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# Supplementary materials for: Heterometallic 3d-4f $\{Co_2Gd_4\}$ phosphonates: new members of the potential magnetic coolers family

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## 1 Experimental part

#### 1.1 Characterization techniques

IR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer with a Bruker Alpha-Platinum ATR system. ICP-OES analyses were done on an ICP-OES spectrometer iCAP 6500 Duo (Thermo, generator 27.12 MHz, amplitude 1.15 kW, plasma gas flow 12 dm<sup>3</sup> min<sup>-1</sup>). Emission lines 335.047 and 336.223 nm for Gd, 228.616 and 238.892 nm for Co, 213.618 and 214.914 nm for P, and 588.995 and 589.952 nm for Na were used. Elemental analysis (C, H, and N) was performed on a Flash 2000 CHNS Elemental Analyzer (Thermo Scientific). The ESI-MS spectra were measured on an Agilent 6224 Accurate-Mass TOF mass spectrometer (Agilent Technologies, Wilmington, DE, USA) with a dual electrospray ionization source from methanol solutions. Following parameters were used: nitrogen flow 7 l min<sup>-1</sup>, gas temperature 325 °C, nebulizer 45 psi, skimmer 65 V, fragmentor 80 V. The solution NMR spectra were recorded on a Bruker Avance II 300 NMR spectrometer at frequencies of (300.1 MHz for <sup>1</sup>H and 121.5 MHz for <sup>31</sup>P) in 5 mm NMR tubes. CD<sub>3</sub>OD was used as an internal lock. The spectra were referenced to the residual proton signal of CHD<sub>2</sub>OD (3.33 ppm) while the <sup>31</sup>P spectra were referenced to 85 % H<sub>3</sub>PO<sub>4</sub> (0 ppm). Thermogravimetric analysis (TG/DSC) was done on a Netzsch 449C Jupiter apparatus in the temperature range 25–1000 °C with the heating rate of 5 K min<sup>-1</sup> under the atmosphere of 90 % of nitrogen and 10 % of synthetic air (70 cm<sup>3</sup> min<sup>-1</sup>). Single crystal X-ray measurements were carried out on a Rigaku diffraction system (MicroMax007HF DW rotating anode source with multilayer optic, partial  $\chi$  axis goniometer, Saturn 724+ HG detector and Cryostream cooling device). The Mo- $K_{\alpha}$  ( $\lambda = 0.7107$  Å) radiation was used. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans<sup>1-3</sup>. CrystalClear (Rigaku 2014) and CrysAlisPro (Agilent Technologies 2013) software packages were used for data collection and data reduction. The structures were solved using SHELXT<sup>4</sup> program and refined (full matrix least-squares refinement on  $F_a^2$ ) using SHELXL<sup>5</sup> program. Magnetic susceptibilities data were obtained from powdered samples in gelatin capsules using a Quantum-Design MPMS-5 SQUID magnetometer equipped with a 5 Tesla magnet in the range from 300 to 2 K. The measured data were corrected for diamagnetism of the sample and the sample holder. Processing of the data was performed with Matlab2018a including the EasySpin<sup>6</sup> package.

#### 1.2 General procedures

All reactions were performed using general synthetic techniques, no special conditions were used. Commercially available  $CoCl_2 \cdot 6H_2O$ ,  $GdCl_3 \cdot 6H_2O$ , NaOH, salicylaldehyde (Sigma), 5-bromosalicylaldehyde (Sigma), 2-hydroxy-1-naphthaldehyde (Sigma), ethanol (pa), and methanol (pa) were used without further purification. (2-aminopropan-2-yl)phosphonic acid (H<sub>2</sub>AIPA) was synthesized by the literature method, <sup>7</sup> commercially available benzylcarbamate, acetone and phosphorous trichloride were used.

