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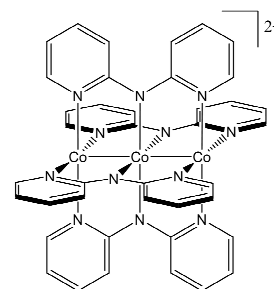
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## ARTICLE TYPE

One-dimensional coordination polymers of  $[\text{Co}_3(\text{dpa})_4]^{2+}$  and  $[\text{MF}_6]^{2-}$  ( $\text{M} = \text{Re}^{\text{IV}}$ ,  $\text{Zr}^{\text{IV}}$  and  $\text{Sn}^{\text{IV}}$ )Vladimir Bulicanu,<sup>a,b</sup> Kasper S. Pedersen,<sup>a,b,c</sup> Mathieu Rouzières,<sup>a,b</sup> Jesper Bendix,<sup>d</sup> Pierre Dechambenoit,<sup>a,b</sup> Rodolphe Clérac<sup>a,b</sup> and Elizabeth A. Hillard<sup>\*a,b</sup>Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX  
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One-dimensional coordination polymers of alternating metal-metal bonded trinuclear  $[\text{Co}_3(\text{dpa})_4]^{2+}$  (dpa = the anion of 2,2'-dipyridylamine) building blocks and  $[\text{ReF}_6]^{2-}$  (1),  $[\text{ZrF}_6]^{2-}$  (2) or  $[\text{SnF}_6]^{2-}$  (3) linkers have been self-assembled and crystallographically characterized. Magnetic measurements reveal a significant ferromagnetic coupling ( $J/k_B = +9.9$  K) between  $S = 1/2$   $\{\text{Co}_3^{6+}\}$  and  $S = 3/2$   $\text{Re}^{\text{IV}}$  magnetic sites through a single, unsupported fluoride bridge in 1.

Chart 1. Schematic representation of the  $[\text{Co}_3(\text{dpa})_4]^{2+}$  unit.

One-dimensional metal-ligand coordination polymers are of particular interest in the molecular magnetism community for their potential as Single-Chain Magnets (SCMs).<sup>1</sup> Because the stereochemistry around the metal ion determines the topology of coordination-driven self-assembled systems, a simple approach to magnetic linear polymers entails the use of paramagnetic metal complexes possessing two empty, or at least kinetically labile, coordination sites. These acceptors can then be associated into chains using paramagnetic linkers with two donor sites, the most common of which have been *trans*-cyanidometallates.<sup>2</sup>

Possessing rich magnetic and electronic properties, in addition to axial geometry, paddlewheel complexes are attractive building blocks for the construction of linear one-dimensional systems. Indeed, many dinuclear metal ion tetracarboxylates, e.g.  $\{\text{Cr}_2^{4+}\}$ ,  $\{\text{Cu}_2^{4+}\}$ ,  $\{\text{Rh}_2^{4+}\}$  and  $\{\text{Ru}_2^{4+}\}$ , have strongly Lewis acidic axial sites and form extended chain structures in the absence of exogenous ligands by coordination of a carboxylate oxygen atom to the axial position of an adjacent molecule.<sup>3</sup> On the other hand, copper and zinc paddlewheels have been extensively used in the formation of three-dimensional metal-organic frameworks,<sup>4</sup> while one-dimensional coordination polymers using exogenous spacers and  $\{\text{Rh}_2^{4+}\}$ ,<sup>5</sup>  $\{\text{Cu}_2^{4+}\}$ ,<sup>6</sup>  $\{\text{Re}_2^{6+}\}$ ,<sup>7</sup>  $\{\text{Zn}_2^{4+}\}$ <sup>8</sup> units are also well represented. Of particular note are magnetic systems, some quite sophisticated, constructed of  $\{\text{Ru}_2^{5+}\}$  ( $S = 3/2$ )<sup>9</sup> and  $\{\text{Ru}_2^{4+}\}$  ( $S = 1$ )<sup>10</sup> building blocks and which display remarkable properties.

