Marie Curie Fellowship Final Report

During the fellowship (from September 2009 to August 2011) I have prepared and investigated the magnetic properties of several series of 3d-4f complexes based on phosphonate ligands. I started from the cobalt-lanthanide phophonate complexes: $[\mathrm{Co}^{\mathrm{II}}_8\mathrm{Ln}^{\mathrm{III}}_8(\mu_3\text{-OH})_4(\mathrm{NO}_3)_4(\mathrm{O}_2\mathrm{C}^t\mathrm{Bu})_{16}(\mathrm{O}_3\mathrm{P}^t\mathrm{Bu})_8]$ (Ln = Gd, Tb, Dy, Er, Ho, Yb and Y) **1**, $[\mathrm{Co}^{\mathrm{II}}_8\mathrm{Ln}^{\mathrm{III}}_4\ (\mathrm{O}_3\mathrm{P}^t\mathrm{Bu})_6(\mathrm{O}_2\mathrm{C}^t\mathrm{Bu})_{16}]$ (Ln = Gd, Dy, and Y) **2** , $[\mathrm{Co}^{\mathrm{II}}_4\mathrm{Ln}^{\mathrm{III}}_6(\mathrm{O}_2\mathrm{C}^t\mathrm{Bu})_{14}(\mathrm{O}_3\mathrm{PCH}_2\mathrm{Ph})_6(\mathrm{MeCN})_2]$ (Ln = Gd, Tb, Dy and Y) **3**, $[\mathrm{Co}^{\mathrm{II}}_6\mathrm{Ln}^{\mathrm{III}}_8(\mu_3\text{-OH})_8(\mathrm{O}_3\mathrm{P}^t\mathrm{Bu})_6(\mathrm{O}_2\mathrm{C}^t\mathrm{Bu})_{16}(\mathrm{H}_2\mathrm{O})_2(\mathrm{MeCN})_2]$, (Ln = Gd, Tb, Dy, Ho, Er, Yb and Y) **4**, $[\mathrm{Co}^{\mathrm{II}}_4\mathrm{Ln}^{\mathrm{III}}_2(\mathrm{O}_3\mathrm{P}^t\mathrm{Bu})_2(\mathrm{O}_2\mathrm{C}^t\mathrm{Bu})_{10}(\mathrm{MeCN})_2](\mathrm{MeCN})_2$, (Ln = Gd and Nd) **5** and $[\mathrm{Co}_8\mathrm{Ln}_2(\mu_3\text{-OH})_2(\mathrm{PO}_3\mathrm{CH}_2\mathrm{Ph})_4(\mathrm{O}_2\mathrm{C}^t\mathrm{Bu})_{12}(\mathrm{HO}_2\mathrm{C}^t\mathrm{Bu})_2](\mathrm{MeCN})_6$ (Ln = Gd and Nd) **6**. The structures and synthetic procedures of these families can be summarised in Figure 1.

