*Supporting Information for*

# Co-Gd Phosphonate Complexes as Magnetic Refrigerants

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## Experimental Details

### Synthesis

Synthesis of starting materials. **4** was synthesized according to the established methods.[8] **5** was synthesized by refluxing $Gd_2O_3$ (3.62 g, 10 mmol) and excess pivalic acid (30 g, 300 mmol) at 160 $^oC$ for 5 hrs to form a clear solution. Followed by cooling the solution to room temperature and white precipate came out. 50 ml toluene were added to dissolve the excess pivalic acid and filtered in vacuum and 50 ml n-hexane were used to wash the product (yield 13 g, 87 %). Single crystals of **5** were grown in the mixed solution of toluene and n-hexane.

Synthesis of compounds **1** to **3**.

Compound **1** was obtained by mixing **4** (0.1 g, 0.1 mmol), $Gd(NO_3)_3$ (0.09 g, 0.2 mmol) and $H_2O_3P^tBu$ (0.014 g, 0.1 mmol) in MeCN (8 ml) and stirring at room temperature for a few minutes. The resulting slurry was transferred into a 10 mL Teflon-lined autoclave, which was heated at 150 $^oC$ for 12 hrs and then cooled to room temperature at a rate of 0.05 $^oC\ min^{-1}$. Purple needle-shape crystals of **1** were collected (yield 5 mg, 4 %, based on **4**). Elemental analysis (EA) for **1**, $C_{112}H_{222}Co_8Gd_8N_4O_{73}P_8$, found (calc); C 28.90 (28.20), H 4.58 (4.69), Co 9.91 (9.88), Gd 26.64 (26.37), N 1.04 (1.17) and P 4.96 (5.19). IR (KBr, $cm^{-1}$): 2964 (m), 2923 (m), 2875 (m), 1549 (vs), 1483 (s), 1455 (m), 1421 (s), 1377 (m), 1364 (m), 1229 (s), 1060 (vs), 988 (m), 895 (w), 877 (w), 830 (w), 785 (w), 665 (w), 612 (w), 534 (w).

Compound **2** was obtained by mixing **4** (0.1 g, 0.1 mmol), **5** (0.075 g, 0.05 mmol) and $H_2O_3P^tBu$ (0.014 g, 0.1 mmol) in MeCN (8 ml) and stirring at room temperature for a few

minutes. The resulting slurry was transferred into a 10 mL Teflon-lined autoclave, which was heated at 150 $^{o}$C for 12 hrs and then cooled to room temperature at a rate of 0.05 $^{o}$C min$^{-1}$. Purple needle-shape crystals of **2** were collected (yield 75 mg, 85 %, based on **4**). EA for $C_{104}H_{198}Co_8Gd_4O_{50}P_6$, found (calc); C 35.43 (35.34); H 5.72 (5.65); Co 7.68 (7.61); Gd 17.37 (17.29) P 5.33 (5.26). IR (KBr, cm$^{-1}$); 2985 (m), 2948 (m), 2838 (m), 1582 (m), 1567 (vs), 1516 (m), 1494 (s), 1467 (m), 1429 (s), 1386 (m), 1372 (m), 1235 (m), 1080 (s), 983 (s), 974 (m), 885 (w), 788 (w), 667 (w), 600 (w), 542 (m).

Compound **3** was obtained by mixing **4** (0.1 g, 0.1 mmol), **5** (0.1 g, 0.075 mmol) and $H_2O_3PCH_2Ph$ (0.017 g, 0.1 mmol) in MeCN (8 ml) and stirring at room temperature for a few minutes. The resulting slurry was transferred into a 10 mL Teflon-lined autoclave, which was heated at 150 $^{o}$C for 12 hrs and then cooled to room temperature at a rate of 0.05 $^{o}$C min$^{-1}$. Purple block crystals of **3** were collected (yield 60 mg, 65 %, based on **5**). EA for $C_{116}H_{174}Co_4Gd_6N_2O_{46}P_6$, found (calc); C 37.63 (37.68); H 4.81 (4.74); N 0.70 (0.76) Co 6.32 (6.38); Gd 25.59 (25.52) P 5.11 (5.03). (KBr, cm$^{-1}$): 2966 (m), 2933 (m), 2834(m), 2020 (m), 1583 (s), 1574 (s), 1511 (m), 1478 (s), 1453 (m), 1414 (s), 1364 (m), 1219 (m), 1031 (s), 993 (s), 964 (m), 895 (m), 834 (s), 798 (s), 754 (m), 687 (w), 606 (w), 546 (m).

