

Serendipitous Assemblies of Two Large Phosphonate Cages: A Co₁₅ Distorted Molecular Cube and a Co₁₂ Butterfly Type Core Structure

Javeed Ahmad Sheikh, Soumyabrata Goswami, Amit Adhikary, and Sanjit Konar*

Department of Chemistry, IISER Bhopal, Bhopal-462023, India

Supporting Information

ABSTRACT: This report describes the synthesis, characterization, and magnetic properties of two novel phosphonate-based Co^{II} cages. Structural investigation reveals some interesting geometrical features in the molecular core that may provide new models in single molecular magnetic materials.

The study of nanoscopic paramagnetic metal-ion aggregates has emerged as a focal point in material chemistry owing to their immense technological applications.¹ In the field of molecule-based magnetic materials, studies have largely been based on discrete transition-metal aggregates, as they typically display properties of a single molecular magnet. A large number of molecular magnetic aggregates have been documented in the literature, where carboxylate, tripodal alkoxide, and related ligands have been used.^{1a,2} In this context, phosphonate ligands are an ideal choice, as they possess three O donors and are capable of binding up to nine metal centers in principle. But, a thorough literature survey reveals that phosphonate-based transition metal complexes have rarely been employed for discrete molecule synthesis owing to their tendency to form layered structures and limited solubility.³ Over the past few years, considerable progress has been achieved by the groups of Winpenny, Clearfield, Chandrasekhar, and others to explore metal-phosphonate cage compounds as magnetic materials.⁴ However, until today, most of the reported metal-phosphonate clusters/cages bear core structures of irregular geometrical pattern. From a magnetic point of view, regular polygonal (Archimedean and Platonic solid) type paramagnetic cores are extremely important and find wide applications.^{2c} Unfortunately, there are rare examples in the literature that demonstrate cages with regular geometrical cores.

As part of the investigation in exploring cages with regular geometrical cores, herein we report the synthesis, structural characterization, and magnetic study of two novel phosphonate-based Co^{II} cage compounds. The geometry of the inorganic core of the molecules can be best described as a combination of Platonic as well as Archimedean type polygons. The phosphonic acid ligand, p-nitrobenzylphosphonic, was synthesized following the Micheliš–Arbusov reaction^{5a,b} from its corresponding bromide. In two similar one pot reactions, the carboxylate bridged cobalt dimer,^{5c} [Co₂(μ-OH₂)(O₂C^tBu)₄](HO₂C^tBu)₄, was reacted with phosphonic acid and 6-chloro-2-hydroxypyridine. A mere change in ratio of the reactants from 1:1:1 to 1:1:0.5 in the above order resulted in the formation of two high nuclearity cages having molecular formulas of

[Co₁₅(chp)₈(chpH)(O₃PR)₈(O₂C^tBu)₆(CH₃CN)₃](CH₃CN) (1) and [Co₁₂(chpH)₂(O₃PR)₄(O₂C^tBu)₁₂(CO₃)₄](CH₃CN) (2), R= p-nitrobenzyl, chpH = 6-chloro-2-hydroxypyridine. All the metals centers in both molecules are at a +II oxidation state as required for the charge balances and confirmed by magnetic measurements and BVS calculations (Table S1, Scheme 2, Supporting Information, SI).⁶ The molecular structure of complex 1 consists of an inorganic core made of 15 Co^{II} that are held together by bridging oxygen atoms from eight doubly deprotonated phosphonates and six carboxylate ligands (Figure 1). Nine 6-chloro-2-hydroxypyridine units are also present per

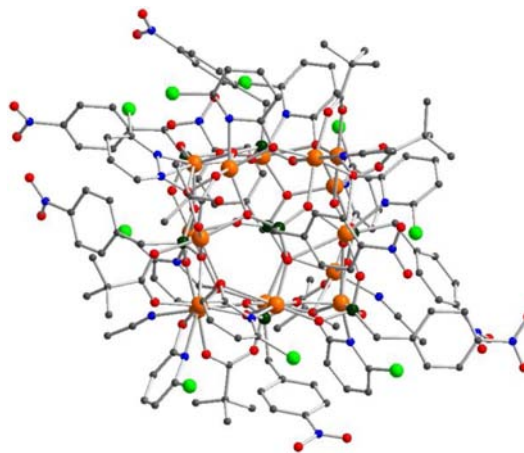


Figure 1. Color code: orange, cobalt; bluish-green, phosphorus; red, oxygen; nitrogen, blue; gray, carbon; and green, chlorine. Hydrogen atoms are omitted for clarity.

