Three-dimensional bimetallic octacyanidometalates
\[ \text{[M}^\text{IV}\{\text{(µ-CN)}_4\text{Mn}^\text{II}(\text{H}_2\text{O})_2\}\_2\cdot 4\text{H}_2\text{O}]_n (M = \text{Nb, Mo, W}) \]:
Synthesis, single-crystal X-ray diffraction and magnetism

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Abstract

We report the synthesis, the single-crystal X-ray crystallographic structures and the magnetic properties of three new isostructural cyanido-bridged networks: \[ \text{[M}^\text{IV}\{\text{(µ-CN)}_4\text{Mn}^\text{II}(\text{H}_2\text{O})_2\}\_2\cdot 4\text{H}_2\text{O}]_n (M = \text{Nb}^\text{IV} (1), \text{Mo}^\text{IV} (2), \text{W}^\text{IV} (3)) \]. For compound 1, the magnetic properties reveal a ferrimagnetic phase below 50 K. In contrast, compounds 2 and 3 show a paramagnetic behaviour with no magnetic ordering down to 2 K. The only electronic difference between the two kinds of compounds is the presence of two paired electrons on \text{Mo}^\text{IV} (2) and \text{W}^\text{IV} (3) (d\textsuperscript{5} electronic configuration, \( S = 0 \)) with no possible exchange interactions with \text{Mn}^\text{II} ions (d\textsuperscript{5} electronic configuration, \( S = 5/2 \)) and one unpaired electron on \text{Nb}^\text{IV} (1) (d\textsuperscript{1}, \( S = 1/2 \)) which allows Nb\textsuperscript{IV}–Mn\textsuperscript{II} antiferromagnetic exchange interactions and the onset of a three-dimensional magnetic ordering under Curie temperature. These three compounds demonstrate how one unpaired electron, well located, can dramatically change the magnetic behaviour of isostructural octacyanido-based three-dimensional networks.

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Résumé

Nous présentons la synthèse et les propriétés structurelles et magnétiques de trois nouveaux composés tridimensionnels isostucturaux, synthétisés à partir des précurseurs octacyanométabalates \([M^{IV}(CN)_8]^{-2}\); \([M^{IV}(\mu-CN)_2Mn^II(H_2O)_2]_2\cdot4H_2O\], \([M^{IV} = Nb^{IV} (1), Mo^{IV} (2), W^{IV} (3)]\). Pour le composé 1, les propriétés magnétiques montrent l’existence d’une phase ferromagnétique en dessous de 50 K. Par contre, les propriétés magnétiques de 2 et 3 correspondent à celles de deux ions MnII magnétiquement isolés. La seule différence électronique dans les deux types des composés est la présence de deux électrons appariés dans les ions MoIV (2) et WIV (3) (configuration électronique d5, S = 0) ce qui rend impossible une interaction d’échange avec le spin des ions MnII voisins (configuration électronique d5, S = 5/2) et d’un électron célibataire dans l’ion NbIV (1) (d1, S = 1/2) qui donne naissance à des interactions d’échange antiferromagnétiques NbIV–MnII et à l’apparition d’un ordre magnétique tridimensionnel sous la température de Curie. Ces trois composés montrent comment un électron célibataire, stratégiquement situé, peut changer de façon dramatique les propriétés magnétiques des composés par ailleurs isostructuraux.

Keywords: Molecule-based magnets; Octacyanidometalates; Magnetic exchange interaction; Cyanido bridge; Crystal structures; Unpaired electrons

Mots-clés : Aimants à précurseurs moléculaires ; Octacyanométabalates ; Interaction d’échange magnétique ; Pont cyanure ; Structure cristalline ; Électrons célibataires

