

## 1 Introduction

Since Werner first alerted the scientific community to the ideas of Coordination Chemistry, progress in the field has been marked by the recognition that beyond the concept of the complex there is a whole field to explore utilising collections of metal ions held together by relatively basic entities such as the chalcogens of species like thiolates, sulfides, oxides, hydroxides, alkoxides, carboxylates and so on. These are increasingly being described as coordination clusters in recognition of the fact that collections of metal ions trapped within ligand shells have the potential for displaying a variety of unusual behaviours resulting from cooperative effects which change the electronic structure both in terms of what might be expected for an isolated case and a bulk solid.

In this work, the properties of coordination clusters which might display the property which has been termed Single-Molecule Magnet (SMM) behaviour have been explored. In particular and as a result of the work already done within the group in Karlsruhe and elsewhere<sup>[1]</sup> it was realised that an area worth exploring was work on 3d/4f systems but including early 3d metal ions into the magnetic blend. Previous work in the group had concentrated on combining the middle to late 3d transition metal ions with various 4f ions and had produced some fascinating systems and very promising clusters such as the  $\{\text{Mn}_5\text{Ln}_4\}$  series<sup>[2]</sup> and the  $\{\text{CuLn}\}$ -propellers,<sup>[3]</sup> for which it was found that the  $\text{Dy}^{\text{III}}$  congeners respectively show high anisotropy barriers and, in the case of  $\text{Dy}^{\text{III}}$  ion, an exotic spin structure derived from a combination of the inherent strong Ising anisotropy of the  $\text{Dy}^{\text{III}}$  ion and the supramolecular imposition of a trigonal geometry.

In this thesis it will be shown how one can begin to understand ways to steer coordination chemistry towards target molecules. It is becoming increasingly clear that the 4f ions are far from being “boring” as a result of their tendency to display such similar chemistries, but rather they actually offer an unexpected means for the coordination chemist to take control of the outcome of a synthesis. As becomes clear, this is, as in all good cookery, not always a simple matter of following the recipe, but needs to take into account potentially subtle influences which may result from small changes to the coordinating ligands or even what the “ambient temperature and humidity” are on any given day.

Below a short summary of the guiding principles in terms of the quest for synthesising interesting 3d/4f coordination clusters displaying SMM properties is given. It should perhaps be noted that in all the work presented here, the real motivation was to expand the field of coordination chemistry. The fact that 3d/4f coordination clusters might possibly show interesting magnetic behaviour was a useful means of supporting this idea and allowing for an investigation into the structures and properties of such species. In this sense, this is the major contribution made by the research presented here.

## 1.1 Overview

Research on the synthesis, structures and magnetic characterisation of polynuclear coordination clusters containing anisotropic paramagnetic centres became an area of great importance in modern coordination chemistry since the discovery that such molecules can act as Single-Molecule Magnets (SMMs).<sup>[4]</sup> The fundamental characteristic of SMM behaviour is the presence of an energy barrier to the reorientation of the spin of the ground state and this can be defined in terms of a large (or at least non-zero) ground spin state ( $S$ ) and a large magnetic anisotropy of the Ising (easy axis) type with a negative zero-field splitting parameter,  $D$ . Coordination clusters containing the  $Mn^{III}$  ion are the richest source of SMMs largely as a result of its favourable Ising anisotropy and, in particular,  $Mn_{12}Ac$  and related carboxylate systems<sup>[4],[5]</sup> provided the first examples of SMMs whilst the recently reported  $Mn_6$  oxime series includes examples with the highest energy barriers so far reported.<sup>[5]</sup> It has been recognised that lanthanide ions also represent a rich source of highly anisotropic spin carriers<sup>[6],[7]</sup> and in the quest for new SMM (Single-Molecule Magnet) compounds attention has recently focused on incorporating such highly anisotropic 4f ions into 3d systems.<sup>[8],[9]</sup> Initially, much work concentrated on mixing 4f ions with the  $Mn^{III}$  ion. However, experience shows that relatively isotropic ions can also be used to help aggregate 3d/4f clusters in such a way as to produce new examples of SMMs often with enhanced SMM properties compared with the pure 3d analogues.

