
 Universidade Federal de Minas Gerais
 Av. Antônio Carlos, 6627, Pampulha, BH, MG, 31270-901 (Brazil)
- Instituto de Ciencia Molecular (ICMol)
 Paterna, Valencia, 46980 (Spain)
- ^d Fundació General de la Universitat de València (FGUV)
 Valencia (Spain)

Experimental

Materials

 $[Cr(H_2O)_6](ClO_4)_2$, 2,9-dimethyl-1,10-phenantroline (dmphen), methanol and dimethylsulfoxide were purchased from Sigma-Aldrich and used as received. The niobium salt $(NH_4)_3[NbO(ox)_3] \cdot 6H_2O$ was a gift from the CBMM company and it was also used without any further treatment.

Preparation of the Complexes

Synthesis of $[{Cr(dmso)_4}_2{NbO_2(ox)_2}]\cdot 2dmso$ (1) and $(NH_4)[Hdmphen]_2[NbO(ox)_3]$ (2). 10.0 mg (21.8 µmol) of Cr(ClO₄)₃·6H₂O was placed at the bottom of a 4.0 cm³ test tube with 0.50 cm³ of dmso. Then, the tube was slowly filled with 2.50 cm³ of a dmso-MeOH mixture (1:4 v/v) containing dmphen (25 mg, 120 μ mol). Finally, 10.0 mg (18.3 μ mol) of (NH₄)₃[NbO(ox)₃]·6H₂O dissolved in 0.50 cm³ of MeOH was layered on the top. The green plates of 1 were manually separated from the colorless prisms of 2, the two type of crystals being formed after ten days on standing at room temperature. Yield: 0.4 mg (2.74 µmol, 30 %) for 1 and 8.6 mg (10.6 μ mol, 58%) for **2**. X-ray absorption microanalysis for **1**: Cr:Nb:S molar ratio = 1:1:5. IR spectrum (KBr/cm⁻¹) for 1: 3015 [v(C-H)], 1710 and 1689 [v(C=O)], 1380 [v(CO₂⁻¹)], 995 [v(S=O)], 930 and 857 [v(Nb=O)], 507 [v(Cr-O)]. Elemental Analysis for 2 (exp. /calc.): C, 49.87/50.44; H, 2.57/3,74; N, 8.55/8.61%. IR spectrum (KBr/cm⁻¹) for 2: 3037 and 2933 [v(C-H)], 1708 and 1679 [v(C=O)], 1376 [v(CO₂-)], 801 [v(Nb=O)].

Physical Techniques

The infrared spectra were recorded on a Perkin-Elmer FTIR spectrophotometer using KBr pellets in the range 4000–400 cm⁻¹ with an average of 32 scans and 2 cm⁻¹ of spectral resolution. The magnetic susceptibility measurements were carried out on crushed single crystals of **1** in the temperature range 4.0–300 K with a Quantum Design SQUID magnetometer and using applied magnetic fields of 0.5 T ($50 < T \le 300$ K) and 250 G ($T \le 50$ K). Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants. Experimental susceptibilities were also corrected for the magnetization of the sample holder (a plastic bag).

Computational Details

All calculations were carried out from a broken symmetry approach to DFT methodology using the B3LYP functional as was implemented in Gaussian 09.¹⁻⁶ The experimental geometry of **1** was used in the theoretical calculations. Double- ζ and Los Alamos effective core potentials proposed by Hay and Wadt were used for the Nb atom.⁷⁻⁹ Ahlrichs' triple- and double- ζ basis set were used for the chromium atom and the rest of atoms, respectively.^{10,11} Electronic effects by surrounding molecules in the network were simulated by a polarizable continuum model with the parameters corresponding to the acetonitrile solvent.¹²