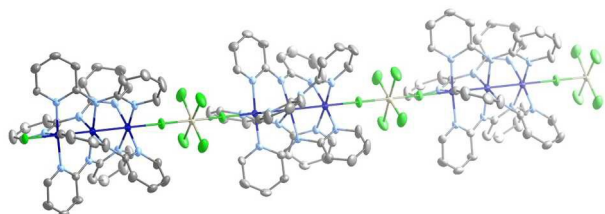
We here turn our attention to Extended Metal Atom Chains (EMACs), which contain three or more metal ions typically supported by oligopyridylamines.<sup>11</sup> While dinuclear divalent paddlewheel complexes are often diamagnetic, EMACs tend to have an odd number of metal centers and to be paramagnetic.

This is due to a variety of factors, including an odd number of electrons, accidental degeneracy of frontier orbitals, or dissymmetry in the linear complex giving rise to an isolated high-

spin metal ion. However, with the exception of a few coordination polymers based on  $[\text{Ni}_3(\text{dpa})_4]^{2+}$ ,<sup>12</sup> (where dpa = the anion of 2,2'-dipyridylamine), EMACs have rarely been used to build extended systems.

The  $[\text{Co}_3(\text{dpa})_4]^{2+}$  unit (Chart 1) is expected to be a useful building block, based on the interesting physical properties of the  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$  analogue. Its core consists of three collinear cobalt metal ions possessing a delocalized 3-electron 3-center bond, and depending on crystal packing effects, the spacing of the Co ions can be equal (as in the orthorhombic  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2$  phase), or unequal, (as in the tetragonal  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2] \cdot 2\text{CH}_2\text{Cl}_2$  phase).<sup>13</sup> Both forms show a spin-crossover (SCO) process from  $S = 1/2$  to  $S = 3/2$  or  $5/2$ . Remarkably, the one electron oxidized compound,  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2](\text{BF}_4)$  undergoes a two-step SCO, from  $S = 0$  to  $S = 1$  to  $S = 2$ .<sup>14</sup> Finally, the axial chloride ligands can be cleanly removed from  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$  using silver salts, generating MeCN,<sup>15</sup>  $\text{BF}_4^-$ ,<sup>16</sup>  $\text{CN}^-$ ,  $\text{N}(\text{CN})_2^-$  or  $\text{SCN}^-$ <sup>17</sup> adducts. Nonetheless,  $[\text{Co}_3(\text{dpa})_4]^{2+}$  has not been widely used in extended structures, even if organization into rigid multi-dimensional systems is an appealing strategy to introduce cooperativity in the SCO process and thus to generate possible spin transition phenomena. Recent work by Shatruk and coworkers on putative 2D grids formed by four ditopic  $[\text{Co}_3(\text{dpa})_4]^{2+}$  units coordinated to  $[\text{Co}(\text{CN})_6]^{3-}$  or  $[\text{Fe}(\text{CN})_6]^{3-}$  is the only example of the assembly of  $[\text{Co}_3(\text{dpa})_4]^{2+}$  units into extended networks.<sup>18</sup> Unfortunately, these materials could not be crystallographically characterized.

In order to obtain 1:1 neutral chains, we have selected the dianionic metalloligands  $[\text{ReF}_6]^{2-}$ ,  $[\text{ZrF}_6]^{2-}$  and  $[\text{SnF}_6]^{2-}$  to link the  $[\text{Co}_3(\text{dpa})_4]^{2+}$  building block.  $(\text{PPh}_4)_2[\text{ReF}_6] \cdot 2\text{H}_2\text{O}$  was recently reported to exhibit a pronounced magnetic anisotropy,<sup>19</sup>



**Fig. 1.** Thermal ellipsoid plot of  $[\text{Co}_3(\text{dpa})_4(\text{ReF}_6)] \cdot 2\text{DMF}$  (C: grey; F: green, Re: light grey; N: light blue; Co: blue). Ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvents of crystallization have been omitted for clarity. Only one of two orientations of the disordered molecule is shown.

a property that was retained in 1D coordination polymers featuring  $\{\text{M}^{\text{II}}\text{--F--Re}^{\text{IV}}\}$  linkages. Furthermore, the  $[\text{Ni}(\text{viz})_4(\text{ReF}_6)]$  ( $\text{viz} = 1\text{-vinylimidazole}$ ) chain additionally exhibits relatively strong fluoride-mediated ferromagnetic coupling between the  $\text{Re}^{\text{IV}}$  and  $\text{Ni}^{\text{II}}$  magnetic sites ( $J/k_{\text{B}} = +17 \text{ K}$ ;  $H = -2JS_1S_2$  Hamiltonian definition).