molecule and are functioning as nitrogen and oxygen donation ligands towards cobalt sites. All the organic parts of the coligands are pointed towards the outer periphery of the molecule. The shape of the inorganic interior can be best described as a distorted cubic unit made of metal and phosphorus tethered by oxygen atoms (Figure 2a, Figure S8, SI). Out of the 15 Co^{II} centers, nine are exhibiting octahedral geometry, five tetrahedral, and one square pyramidal arrangement (Table S1, SI). Six of the eight phosphonate ligands are showing a 5.221 bridging mode and another two are exhibiting a 3.111 mode as per Harris notation⁷ (Scheme S1, SI). Another interesting perspective of the structure was observed after removal of all the atoms except Co and P centers and connecting them through imaginary lines

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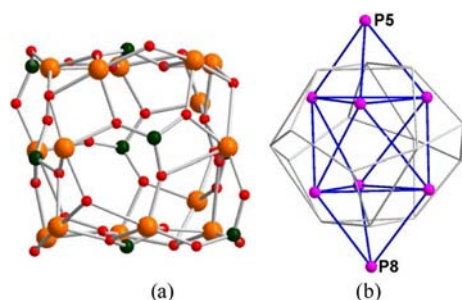


Figure 2. (a) Core structure of **1**, color code same as Figure 1. (b) “Stick” type view of the core after removing all atoms except Co and P.

(Figure 2b). Here, each phosphorus (except P5 and P8) bears five Co^{II} centers as nearest neighbors, and thereby, a pentagonal unit is formed. Each pentagon shares three vertices and an edge with its adjoining pentagons and thereby forms a new type of geometry having total six pentagonal and eight triangular faces with each of the vertices occupied by a metal center. A representative polyhedral view of the core can be seen after the removal of two phosphorus sites, P5 and P8 (Figure 3). The

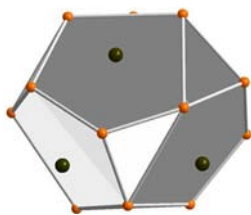


Figure 3. Polyhedral view of the core of complex **1**, central spheres represent P.

remaining two phosphonate groups cap two of the opposite triangular faces and observe a 3.111 bridging mode.⁷ The average distance of cobalt ions of the hexagonal faces is 3.20 Å and that of triangular faces is 3.37 Å. The most recognizable feature of this structure is the presence of paramagnetic pentagonal faces, where each phosphorus at the center of the pentagonal unit is connected to five cobalt, as phosphonate adopts a 5.221 bridging mode.⁷

These pentagonal units bear resemblance to the idea presented by Müller et al.⁸ According to him, the presence of $\{\text{Mo}_6\}$ pentagons is the prime requirement for the formation of nanoscale polyoxometalate cages.^{8c} The generation of pentagonal metal arrays by phosphonate ligands opens up a new avenue in the scientific community for exploring giant phosphonate-based nanoscopic cages. Complex **2** (see Figure 4 for molecular structure) also has an organic outer sheath and inorganic core within. The core is made of 12 octahedral Co^{II} centers held together by four μ_3 oxo groups of four phosphonate ligands, four carboxylates, four carbonates, and two 6-chloro-2-hydroxypyridine coligands. The carbonate ligands came from unreacted cobalt carbonate used in the preparation of cobalt dimer as starting material. All the phosphonate ligands adopt a 6.222 bridging mode as per Harris notation (Scheme S1, SI).⁷ After removing the organic part except selected carbon atoms, the inorganic metal–oxo core of the molecule resembles a butterfly type shape.⁹

Further removal of all atoms except Co and P sites and connecting them through imaginary lines reveals some very interesting geometrical features. Each phosphorus atom is

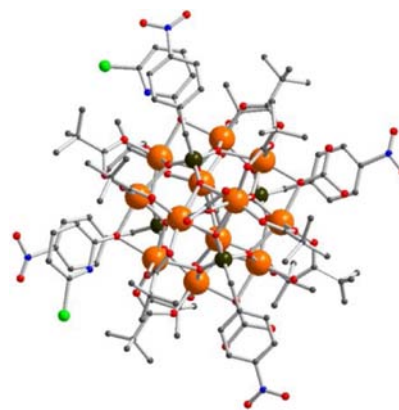


Figure 4. Molecular structure of **2** in the crystal. Color code: Same as in **1**.

surrounded by six cobalt ions and thereby forms four such hexagons (Figure 5a). Consequently, a new geometry consisting

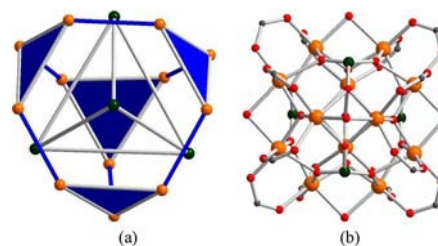


Figure 5. (a) “Stick” type view of the core after removing all atoms except Co and P. (b) Core structure of **2**, color code: same as **1**.

of four hexagonal and four trigonal faces is formed where all the vertices are occupied by metal ions. The average distance of cobalt ions of the hexagonal faces is 3.20 Å and that of triangular faces is 3.37 Å. The interconnection of P atoms resulted in a tetrahedral geometry where four P (P_4) occupied its vertices with an average P–P distance of 5.16 Å. Interestingly, the P_4 tetrahedral structure is surrounded by the Co^{II} polygon, and this feature makes the structure unique. Although the geometry of the core is slightly distorted, it is not difficult to see the presence of four C_3 axes each at the vertex of P_4 T_d and running through the center of each Co_3 triangular unit at the opposite end (Figure 5b). Nine mirror planes are also present along each edge of the tetrahedron and intersecting two opposite edges of the Co_6 hexagonal faces.