1. Introduction

The coordination chemistry of cyanide ligands with transition metal ions has been studied extensively for many years [1]. Spectacular results were achieved in the field of molecular magnetism [2] and photo-magnetism [3]. Cyanide chemistry is particularly attractive since the ambivalent ligand builds stable and inert cyanometalate complexes \([M(CN)_6]^{3-}\); then used as molecular building blocks for the preparation of bimetallic molecules and networks, when combined with metallic complexes M’L. The charge of the precursors and the nature of the ligand L determine the stoichiometry and tune the molecular and crystallographic structures of the resulting compounds. We focus here on octacyanometalates [4] \([M(CN)_8]^{n-}\) and on their magnetic properties, that our groups explore for some years. We omit the exciting photomagnetic properties (for recent works cf. Ref. [5] and references quoted therein). In the field of molecular magnetism, the electronic structure of the octacyanometalate is of the utmost importance: the systems built from MoIV and WIV (d2 electronic configuration, spin zero), present no interaction with the magnetic neighbours; they behave as simple paramagnets, whatever their dimensionality may be [6]. Instead, when combining paramagnetic \([M^{IV/IV}(CN)_8]^{4-}\)– precursors (MIV = Nb; MIV = MoV, WIV, d1 electronic configuration, spin 1/2) [7,8] with MII divalent transition metal ions, a wealth of systems are found ranging from polynuclear clusters [7a–d], including high spin ground state MII\([M^{IV}(CN)_8]_{6-8}\) [7e–g] to two- and three-dimensional magnets [7h–j]. Symmetry and topology determine the interaction between paramagnetic nearest neighbours with localized electrons [1b,7f]: even if the crystallographic structures are often complex and if the analysis is not easy [7f], overlap between singly occupied molecular orbitals leads to an antiferromagnetic interaction whereas orthogonality leads to ferromagnetic exchange.

We would like to demonstrate that one unpaired electron, well located, can dramatically change the magnetic behaviour of octacyanido-based networks presenting isostructural three-dimensional structures. First, one of the condition to get isostructural systems is to choose precursors \([M^{IV}(CN)_8]^{n-}\) having the same charge n–. In polar solvents, neutral entities precipitate and we can expect that tetravalent niobium, molybdenum and tungsten octacyanides \([M^{IV}(CN)_8]^{4-}\)– combined with labile hexaaquamanganese(II) ions (d5 electronic configuration, spin 5/2) can give rise to insoluble neutral MIVMnII networks. Second, we need to choose precursors \([M^{IV}(CN)_8]^{1-}\) with different MIV electronic structures. Indeed, the octacyanidoniobiate \([Nb^{IV}(CN)_8]^{4-}\) (NbIV, d1 electronic configuration, spin 1/2) [8] is a paramagnetic complex, whereas the analogous precursors \([M^{IV}(CN)_8]^{4-}\) (MIV = MoIV, WIV, d2 electronic configuration, spin zero) are diamagnetic. Then, it can be foreseen that in NbIVMnII, the wave function of the unpaired d electron of the niobium will overlap with the ones of the five d electrons of the MnII ion so that antiferromagnetic exchange interactions between these spin carriers appear, leading to an NbIVMnII ferrimagnet. Meanwhile, MoIVMnII and WIVMnII are foreseen to be simple paramagnetic solids.
2. Results and discussion

2.1. Crystal structures of \([M^\text{IV}][(\mu-CN)_2Mn^\text{II}(\text{H}_2\text{O})_2]Z.4H_2\text{O}]_n\) (\(M^\text{IV} = \text{Nb}^\text{IV} (1); \text{Mo}^\text{IV} (2)\) and \(W^\text{IV} (3)\))

