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Miguel Cortijo, Vladimir Bulicanu, Kasper S. Pedersen, Mathieu Rouzières, Jesper Bendix, et al.. Rational self-assembly of tricobalt extended metal atom chains and  $[MF_6]^{2-}$  building blocks into one-dimensional coordination polymers. *European Journal of Inorganic Chemistry*, 2018, Molecular magnetism, 3-4, pp.320-325. 10.1002/ejic.201701084 . hal-01708996

**HAL Id: hal-01708996**

**<https://hal.science/hal-01708996v1>**

Submitted on 5 Jul 2018

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# Rational Self-Assembly of Tricobalt Extended Metal Atom Chains and $[\text{MF}_6]^{2-}$ Building-Blocks into One-Dimensional Coordination Polymers

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**Abstract:** Following our recent work on the first crystallographically characterized coordination polymers based on tricobalt Extended Metal Atom Chains (EMACs),  $[\text{Co}_3(\text{dpa})_4\text{MF}_6]\cdot 2\text{DMF}$  ( $\text{M} = \text{Zr}^{\text{IV}}$  (1),  $\text{Sn}^{\text{IV}}$  (2) and  $\text{Re}^{\text{IV}}$  (3)), we have generalized our synthetic approach based on robust fluoride complexes to prepare new self-assembled one-dimensional (1D) polymers formed by  $[\text{Co}_3(\text{dpa})_4]^{2+}$  and  $5d[\text{MF}_6]^{2-}$  ( $\text{M} = \text{Ir}^{\text{IV}}$  (4), and  $\text{Os}^{\text{IV}}$  (5)) building blocks. These 1D complexes are isostructural, crystallizing in the  $P4/ncc$  space group such that the four-fold axis is coincident with the metal axes of the rigorously linear chains. Magnetic studies reveal ferromagnetic coupling between the  $S = 1/2$   $\{\text{Co}_3\}$  and  $[\text{MF}_6]^{2-}$  units for the complexes 3 and 4, while non-magnetic  $[\text{MF}_6]^{2-}$  linkers of 1 and 5 mediate antiferromagnetic coupling between the  $\{\text{Co}_3\}$  spins. In the case of 2, no significant exchange coupling was observed. Spin-crossover behavior, which was observed in the parent  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$  complex, was not detected in 1-5 up to 300 K. This work demonstrates that EMACs and  $[\text{MF}_6]^{2-}$  complexes can be considered as appealing building-blocks to design new functional coordination networks.

## Introduction

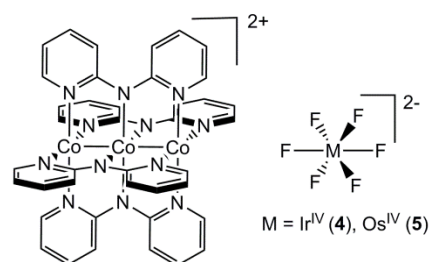
Members of the class of compounds coined “Extended Metal Atom Chains (EMACs)” by F. A. Cotton, or metal strings” by S.-M. Peng, consist of a linear arrangement of three to eleven metal ions, wrapped by four polydentate bridging ligands often based on an oligopyridylamine skeleton.<sup>[1]</sup> Chromium, cobalt, nickel, copper, ruthenium, and rhodium form such structures, which often possess metal-metal bonds. The structure of the first example of this type of complex,  $[\text{Ni}_3(\text{dpa})_4\text{Cl}_2]$ , was reported in 1991.<sup>[2]</sup> Since then, this field has been nourished by notable contributions from the F. A. Cotton, S. M. Peng, and J. F. Berry groups, among others. While Cotton’s group performed many of the seminal studies on tri-metallic and penta-metallic EMACs,<sup>[3]</sup> Peng’s group continues to be particularly active in the synthesis and magnetic

characterization of long EMACs and the development of new bridging ligands,<sup>[4]</sup> and Berry’s group has especially distinguished itself in the synthesis and characterization of heterometallic EMACs.<sup>[5]</sup> These materials often display highly complex crystal and electronic structures, which have been elucidated by theoretical work by the M. Bénard/M. Rohmer<sup>[6]</sup> and J. McGrady<sup>[7]</sup> groups in particular.