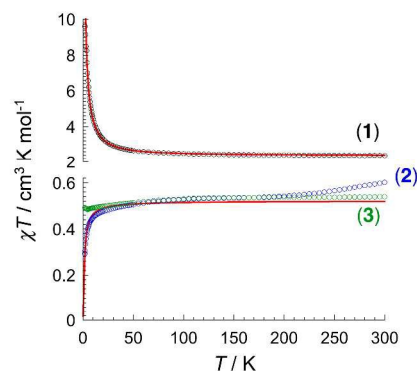
Notably,  $(\text{PPh}_4)_2[\text{ReF}_6] \cdot 2\text{H}_2\text{O}$  can be dehydrated without decomposition and subsequently recrystallized to afford  $(\text{PPh}_4)_2[\text{ReF}_6] \cdot \text{MeCN}$ , (ESI) which is a convenient starting material for assembly reactions with moisture sensitive building blocks. The combination of equimolar solutions of *in-situ* formed  $[\text{Co}_3(\text{dpa})_4(\text{BF}_4)_2]$  and  $(\text{PPh}_4)_2[\text{MF}_6]$  ( $\text{M} = \text{Re}^{\text{IV}}$ ,  $\text{Zr}^{\text{IV}}$  and  $\text{Sn}^{\text{IV}}$ ) immediately gave a dark precipitate, insoluble in all common solvents. In order to obtain crystals, a dilute solution of  $(\text{PPh}_4)_2[\text{MF}_6]$  in MeCN was layered on a DMF solution of  $[\text{Co}_3(\text{dpa})_4(\text{BF}_4)_2]$  in a thin tube and left to slowly diffuse over several weeks.<sup>‡</sup> Green blocks of  $[\text{Co}_3(\text{dpa})_4(\text{ReF}_6)] \cdot 2\text{DMF}$  (**1**),  $[\text{Co}_3(\text{dpa})_4(\text{ZrF}_6)] \cdot 2\text{DMF}$  (**2**) and  $[\text{Co}_3(\text{dpa})_4(\text{SnF}_6)] \cdot 2\text{DMF}$  (**3**) were obtained in moderate yield. Powder X-ray diffraction analysis revealed the presence of only one phase and thermal gravimetric analysis was consistent with the presence of two DMF molecules (SI).

Compounds **1–3** are isostructural. They crystallize in the space group  $P4/ncc$  (Table S1) with the four-fold axis coincident with the rigorously linear  $\text{Co--F--M}$  axis. The chains are racemic, being made up of alternating  $\Delta$  and  $\Lambda$   $[\text{Co}_3(\text{dpa})_4]^{2+}$  helicoidal moieties (Fig. 1). A small disorder is found with respect to the wrapping of the  $\text{dpa}^-$  ligands, and each position is occupied by *ca.* 80% of one enantiomer and 20% of the other. The  $\{\text{Co}_3^{6+}\}$  core is slightly asymmetrical with differences in  $\text{Co--Co}$  distances of 0.008(1), 0.013(1) and 0.013(1) Å in **1**, **2** and **3**, respectively (at 200 K; Table 1). Surprisingly, the  $\text{Co--F}$  distances are quite unequal, with differences of 0.066(4) Å (**1**), 0.059(4) Å (**2**) and 0.069(4) Å (**3**), with the longer distance associated with the terminal cobalt engaged in the longer  $\text{Co--Co}$  bonding interaction. This asymmetry is however not reflected in the two individual  $\text{M--F}_{\text{ax}}$  distances, which are distinctly and equally elongated due to their coordination to the Co centers (Table 1).

**Table 1.** Selected bond distances (Å).

	<b>1</b>	<b>2</b>	<b>3</b>
Co1–Co3	2.270(1)	2.275(1)	2.275(1)
Co2–Co3	2.278(1)	2.288(1)	2.288(1)
Co1–F1	2.115(4)	2.097(4)	2.104(4)
Co2–F2	2.181(4)	2.156(4)	2.173(4)
M–F1	1.962(4)	2.037(4)	2.002(4)
M–F2	1.970(4)	2.044(4)	2.009(4)
M–F <sub>eq</sub>	1.931(3)	1.973(3)	1.928(3)

Magnetic susceptibility measurements were performed on polycrystalline samples of **1–3** between 1.85 and 300 K. At room