Although an increasing number of 3d/4f systems (such as Mn, Fe, Co, Ni and Cu-Ln) have been synthesised and structurally and magnetically characterised, not many compounds of the earlier 3d-transition metals with lanthanides have been reported so far.

For example, very few paramagnetic clusters containing vanadium have been reported<sup>[10]</sup>, with only one structural motif found to show SMM behaviour.<sup>[11]</sup> A  $\{V^{III}_4O_2\}$  butterfly core was obtained in two structures as  $[V_4O_2(O_2CEt)_7(pic)_2]^-$  or a  $[V_4O_2(O_2CEt)_7(bpy)_2]^+$  analogue and both must be prepared under inert gas conditions. The air-sensitivity of vanadium in the (+III) oxidation state is a challenge and may explain why there is a lack of such potentially magnetically interesting compounds. Mostly speaking it is the mid to later transition metal ions which lend themselves to the synthesis of magnetically interesting coordination clusters. This may well be a consequence of the fact that much of the Werner chemistry was developed around these metal ions and thus the ligands coordination chemists tend to choose reflect this. In addition, these metals are not so prone to heading towards the group valency, which is another way of saying that they are not so easily oxidised and, as a consequence, also more amenable to accommodating a variety of oxidation states. Nevertheless, other work has shown that the earlier transition metal ions, with their larger ionic radii and yet relatively hard Pearson character, ought to be useful components in the investigation of magnetically interesting systems in combination with other electronically interesting species.

Taking the specific example of chromium(III) as a potential metal ion to assemble magnetically interesting materials two major problems are obvious. Chromium in the oxidation state of (II) should lead to Jahn-Teller distorted high spin  $d^4$  complexes, leading to a high magnetic anisotropy, but these are hardly accessible due to their extreme air-sensitivity. Oxidation occurs immediately so that even if such a complex is obtained, it is not stable. On the other hand, when using chromium(III) its inertness means that very harsh reaction conditions are required. Thus, although a range of oxo- and hydroxo bridged systems are known these can only be obtained from  $Cr^{III}$  salts in very low yields and although they show a variety of structural and magnetic properties, not surprisingly none has proved to be a SMM.<sup>[12]</sup>

In fact, as will be shown later in this thesis, this idea that it might be best to introduce the required uniaxial magnetic anisotropy into a system via the 3d metal ions, and thereby give SMMs, is not a necessary condition. In fact, the huge anisotropy of certain 4f metal ions makes the choice of the 3d ions almost immaterial apart for tinkering on the peripheries. In line with this, research within this group has amply demonstrated that dysprosium(III), with

its high intrinsic anisotropy, which is one of the requirements to lead to this specific behaviour, is often the best component to choose.

Thus, overall the goal was to discover whether or not combining early transition metal ions with 4f ions in coordination clusters could produce interesting systems as well as new insights into the factors steering the magnetic interactions in these. As will be seen, this proved highly informative and even allowed for the first identification of significant interactions amongst all metal ions within a Cr<sup>III</sup>/Dy<sup>III</sup> coordination cluster. Previous work has suggested that Ln/Ln interactions are inherently weak, as are Ln/3d interactions, and it is the highly anisotropic nature of ions such as Dy<sup>III</sup> which dictates the magnetic behaviour. Yet it seems with the earlier 3d transition metal ions that better exchange pathways for magnetic interaction exist, which also significantly alter our understanding of the electronic structures of such coordination clusters.

Finally, given that within the research group in Karlsruhe, as well as elsewhere, significant contributions towards understanding the magnetic behaviour and interactions in both pure 4f and 3d/4f systems have been made, it seemed useful to explore some simpler pure 3d systems based on the early transition metal ions. As will be seen later in the thesis, this was not such a straightforward undertaking and there is no doubt that much further work is needed in this area.