The most well-studied EMAC is undoubtedly  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$ .<sup>[8]</sup> This complex crystallizes from dichloromethane and hexane as two solvatomorphs, orthorhombic  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2$  and tetragonal  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]\cdot 2\text{CH}_2\text{Cl}_2$ . The Co–Co distances in the orthorhombic form, 2.3369(4) Å, are crystallographically identical at 298 K because the central cobalt lies on a two-fold axis. On the other hand, in the tetragonal form the cobalt atoms lie on general positions, and the Co–Co distances are quite different, 2.299(1) and 2.471(1) Å at 298 K. Both the “symmetrical” and “unsymmetrical” forms of these compounds have an  $S = 1/2$  ground state and show thermal spin-crossover in the solid state due to population of excited magnetic states.<sup>[8]</sup>

One-dimensional coordination polymers have attracted considerable interest in the molecular magnetism community because of their potential as Single-Chain Magnets (SCMs)<sup>[9]</sup> and Spin-Crossover materials.<sup>[10]</sup> An approach to achieve the assembly of such systems consist in the use of paramagnetic building-blocks with two empty or, at least, labile positions, which can be linked by connectors with at least two donor groups. In this regard, it has been shown that the chloride ligands in the axial positions of  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$  can be cleanly substituted by more labile ligands such as  $\text{CH}_3\text{CN}$ ,<sup>[11]</sup> or  $\text{BF}_4^-$ ,<sup>[12]</sup> and the axial positions can then be subsequently replaced with different ligands, such as  $\text{CN}^-$ ,<sup>[13]</sup>  $\text{N}(\text{CN})_2^-$ ,<sup>[14]</sup>  $\text{NCS}^-$ ,<sup>[11]</sup> and  $\text{R-C}\equiv\text{C}^-$ .<sup>[15]</sup> It should be mentioned that materials of higher dimensionality using EMACs are still a great synthetic challenge. For example, the  $[\text{Co}_3(\text{dpa})_4]^{2+}$  moiety (Figure 1) was recently incorporated in two-dimensional materials using  $[\text{M}(\text{CN})_6]^{3-}$  ( $\text{M} = \text{Fe}, \text{Co}$ ) metalloligands<sup>[16]</sup> but obtaining crystalline material proved unsuccessful.

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**Figure 1.** Schematic representation of the building blocks employed in the assembly of the reported 1D coordination polymers.

In the last few years, we became interested in hexafluorometallates  $[\text{MF}_6]^{2-}$  (Figure 1) as connectors between  $\{\text{Co}_3\}$  EMACs. The use of this type of metalloligand for building 1D coordination systems is currently of growing interest,<sup>[17,18]</sup> as fluoride bridges tend to be highly directional, forming a  $180^\circ$  angle between the metal ions with which they are coordinated,<sup>[19]</sup> thus favoring the formation of strictly linear chains. A feature that gives this kind of control over the structure is useful in designing materials and predicting their magnetic properties. In this regard, we recently reported three 1D coordination polymers using  $[\text{ReF}_6]^{2-}$ ,  $[\text{ZrF}_6]^{2-}$ , and  $[\text{SnF}_6]^{2-}$  linkers as  $[\text{Co}_3(\text{dpa})_4\text{MF}_6]\cdot 2\text{DMF}$  (**1**),  $[\text{Co}_3(\text{dpa})_4\text{ZrF}_6]\cdot 2\text{DMF}$  (**2**),  $[\text{Co}_3(\text{dpa})_4\text{SnF}_6]\cdot 2\text{DMF}$  (**3**).<sup>[20]</sup> In the present work, we have selected the paramagnetic  $[\text{IrF}_6]^{2-}$  ( $J = 1/2$ ), and the essentially non-magnetic  $[\text{OsF}_6]^{2-}$  as linkers to apply our synthetic approach to the formation of  $[\text{Co}_3(\text{dpa})_4\text{IrF}_6]\cdot 2\text{DMF}$  (**4**) and  $[\text{Co}_3(\text{dpa})_4\text{OsF}_6]\cdot 2\text{DMF}$  (**5**). These 5d hexafluorometallates have been rarely used as metalloligands in molecular magnetic materials and their detailed electronic structures have been only recently elucidated.<sup>[18,21]</sup>

