One-dimensional coordination polymers of [Co3(dpa)4]2+ and [MF6]2- (M = ReIV, ZrIV and SnIV)

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One-dimensional coordination polymers of alternating metal–metal bonded trinuclear [Co₃(dpa)₄]²⁺ (dpa = the anion of 2,2'-dipyridylamine) building blocks and [ReF₆]²⁻ (1), [ZrF₆]²⁻ (2) or [SnF₆]²⁻ (3) linkers have been self-assembled and crystallographically characterized. Magnetic measurements reveal a significant ferromagnetic coupling (J/K = +9.9 K) between S = 1/2 (Co₃²⁺) and S = 3/2 Re⁶⁺ magnetic sites through a single, unsupported fluoride bridge in 1.

One-dimensional metal–ligand coordination polymers are of particular interest in the molecular magnetism community for their potential as single-chain magnets (SCMs). 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-cyanodimetallates.

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. {Cr₃⁴⁺}, {Cu₃⁴⁺}, {Rh₂⁵⁺} and {Ru₂⁴⁺}, 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. On the other hand, copper and zinc paddlewheels have been extensively used in the formation of three-dimensional metal–organic frameworks, while one-dimensional coordination polymers using exogenous spacers and {Rh₂⁴⁺}, {Cu₃⁴⁺}, {Re₂⁶⁺}, {Zn₄⁴⁺} units are also well represented. Of particular note are magnetic systems, some quite sophisticated, constructed of {Ru₂⁵⁺} (S = 3/2)⁹ and {Ru₂⁴⁺} (S = 1)¹⁰ 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.¹¹ 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 [Ni₃(dpa)]³⁺,¹² EMACs have rarely been used to build extended systems.

The [Co₃(dpa)]¹⁺ unit (Chart 1) is expected to be a useful building block, based on the interesting physical properties of the [Co₃(dpa)Cl₂] analogue. Its core consists of three aligned 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 [Co₃(dpa)Cl₂]₂CH₂Cl₂ phase), or unequal, (as in the tetragonal [Co₃(dpa)Cl₂]₂CH₂Cl₂ phase).¹³ 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, [Co₃(dpa)Cl₂][BF₄] undergoes a two-step SCO, from S = 0 to S = 1 to S = 2.¹⁴ Finally, the axial chloride ligands can be

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**Chart 1** Schematic representation of the [Co₃(dpa)]¹⁺ unit.
fluoride-mediated ferromagnetic coupling between the Re IV (PPh₄)₂[MF₆] (M = Re IV, Zr IV and Sn IV) immediately gave a dark product. The Co₃⁺/Co²⁺ ratio of the Co₃(dpa)₄⁺ units coordinated to [Co(CN)₆]³⁻ or [Fe(CN)₆]³⁻ is the only example of the assembly of [Co₃(dpa)₄]³⁺ units into extended networks. Unfortunately, these materials could not be crystallographically characterized.

In order to obtain 1 : 1 neutral chains, we have selected the dianionic metalloligands [ReF₆]²⁻, [ZrF₆]²⁻ and [SnF₆]²⁻ to link the [Co₃(dpa)₄]³⁺ building block. (PPh₄)₂[ReF₆]·2H₂O was recently reported to exhibit a pronounced magnetic anisotropy, a property that was retained in 1D coordination polymers featuring {Co₃(dpa)₄}⁺ units coordinated to [Co(CN)₆]³⁻ or [Ni(CN)₆]³⁻ by Shatruk and coworkers on putative 2D grids formed by four ditopic [Co₃(dpa)₄]⁺ units coordinated to [Co(CN)₆]³⁻ to generate possible spin transition phenomena. Recent work strategy to introduce cooperativity in the SCO process and thus extend networks. 18 Unfortunately, these materials could not be crystallographically characterized.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Selected bond distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co1-Co3</td>
<td>2.270(1) 2.275(1) 2.275(1)</td>
</tr>
<tr>
<td>Co2-Co3</td>
<td>2.278(1) 2.288(1) 2.288(1)</td>
</tr>
<tr>
<td>Co1-F1</td>
<td>2.115(4) 2.097(4) 2.104(4)</td>
</tr>
<tr>
<td>Co2-F2</td>
<td>2.181(4) 2.156(4) 2.173(4)</td>
</tr>
<tr>
<td>M-F1</td>
<td>1.962(4) 2.037(4) 2.002(4)</td>
</tr>
<tr>
<td>M-F2</td>
<td>1.970(4) 2.044(4) 2.009(4)</td>
</tr>
<tr>
<td>M-Feq</td>
<td>1.931(3) 1.973(3) 1.928(3)</td>
</tr>
</tbody>
</table>

S = 3/2 ([(ReF₆)²⁻], g = 1.76, C = 1.45 cm³ K mol⁻¹) spins (Fig. 2). On lowering the temperature, the χT product increases steadily, with a more abrupt increase below ca. 30 K eventually reaching 9.6 cm³ K mol⁻¹ at 1.85 K, suggestive of a significant ferromagnetic coupling between [Co₆⁺] and Re IV magnetic sites. The data were fit to a Seiden model²⁰ derived from the exchange-coupling Hamiltonian $\hat{H} = -J \sum_{i=1}^{N} (\hat{S}_i \cdot \hat{S}_{i+1})$, where $\hat{S}_i$ and $\hat{S}_{i+1}$ represent spin-operators of [Co₆⁺] and Re IV, yielding g = 2.05(3) and J/K = 9.9(1) K. As expected, this average g value falls in between the previously reported values for [Co₃(dpa)₄Cl₂]·2DMF (g = 2.35) and [PPh₄][ReF₆]·2H₂O (g = 1.76).²¹ Compounds 2 and 3, possessing diamagnetic [ZrF₆]²⁻ and [SnF₆]²⁻ linkers, show an almost constant temperature independent χT product between about 50 and 300 K. The low temperature decrease of the χT product is likely due to weak antiferromagnetic coupling between the...
\(\{\text{Co}^{6+}\}\) centers through the diamagnetic linkers, and fitting the data to a regular quantum \(s = 1/2\) spin chain model\(^{11}\) derived from the Hamiltonian \(\hat{H} = -2J \sum_{i} \delta_{i} \cdot \delta_{i+1}\) yields \(J/k_B = -1.0\) 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 Sn\(^{IV}\) to mediate a superechange interaction, in contrast to Zn\(^{II}\) 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.\(^{13}\) 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 \(\gamma\) 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 \([\text{MeF}_6]\)\(^{2-}\) 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 \((\text{PPh}_4)_2[\text{ReF}_6]\) 2\(\text{H}_2\text{O}\) displays single-molecule magnet (SMM) properties, a behaviour which is retained upon assembly of \([\text{ReF}_6]\)\(^{2-}\) units by diamagnetic linkers.\(^{19}\) In 1, slow dynamics of the magnetization were not detected by ac susceptibility (in zero-dc or applied dc field, up 10 kHz and down to 1.8 K). As we previously discussed,\(^{19,22}\) 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,\(^{1}\) 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 or spin-transition properties.

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**Notes and references**

\(^{\dagger}\) General synthesis of \([\text{Co}_3(\text{dpa})_4(\text{MeF}_6)]\) 2DMF, 1–3: \([\text{Co}_3(\text{dpa})_4\text{Cl}_2]\) (50 mg, 0.05 mmol) and 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 \((\text{PPh}_4)_2[\text{MeF}_6]\) (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, \(\odot\) 10 mm). Dark green blocks were collected from the walls of the tubes after 4 weeks.

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