Crystal Data Collection and Refining

X-ray diffraction data collections on single crystals of 1 and 2 were performed on a Bruker-Saxi diffractometer using Mo- K_{α} radiation ($\lambda = 0.71073$ Å) – SCSIE, Universitad de Valencia. The measurements were performed at room temperature. Data integration and scaling of the reflections for 1 and 2 were carried out with the Crysalis suite of programs.¹³ Final unit cell parameters were based on the fitting of all reflections positions. Empirical absorption corrections were performed using the Crysalis suite of programs based on the chemical formula.¹³ The space group identification was done with XPREP.¹⁴ The structures of 1 and 2 were solved via direct methods using the SUPERFLIP¹⁵ program. The positions of all atoms could be unambiguously assigned on consecutive difference Fourier maps. Refinements were performed by using SHELXL¹⁴ based on F^2 through a full-matrix least-squares routine. All non-hydrogen atoms of 1 and 2 were refined with anisotropic atomic displacement parameters, except the sulfur (S4) and carbon atoms of one disordered coordinated dmso molecule in 1. All hydrogen atoms were located in difference maps and included as fixed contributions according to the riding model.¹⁶ For the organic moieties, C-H = 0.97 Å and $U_{iso}(H) = 1.5 U_{ea}(C)$ for methyl groups (1 and 2) C–H = 0.97 Å and $U_{iso}(H) = 1.2 U_{ea}(C/N)$ for aromatic carbon and protonated dmphen nitrogen atoms (2) and finally N–H = 0.90 Å and $U_{iso}(H) = 1.5$ $U_{eq}(N)$ for the ammonium group (2). A threefold split model for sulfur (S4) and carbon atoms with total occupancy constrained to 1.0(1) and isotropic displacement parameters were applied to treat the disorder of one of the coordinated dmso molecules. Ordinary

double split positions of the sulfur atom of the free dmso molecule (S5) was applied on the refinement of the structure of **1**. The crystal data and details of the structure refinement of **1** and **2** are listed in Table S1 whereas selected bond lengths and angles are given in Tables S2 (**1**) and S3 (**2**).

	1	2
Formula	$C_{28}H_{60}Cr_2Nb_2O_{30}S_{10}$	C ₃₄ H ₃₀ N ₅ Nb O ₁₃
Formula weight	1487.18	809.54
Crystal size (mm)	0.16×0.15×0.08	0.22× 0.16×0.12
Crystal System	Triclinic	Triclinic
Space group	PĪ	PĪ
<i>T</i> (K)	293(2)	293(2)
a (Å)	11.4285(7)	8.9340(12)
<i>b</i> (Å)	12.1741(9)	11.3774(10)
<i>c</i> (Å)	12.1850(10)	17.883(2)
α (Å)	98.122(6)	78.587(9)
β (Å)	116.838(7)	78.363(11)
γ (Å)	94.962(5)	70.115(10)
$V(Å^3)$	1475.7(2)	1657.6(4)
Ζ	1	2
D_{calcd} (g cm ⁻³)	1.673	1.622
μ (mm ⁻¹)	1.171	0.442
<i>F</i> (000)	758	828
$R(F_{o}^{2})[I > 2\sigma(I)]$	0.0538	0.0447
$R_{\rm w} (F_{\rm o}^{2}) [I > 2\sigma(I)]$	0.1532	0.0985

Table S1. Crystal Data Details of the Structure Determination for 1 and 2

Crystallographic data for the structures of **1** and **2** were deposited with the Cambridge Crystallographic Data Centre with reference numbers CCDC 1402553 and CCDC 1402554, respectively.

Niobium enviroment		Chromium enviroment		
Nb1—O2	1.783 (3)	Cr1—O2	1.909 (3)	
Nb1—O1	1.786 (3)	Cr1-O1 ⁱ	1.912 (3)	
Nb1—O7	2.047 (3)	Cr1—O14	1.960 (4)	
Nb1—O3	2.051 (4)	Cr1—O12	1.978 (3)	
Nb1-010	2.167 (3)	Cr1—013	1.992 (3)	

