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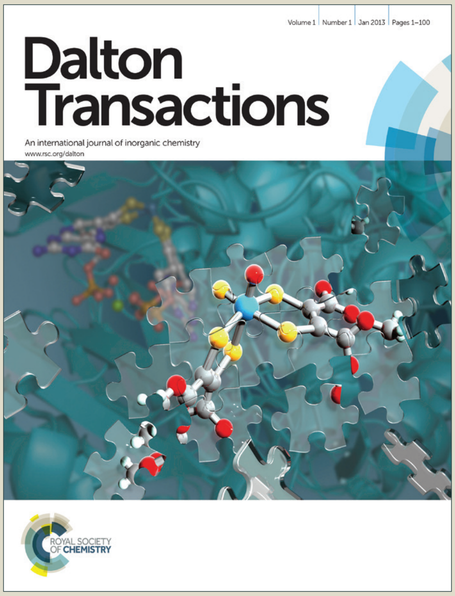

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Discrete $\{Gd^{III}{}_4M\}$ (M = Gd^{III} or Co^{II}) pentanuclear complexes: A new class of metal-organophosphate molecular coolers

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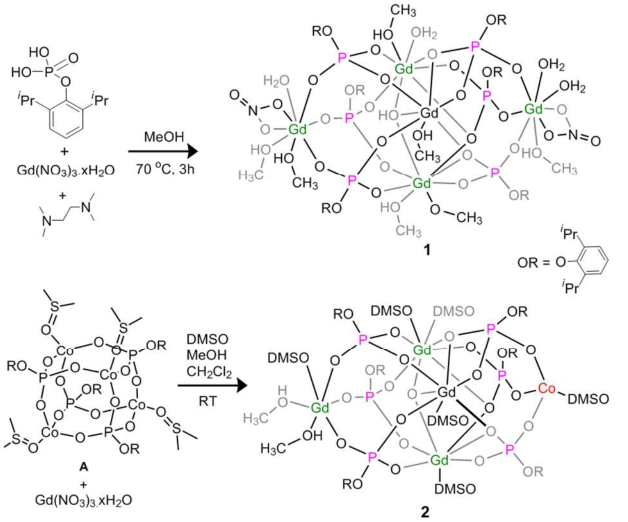
Sandeep K. Gupta,[a] Aijaz A. Dar,[a] Thayalan Rajeshkumar,[a] Subramaniam Kuppuswamy,[a] Stuart K. Langley,[b] Keith S. Murray,[b] Gopalan Rajaraman[a] and Ramaswamy Murugavel[a]

The first examples of homo- and hetero-polymetallic organophosphates of gadolinium are reported. Magnetic measurements reveal a higher magnetic entropy change for the isotropic $\{Gd^{III}{}_5\}$ complex (25.8 J kg^{-1}K^{-1}) as compared to the heterometallic $\{Gd^{III}{}_4Co^{II}\}$ complex (20.3 J kg^{-1}K^{-1}), which is attributable to a change in magnetic coupling as estimated from DFT calculations.

Lanthanide coordination complexes have been widely investigated in recent times due to their interesting magnetic properties and potential technological applications such as low temperature cryogenic coolers,[1] single molecule magnets,[2] and quantum computing devices.[3] In particular, it has been shown that many {3d},[4] $\{Gd^{III}\}$[5] and $\{3d\text{-}Gd^{III}\}$[6] complexes exhibit a significant magneto-caloric effect (MCE). Among these the most effective cooling devices are complexes containing Gd^{III} ion,[5] necessitating further investigations on homo- Gd^{III} and hetero-metallic $\{3d\text{-}Gd^{III}\}$ based systems with newer types of complex forming ligands, such as phosphate monoesters.[7] Since phosphorus based ligands can mediate weak exchange coupling between isotropic ions such as Gd^{III}, organophosphonates and phosphates are ideal candidates to obtain large MCE values.[8] Although several lanthanide organophosphonate complexes have been studied for their MCE properties,[6a-e] to the best of our knowledge, no organophosphate based lanthanide complexes are known to date.

