

Phosphonates as ligands in Co–Cr heterometallic clusters†‡

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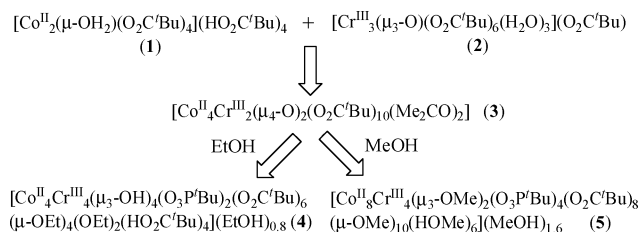
Two new Co(II)–Cr(III) phosphonate clusters with $[\text{Co}^{\text{II}}_4\text{Cr}^{\text{III}}_4]$ and $[\text{Co}^{\text{II}}_8\text{Cr}^{\text{III}}_4]$ cores have been synthesized by a displacement reaction from a pre-formed heterometallic carboxylate cage. Magnetic studies show overall antiferromagnetic interactions are present in these clusters.

Polynuclear clusters have attracted interest not only due to their structural beauty but also because they are nano-sized metal aggregates that can be potentially functionalized as molecule-based catalytic, electronic, optic and magnetic materials.^{1–6} In the family of polynuclear complexes those with two or more kinds of metal ions could have dual or multi-functionality within a single compound. This advantage has led to considerable synthetic effort to make heterometallic clusters.⁷ For 3d–4f heterometallic clusters the established “soft-to-soft and hard-to-hard” principle has often been used (*i.e.* the 4f ions like lanthanides are more oxophilic than 3d transition metal ions, leading to the separated coordination sites when both O and N donors present).⁸ In contrast, investigation of heterometallic 3d–3d transition metal clusters is rare,⁹ with the exception of the Prussian-blue-type family.¹⁰

Within the area of molecular magnetism,¹¹ a particular target are single molecule magnets (SMMs).¹² The requirements of SMMs are for high ground state spin, and high anisotropy of that spin. A strategy which uses two different 3d ions could be interesting here, as we could introduce the high spin through one ion, and the high anisotropy through the other. To do this we have used phosphonate ligands to link together Cr(III) ($S = 3/2$ centres with low anisotropy) with Co(II) centres ($S = 3/2$ centres with first order spin–orbit coupling).

We have previously used $[\text{Co}^{\text{II}}_2(\mu\text{-OH}_2)(\text{O}_2\text{C}^t\text{Bu})_4(\text{HO}_2\text{C}^t\text{Bu})_4]$ (**1**) ($\text{HO}_2\text{C}^t\text{Bu} =$ pivalic acid) as a starting material to make a range of cobalt(II) clusters¹³ and have also reacted **1** with phosphonates.¹⁴ In this paper, we will communicate the synthesis and magnetic properties of two new heterometallic cobalt(II)–chromium(III) phosphonate complexes.

As shown in Scheme 1, the synthesis starts from refluxing **1** and the trinuclear chromium complex, $[\text{Cr}^{\text{III}}_3(\mu_3\text{-O})(\text{O}_2\text{C}^t\text{Bu})_6(\text{H}_2\text{O})_3](\text{O}_2\text{C}^t\text{Bu})_2$ **2**, in toluene, leading to the formation of a hexanuclear secondary starting material, $[\text{Co}^{\text{II}}_4\text{Cr}^{\text{III}}_2(\mu_4\text{-O})_2(\text{O}_2\text{C}^t\text{Bu})_{10}(\text{Me}_2\text{CO})_2]$ **3**, which can be further reacted



Scheme 1 The synthetic procedure of Co–Cr clusters.

with $\text{H}_2\text{O}_3\text{P}^t\text{Bu}$ in EtOH and MeOH to give two larger polynuclear compounds, $[\text{Co}^{\text{II}}_4\text{Cr}^{\text{III}}_4(\mu_3\text{-OH})_4(\text{O}_3\text{P}^t\text{Bu})_2(\text{O}_2\text{C}^t\text{Bu})_6(\mu\text{-OEt})_4(\text{OEt})_2(\text{HO}_2\text{C}^t\text{Bu})_4](\text{EtOH})_{0.8}$ **4** and $[\text{Co}^{\text{II}}_8\text{Cr}^{\text{III}}_4(\mu_3\text{-OMe})_2(\text{O}_3\text{P}^t\text{Bu})_4(\text{O}_2\text{C}^t\text{Bu})_8(\mu\text{-OMe})_{10}(\text{HOME})_6](\text{MeOH})_{1.6}$ **5**, respectively.§

The structure of complex **3** features an edge-sharing bitetrahedral core (Fig. 1(a)),¹⁵ which is almost identical to a $\{\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_2\}$ compound.¹⁶ The body Mn^{III} ions are just replaced by the Cr^{III} ions and the wing Mn^{II} ions are substituted by the Co^{II} ions; other trivalent and divalent metal centres can also be added in the appropriate sites. However, there are only two terminal solvent molecules in **3** rather than four in the $\{\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_2\}$ compound due to the flexibility of the coordination geometry of the Co^{II} ions, in which two of them turn to four-coordinate tetrahedral.

