

*Supporting information for*

## **Serendipitous assemblies of two large phosphonate clusters: A Co<sub>15</sub> distorted molecular cube and a Co<sub>12</sub> butterfly type core structure**

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### **Experimental Section**

**Materials and Methods.** Both the complexes were synthesized from the starting material [Co<sup>II</sup><sub>2</sub>(μ-OH<sub>2</sub>)(O<sub>2</sub>C<sup>t</sup>Bu)<sub>4</sub>](HO<sub>2</sub>C<sup>t</sup>Bu)<sub>4</sub> **Co<sub>2</sub>**, which was made by a literature method<sup>5c</sup>. Other reagents were used as received from Sigma Aldrich without any further purification. Magnetic susceptibility and magnetization measurements were carried out on a Quantum Design SQUID-VSM magnetometer. Direct current magnetic measurements were performed with an applied field of 1000 G in the 2-300 K temperature range. Elemental analysis were done using the Autocube model from Elementar. BVS calculations were done following the procedure given by Liu and Thorpe (*Inorg. Chem.* **1993**, 32, 4102-4105). IR was taken on a Perkin Elmer spectrum BX instrument.

**X-ray Crystallographic Data Collection and Refinement of the Structures.** Data for 1, 2, were collected on a Bruker APEX II diffractometer (Mo KR, λ = 0.71069 Å<sup>o</sup>). Crystal data and refinement parameters are given after synthesis. In all cases the selected crystals were mounted on the tip of a glass pin using Paratone-N oil and placed in the cold flow (140 K) produced with an Oxford Cryo system. Complete hemispheres of data were collected using Φ and ω scans. Integrated intensities were obtained with SAINT+, and they were corrected for absorption using SADABS. Structure solution and refinement was performed with the SHELX package. The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F<sup>2</sup>.

*The quality of both the crystals was not good and we are unable to grow better quality crystals. We are also unable to resolve and refine all the solvents present. Presence of large number of tert-butyl group in the molecules resulted in positional disorders.*

## Synthesis of Ligand

**p-nitrobenzylphosphonic Acid.** The ligand was synthesised following the procedure given by S. Konar and A. Clearfield (*Inorg. Chem.* **2008**, *47*, 5573-5579). A mixture of 4-Nitrobenzylbromide (2.16 g, 10mmol) and triethylphosphite (1.87ml, 11mmol) was heated for 4 h at 165 °C under reflux. Excess triethylphosphite was removed under reduced pressure. Then, the crude product was refluxed with 6 M HCl to be hydrolyzed to the final product 4-Nitrobenzylphosphonic Acid. The acid was recrystallized from aqueous MeOH. The phosphonate ester as well as the acid was characterized by ESI mass spectra. Final yield was 2.04gm, 94.4%.

## Synthesis of Complexes

**[Co<sub>15</sub>(chp)<sub>8</sub>(chpH)(O<sub>3</sub>PR)<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>6</sub>(CH<sub>3</sub>CN)<sub>3</sub>].(CH<sub>3</sub>CN) (R = p-nitrobenzyl) (1)**

[Co<sup>II</sup><sub>2</sub>(μ-OH<sub>2</sub>)(O<sub>2</sub>C<sup>t</sup>Bu)<sub>4</sub>].(HO<sub>2</sub>C<sup>t</sup>Bu)<sub>4</sub> Co<sub>2</sub>, (100 mg, 0.1 mmol), 4-Nitrobenzylphosphonic acid (23 mg, 0.1 mmol), 6-chloro-2-hydroxypyridine (13 mg, 0.1 mmol) were taken in CH<sub>3</sub>CN (8ml) and stirred at ambient temperature for few minutes. This was followed by the addition of NEt<sub>3</sub> (30 mg, 0.3 mmol) and after further stirring for few minutes the contents were transferred into a Teflon lined steel autoclave and heated at 150°C for 18h and then cooled to room temperature at a rate of 0.05°C min<sup>-1</sup>. The resulting solid product was filtered and the deep blue solution was kept in a 15 mL vial for ca. 2 days. Deep blue block shaped crystals suitable for X-ray diffraction were collected by filtration, yield 30-45 mg, 30-45%, based on Co<sub>2</sub>. Elemental analysis, Calculated(found); C 36.82(36.69); N 6.48(5.95); H 3.15(3.27); IR (KBr, cm<sup>-1</sup>); 3430 (w), 3150 (m), 2173 (vw), 1617 (m), 156 (vs), 1445 (s), 1401 (vs), 1345 (m), 1232 (sh), 1160 (s), 1099 (m), 999 (s), 840 (s), 767 (w), 663 (w), 608 (m), 557 (w).