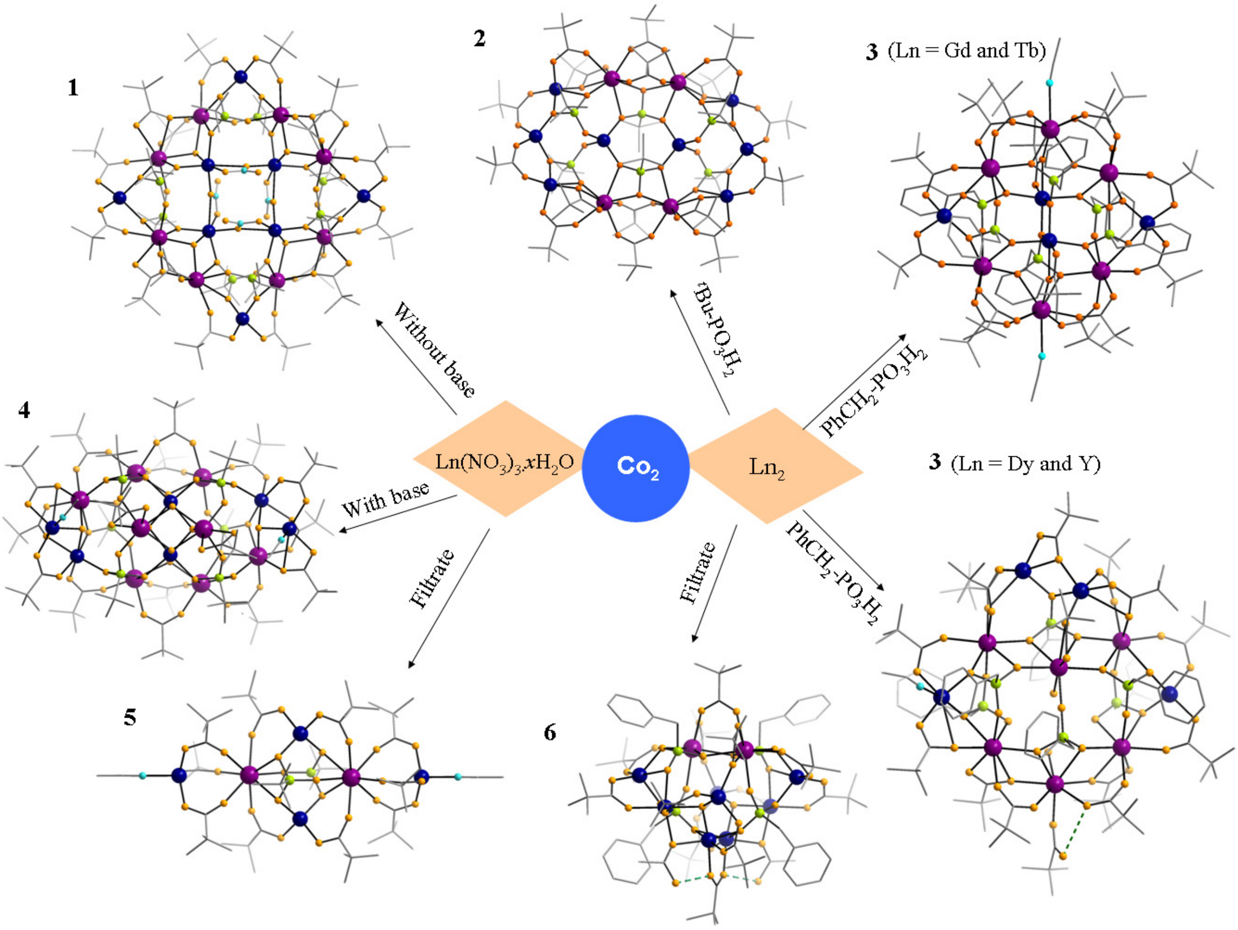


Figure 1. *Synthetic procedures and resulting structures. Colour codes (applied to the following figures) for the structures: Ln, purple; Co, blue; P, green; O, orange; N, cyan; C, grey.*

These six families can be divided into two structural types: grids, where the metal centers lie in a single plane, and cages. The grids include: [4×3] $\{\mathrm{Co}_8\mathrm{Ln}_4\}$ **2**, [3×3] $\{\mathrm{Co}_4\mathrm{Ln}_6\}$ **3** and [2×2] $\{\mathrm{Co}_4\mathrm{Ln}_2\}$ **5** families and a [4×4] $\{\mathrm{Co}_8\mathrm{Ln}_8\}$ **1** family where the central [2 × 2] square is rotated with respect to the external square. The cages include $\{\mathrm{Co}_6\mathrm{Ln}_8\}$ **4** and $\{\mathrm{Co}_8\mathrm{Ln}_2\}$ **6** families.

Magnetic studies have been performed for these compounds, and for each family, the maximum magnetocaloric effect (MCE) has been observed for the Ln = Gd derivative, with a smaller MCE for the compounds containing magnetically anisotropic 4f-ions. The resulting entropy changes of the gadolinium derivatives are (for 3 K and 7 T): 11.8 J kg^{-1} K^{-1} for $\{Co_8Gd_2\}$ **6Gd**; 20.0 J kg^{-1} K^{-1} for $\{Co_4Gd_2\}$ **5Gd**; 21.1 J kg^{-1} K^{-1} for $\{Co_8Gd_4\}$ **2Gd**; 21.4 J kg^{-1} K^{-1} for $\{Co_8Gd_8\}$ **1Gd**; 23.6 J kg^{-1} K^{-1} for $\{Co_4Gd_6\}$ **3Gd**; and 28.6 J kg^{-1} K^{-1} for $\{Co_6Gd_8\}$ **4Gd**, from which we can see these values are proportional to the percentage of the gadolinium in the core.

With the collaboration of Dr. Marco Evangelisti we have also investigated the heat capacity of one of the best magnetic coolers among these six cobalt-lanthanide families, $\{Co_6Gd_8\}$. As shown in Figure 2, the result from the heat capacity agrees well with our magnetic analysis. These results have been published in two papers, Y.-Z. Zheng *et al.*, *Chem. Sci.* **2011**, *2*, 99 and Y.-Z. Zheng *et al.*, *J. Amer. Chem. Soc.* **2011**, in revision.