Reaction of 2,6-di-*iso*-propylphenylphosphate (dippH$_2$)[9] with $Gd(NO_3)_3.6H_2O$ in the presence of tmeda (1:1:2) in methanol yielded $[Gd^{III}{}_5(\mu_3\text{-}OH)(NO_3)_2(dipp)_6(MeOH)_7(H_2O)_4]\cdot5MeOH$ (**1**) (Scheme 1). The introduction of Co^{II} inside the above pentanuclear Gd^{III} complex, **1** has been achieved via a different synthetic strategy, employing the preformed cobalt phosphate $[Co(dipp)(DMSO)]_4$(**A**)[10] complex as a combined source of cobalt and phosphate ligand. Diffusion of a CH_2Cl_2 solution into a DMSO/MeOH solution of $Gd(NO_3)_3.6H_2O$ and **A** resulted in the isolation of single crystals of $[Gd^{III}{}_4Co^{II}(\mu_3\text{-}O)(dipp)_6(DMSO)_6(MeOH)_2]\cdot H_2O$ (**2**), through scrambling (Scheme 1).

Solid state molecular structures of **1** and **2** were determined by single crystal X-ray diffraction studies (Fig. 1). The core of both **1** and **2** are pentanuclear $\{M_5(dipp)_6\}$ units, built around either a triply-bridging μ_3-OH$^-$ (for **1**) or μ_3-O^{2-} (for **2**) ligand, resembling the structure of pentanuclear Ti^{IV} and Fe^{III} complexes recently reported by us.[11] While μ_3-OH or μ_3-O bridged metal-triangular complexes are commonly formed when bridging RCO_2^- carboxylate ligands are employed, due to the presence of an extra oxygen atom and negative charge, organophosphates $((RO)PO_3)^{2-}$ have the ability to embrace two more metal ions and form pentanuclear complexes, as shown in Scheme S1 (ESI). For example, the μ_3-OH$^-$ and six dipp^{2-} ligands in **1** form the $[Gd_3(\mu_3\text{-}OH)(dipp)_6]$ trinuclear unit, utilizing two of phosphate oxygen atoms. A third oxygen atom of the six dangling phosphate ligands then bind to two different Gd^{III} ions on either side of the triangular complex to complete the pentanuclear motif. The coordination unsaturation and charge balance is then taken care of by peripheral nitrate, water, and methanol ligands. The structure of **2** is very similar to **1**, the difference being the substitution of a divalent cobalt ion in place of a trivalent Gd ion and an oxo ligand replacing a hydroxo group at the centre of the complex. Since the charge balance has been achieved from phosphate and oxo ligands, there are no nitrates found in **2**. The phosphate ligands in **1** and **2** on the left side of the complexes exhibit the [3.111] mode of coordination (Harris notation[12]), while those on the right side exhibit the [3.211] mode of coordination (Scheme 1 and Fig. 1).



Scheme 1. Synthesis of Gd_5 and Gd_4Co organophosphate complexes **1** and **2**.