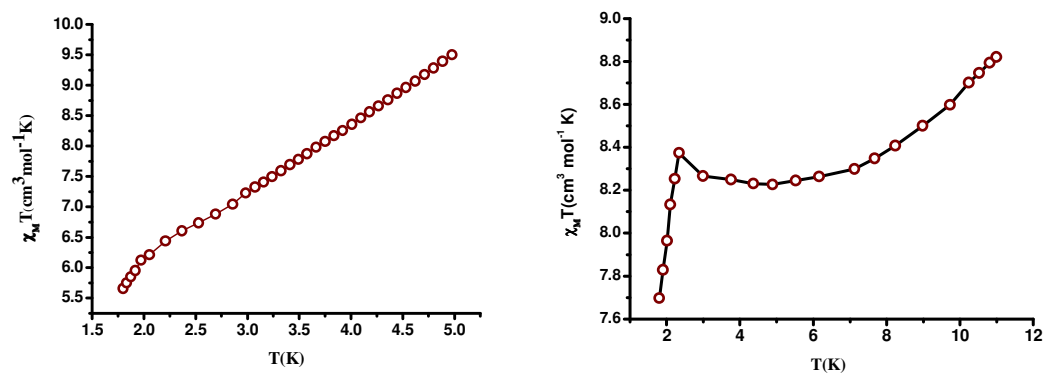
**Crystal data for 1:** C<sub>139</sub>H<sub>142</sub>N<sub>21</sub>Co<sub>15</sub>O<sub>61</sub>P<sub>8</sub>Cl<sub>9</sub>, monoclinic, P21/c, *a* = 17.8914 (15), *b* = 34.494(3), *c* = 32.494(3) Å, β = 104.938(4)°, *V* = 19376(3) Å<sup>3</sup>, *M* = 4533.60, *D<sub>c</sub>* = 1.558 g cm<sup>-3</sup>, *Z* = 4, *R<sub>f</sub>* = 0.0619, *wR<sub>2</sub>* = 0.1663 for 28750 reflections. CCDC no. 892410.

**[Co<sub>12</sub>(μ<sub>3</sub>-(OH)<sub>4</sub>)(chpH)<sub>2</sub>(O<sub>3</sub>PR)<sub>4</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>8</sub>(HO<sub>2</sub>C<sup>t</sup>Bu)<sub>4</sub>(HCO<sub>3</sub>)<sub>4</sub>].(CH<sub>3</sub>CN) (R = p-nitrobenzyl) (2)**

This compound was synthesised following a similar procedure as for **1** but 6-chloro-2-hydroxypyridine was scaled to half (6.5 mg, 0.05 mmol). Purple rectangular shaped crystals suitable for X-ray diffraction were collected by filtration after 4 days, yield 35-45 mg, 35-40%, based on Co<sub>2</sub>. Elemental analysis, Calculated(found); C 37.60 (36.89); N 2.95 (2.58); H

4.33 (4.57); IR (KBr,  $\text{cm}^{-1}$ ); 3443 (w), 2959 (m), 2059(w), 1607 (s), 1562 (vs), 1516 (m), 1484(s), 1423 (s), 1403 (sh), 1343 (vs), 1231 (m), 1146 (m), 1096 (s), 994 (s), 976 (vs), 895 (m), 855 (m), 767 (w), 694 (s), 609 (m), 543 (m).

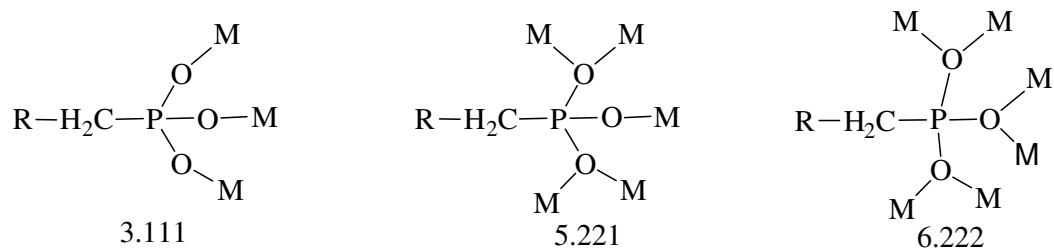
**Crystal data for 2:**  $\text{C}_{104}\text{H}_{155}\text{N}_7\text{Co}_{12}\text{O}_{62}\text{P}_4\text{Cl}_2$ , monoclinic,  $P2_1/c$ ,  $a = 16.7101(17)$ ,  $b = 32.185(3)$ ,  $c = 29.640(3)\text{\AA}$ ,  $\beta = 103.929(6)$ ,  $V = 15472(3)\text{\AA}^3$ ,  $M = 3397.36$ ,  $D_c = 1.410\text{ g cm}^{-3}$ ,  $Z = 4$ ,  $R_I = 0.0792$ ,  $\omega R_2 = 0.2172$  for 22419 reflections. CCDC no. 892411.