#### 1.3 Ligand synthesis

#### 1.3.1 Na<sub>2</sub>HSAA

Into a boiling and stirred suspension of H<sub>2</sub>AIPA (6.28 g, 40.0 mmol) and NaOH (4.80 g, 120.0 mmol) in ethanol (200 cm<sup>3</sup>), neat salicylaldehyde (17.0 cm<sup>3</sup>, 160.0 mmol) was added. The suspension immediately became bright yellow. After several minutes a bright yellow precipitate began to form. The reaction mixture was boiled and stirred under reflux overnight. The yellow precipitate was filtered off, redissolved in methanol (150 cm<sup>3</sup>) and precipitated by addition of acetonitrile. After filtration a yellow precipitate was washed by acetonitrile and dried under vacuum (7.5  $10^{-4}$  Torr) at 80–90 °C for 2 d providing 9.473 g of Na<sub>2</sub>HSAA·H<sub>2</sub>O (yield 77.6 % based on P,  $M_r(C_{10}H_{14}NNa_2O_5P) = 305.18$  g mol<sup>-1</sup>).

Elemental analysis (Calcd for  $C_{10}H_{14}NNa_2O_5P$  / found): Na 15.07/15.80; P 10.15/10.16; C 39.36/38.51; H 4.62/4.74; N 4.59/4.81 %.

IR (cm<sup>-1</sup>): v 3154 vw, 2969 vw, 2908 vw, 2867 vw, 1640 m, 1616 m, 1558 vw, 1524 m, 1494 w, 1470 vw, 1385 vw, 1304 vw, 1246 vw, 1209 w, 1192 w, 1141 m, 1124 s, 1094 vs, 1050 m, 1019 w, 968 s, 901 vw, 863 vw, 836 w, 768 m, 738 s, 690 m, 612 w, 558 s, 528 m, 497 w, 456 m.

<sup>1</sup>H NMR (300.1 MHz, CD<sub>3</sub>OD, ppm):  $\delta$  1.64 (d, <sup>3</sup>*J*<sub>PH</sub> = 11.2 Hz, 6H, CH<sub>3</sub>), 6.46-6.53 (m, 1H), 6.68 (d, *J* = 9.0 Hz, 1H), 7.22–7.30 (m, 2H), 8.47 (m, 1H, NCH).

<sup>31</sup>P {<sup>1</sup>H} NMR (121.5 MHz, CD<sub>3</sub>OD, ppm):  $\delta$  16.30.

ESI-MS (positive ion mode, MeOH): m/z 288.10 [ $C_{10}H_{12}NO_4PNa_2 + H$ ]<sup>+</sup>, 100 %; 310.10 [ $C_{10}H_{11}NO_4PNa_3 + H$ ]<sup>+</sup>, 30 %. ESI-MS (negative ion mode, MeOH): m/z 242.2 [ $C_{10}H_{14}NO_4P - H$ ]<sup>-</sup>, 100 %.

#### 1.3.2 Na<sub>2</sub>HBSAA.

Into a boiling and stirred suspension of H<sub>2</sub>AIPA (4.41 g, 28.0 mmol) and NaOH (3.37 g, 84.0 mmol) in methanol (100 cm<sup>3</sup>), a solution of 5-bromosalicylaldehyde 98 % (6.15 g, 30.0 mmol) in methanol (100 cm<sup>3</sup>) was added. The color immediately changed to bright yellow. After several minutes a bright yellow precipitate began to form. The formed suspension was boiled under reflux with stirring overnight. Then the bright yellow precipitate was filtered off, washed with a small amount of methanol and acetone and dried under vacuum (7.5  $10^{-4}$  Torr) at 80–90 °C for 2 d providing 8.943 g of Na<sub>2</sub>HBSAA·H<sub>2</sub>O (yield 83.2 % based on P,  $M_r(C_{10}H_{13}BrNNa_2O_5P) =$ 

384.07 g mol<sup>-1</sup>).

Elemental analysis (Calcd for  $C_{10}H_{13}BrNNa_2O_5P$  / found): Na 11.97/12.51; P 8.06/8.28; C 31.27/30.81; H 3.41/3.8; N 3.65/3.27 %.

IR (cm<sup>-1</sup>): v 3271 vw, 3050 vw, 2992 vw, 2966 vw, 1635 m, 1598 vw, 1510 m, 1487 m, 1469 w, 1384 vw, 1326 vw, 1285 vw, 1241 vw, 1204 w, 1171 w, 1145 m, 1127 w 1094 vs, 1046 w, 980 vs, 928 vw, 884 vw, 833 m, 785 vw, 711 m, 653 m, 616 m, 564 s, 542 s, 531 s, 505 s, 454 vs.