The three bimetallic, three-dimensional networks 1–3 are isostructural and crystallize in the tetragonal space group \(I4/m\). Crystallographic data and selected bond distances and angles for 1–3 are given in Tables 1 and 2, respectively. The \(M^\text{IV}\) ions and \(Mn^\text{II}\) ions are alternately linked through \(\mu\)-cyanido ligands in a 1:2 ratio. The \(Nb^\text{IV}\) and \(Mn^\text{II}\) coordination spheres of 1 are shown as ORTEP drawing in Fig. 1. The [001] projection of the crystal structure of 1 is shown in Fig. 2. The \(M^\text{IV}\) ion is surrounded by eight carbon atoms from \(\mu\)-cyanido ligands in approximately square antiprismatic coordination. A fourfold rotation axis is passing through the \(M^\text{IV}\) center. The coordination around the \(Mn^\text{II}\) ion is a slightly distorted octahedron: four nitrogen atoms from \(\mu\)-cyanido ligands bind in equatorial positions whereas the axial positions are occupied by oxygen atoms from two water molecules. A mirror plane is passing through the \(Mn^\text{II}\) ion and the two oxygen atoms. The average bond distances (in \(Å\), (1)/(2)/(3)) \(Mn–N\) (2.222/2.203/2.22) and \(Mn–O\) (2.186/2.16/2.20) are similar in the three compounds. Similar conclusions can be drawn for \(C–N\) distances (in \(Å\), (1)/(2)/(3), 1.137/1.13/1.14) in \([M^\text{IV}(\text{CN})_8]\). The only significant difference between 1 and 3 is related to the \(M–C\) bond distances (in \(Å\)), Nb–C (2.248), Mo–C (2.157), W–C (2.17). The Nb–C distances are slightly longer than those of Mo–C or W–C. Such trend was previously observed [7d–e]. The bond angles M–C1–N1 (in \(°\), (1)/(2)/(3), 176.1/176.5/175.5) and M–C2–N2 (177.1/176.8/179.1) deviate only slightly from linearity, whereas the bond angles Mn–N1–C1 (166.6/166.2/164.6) and Mn–N2–C2 (154.1/155.0/153.1) are much less than 180°, as found in other \(\mu\)-cyanido-bridged compounds [3–6]. The shortest distance between the \(M^\text{IV}\) and \(Mn^\text{II}\) ions across the \(\mu\)-cyanido bridge is 5.57 \(Å\) in 1, 5.49 \(Å\) in 2 and 5.51 \(Å\) in 3. These distances and angles are similar to those found in other \([M^\text{IV}(\text{CN})_8]\)/\(Mn^\text{II}\) compounds [5,6]. We would like to point out that our crystallographic results are a very clean and simple demonstration of the structural trends usually observed in the periodic table: (i) contraction of the atomic radii when increasing \(Z\) in the same line [from Nb to Mo, in \(Å\): Nb–C (2.248), Mo–C (2.157)] thanks to the increase of the effective atomic number \(Z_{\text{eff}}\) (due to a reduced screening of the valence electrons of the same valence shell); (ii) moderate increase of the atomic radii in the same column when going to 4d to 5d elements [from Mo to W, in \(Å\): Mo–C (2.157), W–C (2.17)] because of the “lanthanide contraction” due to the filling of the f orbitals before the 5d ones. These data are peculiarly reliable since for the three elements (Nb, Mo, W), the oxidation state (IV), the coordination number (8) and the symmetry of the coordination sphere (square antiprism) are exactly the same and make easy the comparison.