**Crystallography**

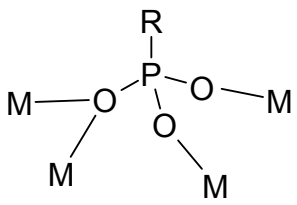
Crystal data. For **1**, $C_{112}H_{222}Co_8Gd_8N_4O_{73}P_8$, $M$ = 4770.14, monoclinic, space group $P2_1/n$, $T$ = 100(2) K, $a$ = 35.6240(18), $b$ = 20.7297(10), $c$ = 25.0866(13) Å, $\beta$ = 101.4160(10)$^{o}$, $V$ = 18159.3(16) Å$^3$, $Z$ = 4, $\rho$ = 1.745 g cm$^{-3}$, total data 85562, unique data 16004 ($R_{int}$ = 0.0616), $\mu$ = 3.737 mm$^{-1}$, 1330 parameters, $R_1$ = 0.0815 for $I \geq 2\sigma(I)$ and $wR_2$ = 0.2154 for all data. For **2**, $C_{104}H_{198}Co_8Gd_4O_{50}P_6$, $M$ = 3534.88, monoclinic, space group $P2_1/n$, $T$ = 100(2) K, $a$ = 22.622(3), $b$ = 11.6300(17), $c$ = 30.189(4) Å, $\beta$ = 97.612(2)$^{o}$, $V$ = 7872.5(19) Å$^3$, $Z$ = 2, $\rho$ = 1.491 g cm$^{-3}$, total data 43509, unique data 13830 ($R_{int}$ = 0.1202), $\mu$ = 2.609 mm$^{-1}$, 775 parameters, $R_1$ = 0.1227 for $I \geq 2\sigma(I)$ and $wR_2$ = 0.3190 for all data. For **3**, $C_{116}H_{174}Co_4Gd_6N_2O_{46}P_6$, $M$ = 3697.61, monoclinic, space group $P2_1/n$, $T$ = 100(2) K, $a$ = 13.5500(13), $b$ = 29.003(3), $c$ = 18.2506(17) Å, $\beta$ = 97.588(2)$^{o}$, $V$ = 7109.4(12) Å$^3$, $Z$ = 2, $\rho$ = 1.727 g cm$^{-3}$, total data 43130, unique data 12527 ($R_{int}$ = 0.0432), $\mu$ = 3.355 mm$^{-1}$, 1032 parameters, $R_1$ = 0.0660 for $I \geq 2\sigma(I)$ and $wR_2$ = 0.1909 for all data. The data of **1**, **2** and **3** were recorded on a Bruker SMART CCD diffractometer with MoKα radiation ($\lambda$ = 0.71073 Å). The structures were solved by direct methods and refined on $F^2$ using SHELXTL. CCDC-784308 to784310 contain the supplementary crystallographic data for this paper. These data

can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

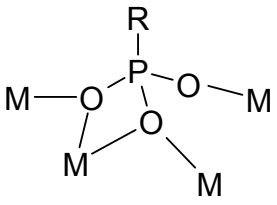
**Magnetic measurements**

Magnetic susceptibility measurements of **1** to **3** were performed with a Quantum Design MPMS-XL7 SQUID. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

**Scheme for Binding Modes by Harris Notation**




4.211

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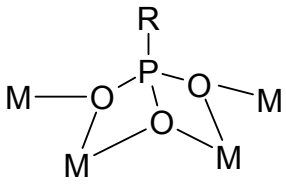


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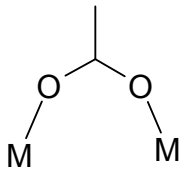
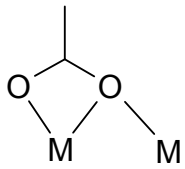



2.11

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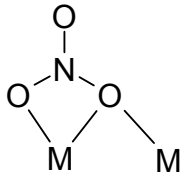


