



Review

The coordination chemistry and magnetism of some 3d–4f and 4f amino-polyalcohol compounds



Joseph W. Sharples*, David Collison

School of Chemistry, The University of Manchester, Oxford Road, Manchester, Lancashire M13 9PL, United Kingdom

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Abbreviations: tacn, 1,4,7-triazacyclononane; bmhH₂, 1,2-bis(2-hydroxy-3-methoxybenzylidene)hydrazone; mshH, 3-methoxysalicylaldehyde hydrazone; 4-Me-py, 4-methyl-pyridine; chpH, 6-chloro-2-hydroxy-pyridine; acacH, acetylacetonate; ΔT_{AD} , adiabatic temperature change; a.c., alternating current; U_{eff} , anisotropy barrier; H , applied magnetic field; D , axial anisotropy; HO₂CPh, benzoic acid; Hbta, benzotriazole; k_B , Boltzmann constant; BVS, bond valence sum; ⁿBudeaH₂, n-butyldiethanolamine; CASPT2, complete active space perturbation theory 2; CASSCF, complete active space self consistent field; J_{12} , coupling constant; d.c., direct current; μ_B , electronic Bohr magneton; fcdCH₂, ferrocene dicarboxylic acid; RdeaH₂, functionalised diethanolamines; HDVV, Heisenberg Dirac van Vleck; ib, isobutyrate; ¹PrO, isopropoxide; JT, Jahn–Teller; g , Landé g -value; $-\Delta S_M$, magnetic entropy change; MCE, magnetocaloric effect; mdeaH₂, methyldiethanolamine; Micro-SQUID, micro-superconducting quantum interference device; m_s , microstate; ⁿBudeaH₃, n-butyldiethanolamine; edteH₄, N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine; sabheaH₃, N-salicylidene-2-(bis(2-hydroxyethyl)amino)ethylamine; NMR, nuclear magnetic resonance; χ'' , out-of-phase susceptibility; H₂Pc, phthalocyanine; HO₂C^tBu, pivalic acid; py, pyridine; QT, quantum tunnelling; RASSI, restricted active space state interaction; E , rhombic ZFS; SMM, single-molecule magnet; χ , susceptibility; χT , susceptibility temperature product; \hat{S}_n , spin operator; τ , tau; teaH₃, triethanolamine; THF, tetrahydrofuran; tpaH, triphenyl acetic acid; ZFS, zero-field splitting.

* Corresponding author. Tel.: +44 0161 306 9260; fax: +44 0161 275 4598.

E-mail address: joseph.sharples@manchester.ac.uk (J.W. Sharples).

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ABSTRACT

Triethanolamine, teaH₃, and diethanolamine, RdeaH₂, 3d–4f and 4f compounds demonstrate an enormous variety in their structure and bonding. This review examines the synthetic strategies to these molecules and their magnetic properties, whilst trying to assess these ligands' suitability towards new SMMs and magnetic refrigerants.

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1. Introduction

1.1. Molecular magnetism and poly-alcohol ligands

Molecular magnetism is a wide ranging area of research that began around 20 years ago, primarily involving the synthesis and study of metal coordination compounds. Twin pillars of this effort, amongst others, are the discovery of single-molecule magnets (SMMs) [1], in which data can in principle be stored at a molecular level; and magnetic refrigerants [2], compounds with a large magnetocaloric effect (MCE) that can be used to cool to and below liquid ⁴He temperatures. Much early research in the former area involved transition metal compounds, such as $[\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]\cdot 2\text{CH}_3\text{COOH}\cdot 4\text{H}_2\text{O}$ [3] and $\{[\text{Fe}^{\text{III}}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]\text{Br}_7\cdot \text{H}_2\text{O}\}\text{Br}\cdot 8\text{H}_2\text{O}$, where tacn is 1,4,7-triazacyclononane [4], whilst the latter topic involved cages such as $[\text{Fe}^{\text{III}}_{14}\text{O}_6(\text{bta})_6(\text{OMe})_{18}\text{Cl}_6]$, where Hbta is benzotriazole [5]. Many subsequent efforts [e.g. 6] used polyalcohol pro-ligands, amongst others, to connect the metals into larger assemblies, so increasing the ground state spin, *S*, as this was initially believed to be the key to increasing the temperatures at which SMMs could maintain magnetised states to a practical level. The challenge of achieving this is still on-going. Selected examples were well reviewed by Brechin in 2005 [7], who showcased the SMM behaviour of mostly Mn^{III} and Fe^{III} cages. The first of these ions was particularly prevalent in early research, having a sizable single-ion anisotropy when in the octahedral configuration, which can define an Ising-type ground state. Introducing lanthanides into molecular magnetism, a more

recent development, led to large improvements in the energy barriers of SMMs, on account of the anisotropy of Ln^{III} ions such as Dy^{III}, Tb^{III} and Ho^{III}, particularly by Ishikawa, with a $[\text{Tb}^{\text{III}}(\text{Pc})_2]^-$ compound [8]. The high spin and isotropy of Gd^{III} has achieved similarly impressive results in increasing the $-\Delta S_M$ (MCE) of molecule-based refrigerants, for example $[\text{Gd}^{\text{III}}_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$ [9].

Therefore, combined with the established benefits of appropriate d-transition metals, or as homometallic species, lanthanide-based compounds impart significant structural and magnetic properties, distinct from their 3d cousins, giving some of the best performing SMMs and magnetic refrigerants.

1.2. Amino-polyalcohol ligands

An extension of this work uses amino-polyalcohol pro-ligands. These would seem an ideal continuation of previous efforts as they possess an affinity to lanthanides due to their O donors, but also incorporate a new N functionality which can take part in bonding, though to date there are significantly fewer 3d–4f and 4f compounds of this type than with 3d metals alone, so this is an ongoing area of research. The focus here will be on those compounds prepared with the pro-ligands teaH₃, triethanolamine, and RdeaH₂, functionalised diethanolamines, where R is H or C_{*n*}H_{2*n*+1}; these being shown in Fig. 1. These are flexible pro-ligands that can bond to metals in many ways, or with many “modes”. Their profligacy also stems from the way they exist in a variety of forms, depending on the basicity of the conditions, as singly, doubly or triply protonated species as appropriate, in addition to their completely

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