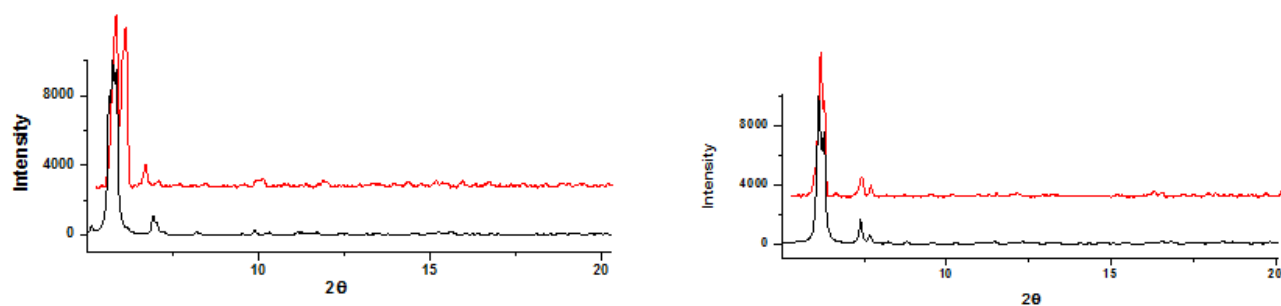
**Figure S1.** Temperature dependence of  $\chi_M T$  measured at 0.1 T for complex **1**(left) and **2**(right)

**Table S1.** BVS Calculation table for Complexes **1** and **2**

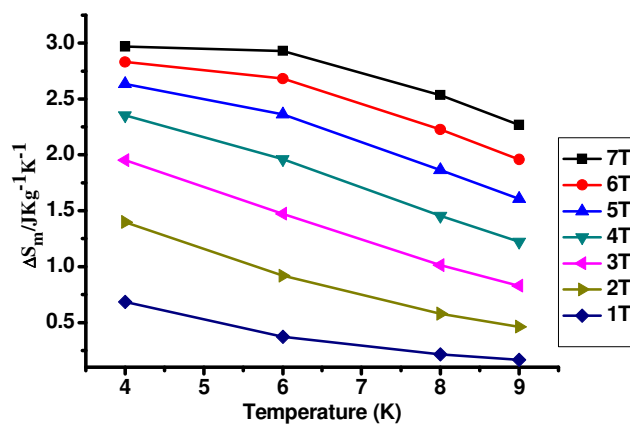
<b>1</b>				<b>2</b>			
Co site	BVS	Assigned Oxidation State	Coordinating atoms(Geometry)	Co site	BVS	Assigned Oxidation State	Coordinating atoms(Geometry)
Co1	1.89	2	6O( $O_h$ )	Co1	1.99	2	6O( $O_h$ )
Co2	1.74	2	3O,1N( $T_d$ )	Co2	1.94	2	6O( $O_h$ )
Co3	1.69	2	3O,1N( $T_d$ )	Co3	1.98	2	6O( $O_h$ )
Co4	1.70	2	3O,1N( $T_d$ )	Co4	2.07	2	6O( $O_h$ )
Co5	1.68	2	3O,1N( $T_d$ )	Co5	1.95	2	6O( $O_h$ )
Co6	1.65	2	3O,1N( $T_d$ )	Co6	2.02	2	6O( $O_h$ )
Co7	1.97	2	5O,1N( $O_h$ )	Co7	2.08	2	6O( $O_h$ )
Co8	1.91	2	6O( $O_h$ )	Co8	1.96	2	6O( $O_h$ )
Co9	1.77	2	4O,1N( $Sq.Py$ )	Co9	2.07	2	6O( $O_h$ )
Co10	1.90	2	6O( $O_h$ ) ( $O_h$ )	Co10	1.96	2	6O( $O_h$ )
Co11	1.95	2	5O,1N( $O_h$ )	Co11	2.10	2	6O( $O_h$ )
Co12	1.94	2	5O,1N( $O_h$ )	Co12	1.96	2	6O( $O_h$ )
Co13	1.99	2	5O,1N( $O_h$ )				
Co14	1.99	2	5O,1N( $O_h$ )				
Co15	1.99	2	5O,1N( $O_h$ )				