Complex **4** has a core with a central planar square of cobalt(II) ions, linked on opposite edges to two dimers of chromium(III) ions, as shown in Fig. 1(b). The two phosphonate ligands bind in the [5.221]¹⁷ mode above and below the plane of cobalts; the two $\mu\text{-O}_p$ bridging adjacent cobalt corners of the square and the other O_p linking these to one of the chromium of each of the dimers. The two opposite sides of the cobalt square not bridged to the dimers are linked by two $\mu\text{-OEt}$ groups and the other two edges of the square are linked to the dimers by two $\mu_3\text{-OH}$, bridging an edge pair of cobalts to a chromium. There are a further two $\mu_3\text{-OH}$ which each bridge the two chromium of a dimer to one of the cobalts. The dimers are linked *via* a $\mu\text{-OEt}$ and a [2.11] pivalate, also each chromium is bridged to its nearest cobalt ion *via* a [2.11] pivalate ligand. There are also four terminal pivalic acids, found on two cobalt ions and two chromium ions, and two terminal ethanol molecules found on two chromium ions. Strong hydrogen bonds form between the O atom of the terminal ethanol molecule and the terminal pivalic acid ($\text{O} \cdots \text{O}$ 2.592 Å); this also allows charge balance as between the ethanol and pivalic acid we have a mono-negative charge. Whether this is best described as ethanol-pivalate or ethoxide-pivalic acid is debatable.

Complex **5** has the largest nuclearity among this series of Co–Cr clusters. The core of **5** features two edge-sharing $[\text{Co}_4\text{Cr}_4]$ hexagons with the shared edge containing a $[\text{Cr}_2]$ fragment, see Fig. 1(c). The near-planar hexagons are hinged along the shared

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† Electronic supplementary information (ESI) available: Selected bond lengths and angles for **3**, **4** and **5**. CCDC reference numbers 767251–767252. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00017e

‡ In memory of Dr Ian J. Hewitt.

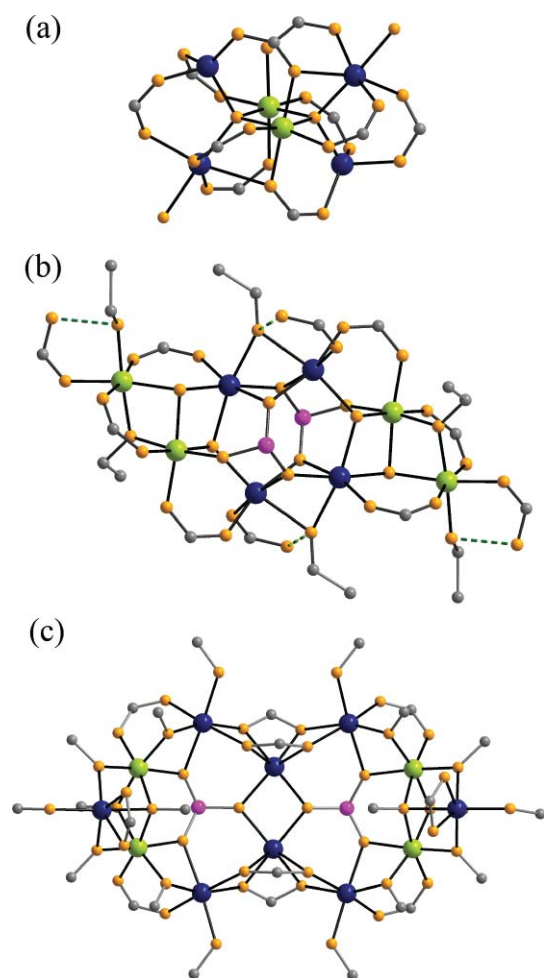


Fig. 1 The cores of compounds **3–5** (a–c). The *tert*-butyl groups, the carbon atoms of Me₂CO and the disordered O₃P-*t*Bu are omitted for clarity. The hydrogen bonds in **4** are shown as dotted lines. Colour codes: Co, blue; Cr, green; P, pink; O, orange; C, grey.