<sup>1</sup>H NMR (300.1 MHz, CD<sub>3</sub>OD, ppm):  $\delta$  1.63 (d, <sup>3</sup>*J*<sub>PH</sub> = 11.2 Hz, 6H, CH<sub>3</sub>), 6.60 (d, *J* = 9.2 Hz, 1H), 7.29 (dd, *J* = 9.2 Hz, 1H), 7.43 (d, *J* = 2.8 Hz, 1H), 8.45 (m, 1H, NCH).

<sup>31</sup>P {<sup>1</sup>H} NMR (121.5 MHz, CD<sub>3</sub>OD, ppm): δ 15.82.

ESI-MS (negative ion mode, MeOH): m/z 319.97/321.97 [C<sub>10</sub>H<sub>13</sub><sup>79/81</sup>BrNO<sub>4</sub>P – H]<sup>-</sup>, 100 %; 341.95/343.95 [C<sub>10</sub>H<sub>12</sub>

 $^{79/81}$ BrNNaO<sub>4</sub>P - H]<sup>-</sup>, 25 %.

#### 1.3.3 Na<sub>2</sub>HNAA.

Into a boiling and stirred suspension of H<sub>2</sub>AIPA (2.00 g, 12.7 mmol) and NaOH (1.52 g, 38.1 mmol) in ethanol (100 cm<sup>3</sup>), a suspension of 2-hydroxy-1-naphthaldehyde (4.38 g, 25.4 mmol) in ethanol was added. The color immediately changed to the bright yellow. After several minutes a bright yellow precipitate began to form. The formed suspension was boiled under reflux with stirring overnight. The precipitate was filtered off, redissolved in methanol (50 cm<sup>3</sup>) and precipitated by the addition of acetone. The bright green-yellow precipitate was filtered off, washed with acetone and dried under vacuum (7.5  $10^{-4}$  Torr) at 80–90 °C for 2 d providing 3.456 g of Na<sub>2</sub>HNAA · H<sub>2</sub>O (yield 76.6 % based on P,  $M_r$ (C<sub>14</sub>H<sub>16</sub>NNa<sub>2</sub>O<sub>5</sub>P) = 355.23 g mol<sup>-1</sup>).

Elemental analysis (Calcd for C<sub>14</sub>H<sub>16</sub>NNa<sub>2</sub>O<sub>5</sub>P/ found): Na 12.94/13.60; P 8.72/8.96; C 47.33/46.79; H 4.54/4.63; N 3.94/3.67 %. IR (cm<sup>-1</sup>): v 3148 vw, 3060 vw, 2991 vw, 1623 vs, 1599 m, 1543 m, 1525 w, 1495 w, 1466 vw, 1448 vw, 1397 vw, 1382 vw, 1353 m, 1327 w, 1280 vw, 1203 w, 1141 s, 1086 vs, 1017 w, 976 vs, 881 w, 859 w, 834 s, 742 s, 684 m, 633 m, 568 vs, 538 s, 508 s, 486 m, 446 s, 413 m.

<sup>1</sup>H NMR (300.1 MHz, CD<sub>3</sub>OD, ppm):  $\delta$  1.69 (d, <sup>3</sup>*J*<sub>PH</sub> = 11.2 Hz, 6H, CH<sub>3</sub>), 6.80 (d, *J* = 9.4 Hz, 1H), 7.17 (m, 1H), 7.42 (m, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 9.4 Hz, 1H), 8.09 (d, *J* = 8.3 Hz 1H), 9.20 (m, 1H, NCH).

<sup>31</sup>P {<sup>1</sup>H} NMR (121.5 MHz, CD<sub>3</sub>OD, ppm):  $\delta$  16.69.

ESI-MS (negative ion mode, MeOH): m/z 292.07  $[C_{14}H_{16}NO_4P - H]^-$ , 100 %.