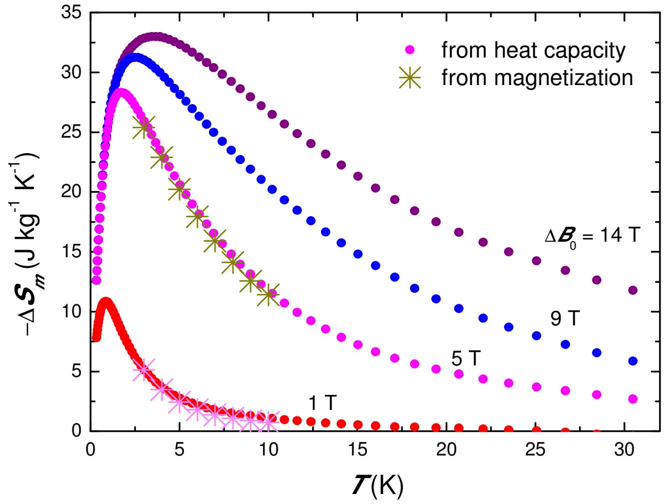


Figure 2. *Experimental ΔS_m for $\{Co_6Gd_8\}$ at various fields and temperatures, as obtained from the heat capacity data. The ΔS_m deduced from the magnetization data is also plotted for comparison, proving the remarkable agreement between these two complementary techniques.*

Indeed, the magnetic anisotropy of the octahedral cobalt(II) ions is theoretically confirmed to be adverse to enhance the magnetocaloric effect (MCE). Therefore, to obtain a 'better' magnetic cooler, I looked also other 3d transition metal ions.

First, I used nickel to replace cobalt in the phophonate complexes and obtained several new families of complexes: $[Ni^{II}_6Ln^{III}_6(\mu_3\text{-}OH)_2(O_3PCH_2Ph)_6(O_2C^tBu)_{16}(Me_2CO)_2](MeCN)x$, (Ln = Gd, Dy, Tb and Y) **7**, $[Ni_5Ln_8(\mu_3\text{-}OH)_7(\mu\text{-}OH_2)(O_3P^tBu)_6(O_2C^tBu)_{15}(MeCN)]\cdot H_2O$ (Ln = Eu, Gd and Tb) **8**, $[Ni^{II}_6Ln^{III}_8(\mu_3\text{-}OH)_8(O_3P^tBu)_6(O_2C^tBu)_{16}(H_2O)_2(MeCN)_2]$, (Ln = Dy, Ho, Er, Yb and Y) **9** and $[Et_3NH]_2[Ni_2Ln_2(\mu_3\text{-}OH)_2(O_2C^tBu)_{10}]$ (Ln = Gd and Dy) **10**. The structures of these families can be summarised in Figure 3. Except that the family **6** is isomorphous to the cobalt analogue **4** the others exhibit new cores. It is worthy note that the core of **7** in many ways the closest structural analogues in the literature is the very beautiful homometallic diamagnetic Wells-Dawson polyoxometallates.

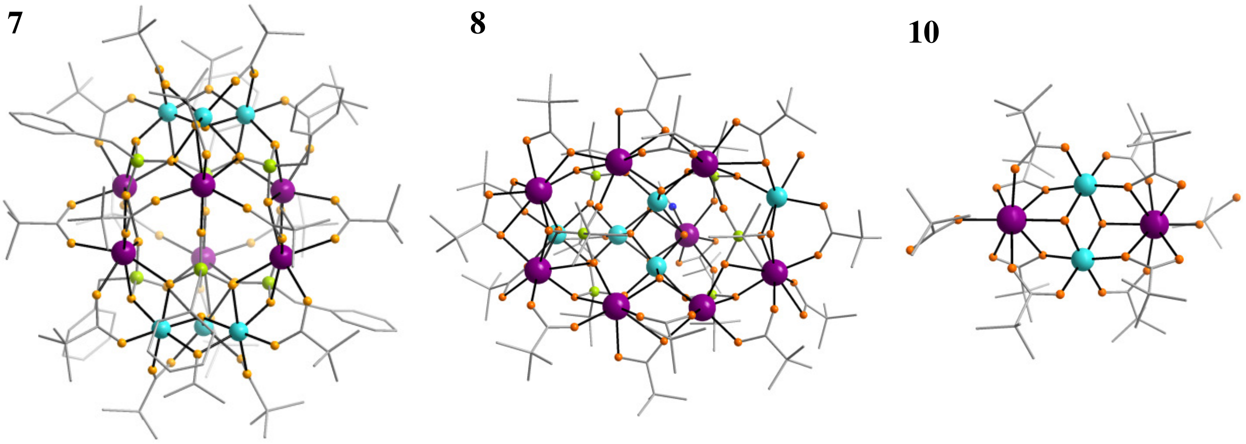
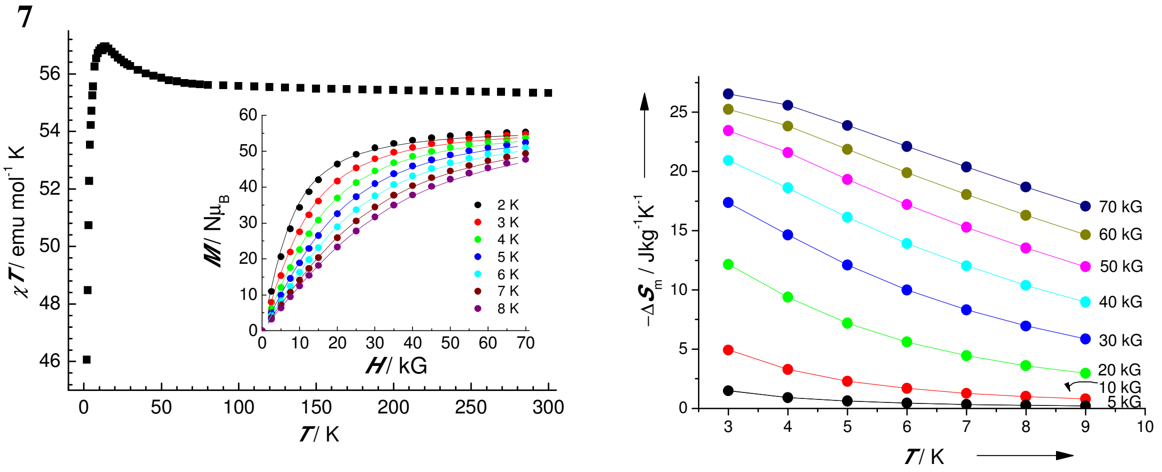