Table S2 – Selected bond length (Å) and angles (°) for $\mathbf{1}^*$

Nb1—O6	2.180 (3)	Cr1-011	2.002 (3)	
Nb1—Nb1 ⁱ	4.957 (6)	Cr1—Cr1 ⁱ	5.439 (1)	
O2—Nb1—O1	102.77 (13)	O2-Cr-O1 ⁱ	91.99 (13)	
O3—Nb1—O6	73.82 (14)	Intermolecular distance		
O7—Nb1—O10	73.92 (14)	Square-Square&	11.43 (5)	
Oxalate important parameters				
Oxalate 1 [#] b	oond lengths	Oxalate 2 [#] t	oond lengths	
Oxalate 1 [#] t O3—C1	oond lengths 1.287 (7)	Oxalate 2 [#] t O7—C3	oond lengths 1.317 (6)	
Oxalate 1 [#] t O3—C1 O4—C1	oond lengths 1.287 (7) 1.212 (7)	Oxalate 2 [#] b O7—C3 O8—C3	oond lengths 1.317 (6) 1.209 (7)	
Oxalate 1 [#] t O3C1 O4C1 O5C2	00000 lengths 1.287 (7) 1.212 (7) 1.208 (6)	Oxalate 2 [#] t O7—C3 O8—C3 O9—C4	bond lengths 1.317 (6) 1.209 (7) 1.217 (7)	
Oxalate 1 [#] t O3C1 O4C1 O5C2 O6C2	00000 lengths 1.287 (7) 1.212 (7) 1.208 (6) 1.272 (6)	Oxalate 2 [#] t O7—C3 O8—C3 O9—C4 O10—C4	bond lengths 1.317 (6) 1.209 (7) 1.217 (7) 1.278 (6)	

*Symmetry codes: (i) = 1-x, -y, 1-z; (ii) = -1+x, y, z. *Distance between the centroids of adjacent Cr^{III}₂Nb^V₂ molecular squares. #Oxalate 1 (Ox1) and Oxalate 2 (Ox2) are the mean planes defined by the O3C1O4O5C2O6 and O7C3O8O9C4O10 set of atoms, respectively.

(a)





Figure S1 – (a) Asymmetric unit of **1** showing the atom numbering of the nonhydrogen atoms except the carbon atoms of the dmso molecules. Free dmso molecules and the hydrogen atoms were omitted for clarity. (b) Projection of the structure of **1** in the crystallographic *bc* plane showing the separation of the $Cr_2^{III}Nb_2^V$ molecular squares by the non-coordinated dmso molecules along the crystallographic *b* axis. Only the oxygen atom of the coordinated dmso molecules are shown for clarity. The same colour code was used for both images.

Niobium bond Lenghts / Å		Niobium-Oxygen important angles / °			
Nb1—O1	1.713 (2	2)	O1—Nb1—O2	96.31 (10)	
Nb1—O6	2.087 (2	2)	O1—Nb1—O5	96.53 (10)	
Nb1—O13	2.1098	(19)	01—Nb1—06	94.42 (10)	
Nb1—O2	2.118 (2	2)	O1—Nb1—O9	168.59 (9)	
Nb1—O5	2.143 (2	2)	O1-Nb1-O10	93.99 (10)	
Nb1—O10	2.156 (2	2)	O1—Nb1—O13	99.35 (10)	
Nb1—O9	2.239 (2	2)	O2—Nb1—O5	71.90 (8)	
Intermolecular d	listance / Å		O6—Nb1—O9	74.35 (8)	
Nb1—Nb1 ^{iv}	8.403 (5	j)	O10—Nb1—O13	72.14 (7)	
Oxalate important parameters					
Oxalate 1 ^{&} bond	lengths / Å	Oxalate 2 ^{&} bo	nd lengths / Å	Oxalate 3 ^{&} bond	lengths / Å
O2—C1	1.294 (4)	O6—C3	1.284 (4)	O10—C5	1.296 (3)