**Fig. 2.** Temperature dependence of the  $\chi T$  product for **1** (●), **2** (○) and **3** (◐) at 1000 Oe ( $\chi$  is defined as molar magnetic susceptibility equal to  $M/H$ ). The red lines are the fits discussed in the text.

temperature, the  $\chi T$  product of **1** amounts to  $2.4 \text{ cm}^3 \text{ K mol}^{-1}$ , slightly higher than the theoretical value of  $1.97 \text{ cm}^3 \text{ K mol}^{-1}$  for isolated  $S = 1/2$  ( $[\text{Co}_3(\text{dpa})_4]^{2+}$ ,  $g = 2.35$ ,  $C = 0.52 \text{ cm}^3 \text{ K mol}^{-1}$ ) and  $S = 3/2$  ( $[\text{ReF}_6]^{2-}$ ,  $g = 1.76$ ,  $C = 1.45 \text{ cm}^3 \text{ K mol}^{-1}$ ) spins (Fig. 2). On lowering the temperature, the  $\chi T$  product increases steadily, with a more abrupt increase below *ca.* 30 K eventually reaching  $9.6 \text{ cm}^3 \text{ K mol}^{-1}$  at 1.85 K, suggestive of a significant ferromagnetic coupling between  $\{\text{Co}_3^{6+}\}$  and  $\text{Re}^{\text{IV}}$  magnetic sites. The data were fit to a Seiden model<sup>20</sup> derived from the exchange-coupling Hamiltonian  $\hat{H} = -2J \sum_{i=1}^N (\hat{s}_i \cdot (\hat{S}_i + \hat{S}_{i+1}))$ , where  $\hat{s}_i$  and  $\hat{S}_i$  represent spin-operators of  $\{\text{Co}_3^{6+}\}$  and  $\text{Re}^{\text{IV}}$ , yielding  $g = 2.05(5)$  and  $J/k_{\text{B}} = +9.9(1) \text{ K}$ . As expected, this average  $g$  value falls in between the previously reported values for  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2$  ( $g = 2.35$ )<sup>13</sup> and  $(\text{PPh}_4)_2[\text{ReF}_6] \cdot 2\text{H}_2\text{O}$  ( $g = 1.76$ ).<sup>19</sup> Compounds **2** and **3**, possessing diamagnetic  $[\text{ZrF}_6]^{2-}$  and  $[\text{SnF}_6]^{2-}$  linkers, show an almost temperature independent  $\chi T$  product between about 50 to 300 K. The low temperature decrease of the  $\chi T$  product is likely due to weak antiferromagnetic coupling between the  $\{\text{Co}_3^{6+}\}$  centers through the diamagnetic linkers, and fitting the data to a regular quantum  $s = 1/2$  spin chain model<sup>21</sup> derived from the Hamiltonian  $\hat{H} = -2J \sum_{i=1}^N \hat{s}_i \cdot \hat{s}_{i+1}$  yields  $J/k_{\text{B}} = -1.0 \text{ K}$  for **2** while magnetic interactions are virtually undetectable above 1.85 K for **3** (with  $g = 2.36$  for both). The difference in the magnetic coupling between **2** and **3** may be attributed to the lack of empty d orbitals in  $\text{Sn}^{\text{IV}}$  to mediate a superexchange interaction, in contrast with  $\text{Zr}^{\text{IV}}$  in **2**.

The magnetic behaviour of these coordination polymers is significantly different to that of their building units. For example, the parent compound  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2$  demonstrates a SCO event above 200 K.<sup>13</sup> No such thermal behaviour is observed in **1** and **3** up to 300 K, while for **2**, an onset of what may be a SCO event appears reversibly above 250 K. However, above 300 K, a rapid and irreversible rise in the  $\chi T$  product of these compounds was observed in concert with DMF loss. Therefore, the assembly of ostensibly SCO  $[\text{Co}_3(\text{dpa})_4]^{2+}$  units with  $[\text{MF}_6]^{2-}$  linkers into chains increased the SCO temperature to inaccessible temperatures without evidence of cooperativity increase. As previously reported, the  $[\text{ReF}_6]^{2-}$  anion in  $(\text{PPh}_4)_2[\text{ReF}_6] \cdot 2\text{H}_2\text{O}$  displays Single-Molecule Magnet (SMM) properties, a behavior which is retained upon assembly of  $[\text{ReF}_6]^{2-}$  units by diamagnetic linkers.<sup>19</sup> In **1**, the slow dynamics of the magnetization was not detected by ac susceptibility (in zero-dc or applied dc field, up to 10 kHz and down to 1.8 K). As we previously discussed,<sup>19,22</sup> an

electronic elongation of the  $[\text{ReF}_6]^{2-}$  octahedron, while keeping the tetragonal symmetry implies the axial zero-field splitting parameter,  $D$ , to be positive. Therefore, despite relatively strong intra-chain ferromagnetic interactions, magnetic bistability, e.g. single-chain magnet behavior,<sup>1</sup> is not expected nor experimentally observed in the present system.