Table 1
Summary of crystal, data collection and refinement details for 1, 2 and 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>NbMn_2C_8N_8O_8H_16</td>
<td>MoMn_2C_8N_8O_8H_16</td>
<td>WMn_2C_8N_8O_8H_16</td>
</tr>
<tr>
<td>Molecular weight</td>
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<td>558.1</td>
<td>646.0</td>
</tr>
<tr>
<td>Crystallographic system</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>(I4/m)</td>
<td>(I4/m)</td>
<td>(I4/m)</td>
</tr>
<tr>
<td>(a, Å)</td>
<td>12.080(2)</td>
<td>11.894(5)</td>
<td>11.903(5)</td>
</tr>
<tr>
<td>(b, Å)</td>
<td>12.080(2)</td>
<td>11.894(5)</td>
<td>11.903(5)</td>
</tr>
<tr>
<td>(c, Å)</td>
<td>13.375(4)</td>
<td>13.236(3)</td>
<td>13.235(9)</td>
</tr>
<tr>
<td>(α, °)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(β, °)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(γ, °)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(V, Å^3)</td>
<td>1951.6(8)</td>
<td>1873.1(1)</td>
<td>1875.2(2)</td>
</tr>
<tr>
<td>(Z)</td>
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<td>4</td>
<td>4</td>
</tr>
<tr>
<td>(ρ, \text{g cm}^{-3})</td>
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<td>1.98</td>
<td>2.288</td>
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<td>(μ, \text{mm}^{-1})</td>
<td>18.3</td>
<td>19.7</td>
<td>7.58</td>
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<tr>
<td>Temperature, (K)</td>
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<td>298</td>
<td>298</td>
</tr>
<tr>
<td>Color, habit</td>
<td>Red, box</td>
<td>Yellow, box</td>
<td>Yellow-orange, box</td>
</tr>
<tr>
<td>Crystallographic size, (\text{mm}^3)</td>
<td>0.2 (\times) 0.2 (\times) 0.4</td>
<td>0.4 (\times) 0.4 (\times) 0.35</td>
<td>0.2 (\times) 0.2 (\times) 0.4</td>
</tr>
<tr>
<td>No. of reflections/unique</td>
<td>1860/902</td>
<td>1935/1183</td>
<td>1988/902</td>
</tr>
<tr>
<td>Final (R1, wR2)</td>
<td>0.0516, 0.050</td>
<td>0.081, 0.062</td>
<td>0.0564, 0.0487</td>
</tr>
</tbody>
</table>
magnetization data demonstrate a three-dimensional ferrimagnetic ordering in 1.

Instead, compounds 2 and 3 present no magnetic order. The magnetization of 2, in Fig. 4, in contrast to the high zero-field susceptibility shown by compound 1, shows the expected behaviour for practically uncoupled Mn\textsuperscript{II} ions, approaching 9.7 Bohr magnetons per formula unit, at 50 K, close to the expected value of 10 (g = 2). Furthermore, the variable-temperature magnetic susceptibility data for 2–3 are very similar and consistent with two uncoupled Mn\textsuperscript{II} ions as shown in Fig. 5. At T > 50 K, χ\textsubscript{MT} is constant with 8.8 cm\textsuperscript{3} K mol\textsuperscript{-1} value, close to the χ\textsubscript{MT} value of 8.75 cm\textsuperscript{3} K mol\textsuperscript{-1} calculated for two uncoupled Mn\textsuperscript{II} (S = 5/2, g = 2). Below 50 K, the χ\textsubscript{MT} decrease points out the existence of a weak antiferromagnetic exchange interactions between next nearest Mn\textsuperscript{II} neighbours. The Mn\textsuperscript{II}–NC–M–CN–Mn\textsuperscript{II} pathway is rather long since the Mn–M–Mn distances are around 10.9 Å but the overlap between Mn\textsuperscript{II} magnetic orbitals is not strictly zero.

The antiferromagnetic interaction Nb\textsuperscript{IV}–Mn\textsuperscript{II} is simply explained by a “trough-bond” interaction, i.e. the overlap between the magnetic orbital centered on the 4dz\textsuperscript{2} orbital of niobium and some of the 3d orbitals of manganese\cite{1b,7f}. The magnetic orbital (singly occupied molecular orbital) centered on the dz\textsuperscript{2} orbital of Nb(IV) is partially delocalized on the carbon and nitrogen (π symmetry) of the cyanide (Scheme 1a).
Among the five magnetic orbitals centered on the d orbitals of manganese, at least one of them (xz for example, t2g type) is also delocalized on the nitrogen and the carbon of the cyanide (with the same \( \pi \) symmetry) (Scheme 1a). These two basis orbitals overlap to give two molecular orbitals in the complex Nb–Mn. For two electrons, the Kahn’s model

\[
J = 2k + 4\beta S,
\]

where \( J \) is the coupling constant, energy difference between the singlet and the triplet, \( k \) is the exchange integral (>0),

Fig. 2. [001] Projection of the crystal structure of 1. The H atoms and the water molecules of crystallization are omitted for clarity.