For magnetic characterization, dc susceptibility data of **1** and **2** were collected on polycrystalline samples in the range 1.8–300 K at 0.1 T. The magnetic measurements for **1** and **2** are shown in the form of a $\chi_M T$ ($\chi_M T$ is the molecular magnetic susceptibility) versus temperature (T) plot in Figure 6. The room temperature $\chi_M T$ value for **1** is 36.45 $\text{cm}^3 \text{Kmol}^{-1}$ and for **2** it is 30.07 $\text{cm}^3 \text{Kmol}^{-1}$. Both values are significantly higher than the calculated spin only values of 28.12 $\text{cm}^3 \text{Kmol}^{-1}$ ($g = 2$) and 22.50 $\text{cm}^3 \text{Kmol}^{-1}$ ($g = 2$) for isolated 15 and 12 Co^{II} centers, respectively. This can be explained on the basis of the orbital contribution of Co^{II} , which is known to be significant in an octahedral field. The $\chi_M T$ value decreases gradually from room temperature to 13.63 $\text{cm}^3 \text{Kmol}^{-1}$ for **1** at 55 K and then sharply to 2.05 $\text{cm}^3 \text{Kmol}^{-1}$ at 1.9 K. For **2**, the $\chi_M T$ value decreases gradually from room temperature to 21.99 $\text{cm}^3 \text{Kmol}^{-1}$ at 150 K and then sharply to 5.07 $\text{cm}^3 \text{Kmol}^{-1}$ at 4.5 K, followed by an

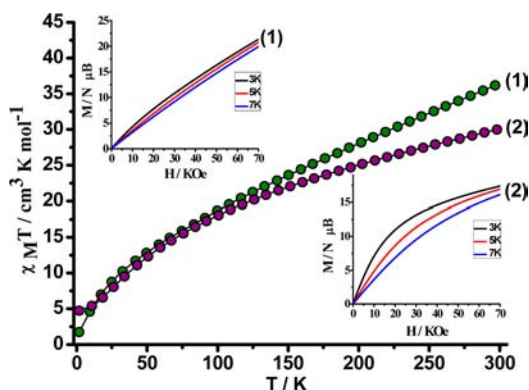


Figure 6. Temperature dependence of $\chi_M T$ measured at 0.1 T and magnetization curves (inset graphs) measured at 3, 5, and 7 K for complex 1 (top) and 2 (bottom).

increase to $5.16 \text{ cm}^3 \text{ K mol}^{-1}$ at 2.3 K before dropping sharply to $4.73 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. The gradual decline at higher temperatures may be attributed to the presence of intramolecular antiferromagnetic interaction in the molecules. Further decrease of $\chi_M T$ values at lower temperatures for both compounds could be due to the presence of intercage antiferromagnetic interactions and/or zero field splitting of the ground state. Above 55 K (for 1) and 150 K (for 2), the magnetic susceptibilities follow a Curie–Weiss behavior with $C = 28.12 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $C = 22.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, respectively. The M vs H plots for compounds 1 and 2 from 3 to 7 K (inset of Figure 6) show a steady increase that reaches 21.3 and $17.4 \mu_B$, respectively, at 7 T and 3 K without any saturation. These values are inconsistent with 15 and 12 uncoupled Co^{II} ions, and it can be assumed that the Co^{II} ions are strongly antiferromagnetically coupled in both cases. The unsaturated behavior of the plots can be explained by assuming strong magnetic anisotropy of the ions present with high nuclearity resulting in many spin states populated at low temperature.¹⁰ The entropy changes (ΔS_m) and hence the MCE for both compounds were performed according to the Maxwell equation $\Delta S_m(T)_{\Delta H} = \int [\partial M(T, H) / \partial T]_H dH$.

In conclusion, an attempt has been made to explore the geometry of the core of two serendipitously formed metal-phosphonate cage compounds. The slight variation of the coligand ratio in the synthesis resulted in a dramatic change in the core structure. Therefore, exploring symmetry and regular geometry of the paramagnetic core is very important in terms of understanding the magnetic properties of the molecular systems. Further work along this line is in progress in our group.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, synthesis of both compounds, crystallographic data, BVS calculations, and PXRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: skonar@iiserb.ac.in.

Notes

The authors declare no competing financial interest.

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