Figure 3. *Synthetic procedures and resulting structures. Colour code of Ni, cyan.*

Magnetic studies show that both **7Gd** and **8Gd** are promising coolers. As shown in Figure 4, both compounds show weak ferromagnetic interactions. Calculating the magnetic entropy changes obtained from the magnetisation data (Figure 3) gives values at 3 K and for a field change ΔH = 70 kG of: for **7Gd**, 26.5; for **8Gd**, 30.5 J kg^{-1} K^{-1}. The later value is slightly larger than **4Gd**. However, the performance of the magnetic cooling materials doesn't simply rely on the maximum value of the entropy change, but also the cooling rate at lower magnetic fields. For pragmatic application the magnetic field is better lower than 2 T. The fast cooling rate mostly depends on the ferromagnetic interactions and isotropy. That's way these two complexes are actually 'better' candidates in terms of the application. As we can see that at 2 T, the entropy changes of these two complexes have already reached half value of the maxima at 7 T. Part of this result has been published in a high-impact journal, Y.-Z. Zheng *et al.*, *Angew. Chem. Int. Ed.* **2011**, 50, 3692. Further results are in preparation for a full paper.



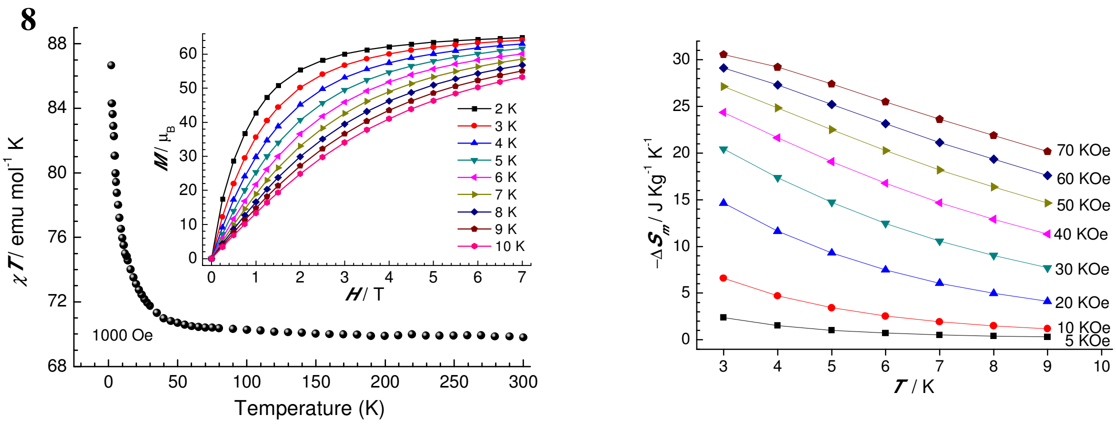


Figure 4. *The χT vs T plot of **7** and **8** under 1000 Oe dc field. Inset: the filed-dependent magnetization plots at indicated temperatures and the calculation of ΔS for **7** and **8** at various fields and temperatures.*

Inspired by the exciting results from the nickel complexes I extended this method to the 3d transition metal ions with more unpaired electrons and magnetically more isotropic. Manganese(II) and iron(III) who have five unpaired electrons ($s = 5/2$) are exactly those candidates.