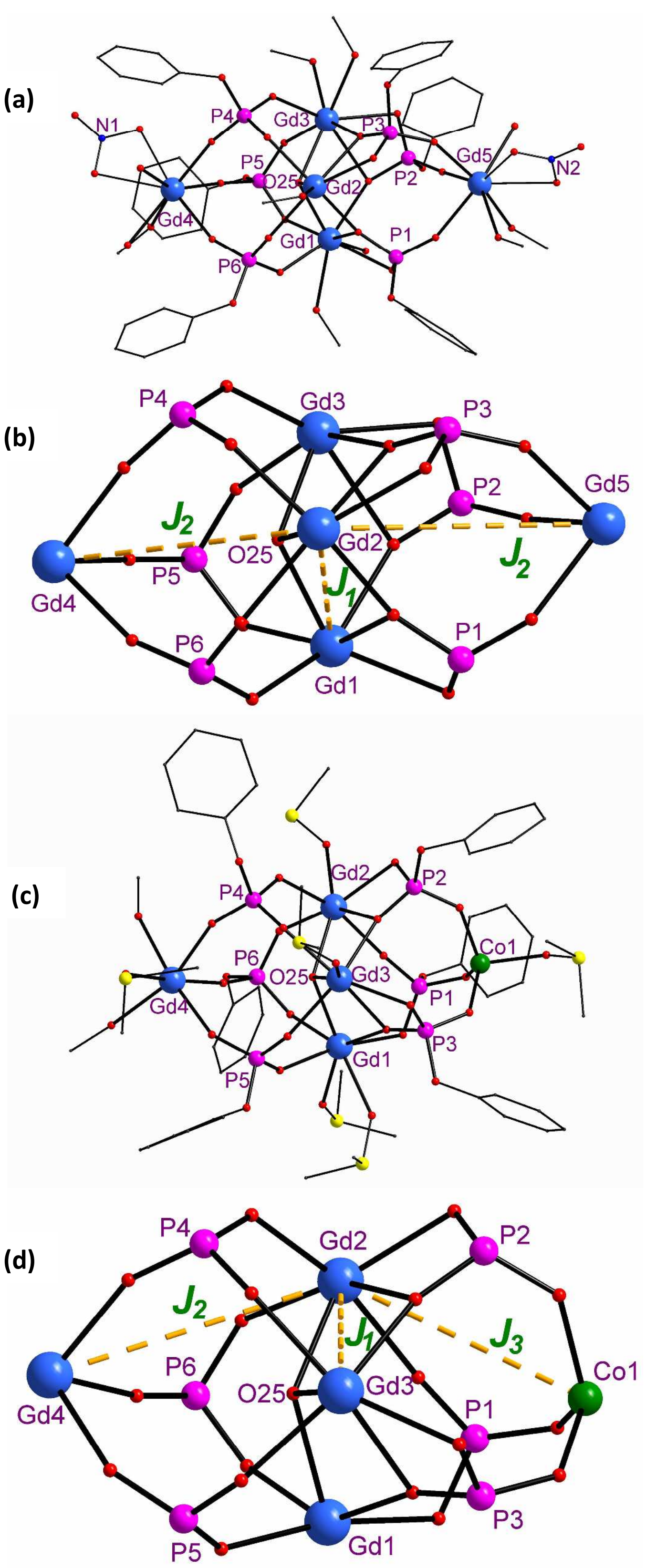


Fig. 1. (a & b) Molecular and core structure of **1**; (c & d) Molecular and core structure of **2**. Lattice solvent molecules, isopropyl groups and H-atoms are omitted for clarity. Dotted lines indicate the different magnetic exchange interaction pathways.

The distance between the three central triangle of Gd^{III} ions, Gd1···Gd2, Gd2···Gd3 and Gd1···Gd3 in **1** are 3.8865(8), 3.9399(9), and 3.9192(8) Å, respectively, with the central hydroxo oxygen lying 0.893 Å above the triangle. The eight-coordinate Gd1, Gd3, Gd4, and Gd5 ions exhibit distorted triangular dodecahedral geometries, whereas the seven coordinate Gd2 ion adopts a distorted pentagonal bipyramidal geometry.[13] The distance between the two terminal, Gd4 and Gd5 ions is 10.149(2) Å. The Gd1···Gd2, Gd2···Gd3 and Gd1···Gd3 metal-metal distances in the central triangular unit of **2** are 4.140(1), 3.888(1) and 3.903(1) Å, respectively, with the central oxo ligand lying 0.736 Å above the metal triangle. The distance of the tetrahedral Co1 ion from Gd1, Gd2 and Gd3 are 4.944(1), 4.739(1) and 4.838(8) Å, respectively, whereas the distance to the terminal Gd4 ion is 9.17(2) Å. The central seven-coordinate Gd1, Gd2 and Gd3 ions adopt distorted pentagonal bipyramidal geometries, while the terminal Gd4 ion exhibits a distorted octahedral geometry.

Variable temperature direct current (dc) magnetic susceptibility measurements were performed for complexes **1** and **2** between 2 and 300 K under an applied field of 1.0 T (Fig. 2). The $\chi_M T$ value of 39.58 cm^3 K mol^{-1} at 300 K for **1** is in good agreement with the calculated value of 39.40 cm^3 K mol^{-1} (g = 2) for five non-interacting Gd^{III} ions. The $\chi_M T$ value for **2** at ~300 K is 33.17 cm^3 K mol^{-1} similar to the value expected for non-interacting four Gd^{III} and one Co^{II} ions . For complex **1,** as the temperature is reduced, the $\chi_M T$ product remains almost constant reaching 37.71 cm^3 K mol^{-1} at 8.7 K, with complex **2** displaying similar behaviour, reaching 30.7 cm^3 K mol^{-1} at 8.7 K. Below 8.7 K the $\chi_M T$ value decreases drastically reaching 26.40 cm^3 K mol^{-1} for **1** and 20.87 cm^3 K mol^{-1} for **2** and suggests the presence of weak antiferromagnetic interactions. Magnetization measurements reveal the magnetization value saturates for **1** and **2** in an applied field of 7 T at 2 K, reaching a value of 34.9 and 30.12 μ_B, respectively. These values approach closely to that expected for five non-interacting Gd^{III} ions for **1** and four non-interacting Gd^{III} ions and a Co^{II} ion for **2**.