Fig. 3. Thermal dependence of the magnetization (M vs T) for a polycrystalline sample of 1: FCM, cooling the sample with a 30 Oe applied magnetic field (•), ZFCM, cooling in zero field and warming in a 30 Oe applied field, (▲), and RM (■).

Fig. 4. Field dependence of the magnetization, \( M/N_A\beta \), at 2 K for polycrystalline samples of 1 (■) and 2 (○) (\( N_A \) is the Avogadro’s constant and \( \beta \) the electron Bohr magneton).
β is the resonance integral (<0), and S is the overlap integral [9] allows to foresee an antiferromagnetic interaction \((2k << |4βS|)\). Furthermore, for two metals located at \(\approx 5.5\) Å the ferromagnetic terms arising from the orthogonality of the \(dz^2\) niobium orbital with some of the manganese orbitals are weak and can be neglected.

The antiferromagnetic coupling between nearest neighbour spins with different values \((\text{Nb}^{IV}, S = 1/2; \text{Mn}^{II}, S = 5/2)\) leads then to ferrimagnetism (\(\downarrow \uparrow \)) and to the observed long range ferrimagnetic order.

3. Experimental section

3.1. Materials

All solid reactants were reagent grade, purchased from Acros or Aldrich and used as-received. Absolute methanol was obtained over magnesium before use.

3.2. Syntheses

The precursors \(\text{K}_4[\text{M(CN)}_8]\cdot2\text{H}_2\text{O} (\text{M} = \text{Mo}, \text{W})\) were made according to previously published procedures [10]. The precursor \(\text{K}_4[\text{Nb(CN)}_8]\cdot2\text{H}_2\text{O}\) was prepared using a procedure slightly modified compared to the literature [11]. In 25 mL of methanol was dissolved 20 g of \(\text{NbCl}_5\) under inert argon atmosphere using Schlenk technique. After the vigorous \(\text{HCl}\) evolution stopped, the light-yellow solution was diluted with an additional 50 mL of methanol. The resulting solution was electrochemically reduced on carbon electrodes for 24 h at a constant voltage of 35 V. After reduction, the green-brown solution was slowly added to a solution of 100 g \(\text{KCN}\) dissolved in 150 mL \(\text{H}_2\text{O}\), cooled in an ice/\(\text{NaCl}\) bath. The mixture was stirred for 1 h under cooling and for additional 24 h at ambient temperature. Brick red \(\text{K}_5[\text{Nb}^{III}(\text{CN})_8]\) precipitated by this time. After centrifugation, \(\text{K}_5[\text{Nb}^{III}(\text{CN})_8]\) was added under stirring to 100 mL of \(\text{H}_2\text{O}\) and then 15 mL of a 10% aqueous solution of hydrogen peroxide were slowly added. Yellow \(\text{K}_4[\text{Nb}^{IV}(\text{CN})_8]\cdot2\text{H}_2\text{O}\) precipitated by addition of methanol. The product was recrystallized from water/methanol. Yield \(\sim 25\%\).

\([\text{Nb}^{IV}\{\text{\(\mu\)}\cdot\text{CN}\}_2\text{Mn}^{II}(\text{H}_2\text{O})_2]_2\cdot4\text{H}_2\text{O}\]_n (1) was prepared by the addition, in the dark, of 0.4 mmol (197.2 mg) of \(\text{K}_4[\text{Nb(CN)}_8]\cdot2\text{H}_2\text{O}\) in 15 mL of \(\text{H}_2\text{O}\) to 1.0 mmol (0.198 g) of \(\text{MnCl}_2\cdot4\text{H}_2\text{O}\) in 15 mL of \(\text{H}_2\text{O}\) (without stirring). The resultant yellow suspension was kept at 4 °C. After a few days, dark-red polyhedral crystals formed. The crystals were washed with a few small portions of distilled water and ethanol and dried in air. Calcd for I: C, 17.3; H, 2.9; N, 20.2. Found: C, 17.2; H, 3.1; N, 20.1.