## Results and Discussion

### Synthesis and spectroscopic characterization.

The synthesis of **1-5** was accomplished by slow diffusion of a MeCN solution of the corresponding anhydrous  $(\text{PPh}_4)_2[\text{MF}_6]$  salt into a DMF solution of the *in-situ* formed  $[\text{Co}_3(\text{dpa})_4(\text{BF}_4)_2]$  precursor as described previously.<sup>[20]</sup> The FT-IR analysis of the  $[\text{Co}_3(\text{dpa})_4\text{MF}_6]\cdot 2\text{DMF}$  compounds ( $M = \text{Zr}$  (**1**),  $\text{Sn}$  (**2**),  $\text{Re}$  (**3**),  $\text{Ir}$  (**4**), and  $\text{Os}$  (**5**)) in the range of 600-1800  $\text{cm}^{-1}$  yielded, in all cases, spectra similar to that of  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]\cdot \text{CH}_2\text{Cl}_2$  (Figure S1) with the exception of the bands corresponding to the DMF molecules present in the crystal structure of the coordination polymers. In general, the FT-IR analysis in this range shows very similar features to those of the Hdpa ligand. However, symmetrical and unsymmetrical EMACs give slightly different solid-state IR spectra, as illustrated by the IR spectrum of  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]\cdot x\text{CH}_2\text{Cl}_2$  obtained as a mixture of symmetrical and unsymmetrical forms.<sup>[22]</sup> This spectrum shows a splitting of the band around 1153  $\text{cm}^{-1}$ , related to pyridine vibrations, into two peaks at 1153 and 1164  $\text{cm}^{-1}$ , corresponding to the symmetrical and unsymmetrical form, respectively. On the other hand, the IR spectra of **1-5** (Figure S1) do not display a peak at 1164  $\text{cm}^{-1}$  suggesting that there are no unsymmetrical  $\{\text{Co}_3\}$  moieties in these materials.

The decomposition of  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$  precursor, when exposed to humid air, occurs within a few weeks resulting in the formation of blue products, characteristic of mononuclear  $\text{Co}(\text{II})$  products. To test the stability of the 1D assemblies, a sample of **2** was left open to air for 4 months and then an IR spectrum was collected. As seen in Figure S2, the spectrum is identical to that obtained from freshly-filtered crystals. This result thus suggests that connecting the  $\{\text{Co}_3\}$  clusters into coordination polymers improves the stability of the  $\{\text{Co}_3\}$  unit.

Far IR spectra are more informative for characterizing **1-5**, as the M-F bond vibrations are typically found in the 600-150  $\text{cm}^{-1}$  range.<sup>[23]</sup> The far-IR spectrum of  $\text{Cs}_2[\text{Os}^{\text{IV}}\text{F}_6]$  has been reported and consists of one characteristic band at 547  $\text{cm}^{-1}$  for the F-

**Table 1.** Bands related to the M-F bond in the far IR region.

Compound	M-F stretching / $\text{cm}^{-1}$	F-M-F bending / $\text{cm}^{-1}$
$(\text{PPh}_4)_2[\text{ZrF}_6]\cdot 2\text{H}_2\text{O}$	456, 496	218
$(\text{PPh}_4)_2[\text{ZrF}_6]$	480	218
<b>1</b>	450b, 510	218
$(\text{PPh}_4)_2[\text{SnF}_6]\cdot 2\text{H}_2\text{O}$	511, 556	246
$(\text{PPh}_4)_2[\text{SnF}_6]$	548	246
<b>2</b>	500b, 570	246
$(\text{PPh}_4)_2[\text{ReF}_6]\cdot 2\text{H}_2\text{O}$	499, 520*	237
$(\text{PPh}_4)_2[\text{ReF}_6]$	511	236
<b>3</b>	500b, 539	238
$(\text{PPh}_4)_2[\text{IrF}_6]\cdot 2\text{H}_2\text{O}$	521*, 554	256
$(\text{PPh}_4)_2[\text{IrF}_6]$	546	256
<b>4</b>	504b, 562	259
$(\text{PPh}_4)_2[\text{OsF}_6]\cdot 2\text{H}_2\text{O}$	509, 543	244
$(\text{PPh}_4)_2[\text{OsF}_6]$	539	244
<b>5</b>	492b; 549	250

\* The P-C stretching of the  $\text{PPh}_4^+$  cation also appears at this energy. b = broad band