#### 1.4 Test for the Cl<sup>-</sup> anions

The complex (0.070 g, 0.024 mmol of 1; 0.080 g, 0.024 mmol of 2; 0.071 g, 0.022 mmol of 3) was placed into an empty closed vial (20 cm<sup>3</sup>) with a Teflon-covered silicon septum. Approximately 1 cm<sup>3</sup> (STP) of HCl should be released from the given portions of the complexes, in the case that 2 Cl<sup>-</sup> anions are present in one molecular unit. The reaction vial was connected with a similar vial by a cannula. The end of the cannula in the first vial was fitted directly under the cap, while in the second vial it reached completely to the bottom. AgNO<sub>3</sub> (0.100 g) was dissolved in 2 cm<sup>3</sup> of H<sub>2</sub>O in the second vial. The end of the cannula was under the solution surface. The septum was pierced by a syringe needle in the second vial. Then 1 cm<sup>3</sup> of concentrated H<sub>2</sub>SO<sub>4</sub> was added to the complex by the syringe. No evidence of the gas formation was observed. Gas in the first vial was slowly transported into the second vial by the airflow from the empty syringe. No evidence of the formation of AgCl was observed.

The control experiment with corresponding amounts of a known complex, which contains  $Cl^-$ , and  $DyCl_3 \cdot 6 H_2O$  (0.006 g, 0.016 mmol) showed clear formation of an insoluble white precipitate of AgCl.

# 2 Figures SI:



Fig. S1 Comparison of the IR spectra of 1, recorded immediately after separation from the mother liquor and washing by methanol (a) and after storing for a month (b).



Fig. S2 Comparison of the IR spectra of 2, recorded immediately after separation from mother liquor and washing by methanol (a) and stored for a month (b).



Fig. S3 Comparison of the IR spectra of 3, recorded immediately after separation from mother liquor and washing by methanol (a) and stored for a month (b).



Fig. S4 Ball and stick representation of the molecule of 2. Color code: Gd cyan, Co blue, Na magenta, N pale-blue, O red, P orange, C black, Br brown. All hydrogen atoms and carbon atoms of the coordinated methanol molecules were omitted for the sake of clarity.



Fig. S5 Ball and stick representation of the molecule of 3. Color code is the same as in Figure S4. The alternative positions of two sodium cations, methanol molecules coordinated to the sodium cations (left in the picture), all hydrogen atoms, and all carbon atoms of the coordinated methanol molecules were omitted for the sake of clarity.



Fig. S6 Ball and stick representation of coordination spheres of Gd1, Gd2, Gd3, and Gd4 in 2 (Gd - green).



Fig. S7 Ball and stick representation of coordination spheres of Gd1, Gd2, Gd3, and Gd4 in 3 (Gd - magenta).



**Fig. S8** Representation of  $\chi T$  as a function of temperature for **2** (top) and **3** (bottom). The solid lines represent the simulated values for the Hamiltonian given in eqn 1 from the main text, see text for details.



Fig. S9 Representation of the Curie-Weiss plots  $\chi^{-1}$  as a function of temperature for 1 (top), 2 (middle), and 3 (bottom). The solid lines represent the simulated values, see text for details.



Fig. S10 Magnetization data as a function of applied field for 1 (top), 2 (middle), and 3 (bottom), measured in the temperature range 2–5 K.



Fig. S11 Representation of the magnetic entropy change  $\Delta S_m$  for complexes 2 (top), and 3 (bottom) obtained from magnetization data dependent on temperature and applied maximal magnetic field (lines are guides to the eye).

# 3 Tables SI:

**Table S1** Selected distances (Å) between the Gd<sup>3+</sup> cations, angles Gd–O–Gd, and selected torsion angles (°) present in the structures of **1**, **2**, and **3**.

	1	2	3
Gd1–Gd2	3.920	3.889	3.891
Gd1–Gd3	5.682	5.655	5.727
Gd1–Gd4	5.137	5.387	5.188
Gd2–Gd3	5.169	5.056	5.170
Gd2–Gd4	5.712	5.726	5.645
Gd3–Gd4	3.924	3.886	3.897
Gd101_1Gd2	107.77	106.28	106.77
Gd1-01_2-Gd2	107.83	106.53	107.88
Gd3-01_3-Gd4	108.10	107.36	106.94
Gd3-01_4-Gd4	107.45	105.13	106.36
Gd1–Gd2–Gd3–Gd4	-62.19	-66.47	-63.59
Gd2-Gd1-Gd3-Gd4	101.84	99.85	100.31