By using two precursors, $[\mathrm{Mn^{II}(O_2C^tBu)_4(EtOH)}]_n$ and $[\mathrm{Ln_2(O_2C^tBu)_6\text{-}(HO_2C^tBu)_6}]$ (Ln = Gd and Dy) [12,13] to react with phosphonic acids. With methylphosphonic acid ($\mathrm{H_2O_3PMe}$) we found $[\mathrm{Mn^{II}_9Gd^{III}_9(O_3PMe)_{12}(O_2C^tBu)_{18}(L)}]$, **11** and $[\mathrm{Mn^{II}_8Gd^{III}_4(O_3P\text{-}^tBu)_6(O_2C\text{-}^tBu)_{16}(MeCN)}]$ **12**, where L = $(\mu_3\text{-OH})_{1.5\text{-}}(\mathrm{O_2C^tBu})_{1.5}$. With benzylphosphonic acid we isolated $[\mathrm{Mn^{II}_4Gd^{III}_6(O_3PCH_2Ph)_6(HO_2C^tBu)_{13}(O_2CMe)(HO_2C^tBu)(OH_2)_{2\text{-}}(MeCN)_2](MeCN)_3}$ **13** and $[\mathrm{Mn^{II}_6Dy^{III}_6(\mu_3\text{-}OH)_2(O_3PCH_2Ph)_{6\text{-}}(O_2C^tBu)_{16}](MeCN)_5}$ **14**. Except that compounds **12** and **13** exhibit similar cores as compounds **2** and **3** the other two compounds **11** and **14** show brand-new type of cores in 3d-4f coordination chemistry, that is, for **11**, a highly symmetric trigonal-bipyramidal $\{\mathrm{Mn^{II}_9Gd^{III}_9}\}$ core; for **14**, a truncated-ball shaped $\{\mathrm{Mn^{II}_6Dy^{III}_6}\}$ core, as shown in Figure 5.

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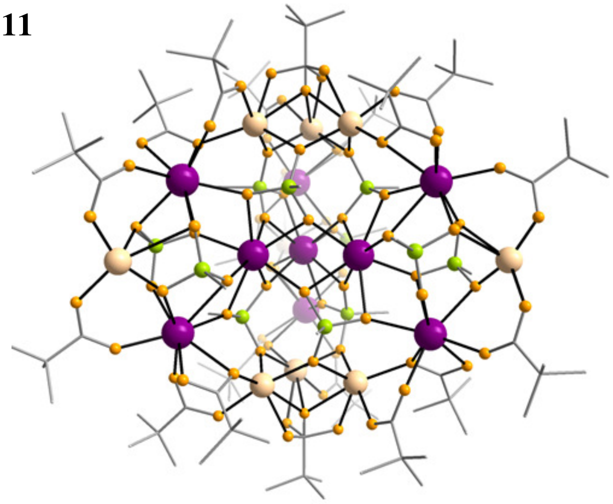

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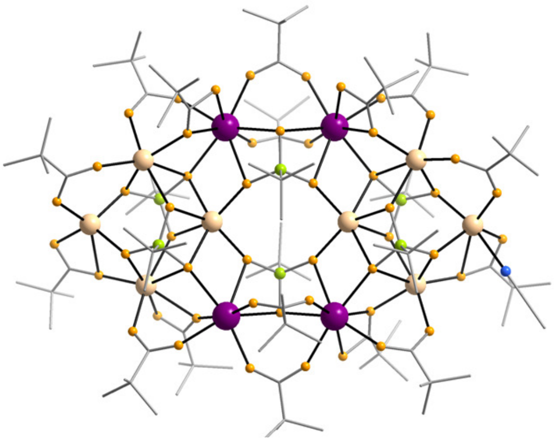

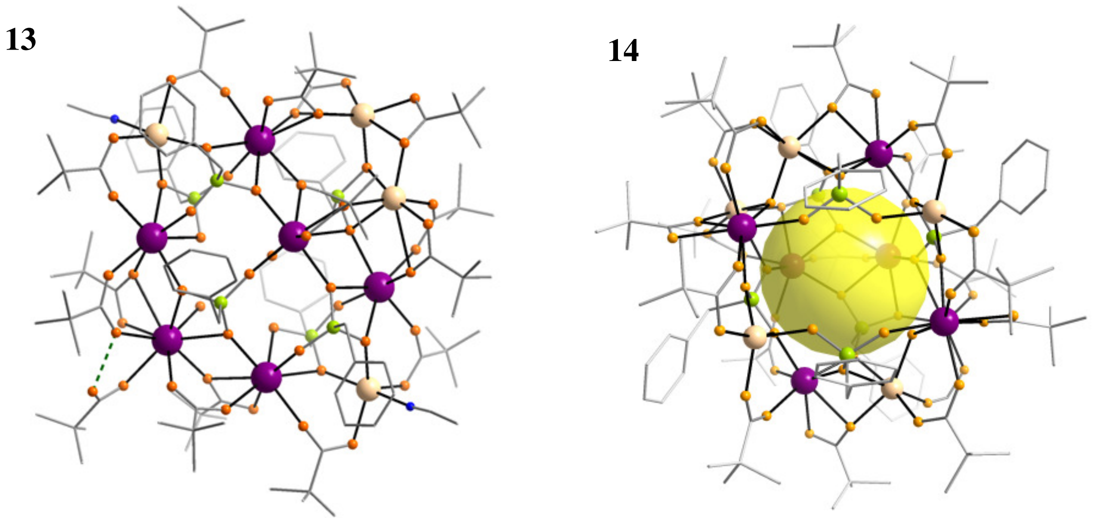

Figure 5. *Crystal structures of **11-14**. Colour codes: Mn, pink.*

Magnetic properties of **11-14** have been studied, which show an overall antiferromagnetic interaction, as shown in Figure 6.