$\text{Os}(\text{IV})$  stretching mode and two bands at 259  $\text{cm}^{-1}$  and 231  $\text{cm}^{-1}$  corresponding to F- $\text{Os}^{\text{IV}}$ -F bending modes.<sup>[23a]</sup> The far FT-IR spectra of the  $(\text{PPh}_4)_2[\text{MF}_6]\cdot 2\text{H}_2\text{O}$  salts ( $M = \text{Zr}$ ,  $\text{Sn}$ ,  $\text{Re}$ ,  $\text{Ir}$ , and  $\text{Os}$ ) measured in the 600-150  $\text{cm}^{-1}$  range (Table 1 and Figures S3-S7) consist mainly of a broad band that appears in the 180-260  $\text{cm}^{-1}$  range corresponding to the F- $M^{\text{IV}}$ -F bending mode, a very strong band at ca. 520  $\text{cm}^{-1}$  corresponding to a P-C stretching mode of the  $\text{PPh}_4^+$  cation,<sup>[24]</sup> and one ( $M = \text{Re}$  and  $\text{Ir}$ ) or two ( $M = \text{Zr}$ ,  $\text{Sn}$  and  $\text{Os}$ ) additional bands in the 450-560  $\text{cm}^{-1}$  region corresponding to F- $M^{\text{IV}}$  stretching modes. Considering that the  $(\text{PPh}_4)_2[\text{MF}_6]\cdot 2\text{H}_2\text{O}$  compounds are isostructural for  $M = \text{Sn}$  (ESI),  $\text{Re}$ ,  $\text{Ir}$ , and  $\text{Os}$ ,<sup>[17,18,21]</sup> it seems reasonable to consider that the P-C stretching band of the  $\text{PPh}_4^+$  cation masks a F- $M^{\text{IV}}$  stretching band for the compounds where  $M = \text{Re}$  and  $\text{Ir}$ . After drying the crystals under vacuum, only one M-F stretching band is observed in all cases due to the removal of interstitial water molecules, which are hydrogen bonded to the apical fluoride ions. The far IR spectra of the coordination polymers **1-5** display in all cases a strong band in the 510-570  $\text{cm}^{-1}$  region and a broad band in the 450-500  $\text{cm}^{-1}$  range corresponding to F- $M^{\text{IV}}$  stretching modes. A broad and strong band in the 260-220  $\text{cm}^{-1}$  range corresponding to the F- $M^{\text{IV}}$ -F bending mode is also observed (Tables 1 and 2 and Figure S8-S12). The rest of the bands agree

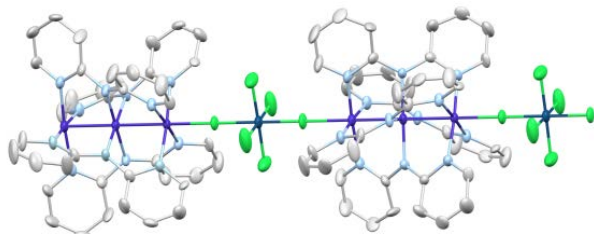
**Table 2.** Assignment of the bands observed in the far FT-IR spectra of **5** and analogues of the building units.

	$\text{Cs}_2[\text{OsF}_6]^{[23]}$ $\bar{\nu} / \text{cm}^{-1}$	$[\text{Co}_3(\text{dpa})_4\text{Cl}_2]^{[22]}$ $\bar{\nu} / \text{cm}^{-1}$	<b>5</b> $\bar{\nu} / \text{cm}^{-1}$
Co-N bend.	-	178	173
Co-Cl str.	-	187	-
$\Gamma$ (ring-ring)	-	215	217
F-Os-F bend.	259, 231	-	250
Co-Co-Co bend.	-	251	252
C-N-C bend.	-	270	273
Co-N str.	-	291	287
Co-Co-Co asym. str.	-	313	317
Co-F str.	-	-	347
$\Delta$ (ring-ring)	-	359	365
Co-N str.	-	401	398
$\Gamma$ (ring)	-	429, 456, 518, 540	428, 462 519b
Os-F str.	547	-	492b, 549

well with that reported for  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$  in the literature<sup>[22]</sup> with the exception of (i) a band at  $193\text{ cm}^{-1}$  attributed to the Co–Cl stretch that is absent in the coordination polymers **1–5** and (ii) the presence of bands at ca.  $345\text{ cm}^{-1}$  attributed to Co–F stretching vibrations.

### Description of the crystal structures.

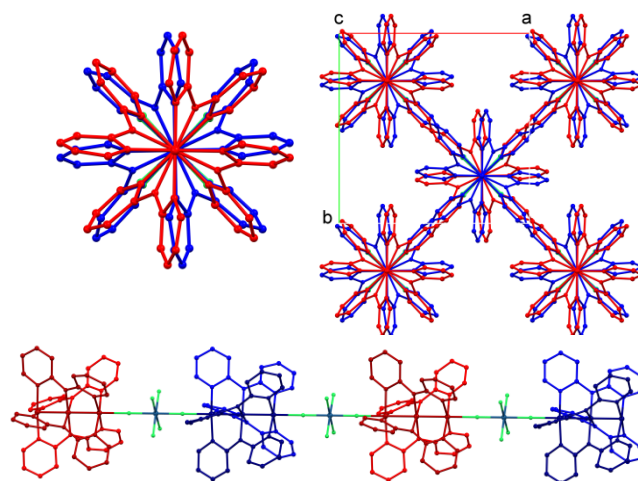
Compounds **1–5** are isostructural, crystallizing in the tetragonal  $P4/ncc$  space group. The structures consist of perfectly linear neutral coordination polymers formed of alternating  $[\text{Co}_3(\text{dpa})_4]^{2+}$  and  $[\text{MF}_6]^{2-}$  units in which the four-fold axis is coincident with the chain direction and the  $c$  axis (Figure 2). In the new compounds **4** and **5**, the  $\{\text{Co}_3\}$  units are slightly unsymmetrical with Co–Co distances of 2.267(1) and 2.274(1) Å in the case of **4** and 2.270(1) and 2.279(1) Å in the case of **5**. The  $[\text{MF}_6]^{2-}$  octahedra are axially elongated in both structures ( $\sim 2\%$ ) with all the  $\text{cis-F–M–F}$  bond angles in the range of  $90.0 \pm 0.6^\circ$ . Co–F distances are 2.117(3) and 2.178(3) Å for **4** and 2.117(3) and 2.175(3) Å for **5**. More detailed crystallographic data can be found in Table 3 and Tables S1–S4.