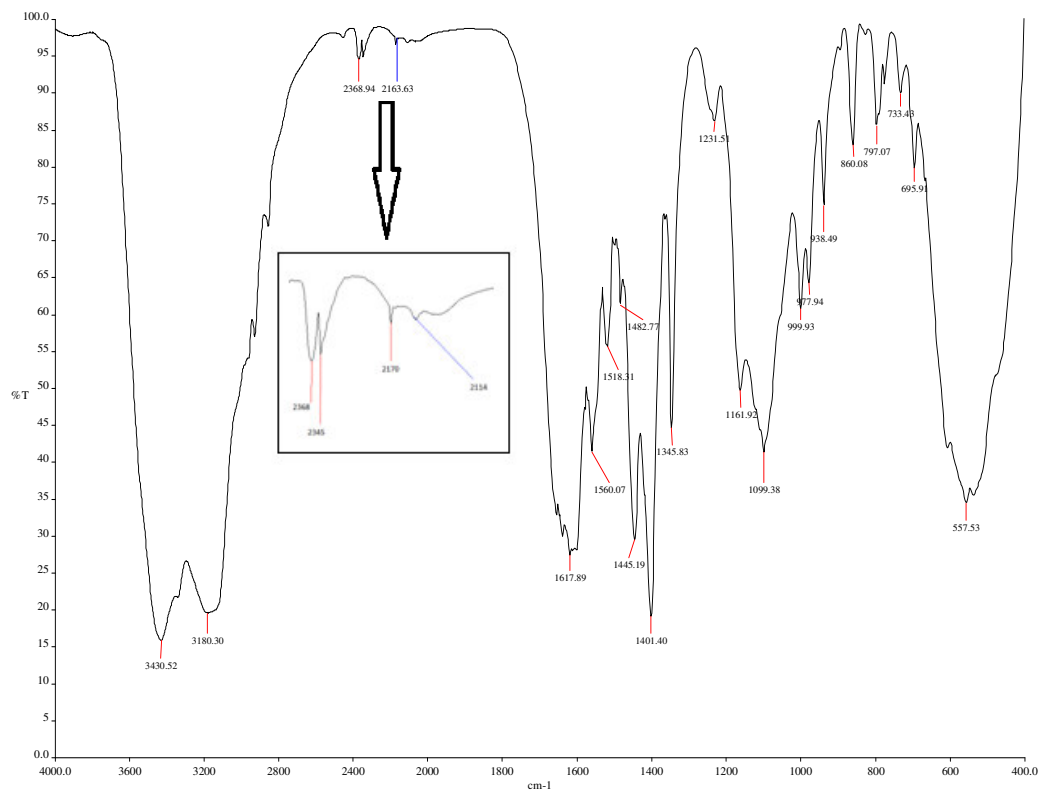
Scheme 1. Bridging modes of phosphonates in complexes **1** and **2**