In summary, the metal-metal bonded  $[\text{Co}_3(\text{dpa})_4]^{2+}$  moiety has been used for the first time as a building block in a structurally characterized coordination network leading to one-dimensional extended architectures. These unique systems pave the way toward the synthesis of new bistable coordination networks incorporating metal-metal bonding clusters with spin-crossover and/or spin-transition properties.

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## Notes and references

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<sup>†</sup>Electronic Supplementary Information (ESI) available: Physical methods, crystal structure data for **1–3** and  $(\text{PPh}_4)_2[\text{ReF}_6]\cdot\text{MeCN}$ . CCDC 1415823–1415826. See DOI: 10.1039/b000000x/

<sup>‡</sup> General synthesis of  $[\text{Co}_3(\text{dpa})_4(\text{MF}_6)]\cdot 2\text{DMF}$ , **1–3**:  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$  (50 mg, 0.05 mmol) and  $\text{AgBF}_4$  (20 mg, 0.10 mmol) were combined in 10 mL of DMF in a glovebox. The mixture was stirred overnight and filtered. Anhydrous  $(\text{PPh}_4)_2[\text{MF}_6]$  (1 eq) was dissolved in 10 ml of MeCN. The MeCN solution was layered upon the DMF solution, separated by a 1:1 mixture of DMF:MeCN in glass tubes (200 mm,  $\varnothing$  10 mm). Dark green blocks were collected from the walls of the tubes after 4 weeks.

**1**:  $[\text{Co}_3(\text{dpa})_4(\text{ReF}_6)]\cdot 2\text{DMF}$ . Yield 30.2 mg (46%). FT-IR ( $\bar{\nu}$ ,  $\text{cm}^{-1}$ ): 657, 740, 761, 885, 1024, 1089, 1153, 1283, 1314, 1366, 1421, 1457, 1466, 1550, 1595, 1606, 1668. Elemental anal. for  $\text{C}_{40}\text{H}_{32}\text{Co}_3\text{F}_6\text{N}_{12}\text{Re}$ ,  $2(\text{C}_3\text{H}_7\text{NO})$ , % calc. C 42.37, H 3.56, N 15.04; % found C 42.48, H 3.52, N 15.26.

**2**:  $[\text{Co}_3(\text{dpa})_4(\text{ZrF}_6)]\cdot 2\text{DMF}$ . Yield 35.1 mg (58%). FT-IR ( $\bar{\nu}$ ,  $\text{cm}^{-1}$ ): 656, 741, 763, 885, 1025, 1084, 1152, 1284, 1316, 1363, 1421, 1459, 1471, 1550, 1596, 1606, 1671. Elemental anal. for  $\text{C}_{40}\text{H}_{32}\text{Co}_3\text{F}_6\text{N}_{12}\text{Zr}$ ,  $2(\text{H}_2\text{O})$  % calc. C 43.72, H 3.30, N 15.30; % found C 43.86, H 3.52, N 15.32.

**3**:  $[\text{Co}_3(\text{dpa})_4(\text{SnF}_6)]\cdot 2\text{DMF}$ . Yield 32.2 mg (53%). FT-IR ( $\bar{\nu}$ ,  $\text{cm}^{-1}$ ): 656, 740, 761, 884, 1024, 1084, 1150, 1280, 1315, 1363, 1421, 1457, 1470, 1551, 1596, 1606, 1671. Elemental anal. for  $\text{C}_{40}\text{H}_{32}\text{Co}_3\text{F}_6\text{N}_{12}\text{Sn}$ ,  $(\text{C}_3\text{H}_7\text{NO})(\text{H}_2\text{O})$  % calc. C 43.72, H 3.50, N 15.41; % found C 44.30, H 3.76, N 15.15.

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