

## Electronic Supplementary Information (ESI)

### A Unique type of a Dicobalt Cage Templated by weakly Coordinated Hexafluorophosphate Anion: Design, Structure and Solid-State NMR Investigations.

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**Synthesis of L = bis-benzimidazole-1, 3-phenylene:** The bidentate ligand **L** was prepared by addition of 1,3-dichloromethyl-2,5-dimethoxy-4,6-dimethylbenzene (1.09 g, 4.41 mmol) in CH<sub>3</sub>CN (50 ml) to benzimidazole (0.98 g, 8.3 mmol) in the presence of K<sub>2</sub>CO<sub>3</sub> (1.14 g, 8.24 mmol). The reaction was stirred for 30 minutes before being refluxed for 12 hours. The resulting precipitate was filtered and extracted with CHCl<sub>3</sub>. After being washed with distilled water the organic phase was isolated before being dried over MgSO<sub>4</sub>. The solvent was removed on a rotary evaporator to yield an off-white microcrystalline substance. Yield: 1.58 g (90%). C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>.H<sub>2</sub>O: calcd C 70.27, H 6.30, N 12.61; found C 70.64, H 6.10, N 12.57. <sup>1</sup>H NMR (400 MHz, DMSO-d<sup>6</sup>): δ = 8.10 ppm (s, =CH, 2H), 7.63(d, =CH, 2H), 7.47(d, =CH, 2H), 7.16(m, H-aromatic, 4H), 5.49(s, -CH<sub>2</sub>-, 4H), 3.70(s, MeO-, 3H), 3.50(s, MeO-, 3H), 2.12(s, CH<sub>3</sub>-, 6H).

X-ray Structural determination of {[PF<sub>6</sub>-(CH<sub>3</sub>-CN)<sub>2</sub>Co<sub>2</sub>(L)<sub>4</sub>][PF<sub>6</sub>]<sub>3</sub>} (**2**)

Crystals were mounted on fiberglass using paratone oil and immediately cooled to 150 K in a cold stream of nitrogen. All data were collected on a Nonius Kappa CCD diffractometer at 150(1) K using Mo K<sub>α</sub> (λ = 0.71073 Å) X-ray source and a graphite monochromator. The cell parameters were initially determined using more than 50 reflections. The crystal structures were solved in SIR 97<sup>1</sup> and refined in SHELXL-97<sup>2</sup> by full-matrix least-squares using anisotropic thermal displacement parameters for all non-carbon and non-hydrogen atoms. All the hydrogen atoms were placed in geometrically calculated positions.

1. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single crystal data*, *J. Appl. Cryst.* **32**, 115-119, **1999**.
2. Sheldrick, G. M. *SHELXL-97*, Universität Göttingen, Göttingen, Germany, **1997**.

## **I. Solid-State MAS NMR Measurement**

$^{31}\text{P}$  and  $^{19}\text{F}$  solid-state NMR measurements were performed on a Varian Infinity Plus 400 NMR spectrometer, operating at a static magnetic field of 9.39 T ( $^{19}\text{F}$  frequency: 376.11 MHz;  $^{31}\text{P}$  frequency: 161.79 MHz). All measurements were run at the spinning speed of 25 kHz using a 2.5 mm magic angle spinning (MAS) probe.

Single pulse  $^{31}\text{P}$  and  $^{19}\text{F}$  NMR spectra were acquired using  $90^\circ$  pulse lengths of 3 and 2  $\mu\text{s}$ , respectively, and recycle delays of 20 s for the diamagnetic and 5 s for the paramagnetic samples. The  $^{19}\text{F}$  resonance of the paramagnetic inclusion compound covers a range of about 200 kHz and therefore was acquired using the spin-echo sequence.

$^{31}\text{P}$  and  $^{19}\text{F}$   $T_1$  relaxation times were measured by the standard ( $180^\circ$ - $\tau$ - $90^\circ$ -acq) inversion-recovery experiment. However, in case of the broad  $^{19}\text{F}$  NMR signal of the paramagnetic inclusion compound, an additional  $180^\circ$  pulse was applied before the acquisition to avoid baseline distortions.

## II. Line fitting of the $^{31}\text{P}$ and $^{19}\text{F}$ NMR spectra