The magnetic data of **1** and **2** were fitted using PHI software[14] employing the following exchange interactions for **1** and **2**, respectively (zero field splitting is assumed to be zero; see below for the rationale for the use of two and three different exchange constants for **1** and **2**, respectively).

$$\begin{aligned}\hat{H}_{Ex} = &-J_1(\hat{S}_{Gd1}.\hat{S}_{Gd2} + \hat{S}_{Gd2}.\hat{S}_{Gd3} + \hat{S}_{Gd1}.\hat{S}_{Gd3}) \\ &-J_2(\hat{S}_{Gd1}.\hat{S}_{Gd4} + \hat{S}_{Gd2}.\hat{S}_{Gd4} + \hat{S}_{Gd3}.\hat{S}_{Gd4} + \hat{S}_{Gd1}.\hat{S}_{Gd5} \\ &+ \hat{S}_{Gd2}.\hat{S}_{Gd5} + \hat{S}_{Gd3}.\hat{S}_{Gd5}) \qquad (eqn\ \mathbf{1})\end{aligned}$$

$$\begin{aligned}\hat{H}_{Ex} = &-J_1(\hat{S}_{Gd1}.\hat{S}_{Gd2} + \hat{S}_{Gd2}.\hat{S}_{Gd3} + \hat{S}_{Gd1}.\hat{S}_{Gd3}) \\ &-J_2(\hat{S}_{Gd1}.\hat{S}_{Gd4} + \hat{S}_{Gd2}.\hat{S}_{Gd4} + \hat{S}_{Gd3}.\hat{S}_{Gd4}) \\ &-J_3(\hat{S}_{Gd1}.\hat{S}_{Co5} + \hat{S}_{Gd2}.\hat{S}_{Co5} + \hat{S}_{Gd3}.\hat{S}_{Co5}) \qquad (eqn\ \mathbf{2})\end{aligned}$$

The best fit parameters obtained for complex **1** are J_1 = -0.011 cm^{-1} and J_2 = -0.001 cm^{-1} (spin ground state, S=13/2) and in the case of **2**: J_1 = -0.0023 cm^{-1},J_2 = -0.0092 cm^{-1} and J_3= -0.0755 cm^{-1} (Fig. 2) (spin ground state, S=11/2). As Gd^{III} containing complexes are of major interest in understanding and developing the MCE in molecular coordination complexes, the entropy change has been evaluated for **1** and **2** from the magnetization data using the Maxwell relationship;

$$\Delta S_m(T)_{\Delta B} = \int \left[\frac{\partial M(T,B)}{\partial T}\right]_B dB$$

, (see Fig.2 (c) and (d)). The maximum theoretical entropy values are evaluated as 29.6 and 27 J kg^{-1} K^{-1} for **1** and **2** (at 3 K and 7 T), respectively, using the relationship S_m = nRln(2S+1). The experimentally determined maximum change in magnetic entropy are found to be 25.8 and

20.3 J kg^{-1} K^{-1} for **1** and **2**, respectively for a field change of 7 T at 3 K. These -ΔS_m values are significant for the first generation Gd-phosphates, although much larger values have been found for other gadolinium systems.[5i] Despite the very small J values, there is a significant reduction on the MCE values, particularly so in the case of **2**. To probe this observation/effect further, we have evaluated the exchange interaction pathways in both **1** and **2** using DFT calculations (see ESI). The calculations have been performed starting from the crystal structures of **1** and **2**.