\([\text{Mo}^{IV}\{\text{\(\mu\)}\cdot\text{CN}\}_2\text{Mn}^{II}(\text{H}_2\text{O})_2]_2\cdot4\text{H}_2\text{O}\]_n (2) and \([\text{W}^{IV}\{\text{\(\mu\)}\cdot\text{CN}\}_2\text{Mn}^{II}(\text{H}_2\text{O})_2]_2\cdot4\text{H}_2\text{O}\]_n (3) were prepared by reacting aqueous solutions, in the dark, of...
MnCl₂·4H₂O and K₄[Mo(CN)₈]·2H₂O for 2 or K₄[W(CN)₈]·2H₂O for 3 by slow diffusion in an H-tube. After a few weeks, yellow-orange polyhedral crystals formed. The crystals were washed with a few small portions of distilled water and ethanol and dried in air. Calcld for 2: C, 17.2; H, 2.9; N, 20.1. Found: C, 17.1; H, 3.0; N, 20.0. Calcld for 3: C, 14.9; H, 2.5; N, 17.3. Found: C, 14.8; H, 2.9; N, 17.3.

3.3. Crystallographic data collection and structure determination

The determination of the unit cell parameters and the collection of intensity data for 1, 2 and 3 were made at 295 K on a Enraf Nonius CAD4 diffractrometer using crystals of dimensions 0.2 × 0.2 × 0.4 mm³ (1), 0.4 × 0.4 × 0.35 mm³ (2) and 0.2 × 0.2 × 0.4 mm³ (3). Of the 902 (1), 1183 (2) and 902 (3) unique reflections, 838 (1), 856 (2) and 720 (3) with I > 3σ(I) were used to solve the structure with SHELXS-86 program [12]. Computations were performed by using PC versions of CRYSALS [13]. Least-squares refinements of 68 (for 1), 67 (for 2) and 67 (for 3) parameters with approximations to the normal matrix were carried out by minimizing the function Σw(|F₀| − |Fₑ|)², where F₀ and Fₑ are the observed and calculated structure factors. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections based on ψ scan curves were applied. The models reached convergence with R = 0.0516 and R_w = 0.050 for 1, R = 0.081 and R_w = 0.062 for 2 and R = 0.0564 and R_w = 0.0487 for 3. The hydrogen atoms were not included in the refinement. All non-hydrogen atoms were refined anisotropically. The crystallographic data for 1, 2 and 3 are summarized in Table 1. Main bond lengths and angles are listed in Table 2.

3.4. Magnetic measurements

Magnetic susceptibility data of polycrystalline samples of 1, 2 and 3 were collected with an MPMS Quantum Design SQUID magnetometer (XL5S) in the temperature range 300–302 K. Pascal’s constants were used for the diamagnetic corrections [14].

4. Conclusions

We have presented an example of isostructural octacyanidometalate-based three-dimensional bimetallic networks that present striking different magnetic properties, due to the presence of an unpaired electron on the octacyanidometalate (Nb⁴⁺) or its absence (Mo⁴⁺ and W⁴⁺); (1), Nb⁴⁺Mn²⁺ is a ferrimagnet below T_C = 47 K, whereas (2) (Mo⁴⁺Mn²⁺) and (3) (W⁴⁺Mn²⁺) are simple paramagnets. Besides the amazing saga of magnetic Prussian blues [1b], the chemistry of octacyanidometalates is bringing new perspectives in molecular magnetism, including multifunctional materials [5].

Supporting information available. X-ray crystallographic files in CIF format for the structures of compounds 1, 2 and 3. This material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (CCDC 679635–679637).

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References