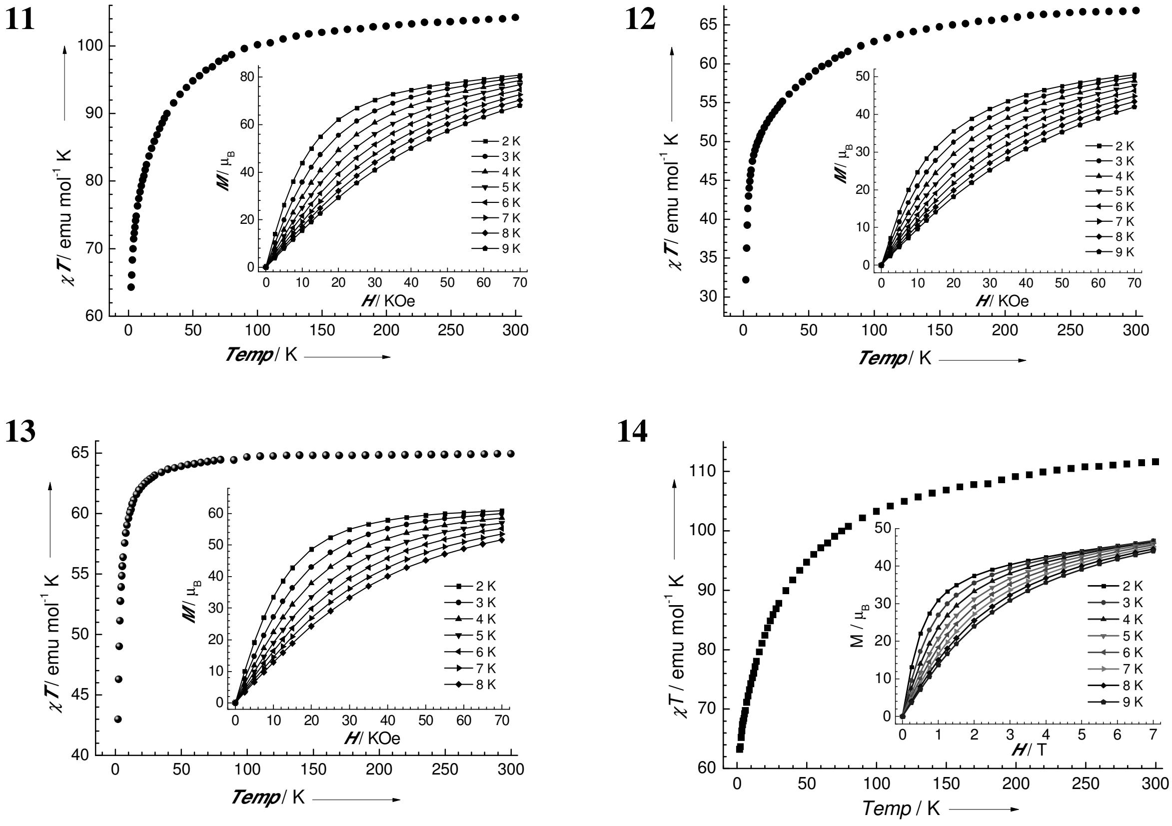

Figure 6. *The χT vs T plot of **11-14** under 1000 Oe dc field. Inset: the filed-dependent magnetization plots at indicated temperatures.*

Interestingly, complex **11** and **13** still exhibit very large entropy changes despite the overall antiferromagnetic interaction within the manganese centres (Figure 7). This is most likely due to the presence of large number of weakly coupled gadolinium centres. Moreover, by comparing the anisotropic Dy(III)-containing complex **14** the advantage of isotropic effect from both Mn(II) and Gd(III) are prominent. This result has been prepared for submitting to a high-impact journal.