**Figure 2.** Thermal ellipsoid (50% probability) plot of **4**. Only one of the two orientations of the disordered molecule is shown. (C: grey; F: light green; Ir: dark green; N: pale blue; Co: dark blue). H atoms and solvent molecules are omitted for clarity. Selected bond distances for **4**: Co–Co: 2.2674(10) and 2.2736(10) Å; Co–F: 2.117(3) and 2.178(3) Å; Ir–F<sub>ax</sub>: 1.951(3) and 1.965(3) Å; IrF<sub>eq</sub>: 1.919(2) Å; for **5**: Co–Co: 2.2699(9) and 2.2793(10) Å; Co–F: 2.117(3) and 2.175(3) Å; Os–F<sub>ax</sub>: 1.963(3) and 1.975(3) Å; Os–F<sub>eq</sub>: 1.917(2) Å.

The tricobalt units present helicoidal chirality, but the chains themselves are racemic with the  $[\text{Co}_3(\text{dpa})_4]^{2+}$  units in the  $\Delta$  and  $\Lambda$  configurations alternating along the one-dimensional structure (Figure 3). The structures are disordered on the position of the  $\text{dpa}^-$  ligands, such that both enantiomers are found in the same position with a ca. 60 and 40 % occupancy.

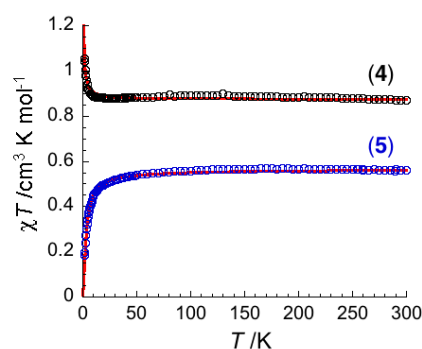
Two molecules of DMF per structural unit of the  $[\text{Co}_3(\text{dpa})_4\text{MF}_6]$  polymer are found in the crystal structures. These molecules are severely disordered with two molecules of DMF occupying four positions with 1/2 occupancy (Figure S5). Thermogravimetric analysis was performed to confirm the number of solvent molecules in the structures and also to determine their thermal stability (Figure S6). The analysis shows a loss in mass at about  $150\text{ }^\circ\text{C}$  of  $\sim 12\%$  for the two samples, which is the equivalent of two molecules of DMF per structural unit.



**Figure 3.** Ball and stick views along (top)  $c$  axis and (bottom)  $b$  axis of the polymeric species in **4** (red:  $\Delta$ - $\{\text{Co}_3\}$  helix, blue:  $\Lambda$ - $\{\text{Co}_3\}$  helix, green: fluoride, and blue: iridium). Only one of the two orientations of the disordered molecule is shown. H atoms and solvent molecules have been omitted for clarity.