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			1	2	3
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		01 1	2.406(7)	2.399(3)	2.396(4)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		012	2.491(7)	2.460(3)	2.451(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		01_5	2.282(7)	2.294(3)	2.322(4)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Gd1	O3_4	2.257(7)	2.251(3)	2.262(4)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		041	2.239(7)	2.239(5)	2.237(5)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$O^{a}$	2.439(7)	2.403(5)	2.423(5)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		N1_1	2.599(9)	2.574(4)	2.576(5)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		O1_1	2.446(6)	2.461(3)	2.452(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		012	2.359(7)	2.392(3)	2.363(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		O3 <sup>-</sup> 3	2.236(8)	2.226(3)	2.233(3)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Gd2	O4 <sup>2</sup>	2.293(7)	2.277(5)	2.285(5)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		O2_5	2.318(8)	2.306(3)	2.334(3)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		0 -	2.463(7)	2.459(4)	2.467(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		N1_2	2.58(1)	2.612(4)	2.510(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		O1_3	2.429(7)	2.423(3)	2.402(4)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		01_4	2.512(7)	2.509(3)	2.504(3)
		O1_6	2.285(7)	2.263(3)	2.300(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Gd3	O3_2	2.242(7)	2.261(4)	2.244(3)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		O4_3	2.242(8)	2.232(3)	2.220(4)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		0	2.441(7)	2.435(4)	2.441(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		N1_3	2.613(9)	2.612(5)	2.569(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		O1_3	2.418(7)	2.399(3)	2.447(3)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		01_4	2.354(7)	2.384(3)	2.362(4)
		O3_1	2.232(8)	2.248(3)	2.246(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Gd4	O4_4	2.285(7)	2.274(4)	2.285(4)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		O2_6	2.324(8)	2.298(3)	2.304(3)
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		0	2.444(7)	2.464(5)	2.467(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		N1_4	2.551(8)	2.522(5)	2.525(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		N1	1.95(1)	1.958(5)	1.958(6)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		N2	1.971(8)	1.976(7)	1.982(6)
		N1_5	1.92(1)	1.916(4)	1.906(6)
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Co1	O3_5	1.976(8)	1.953(4)	1.927(3)
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		O4_5	1.874(8)	1.888(4)	1.889(4)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		0	1.877(7)	1.890(5)	1.883(5)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		N3	1.91(1)	1.945(5)	1.951(6)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		N4	1.963(9)	1.971(5)	1.971(5)
Co2 O3_6 1.920(8) 1.934(3) 1.932(3)   O4_6 1.860(9) 1.882(3) 1.871(3)   O 1.89(1) 1.897(5) 1.894(4)		N1_6	1.88(1)	1.922(5)	1.913(6)
O4_6 1.860(9) 1.882(3) 1.871(3)   O 1.89(1) 1.897(5) 1.894(4)	Co2	O3_6	1.920(8)	1.934(3)	1.932(3)
0 1.89(1) 1.897(5) 1.894(4)		O4_6	1.860(9)	1.882(3)	1.871(3)
		0	1.89(1)	1.897(5)	1.894(4)

### Table S2 Bond lengths (Å) in $Co^{3+}$ and $Gd^{3+}$ polyhedra in 1, 2, and 3.

a Oxygen atoms without labels belong to the methanol molecules coordinated to the corresponding metal cation. Labeling was not used due to their different numbering, which depends on a particular structure.

Table S3 BVS<sup>*a*</sup> calculated for the Co cations in 1, 2, and 3.