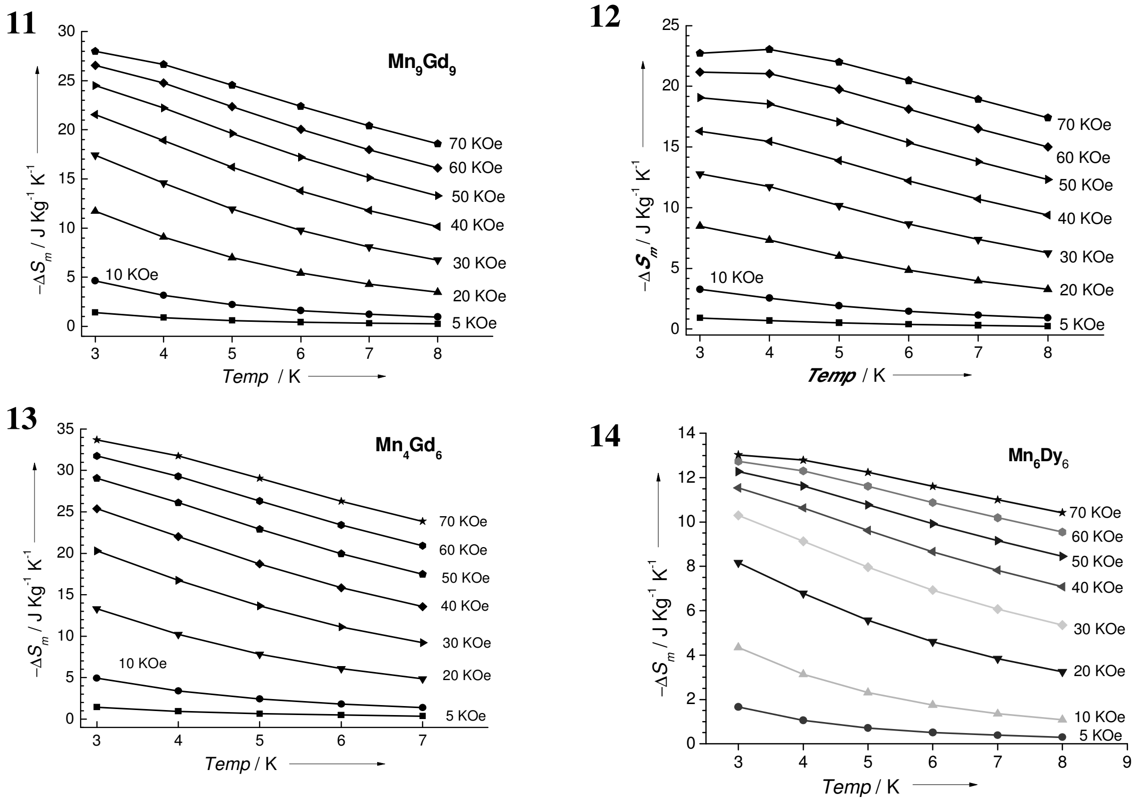

Figure 7. *Calculation of ΔS for **11-14** at various fields and temperatures.*

The extending to iron analogues leads to the isolation of two new families, $[\mathrm{Fe}^{\mathrm{III}}_{17}\mathrm{Ln}^{\mathrm{III}}_{2}(\mu_4\text{-O})_{10}(\mu_3\text{-O})_3(\mathrm{O_3P}^t\mathrm{Bu})_{14}(\mathrm{O_2C}^t\mathrm{Bu})_3(\mathrm{Me_2CO})_3](\mathrm{H_2O})x$, (Ln = Pr, Sm, Gd, Tb, Dy and Ho) **15** and $[\mathrm{Fe_6Gd_2(O_3P}^t\mathrm{Bu)_4(O_2C}^t\mathrm{Bu)_{12}(H_2O)_4(MeCN)_2}]$ (Ln = Sm and Gd) **16**. The structures of these families are shown in Figure 8, from which we can see compound **15** has much higher percentage of iron compared to **16**. Unfortunately, primitive magnetic studies show these two complexes show overall strong antiferromagnetic interactions within the iron centres, leading to a smaller MCE.

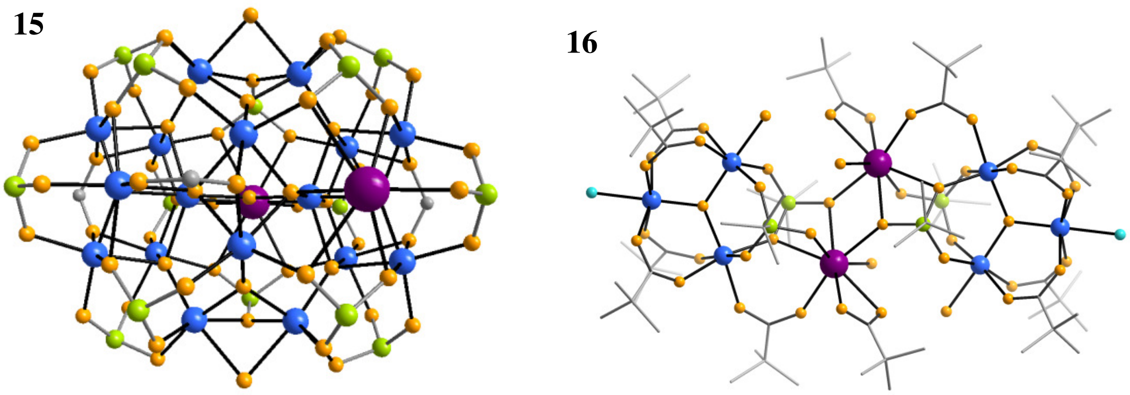

Figure 8. *Crystal structures of **15** and **16**. Colour codes: Fe, blue; N, light blue.*

There are also some unsuccessful examples, particularly the iron complexes obtained below (Figure 9), which have no lanthanide ions in them.