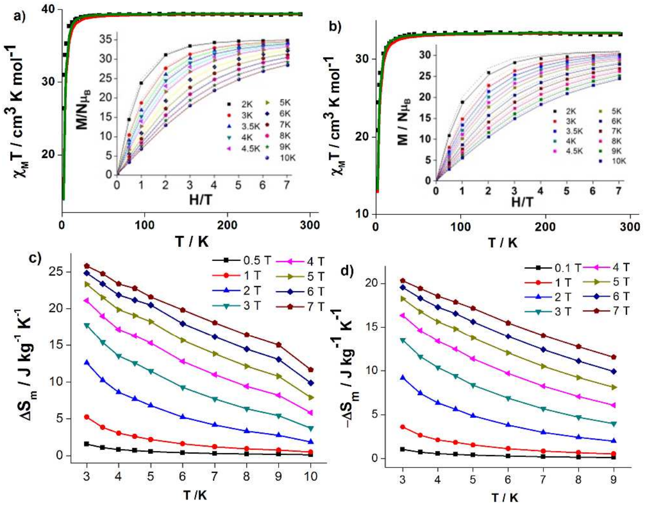


Fig. 2. (a & b) Temperature dependence of $\chi_M T$ under an applied field 1.0 T for **1** and **2** respectively (black squares-experimental points; red line-fit; green line-DFT simulated).Insets are corresponding magnetization plots for **1** and **2** [black squares-experimental points; solid lines-fit; dotted lines-DFT simulated, see ESI for enlarged plots]. c) $-\Delta S_m$ values calculated from magnetization data of **1** at different temperatures and fields. (d) $-\Delta S_m$ values calculated from magnetization data of **2** at different temperatures and fields.

In complex **1** two exchange interactions are modelled. The first is between the Gd^{III} ions within the gadolinium triangular unit, Gd1 – Gd3, present at the centre of the complex (see Fig.1) (J_1). The second interaction J_2 describes the interaction between the central triangular Gd^{III} ions with the terminal Gd^{III} ions, Gd4 and Gd5 (Fig. 1). In the case of complex **2**, the J_1 and J_2 interactions are similar to that in complex **1** and, in addition to these interactions, the exchange between Co^{II} and Gd^{III} ions are treated as J_3. The DFT computed exchange interactions for **1** are, J_1= -0.0013 cm^{-1}, J_2= 0.0001 cm^{-1} and for **2** J_1= -0.0502 cm^{-1}, J_2= 0.0001 cm^{-1}, J_3= -0.0159 cm^{-1}. The magnetic data have been simulated using the DFT computed J values (PHI software) and there is a striking match between the experimental data and the DFT simulated curve offering confidence on the computed J parameters. (See Fig. 2). Minor deviations are however found compared to J values obtained by fitting the experimental data. Since the Js are extremely small (both experimental and DFT), multiple solutions are possible for fitting the featureless curves.

The J_1 interaction mediates via the μ_3-O(H) and the phosphate bridges in **1** and the μ_3-O and the phosphate bridges in **2**. This interaction is found to be antiferromagnetic in both **1** and **2**. From our earlier studies on acetate bridged binuclear {Gd^{III}-Gd^{III}} complexes, the Gd-O-Gd angle was demonstrated to be an important parameter in controlling the nature of the exchange interaction.[15] Here the average Gd-O-Gd angle for **1** and **2** are 108.8°and 110.9°, respectively. From these angles the exchange is therefore predicted to be very weak, at the boundary of the crossover from ferro-to-antiferro-magnetic coupling. This therefore supports the small J value calculated via DFT. The J_2 interaction is found to be weakly ferromagnetic and is rationalized using a spin polarization model.[16] The -ΔS_m values for **1** and **2** were then calculated from the DFT J values and are found to be 26.9 and 23.9 J kg^{-1}K^{-1}, which are in fair agreement to the experimentally obtained -ΔS_m values. The combination of weak antiferro/ferro exchange interactions result in spin frustration within the system which brings the excited states closer to the ground state, resulting in large MCE values for **1** and **2**. The computed J_3 interaction between the Co^{II} and Gd^{III} ions in **2** is stronger than the J_2 interaction. The stronger exchange along with magnetic anisotropy associated with Co(II)[17] therefore lowers the MCE values compared to **1** (see ESI).

The computed spin density plots for the high spin states for **1** and **2** are shown in Fig. 3. The larger spin density values on the Gd^{III} ions (7.03) and lower spin density on Co^{II} ion (2.73) than the expected values suggest spin polarization and spin delocalization mechanisms around the respective ions. The mechanism operating in **1** and **2** can be understood from the negative spin densities on the atoms attached to the Gd^{III} ions and positive spin densities on the atoms attached to Co^{II} ions (Fig. 3). To further understand the effect of different transition metal ions, a simple dimeric model is constructed out of **2** (see ESI) and the exchange interaction (J_3) is computed in which the sign (-0.037 cm^{-1}) is reproducible. As the antiferromagnetic interaction between the Co-Gd ions is found to reduce the -ΔS_m value, the role of other first transition metal ions was probed using **2** as a model by replacing Co^{II} by Mn^{II}, Fe^{II}, Ni^{II}, and Cu^{II}. The computed J values for these models are -0.027, -0.035, -0.003, -0.079 cm^{-1} for Mn^{II}, Fe^{II}, Ni^{II} and Cu^{II}, respectively. The Ni^{II} ion mediates the weakest exchange followed by Mn^{II} ion. Since the Ni^{II} ion is likely to possess significant anisotropy, the isotropic Mn^{II} is therefore likely to be the best candidate to enhance the entropy change compared to the Co^{II} analogue.

