**Synthesis and structural and magnetic characterization of a hexadecanuclear cobalt phosphonate compound†**

**Yun-Sheng Ma,**a You Song,b Xiao-Yan Tanga and Rong-Xin Yuana

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A wheel-like hexadecanuclear cobalt phosphonate [Co₁₆(OH)₆(chp)₂₂(O₃PC₆H₉)₂(H₂O)₄] has been synthesized by reactions of cobalt perchlorate with cyclohexenephosphonic acid (H₂O₃PC₆H₉) and 6-chloro-2-pyridone (chp) in the presence of Et₃N. Magnetic studies on the compound show a general decline of χₚT with decreasing T. The appeared maximum of χₚT at low temperature suggests the presence of a non-diamagnetic ground state. The alternating current susceptibilities show frequency-dependent signals.

**Introduction**

Research on single-molecule magnets (SMMs), has been a focal point in the magnetochemistry field in the past decade, and is still rapidly growing. The requirements for SMM behavior are well established: the presence of a large-spin ground state (S) and an Ising-type magnetic anisotropy (D < 0) leads to an energy barrier (ΔE) to reorientation of the magnetization. Thus, great efforts have been mainly made on Mn(III) containing clusters, to exploit the associated large single-ion anisotropy. To date, a large number of oxo-bridged Mn(III)-based SMMs with nuclearity as high as [Mn₈₄] and SMMs incorporating lanthanide ions associated with a large spin and/or large anisotropy have been reported. Co(II) with a large anisotropy due to an orbitally degenerate ground state is another promising candidate ion for the isolation of SMMs. Hendrickson and coworkers reported a cube-like core containing a [Co₄] cluster as the first Co-based SMM. To date, several groups have exploited a number of synthetic strategies to obtain the Co-based SMMs and shown some interesting results.

Phosphonates have been proved to be versatile ligands in the construction of polynuclear clusters. We have been exploiting poly metallic complexes with phosphonate as ligands, and found Mn₁₃, Mn₂₃ and Mn₃₇Cl₄ clusters show slow magnetic relaxation. To seek new structural types of SMMs, we exploit the Co(II) phosphonate chemistry. Here we report a hexadecanuclear cobalt cage, related to the Chandrasekhar approach, by using deprotonated 6-chloro-2-pyridone (chp⁻) as the co-ligand.

**Experimental**

**Synthesis**

Cyclohexene phosphonic acid (H₂O₃PC₆H₉) was prepared according to the literature method. All other starting materials were used as obtained from Aldrich.

\[\text{[Co₆(OH)₆(chp)₂₂(O₃PC₆H₉)₂(H₂O)₄]·10CH₂Cl₂·2H₂O.}\]

Co(ClO₄)₂·6H₂O (0.73 g, 2 mmol) was dissolved in CH₃CN (25 mL). To this was added Hchp (0.5182 g, 4 mmol), H₂O₃PC₆H₉ (0.0535 g, 0.33 mmol) and triethylamine (0.64 mL, 4.7 mmol); this resulted in a deep purple solution, which was stirred for 48 h. The resulting purple micro-crystals were collected by filtration. The crystals were dissolved in CH₂Cl₂ and layered with hexane to give deep-purple block crystals of 1·10CH₂Cl₂·2H₂O. Yield: 15% (based on Co). Elemental analysis calc (%) for C₁₃₂H₂₂₆Cl₈Co₆N₁₉O₄P₂: C 30.78, H 2.39, N 5.98. Found: C 30.61, H 2.55, N 5.78. IR (KBr, cm⁻¹): 3482 (br), 1638 (m), 1444 (s), 1342 (m), 1168 (s), 1069 (m), 1004 (s), 933 (s), 786 (s), 728 (m), 700 (m), 613 (s), 478 (s), 406 (s).

**Measurements**

The elemental analyses were performed on a PE 240 elemental analyzer. The IR spectra were recorded on a NICOLET 380 spectrometer with pressed KBr pellets. All the magnetic studies were performed on microcrystalline samples. The magnetic susceptibilities were measured on a Quantum Design MPMS SQUID-XL7 magnetometer. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal’s constants.

**X-Ray crystallographic analysis**

A single crystal of dimensions 0.40 × 0.38 × 0.32 mm³ was used for structural determination on a Rigaku SCX mini diffractometer using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) at room temperature. A hemisphere of data were collected in the θ range of 3.01–25.00° using a narrow frame method with scan widths of 0.30° in ø and an exposure time of 15 s per frame. Numbers of collected and unique reflections are 40839 and 16833.
Fig. 1 The structure of **I** in the crystal. Colour scheme: Co, green; P, magenta; N, blue; O, red; C, black line; Cl, light green; H, pale.

(R_{int} = 0.0736). Cell parameters were refined by using the program **CrystalClear** on all observed reflections. The collected data were reduced by using the program **CrystalClear**, and an absorption correction (multiscan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined on \( F^2 \) by full matrix least squares using **SHELXTL**. All the non-hydrogen atoms were located from the Fourier maps and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. Crystallographic and refinement details are listed in Table S1†. Selected bond lengths and angles are given in Table S2†.