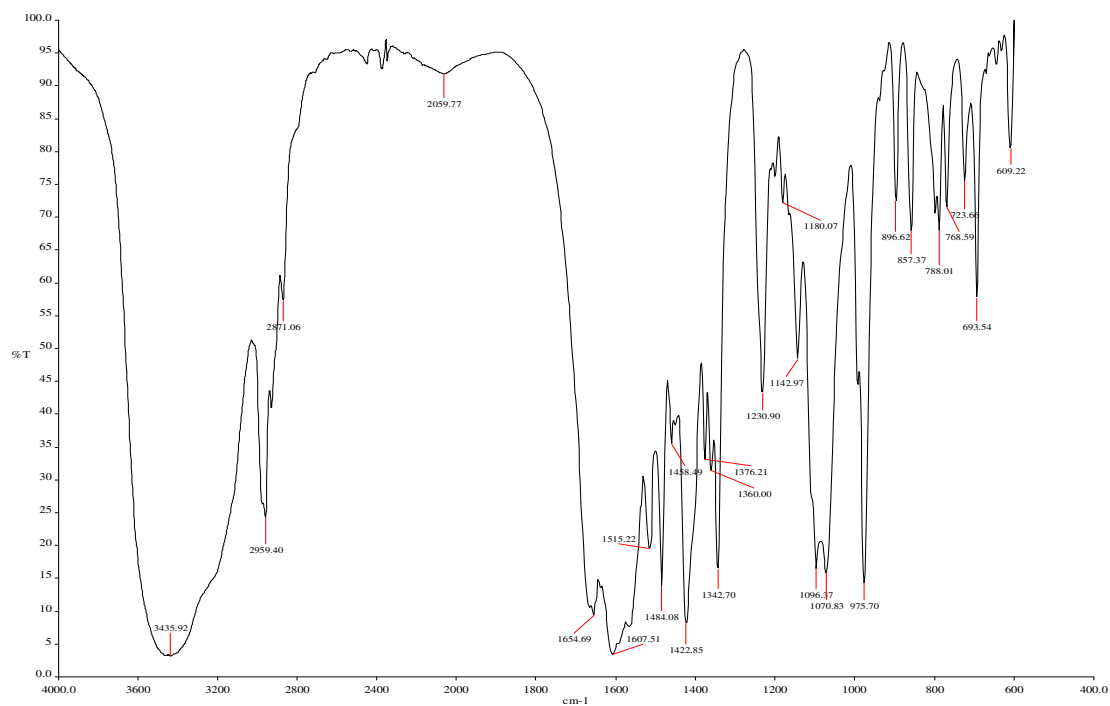
**Figure S2.** Powder XRD pattern for complexes **1** (left) and **2** (right), top pattern (experimental) and bottom (simulated).



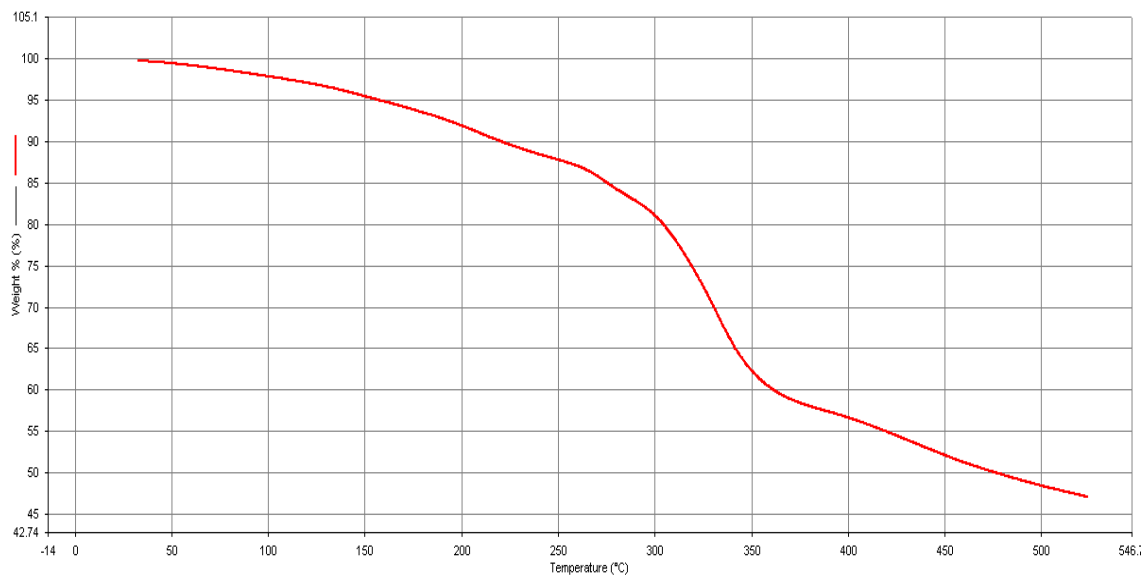
**Figure S3.** Calculation of  $\Delta S_m$  for complex **2** at different fields and temperatures.