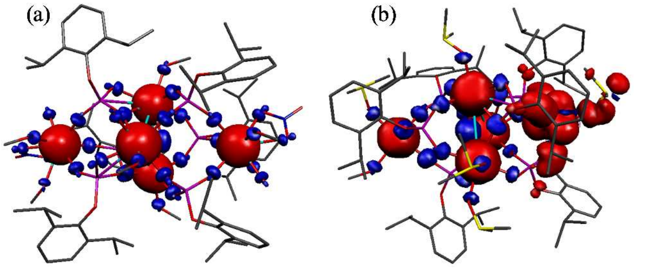


Fig. 3. Computed High Spin (HS)-spin density plots for (a) **1** and (b) **2.** Red and blue represent positive and negative spin densities, respectively.

In conclusion, we have synthesized a novel pentanuclear organophosphate complex of Gd^{III} using a phosphate monoester and a structurally similar 3d-4f analogue with Co^{II}, which are the first examples of organophosphate complexes of any lanthanide ion. The {Gd$^{III}_5$} complex reveals a significant entropy change (-ΔS_m) of 25.8 J kg^{-1}K^{-1}, at ΔH = 7 T. The high -ΔS_m values show that the organophosphate ligands based gadolinium complex display promising MCE properties for cryogenic applications. As the maximum -ΔS_m value (ΔH = 7 T) of the {Gd$^{III}_5$} complex is close to the maximum attainable value, the replacement of the bulky aryl phosphate ligand with a lower molecular weight phosphate ligands would enhance the entropy change (-ΔS_m). Work in this direction is currently underway, apart from incorporating other 3d metal ions.

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Notes and references

[a]Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, Maharashtra, India-400076; E-mail: rmv@chem.iitb.ac.in

[b]School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

† Electronic Supplementary Information (ESI) available: Experimental and computational details as a PDF; CIF for **1** (CCDC 1030609) and **2** (CCDC 1030610); See DOI: 10.1039/c000000x/

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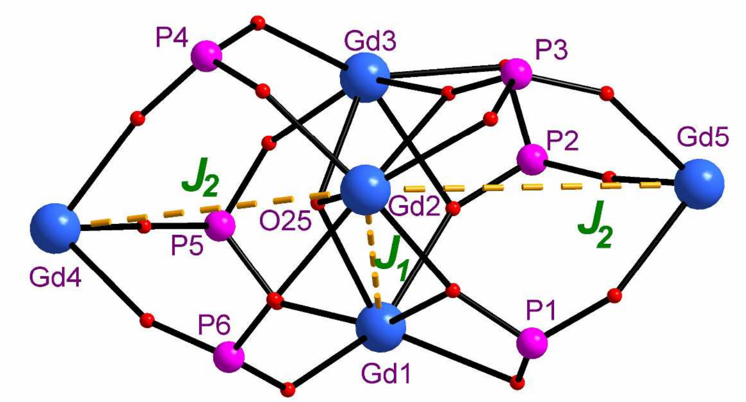
Discrete $\{Gd^{III}_4M\}$ (M = Gd^{III} or Co^{II}) pentanuclear complexes: A new class of metal-organophosphate molecular coolers

Sandeep K. Gupta,[a] Aijaz A. Dar,[a] Thayalan Rajeshkumar,[a] Subramaniam Kuppuswamy,[a] Stuart K. Langley,[b] Keith S. Murray,[b] Gopalan Rajaraman[a] and Ramaswamy Murugavel[a]



Magnetic measurements of the first examples of homo- and hetero-pentanuclear organophosphates of gadolinium reveal a higher magnetic entropy change for the isotropic $\{Gd^{III}_5\}$ complex (25.8 J $kg^{-1}K^{-1}$) as compared to the heterometallic $\{Gd^{III}_4Co^{II}\}$ complex (20.3 J $kg^{-1}K^{-1}$).