## Results and discussion

### Synthesis

Reactions of cobalt perchlorate with 1/6 equiv of \( \text{H}_2\text{O}_3\text{PC}_6\text{H}_9 \), 2 equiv of Hchp, and 7/3 equiv of \( \text{Et}_3\text{Ni} \) give deep-purple crystals. Et\( _3\)Ni was added to deprotonate the phosphonic acid and Hchp. Increasing the amount of \( \text{H}_2\text{O}_3\text{PC}_6\text{H}_9 \) in the system yielded gel which could not be dissolved in common solvents. The synthetic approach adopted is similar to those reported but if the phosphonate ligand is replaced with cyclohexenephosphonate, the structures of the crystalline materials are different in all cases. With phenylphosphonate, a tridecanuclear compound \( [\text{Co}_{13}(\text{OH})_3(\text{chp})_{19}(\text{O}_3\text{PPh})_2(\text{H}_2\text{O})_2(\text{EtOAc})_2] \) results. While with benzylphosphonate and ethylphosphonate, a tetradecanuclear compound results: \( [\text{Co}_{14}(\text{OH})_3(\text{chp})_{20}(\text{O}_3\text{PR})_2(\text{H}_2\text{O})_2](\text{R} = \text{benzyl and Et}) \). These results indicate that the steric effects and solubility of the organic groups of the ligands may influence the crystallization of the clusters.

### Crystal structure

Single-crystal X-ray diffraction studies reveal that complex \( \text{I} \cdot 10\text{CH}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O} \) crystallizes in a triclinic space group \( \text{P}\overline{1} \). The asymmetric unit of \( \text{I} \) contains eight cobalt atoms, three \( \mu_3-\text{OH}^- \), one \( \text{C}_6\text{H}_9\text{PO}_3^- \), eleven chp\(^-\) and two \( \text{H}_2\text{O} \) molecules (Fig. 1). The core structure of \( \text{I} \) is centrosymmetric, and may be described as two equivalent \( \mu_3\) segments bridged together through the \( \mu_3\)-O16 and \( \mu_3\)-O16A atoms of chp\(^-\). Ten of the cobalt centers make up a distorted wheel, with the six remaining sites lying above and below the plane of the wheel. In the asymmetric unit, three \( \{\text{Co}_{(\mu_3-\text{OH})}\} \) units are corner shared at Co1 and Co3 sites to form an irregular heptametallic fragment. The other cobalt site in the asymmetric unit Co4 is attached to this heptametallic fragment through the phosphonate and the \( \mu_3\)-O atoms of chp\(^-\) ligands. The Co–O/N bond distances (1.944(7)–2.277(5) Å) and O–Co–O/N bond angles (60.9(2)–172.2(2)°) and Co–O–Co bond angles (94.8–129.6(3)°) are similar to those found in other polynuclear cobalt complexes. All the Co ions are divalent. The metal oxidation states and the protonation of \( \text{OH}^- \) are established by the Co and O bond valence sum calculations and by consideration of bond lengths and charge balance (Table S3†).

The structure of the Co\(^{II}\) segment is different from that reported. In \( [\text{ET}_{3}\text{NH}]_2[\text{Co}_{8}(\text{chp})_{10}(\text{O}_3\text{PPh})_2(\text{NO}_3)_2(\text{Hchp})_2] \), two P atoms from phosphonate and four Co atoms lie on the vertices of a central trigonal prism. The final four Co atoms lie above the triangular faces of the prism.

One of the three oxygen atoms of each phosphate bridges two cobalt sites (Co1 and Co2) while each of the remaining two oxygen atoms binds only to one Co site. The phosphonate therefore shows the \( \eta^1,\eta^1,\eta^2-\mu_2 \) bridging mode (Scheme 1). The chp\(^-\) ligands coat the exterior of the cluster, and as is typical, show a variety of coordination modes. Of the 11 chp\(^-\) ligands in the asymmetric unit, 5 show the \( \eta^1,\eta^2-\mu_2 \) mode, 2 show the \( \eta^1,\eta^1-\mu_3 \) mode, 2 show the \( \eta^1,\eta^1-\mu_1 \) mode, etc.
of saturating up to a field of 7 T at 1.8 K (Fig. S1†). Given the high anisotropy of the ions present and the high nuclearity of the cluster with many spin states populated at low temperature this is unsurprising.

The temperature-dependent ac magnetic susceptibilities for I-10CH2Cl2·2H2O were collected in zero-applied dc field with a 5 G ac field oscillating at frequencies in the range of 1–1500 Hz and in the temperature range of 1.8–10 K. Fig. 3 shows the in-phase ($\chi''_m T$) and out-of-phase signals ($\chi''''_m$) versus $T$ curves. These showed frequency-dependent out-of-phase signals below 3 K, which may be attributed to superparamagnetic relaxation of the magnetization of I-10CH2Cl2·2H2O. However, since no maxima were observed down to 1.8 K, quantitative estimation of the relaxation kinetics was not possible.\(^5\)

\begin{figure}
\centering
\includegraphics[width=\linewidth]{fig3}
\caption{Plots of $\chi''_m T$ (upper) and $\chi''''_m$ (lower) versus $T$ for I-10CH2Cl2·2H2O. $\chi''_m T$ and $\chi''''_m$ are the molar in-phase and out-of-phase ac susceptibilities, respectively.}
\end{figure}

Conclusions

In conclusion, we have obtained a novel wheel-like hexadecanuclear cobalt phosphonate [Co16(OH)6(chp)22(O3PC6H9)2(H2O)4]. The complex displays frequency-dependent out-of-phase signals below 3 K, and more evidence is required to determine if it is an SMM. Further work is in progress to obtain new cobalt
phosphonate clusters by systematic exploration of the variable synthetic parameters.

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Notes and references


14 In pentacoordinated systems, the actual geometry of the complex can be described by a structural index parameter $\tau$ such that $\tau = (\beta - \alpha)/60^\circ$, where $\beta$ and $\alpha$ are the two largest angles ($\beta > \alpha$). For details see: A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, J. Chem. Soc., Dalton Trans., 1984, 1349–1356.