edge, with the angle between the hexagons roughly 20°. There are two [6.222] phosphonate ligands, one located in the centre of each hexagon, with the central shared edge bridged by a μ -O_p from each phosphonate. Four unusual [3.220] phosphonates are disordered with four [3.22] pivalate ligands, these chelate and bridge the metals of the shared edge linking the metal of the shared edge with an adjacent metal of each of the hexagons. Modelling this disorder gives 2.1 phosphonates to 1.9 carboxylates, however we give the formula for which charge balances. Four of the edges of the hexagons are bridged by a μ -OMe and a [2.11] pivalate and the two edges which bridge the additional metal are bridged by a μ_3 -OMe and a μ -OMe. A chelating pivalate is found on each of the cobalts not associated with the hexagons, also two μ -OMe link the addition cobalt to two of the chromium of the hexagons, forming a {CoCr₂(OMe)₄} cube with a vertex missing.

The magnetic properties of **3** to **5** have been studied with powder samples (Fig. 2). At room temperature, the $\chi_M T$ value of **3** is 11.1 emu K mol⁻¹, which is slightly less than a spin-only value (11.3 emu K mol⁻¹) for four cobalt(II) ions and two chromium(III) ions. This is reasonable if considering the combined actions of the unquenched orbital momentum of octahedral cobalt(II)

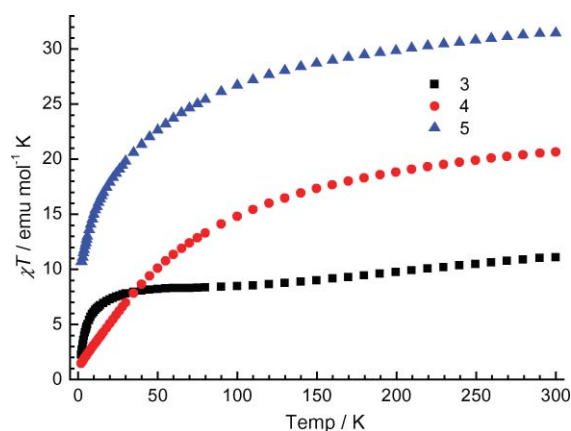


Fig. 2 Plots of $\chi_M T$ vs. T under an applied field of 1 KOe for **3** to **5**.

ions, the less half-filled chromium(III) ions and antiferromagnetic interactions between them. Upon cooling, the $\chi_M T$ vs. T curve decreases steadily with decreasing temperature to a platform between 75 and 50 K with a value around 8.3 emu K mol⁻¹. The presence of this platform might indicate a non-diamagnetic ground state of **3**. However, there is no out-of-phase signal in ac susceptibility data which means **3** is not an SMM.

For **4**, the room temperature $\chi_M T$ value is 20.6 emu K mol⁻¹, which is consistent with four cobalt(II) ions and four chromium(III) ions with a g value of just over 2. This is reasonable if considering the combined actions of the unquenched orbital momentum of octahedral cobalt(II) ions and the less half-filled chromium(III) ions. Upon cooling, the $\chi_M T$ vs. T curve decreases steadily with decreasing temperature to a value around 1.0 emu K mol⁻¹ at 2 K. This decrease is probably due to a mixture of antiferromagnetic coupling between the metal centres and single ion effects for the cobalt(II) centres. It seems that the ground state in **4** is likely to be low.

For **5**, the room temperature $\chi_M T$ value of 31.4 emu K mol⁻¹ is consistent with eight cobalt(II) ions and four chromium(III) ions with a g value of ~ 2.4 . The larger g value is consistent with the majority of octahedral cobalt(II) ions with unquenched orbital momentum. Upon cooling, the $\chi_M T$ vs. T curve decreases steadily with decreasing temperature to a value around 11 emu K mol⁻¹ at 2 K. This decrease is again likely to be due to a mixture of antiferromagnetic interactions and crystal field effects at cobalt(II). The rapid low temperature fall in $\chi_M T$ for **5** suggests it will have a very low spin ground state.

In summary, we have successfully used a secondary starting material **3** to further react with the phosphonic acid, leading to two new larger heterometallic clusters **4** and **5**. The reason of the solvent-dependent nuclearity is probably associated with the coordination of the solvent molecules in these structures. Although these complexes do not lead to high-spin ground states, it does provide a route to fabricate 3d–3d heterometallic clusters.