2.21

## FIGURES

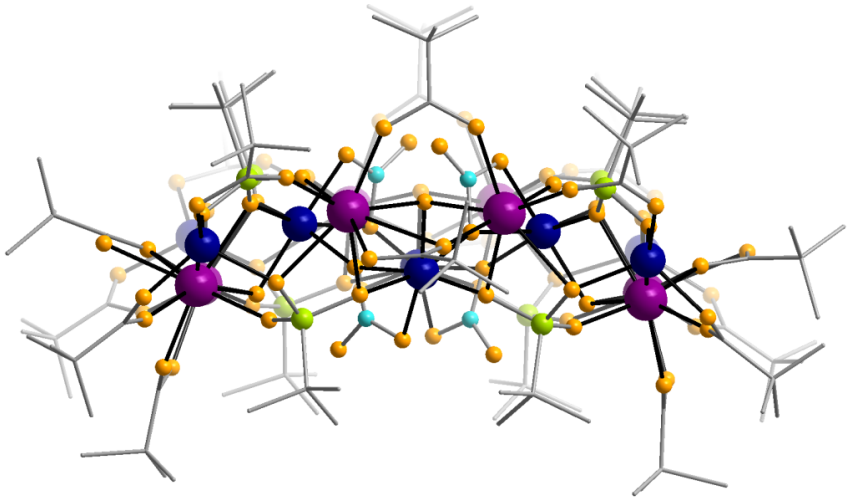

**Fig. S1.** Side view of compound **1** in the crystal.

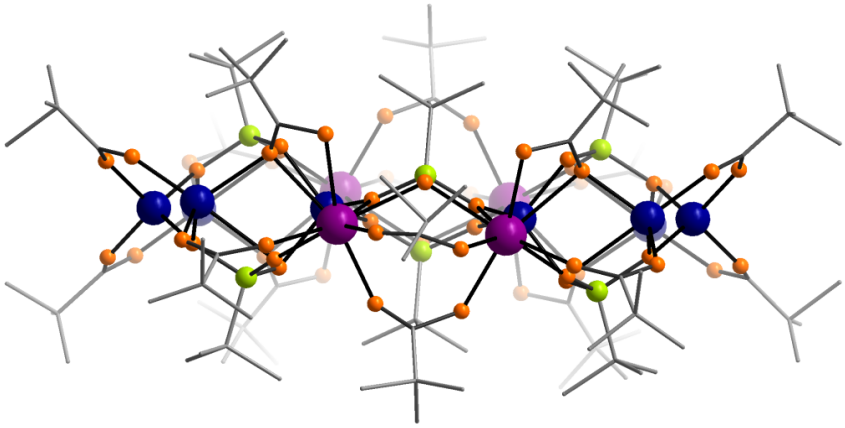

**Fig. S2.** Side view of compound **2** in the crystal.

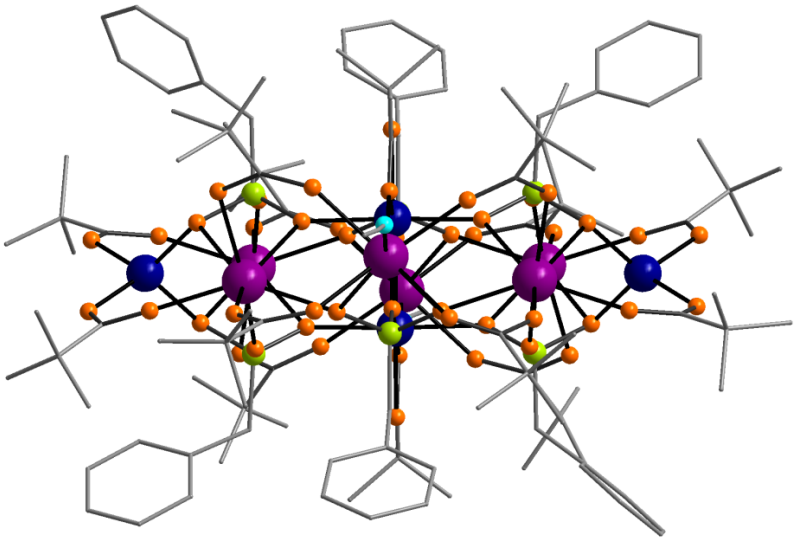

**Fig. S3.** Side view of compound **3** in the crystal.