Table S3 – Selected bond length and angles for 2^*

O3—C1 1	.211 (4)	O7—C3	1.217 (3)	011—C5	1.220 (3)
O4—C2 1	.214 (4)	O8—C4	1.225 (4)	O12—C6	1.210 (3)
O5—C2 1	.283 (4)	O9—C4	1.295 (3)	O13—C6	1.289 (3)
Diedral Angle Ox1	—Ox2	87.25(3)°			
Diedral Angle Ox1	—Ox3	13.51(2)°			
Diedral Angle Ox2	e—Ox3	79.83(3)°			
		Hydrogen Bor	d Parameters#		
D—H···A	D—H / Å	. H·…A /	Å D····	4 / Å	<i>D</i> —Н…А / ∘
N5—H5 <i>C</i> ⋯O3	0.91	2.16	2.795 (3)	127	
N5—H5 <i>C</i> ⋯O4	0.91	2.09	2.912 (3)	151	
N2— $H2$ ···O7 ⁱ	0.86	2.56	2.826 (3)	99	
$N1 - H1 \cdots O8^i$	0.86	2.40	3.256 (3)	173	
N2— $H2$ ···O8 ⁱ	0.86	2.16	2.990 (3)	163	
N3—H3…O9 ⁱⁱ	0.86	2.64	3.418 (3)	151	
N4—H4…O9 ⁱⁱ	0.86	2.18	2.898 (3)	141	
N5—H5 <i>D</i> ···O11 ⁱⁱⁱ	0.91	2.12	2.954 (3)	152	
N5—H5 <i>D</i> ···O12 ⁱⁱⁱ	0.91	2.17	2.770 (3)	123	
N5—H5 <i>C</i> ⋯O3	0.91	2.16	2.795 (3)	127	
N5—H5 <i>C</i> ⋯O4	0.91	2.09	2.912 (3)	151	
N5—H5 <i>B</i> ⋯O1 ^{iv}	0.91	2.64	3.221 (3)	122	
N5—H5 A ···O2 ^{iv}	0.91	2.30	3.093 (3)	145	
N5—H5A…O13 ^{iv}	0.91	2.48	3.246 (3)	143	

*Symmetry codes: (i) = -x+1, -y+1; -z+1; (ii) = x, y+1, z; (iii) = x-1, y+1, z; (iv) = -x+1, -y+1, -z. &Oxalate 1 (Ox1), Oxalate 2 (Ox2) and Oxalate 3 (Ox3) are the mean planes defined by the O2C1O3O4C2O5, O6C3O7O8C4O9 and O10C5O11O12C6O13 set of atoms, rerspectively. #D = Donor and A = acceptor.

(a)





Figure S2 – Packing of **2** featuring the main hydrogen bonds and π - π stacking interactions (both in dotted lines): (a) the ammonium cation give rise to a supramolecular linear chain by interacting with the oxalate groups of the [NbO(ox)₃]³-units; (b) these chains are interconnected by π - π type stacking interactions as well as by hydrogen bonds of the ammonium cation and the oxygen atom from Nb=O group to afford a supramolecular three-dimensional network. Colour code follows that used in Figure S1 and the nitrogen atoms are drawn as pale blue ellipsoids.

References

- 1 Frisch, M. J. et al., Gaussian 09, (Rev. D01); Gaussian, Inc., Wallingford, CT, 2009.
- 2 Becke, A. D. J. Chem. Phys. 1993, 98, 5648.
- 3 Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. J. Am. Chem. Soc. 1997, 119, 1297-1303.
- 4 Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P., J. Comp. Chem. 1999, 20, 1391.
- 5 Ruiz, E.; Rodríguez-Fortea, A.; Cano, J.; Alvarez, S.; Alemany, P., *J. Comp. Chem.* 2003, 24, 982.
- 6 Ruiz, E.; Alvarez, S.; Cano, J.; Polo, V. J. Chem. Phys. 2005, 123, 164110.
- 7 Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 270-283.
- 8 Wadt, W. R.; Hay, P. J. J. Chem. Phys. 1985, 82, 284-298.
- 9 Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299-310.
- 10 Schafer, A.; Horn, H.; Ahlrichs, R. J. Chem. Phys. 1992, 97, 2571-2577.
- 11 Schafer, A.; Huber, C.; Ahlrichs, R. J. Chem. Phys. 1994, 100, 5829-5835.
- 12 Tomasi, J.; Mennucci, B.; Cammi, R. Chem. Rev. 2005, 105, 2999-3093.
- 13 Xcalibur CCD system, CrysAlisPro Software system, version 1.171.35.15 (Agilent Technologies UK Ltd, Oxford 2011).
- 14 G. M. Sheldrick, Acta Crystallogr., 2008, A64, 112.

- 15 L. Palatinusz, G. Chapuis, SUPERFLIP a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J. Appl. Cryst.*, 2007, **40**, 786.
- 16 C. K. Johnson, ORTEP, Crystallographic Computing, edited by F. R. Ahmed, pp 217-219, Copenhagen, Denmark.