### Magnetic properties

Magnetic susceptibility measurements on polycrystalline samples of **4** and **5** were carried out from 1.9 to 300 K (Figures 4 and S7). The  $\chi T$  product measured for  $[\text{Co}_3(\text{dpa})_4\text{IrF}_6] \cdot 2\text{DMF}$  (**4**) is roughly constant ( $0.91\text{ cm}^3\text{ K mol}^{-1}$ ) in the 20–300 K range of temperatures. This value is in agreement to that expected for an  $S = 1/2$   $[\text{Co}_3(\text{dpa})_4]^{2+}$  cluster ( $g = 2.40(5)$ ,  $C = 0.54\text{ cm}^3\text{ K mol}^{-1}$ )<sup>[9]</sup> and an  $[\text{IrF}_6]^{2-}$  unit with an effective  $J = 1/2$  ground state ( $g = 2$ ,  $C = 0.38\text{ cm}^3\text{ K mol}^{-1}$ ).<sup>[18]</sup> On cooling, the  $\chi T$  product increases giving a value of  $1.06\text{ cm}^3\text{ K mol}^{-1}$  at 1.85 K, suggesting the presence of ferromagnetic interactions in the system. The magnetic data were fitted using the Baker model for a  $S = 1/2$  Heisenberg chain model,<sup>[25]</sup> on the basis of the Hamiltonian  $\hat{H} = -2J \sum_{i=1}^N \hat{S}_i \cdot \hat{S}_{i+1}$ , yielding  $g = 2.16(5)$  and  $J/k_B = +0.13(6)$  K. The ferromagnetic interactions between the magnetic  $[\text{Co}_3(\text{dpa})_4]^{2+}$  and  $[\text{IrF}_6]^{2-}$  building-blocks along the chain are significantly weaker than those observed in **3** involving the  $S = 3/2$   $[\text{ReF}_6]^{2-}$  moiety ( $J/k_B = +9.9(1)$  K).



**Figure 4.** Temperature dependence of the  $\chi T$  product for **4** (red) and **5** (blue) at 1000 Oe ( $\chi$  is defined as molar magnetic susceptibility equal to  $M/H$  per mole of  $[\text{Co}_3(\text{dpa})_4\text{MF}_6]$ ). The solid lines are the fits as discussed in the text.



[Co<sub>3</sub>(dpa)<sub>4</sub>OsF<sub>6</sub>]<sub>2</sub>DMF (**5**) shows a temperature-independent  $\chi T$  value between 100 and 300 K of 0.56 cm<sup>3</sup> K mol<sup>-1</sup>, close to what is expected for an  $S = 1/2$  system with  $g = 2.40(5)$  (0.54 cm<sup>3</sup> K mol<sup>-1</sup>) typical of tricobalt EMACs. Upon cooling, a decrease of  $\chi T$  is observed, suggesting weak antiferromagnetic interactions between the {Co<sub>3</sub>} magnetic site via the virtually nonmagnetic [OsF<sub>6</sub>]<sup>2-</sup> linkers.<sup>[21]</sup> Fitting the experimental susceptibility data of **4** using the Bonner-Fisher<sup>[26]</sup> model for linear  $S = 1/2$  chains, on the basis of the Hamiltonian  $\hat{H} = -2J \sum_{i=1}^N \hat{S}_i \cdot \hat{S}_{i+1}$ , gave values of  $g = 2.45(5)$  and  $J/k_B = -1.9(4)$  K. In this case, [OsF<sub>6</sub>]<sup>2-</sup> mediates stronger antiferromagnetic interactions than those previously found in **1** or **2** through [ZrF<sub>6</sub>]<sup>2-</sup> ( $J/k_B = -0.82(4)$  K) or [SnF<sub>6</sub>]<sup>2-</sup> ( $J/k_B \approx \pm 0.0(5)$  K).<sup>[20]</sup>

Unlike [Co<sub>3</sub>(dpa)<sub>4</sub>Cl<sub>2</sub>], but in line with previous findings for **1-3**, these coordination polymers do not show any sign of spin crossover behavior up to 300 K confirming that the axial substitution of Cl<sup>-</sup> by [MF<sub>6</sub>]<sup>2-</sup> stabilizes the  $S = 1/2$  low spin state in tricobalt EMACs.

## Conclusions

Two new self-assembled one-dimensional polymers formed by [Co<sub>3</sub>(dpa)<sub>4</sub>]<sup>2+</sup> and [MF<sub>6</sub>]<sup>2-</sup> (M = Ir<sup>IV</sup> (**4**), and Os<sup>IV</sup> (**5**)) building blocks have been prepared and studied. Both compounds are isostructural, crystallizing in the same tetragonal space group but ferromagnetic interactions between [Co<sub>3</sub>(dpa)<sub>4</sub>]<sup>2+</sup> and [IrF<sub>6</sub>]<sup>2-</sup> magnetic sites are observed ( $J/k_B = +0.13(6)$  K) whereas [OsF<sub>6</sub>]<sup>2-</sup> mediates significant antiferromagnetic interactions ( $J/k_B = -1.9(4)$  K). As observed in the Zr, Sn and Re analogues (**1-3**), no spin crossover behavior is detected below 300 K. In order to clarify the impact of the axial ligand on the  $T_{1/2}$  characteristic temperature of the spin crossover, we are currently studying the effects of various axial halide ligands on the magnetic properties of tricobalt EMACs. The present results further demonstrate the utility of [MF<sub>6</sub>]<sup>2-</sup> anions to rationally build coordination architectures using Extended Metal Atom Chains. Future work in this line will be dedicated to the assembly of other EMACs using hexafluorometallates. For example, single-molecule magnet properties for [Cr<sub>3</sub>(dpa)<sub>4</sub>Cl<sub>2</sub>] have recently been discovered, and therefore the combination of [Cr<sub>3</sub>(dpa)<sub>4</sub>]<sup>2+</sup> with paramagnetic [MF<sub>6</sub>]<sup>2-</sup> are of interest for the design of novel single-chain magnets.