	1	2	3
Co1	2.83	2.80	2.85
Co2	2.99	2.84	2.87

a The bond valence sums (BVS) were calculated for the cobalt ions to establish their oxidation state  $Z_j$  from the bond valence  $S_{ij}$  using the the following equations:

$$Z_j = \sum_i S_{ij}; \ S_{ij} = \exp[(R_0 - r_{ij})/b]$$

The parameter values for R<sub>o</sub> equal 1.685 and 1.600 for Co–O and Co–N bonds, respectively. The usual value of 0.37 was used for b in both cases.<sup>8</sup>

	Table S4 The geometr	y analysis of Gd <sup>3+</sup>	polyhedra in 1, 2,	and 3 by	the SHAPE 2.1.9-12
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Product	Central atom	HP-7 <sup>a</sup>	HPY-7 <sup>b</sup>	PBPY-7 <sup>c</sup>	COC-7 <sup>d</sup>	CTPR-7 <sup>e</sup>	JPBPY-7 <sup>f</sup>	JETPY-7 <sup>g</sup>
	Gd1	26.980	22.726	2.075	8.016	5.576	4.588	19.949
1	Gd2	31.508	20.558	2.385	5.347	4.563	3.239	21.635
	Gd3	26.469	22.181	2.345	8.165	5.787	4.834	19.818
	Gd4	31.469	20.570	2.350	5.295	4.522	3.285	21.680
	Gd1	29.097	22.044	8.835	12.209	10.867	18.740	21.624
2	Gd2	27.056	16.198	8.822	10.362	9.934	17.319	22.716
	Gd3	30.423	24.592	9.049	14.497	13.564	19.731	25.834
	Gd4	19.145	21.946	10.832	11.172	9.227	18.104	19.748
	Gd1	24.131	20.786	8.991	14.438	12.630	19.508	23.194
3	Gd2	28.574	15.118	10.713	12.409	11.181	18.607	20.857
	Gd3	28.580	24.652	9.169	14.985	13.250	19.654	24.508
	Gd4	17.491	17.280	10.654	11.883	9.495	17.997	20.986

a Heptagon  $D_{7h}$ 

*b* Hexagonal pyramid C<sub>6v</sub> *c* Pentagonal bipyramid D<sub>5h</sub>

d Capped octahedron  $C_{3v}$ 

e Capped trigonal prism  $C_{2\nu}$ 

f Johnson pentagonal bipyramid J13 D<sub>5h</sub>

g Johnson elongated triangular pyramid J7  $C_{3\nu}$ 

Table S5 The geometry analysis of Co<sup>3+</sup> polyhedra in 1, 2, and 3 by the SHAPE 2.1.<sup>9–11,13</sup>

Central atom	HP-6 <sup>a</sup>	PPY-6 <sup>b</sup>	OC-6 <sup>c</sup>	TPR-6 <sup>d</sup>	JPPY-6 <sup>e</sup>
Co1	28.748	27.001	1.809	15.644	29.372
Co2	29.654	27.970	1.928	15.784	30.267
Co1	19.516	23.451	9.134	21.430	22.660
Co2	19.089	24.891	9.290	17.924	25.102
Co1	21.160	23.612	9.587	21.104	22.664
Co2	14.055	22.259	10.296	19.645	22.042
	Central atom Co1 Co2 Co1 Co2 Co1 Co1 Co2	Central atom HP-6 <sup>a</sup> Co1 28.748   Co2 29.654   Co1 19.516   Co2 19.089   Co1 21.160   Co2 14.055	Central atom HP-6 a PPY-6 b   Co1 28.748 27.001   Co2 29.654 27.970   Co1 19.516 23.451   Co2 19.089 24.891   Co1 21.160 23.612   Co2 14.055 22.259	Central atom HP-6 <sup>a</sup> PPY-6 <sup>b</sup> OC-6 <sup>c</sup> Co1 28.748 27.001 1.809   Co2 29.654 27.970 1.928   Co1 19.516 23.451 9.134   Co2 19.089 24.891 9.290   Co1 21.160 23.612 9.587   Co2 14.055 22.259 10.296	Central atom HP-6 a PPY-6 b OC-6 c TPR-6 d   Co1 28.748 27.001 1.809 15.644   Co2 29.654 27.970 1.928 15.784   Co1 19.516 23.451 9.134 21.430   Co2 19.089 24.891 9.290 17.924   Co1 21.160 23.612 9.587 21.104   Co2 14.055 22.259 10.296 19.645

a Hexagon  $D_{6h}$ 

b Pentagonal pyramid C5v

c Octahedron  $O_h$ 

d Trigonal prism  $\mathrm{D}_{3h}$ 

*e* Johnson pentagonal pyramid J2  $C_{5\nu}$ 

## Notes and references

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