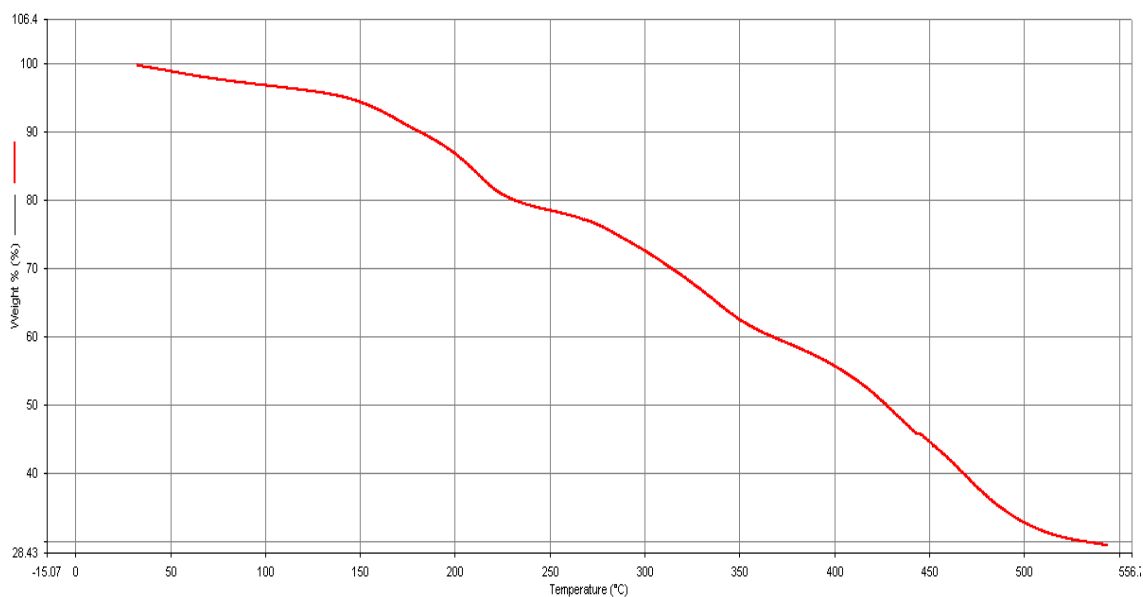
**Figure S4.** IR spectra of complex **1** (inset plot shows the magnified view of CN stretching region)



**Figure S5.** IR spectra of complex **2**



**Figure S6.** TGA plot of complex 1



**Figure S7.** TGA plot of complex 2

**Discussion on TGA results:** TG Analysis of both complexes reveals a weight loss of around 5% upto 150°C that may be assigned to the coordinated and non coordinated solvent molecules. Further weight loss of around 15% upto 250 °C probably corresponds to the aromatic nitro ligands, after which the complexes decompose completely.

**Scheme 2: Overall charge balance for the complexes are as follows:**

**Complex 1:**  $[\text{Co}_{15}(\text{chp})_8(\text{chpH})(\text{O}_3\text{PR})_8(\text{O}_2\text{C}^t\text{Bu})_6(\text{CH}_3\text{CN})_3] \cdot (\text{CH}_3\text{CN})$

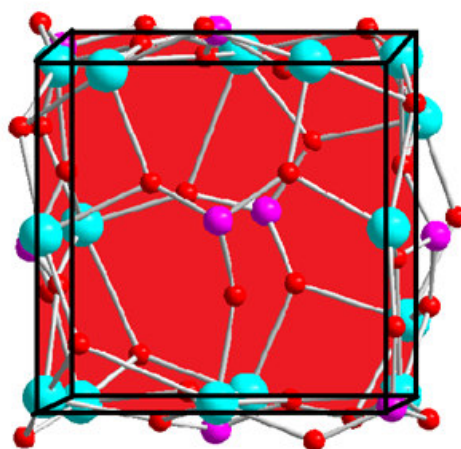
$15\text{Co} \times 2 = +30$  (total +ve charge = 30)

$8\text{chp} \times -1 = -8$ ,  $8\text{RPO}_3 \times -2 = -16$ ,  $6 \text{O}_2\text{C}^t\text{Bu} \times -1 = -6$ , (total -ve charge = 30)

**Complex 2:**  $[\text{Co}_{12}(\mu_3\text{-(OH)}_4)(\text{chpH})_2(\text{O}_3\text{PR})_4(\text{O}_2\text{C}^t\text{Bu})_8(\text{HO}_2\text{C}^t\text{Bu})_4(\text{HCO}_3)_4] \cdot (\text{CH}_3\text{CN})$

$12 \text{Co} \times 2 = +24$  (total +ve charge = 24)

$4\text{RPO}_3 \times -2 = -8$ ,  $8 \text{O}_2\text{C}^t\text{Bu} \times -1 = -8$ ,  $4\text{HCO}_3 \times -1 = -4$ ,  $4 \mu_3\text{-OH} \times -1 = -4$  (total -ve charge = 24)



**Figure S8.** Distorted Cubic view of Complex 1