## Experimental Section

**General Comments.** All reactions were carried out under a dry argon or nitrogen atmosphere using Schlenk or glovebox techniques. Tetrahydrofuran (THF), diethyl ether (Et<sub>2</sub>O), acetonitrile (CH<sub>3</sub>CN) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were purified using an Innovative Technologies solvent purification system. Anhydrous dimethylformamide (DMF) was purchased from Alfa Aesar and used as received. 2,2'-dipyridylamine (Hdpa) was purchased from Aldrich and recrystallized from hot petroleum ether before use. Anhydrous CoCl<sub>2</sub> was purchased from Aldrich and stored in an oven at 130 °C several days before use. [Co<sub>3</sub>(dpa)<sub>4</sub>Cl<sub>2</sub>]·xCH<sub>2</sub>Cl<sub>2</sub> was prepared as previously reported.<sup>[8]</sup> (PPh<sub>4</sub>)<sub>2</sub>[MF<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O, M = Ir,<sup>[18]</sup> Os,<sup>[21]</sup> were prepared according to the respective literature procedures. The

**Table 3.** Crystal and structure refinement data for **4-5**.

	<b>4</b>	<b>5</b>
Empirical formula	C <sub>46</sub> H <sub>46</sub> Co <sub>3</sub> F <sub>6</sub> N <sub>14</sub> O <sub>2</sub> Ir	C <sub>46</sub> H <sub>46</sub> Co <sub>3</sub> F <sub>6</sub> N <sub>14</sub> O <sub>2</sub> Os
Formula weight / g mol <sup>-1</sup>	1309.97	1307.98
Temperature / K	200(2)	200(2)
Space group	P4/ncc	P4/ncc
a / Å	13.7071(13)	13.6719(13)
b / Å	13.7071(13)	13.6719(13)
c / Å	25.505(3)	25.558(2)
Volume / Å <sup>3</sup>	4791.9(10)	4777.3(10)
Z	4	4
Calculated density / g cm <sup>3</sup>	1.816	1.819
$\mu$ / mm <sup>-1</sup>	3.868	3.754
Goodness-of-fit on $F^2$	$R_1^{[a]} = 0.0449$ ,	$R_1^{[a]} = 0.0440$ ,
R indices (all data)	$wR_2^{[b]} = 0.0608$	$wR_2^{[b]} = 0.0609$

<sup>[a]</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>[b]</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ ,  $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$ , where  $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$ .

crystals of (PPh<sub>4</sub>)<sub>2</sub>[MF<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O were dried under vacuum (10<sup>-3</sup> Torr) at 80 °C overnight to eliminate the water molecules prior to their use.

**Physical measurements.** Elemental analyses were carried out by the Service d'Analyse Élémentaire of the University of Lorraine, Nancy. IR spectra were measured on a Nicolet 6700 FT-IR using Smart iTR accessories between 450-4000 cm<sup>-1</sup> and 150-600 cm<sup>-1</sup>. The magnetic measurements were carried out with the use of an MPMS-XL Quantum Design SQUID magnetometer. This instrument works between 1.8 and 400 K with applied dc fields ranging from -7 to 7 T. Measurements were performed on finely ground polycrystalline samples of **4** and **5** (20.29 and 18.66 mg respectively) sealed in a polypropylene bag (typical sizes and mass: 3 × 0.5 × 0.02 cm; 15-30 mg). Prior to the experiments, the field-dependent magnetization was measured at 100 K in order to detect the presence of any bulk ferromagnetic impurities. Ac susceptibility measurements were made with an oscillating field of 3 Oe with a frequency from 1 to 1500 Hz but no out-of-phase signal was detected above 1.8 K. The magnetic data were corrected for the sample holder, intrinsic diamagnetic contributions, minor ferromagnetic impurities, and temperature-independent paramagnetism.