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Notes and references

§ Synthesis. Compounds **1** and **2** were synthesized according to the established methods.¹⁸ Compound **3** was obtained by refluxing **1** (1.0 g, 1.05 mmol) and **2** (0.7 g, 0.7 mmol) in toluene (30 ml) for 3–5 h to give a blue solution. The solution was filtered and acetone (30 ml) added. Crystals form after 24–48 h (yield 87%). Compound **4** was obtained by mixing **3** (0.2 g, 0.14 mmol) and H₂O₃PⁿBu (0.02 g, 0.16 mmol) in EtOH (20 ml) and stirring at room temperature overnight. Pale blue needles were isolated from the mother solution after standing for a few days. Yield 55%, based on M₆. EA for C_{73.20}H_{153.60}Co₄Cr₄O_{37.60}P₂, found (calc): C 40.90 (41.06), H 7.28 (7.23), P 2.96 (2.89), Cr 9.64 (9.71), Co 11.11 (11.01). IR: 2961 (m), 2929 (m), 2871 (m), 1548 (broad, s), 1485 (s), 1458 (m), 1423 (s), 1376 (m), 1361 (m), 1228 (s), 1082 (broad, s), 984 (m), 899 (w), 876 (w), 832 (w), 787 (w), 668 (w), 613 (w), 539 (w) cm⁻¹. Compound **5** was obtained by mixing **3** (0.1 g, 0.07 mmol) and H₂O₃PⁿBu (0.009 g, 0.07 mmol) in MeOH (20 ml) and stirring at room temperature overnight. Pale pink needles were isolated from the mother solution after standing for several weeks. Yield 40%, based on M₆. EA for C₇₂H₁₈₂Co₈Cr₄O₅₅P₄, found (calc): C 31.69 (31.64); H 6.23 (6.72); P 4.53 (4.54); Cr 7.68 (7.61); Co 17.37 (17.27). IR: 2959 (m), 2928 (m), 2818 (m), 1579 (m), 1563 (s), 1506 (m), 1484 (s), 1457 (m), 1419 (s), 1376 (m), 1362 (m), 1229 (m), 1020 (broad, s), 993 (s), 964 (m), 895 (w), 834 (vw), 788 (w), 667 (w), 600 (w), 542 (m) cm⁻¹. Crystal data. For **3**, C₅₆H₁₀₂Co₄Cr₂O₃₄, M = 1499.10, monoclinic, space group P2₁/n, T = 100(2) K, a = 23.599(5), b = 16.080(4) Å, c = 18.887(4) Å, β = 94.36(1)°, V = 7146(3) Å³, Z = 4, ρ = 1.393 g cm⁻³, total data 41 853, unique data 15 455 (R_{int} = 0.0630), μ = 1.270 mm⁻¹, 964 parameters, R₁ = 0.0625 for I ≥ 2σ(I) and wR₂ = 0.1509 for all data. For **4**, C_{73.20}H_{153.60}Co₄Cr₄O_{37.60}P₂, M = 2141.22, monoclinic, space group P2₁/n, T = 150(2) K, a = 14.0004(11), b = 23.3797(18), c = 16.6605(13) Å, β = 95.0510(10)°, V = 5432.2(7) Å³, Z = 2, ρ = 1.309 g cm⁻³, total data 182 988, unique data 12 863 (R_{int} = 0.0467), μ = 1.080 mm⁻¹, 742 parameters, R₁ = 0.0793 for I ≥ 2σ(I) and wR₂ = 0.2306 for all data. For **5**, C_{75.15}H₁₇₅Co₈Cr₄O_{47.75}P_{4.10}, M = 2649.37, monoclinic, space group P2₁/c, T = 150(2) K, a = 23.670(3), b = 15.1475(10), c = 35.695(8) Å, β = 109.321(9)°, V = 12 077(3) Å³, Z = 4, ρ = 1.457 g cm⁻³, total data 119 625, unique data 29 974 (R_{int} = 0.0723), μ = 1.544 mm⁻¹, 1717 parameters, R₁ = 0.0639 for I ≥ 2σ(I) and wR₂ = 0.1883 for all data. The data of **3** were recorded on a Bruker SMART CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The data of **4** and **5** were recorded on a Bruker APEX II CCD diffractometer with synchrotron radiation (λ = 0.78480 and 0.69070 Å for **4** and **5**, respectively). The structures were solved by direct methods and refined on F² using SHELXTL. The chromium and cobalt were distinguished based on structure, elemental analysis and charge considerations. The chromium centres have much more regular octahedra with shorter bond lengths, chromium bond range 1.941(1)–2.013(2) Å (average 1.98 Å) for **3**, 1.927(4)–2.050(3) Å (average 1.97 Å) for **4** and range 1.939(4)–2.043(4) Å (average 1.98 Å) for **5** and octahedral cobalt bond range 2.008(1)–2.656(2) Å (average 2.14 Å) for **3**, 1.976(3)–2.37(5) Å (average 2.13 Å) for **4** and range 2.022(4)–2.272(4) Å (average 2.11 Å) for **5** (see Tables S1, S2 and S3 in ESI†).

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