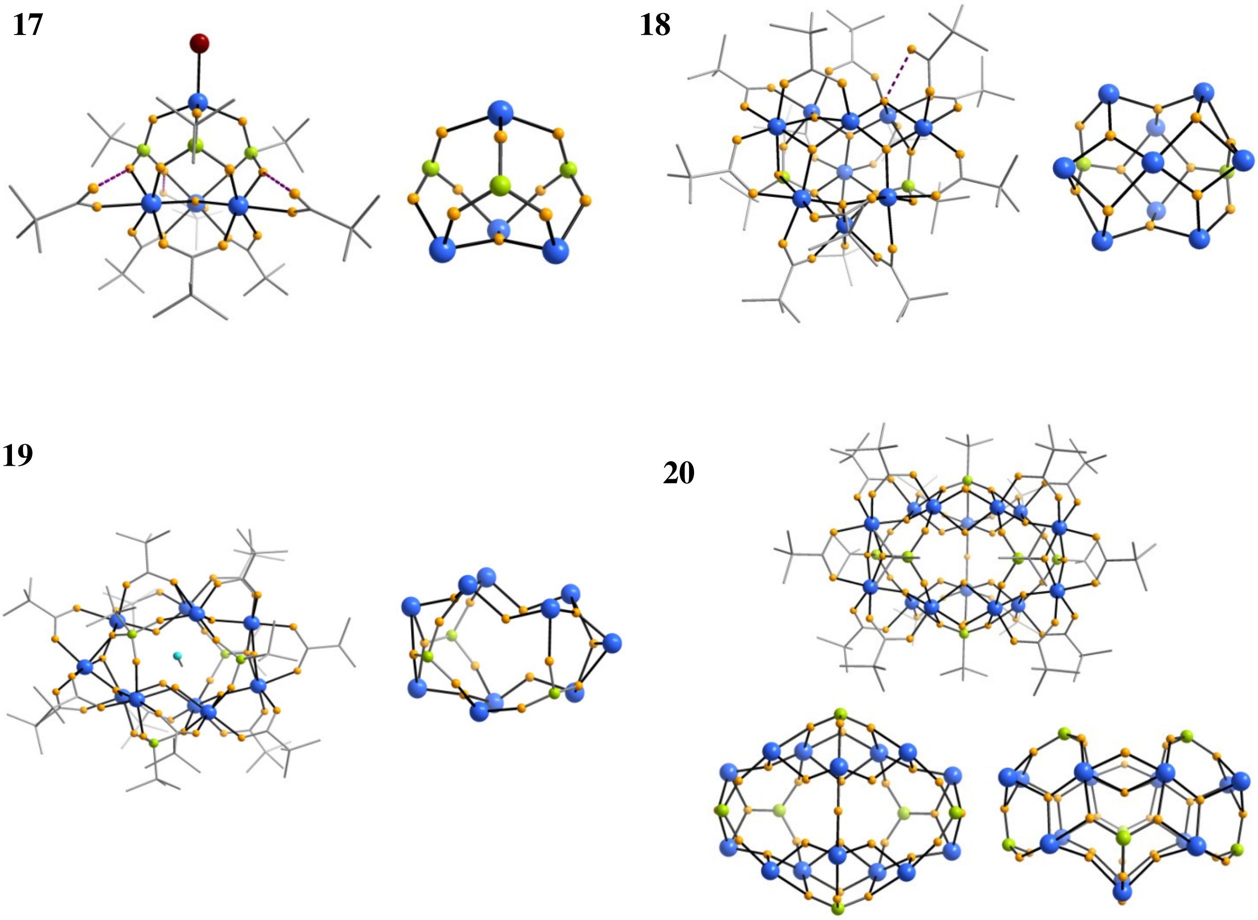

Figure 9. *Crystal structures of* ***17*** *-* ***20****.*

To summarize, during these two years as a Marie Curie International Incoming Fellow in the University of Manchester I have successfully finished the task as proposed, opening a new era of 3d-4f cooler in molecular magnetism. The creativity of this work lies in the exploit of different functions of metal centres to reach a magnetic combination, that is, the stronger interaction of the 3d transition metal and the larger spin state of the 4f lanthanide. This combination has been confirmed in this project to be a great success. Therefore, my research result in Manchester is fruitful. So far I have published four high-impact papers in *Chemical Science, Angewandte Chemie, Chemical Communications* and *Dalton Transactions*; and there are more papers are coming, one has been accepted by the *Journal of American Chemical Society*, one is in the process of reviewing by *Angewandte Chemie* and one invited review is in preparation.

Other than the success in science, technically I have been trained on the operation of SQUID and EPR spectroscopy. Moreover, I have also acquired many essential skills in teaching such as I have successfully passed the 40 hours training course of ‘Teaching for Researcher’, supervised one PhD, one master and one undergraduate students, assisted supervising a workshop of a EPR course and a tutorial course of undergraduate Chemical Physics. These experiences greatly helped me to earn a faculty position before I returned to China. Now I am a principal investigator in the Frontier Institute of Science and Technology, Xi’an Jiaotong University, in Xi’an, China. Supported by this fellowship I am fully confident to be an independent academia, leading a research group in an internationally competitive environment.