X-ray diffraction measurements were carried out on single crystals selected under immersion oil in ambient conditions and attached to a MiTeGen microloop. The crystals were mounted in a stream of cold nitrogen at 200(2) K and centered in the X-ray beam using a video camera. Data collection was performed on a Bruker APEX II Quasar diffractometer with Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. The data were collected using a routine to survey reciprocal space, and were indexed by the APEX II program.<sup>[27]</sup> The structures were solved using direct methods and refined by least-squares refinement on  $F^2$  followed by difference Fourier synthesis.<sup>[28]</sup> All hydrogen atoms were introduced at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. CCDC 1573012, 1573013 and 1586059 contain the crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). A summary of crystal and refinement data is shown in Table 3.

**Synthesis of [Co<sub>3</sub>(dpa)<sub>4</sub>MF<sub>6</sub>]<sub>2</sub>DMF (M = Ir (**4**) or Os (**5**)).** A mixture of [Co<sub>3</sub>(dpa)<sub>4</sub>Cl<sub>2</sub>]·xCH<sub>2</sub>Cl<sub>2</sub> (50 mg, 0.05 mmol) and AgBF<sub>4</sub> (20 mg, 0.10 mmol) in 10 mL of DMF was stirred overnight and filtered to remove AgCl. A solution of the corresponding anhydrous (PPh<sub>4</sub>)<sub>2</sub>[MF<sub>6</sub>] salt (0.05 mmol) in 10 mL of CH<sub>3</sub>CN was prepared and layered over the DMF solution in a glass tube (200 mm,  $\varnothing$  10 mm). The DMF and CH<sub>3</sub>CN solution were separated by 4 mL of a 1:1 mixture of DMF and CH<sub>3</sub>CN. Dark green blocks were collected from the walls of the tubes after 3-4 weeks. **4:** Yield 37 mg

(58%). 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  $\text{C}_{40}\text{H}_{32}\text{Co}_3\text{F}_6\text{N}_{12}\text{Ir}$ ,  $2(\text{C}_3\text{H}_7\text{NO})$ , % calc. C 42.10, H 3.51, N 14.97; found C 41.63, H 3.37, N 14.81. **5** Yield 47 mg (72.5%). 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  $\text{C}_{40}\text{H}_{32}\text{Co}_3\text{F}_6\text{N}_{12}\text{Os}$ ,  $2(\text{C}_3\text{H}_7\text{NO})$ , % calc. C 42.20, H 3.52, N 14.99; % found C 41.93, H 3.44, N 14.91.

## Acknowledgements

This work was supported by the CNRS, the University of Bordeaux, the Conseil Régional de la Nouvelle Aquitaine, the Marie Skłodowska-Curie grant 706556 CHIMMM (Postdoctoral fellowship for MC) and the Erasmus Mundus European program (PhD fellowship for VB). JB acknowledges support from The Danish Research Council under grant 12-125226. KSP thanks The Danish Research Council for a DFF | Sapere Aude: Research Talent award (grant 4090-00201). The authors thank the GdR MCM-2 (Magnétisme et Commutation Moléculaires), the MOLSPIN COST action CA15128, L. Favello (for crystallographic assistance), P. Dagault (for TGA analysis), I. Oyarzabal (for useful scientific discussions), and E. Durand and A. Tressaud (for the synthesis of the  $[\text{MF}_6]^{2-}$  precursors).

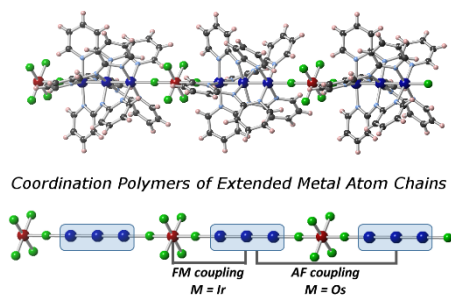
**Keywords:** Coordination polymers • Cobalt Extended Metal Atom Chains • Hexafluoridometallates • Magnetic properties

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### FULL PAPER

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Two new 1D coordination polymers based on tricobalt EMACs and 5d-hexafluoridometallates ( $M = \text{Ir}^{\text{IV}}$ ,  $\text{Os}^{\text{IV}}$ ) are reported. Magnetic studies show the presence of ferromagnetic interactions between  $[\text{Co}_3(\text{dpa})_4]^{2+}$  and  $[\text{IrF}_6]^{2-}$  magnetic sites ( $J/k_{\text{B}} = +0.13(6)$  K) while  $[\text{OsF}_6]^{2-}$  mediates significant antiferromagnetic interactions ( $J/k_{\text{B}} = -1.9(4)$  K).



#### **Sticking together: Tricobalt EMACs and 5d-hexafluoridometallates**

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**Rational Self-Assembly of Tricobalt Extended Metal Atom Chains and  $[\text{MF}_6]^{2-}$  Building-Blocks into One-Dimensional Coordination Polymers**