Solvothermal Synthesis of Paramagnetic Molecular Clusters

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A brief overview is given of the literature of the use of solvothermal techniques – chemistry in superheated solvents – towards paramagnetic cluster synthesis. Although these techniques have been used extensively to prepare infinite lattice magnetic materials, there is much less work on preparing discrete molecular clusters other than the polyoxovanadates and -molybdates. This microreview details some of our early success in using these techniques towards high-nuclearity vanadium(III), chromium(III), manganese(II/III), iron(III) and nickel(II) clusters, including some very high spin ground state clusters ($S \leq 25$), and therefore demonstrates the potential in the synthesis of molecular materials such as single-molecule magnets.

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Introduction

Interest in polymetallic cluster complexes of paramagnetic transition metal ions has increased hugely since the discovery of "single-molecule magnets" (SMMs).[1] This remarkable class of molecules displays magnetic bistability that is entirely of a molecular origin, and arises from the combination of a high ground state electron spin (S, resulting from the magnetic exchange interactions between the individual ions within the cluster), and a large negative zero-field splitting (D) within this ground state.[2] The first SMM discovered was the dodecametallic, mixed-valence manganese(III/IV) cluster[1] $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$, trivially known as "Mn12", that has an $S = 10$ ground state. Magnetic hysteresis (due to retention of magnetisation in the absence of an applied magnetic field) in SMMs is only observed below a certain blocking temperature, and in Mn12 this is ca. 4 K − this is still the highest recorded for an SMM. The blocking temperature is controlled in part by the product DS^2. Clearly, if SMMs are to be exploited in, for example, memory devices there is a need to synthesise new SMMs with higher blocking temperatures. Thus, the primary challenge in this field is still the synthesis of new cluster molecules.

The vast majority of paramagnetic cluster compounds have been synthesised by what might be termed "conventional" coordination chemistry techniques − a source of metal ion and bridging and terminal ligands in a common solvent at temperatures limited by the boiling point of that solvent at atmospheric pressure. Although these methods have been superbly successful in producing a bewildering array of clusters (see ref.[3] for a recent review of structures

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MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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with more than 6 metal ions), there is no reason to confine synthetic methods to this limited temperature/pressure regime as this can only limit the range of products available. A few groups have explored higher temperature routes to clusters – for example, high-nuclearity chromium(III) clusters, including very high spin ground state examples,[4] have been made by solid-state thermolysis reactions followed by extraction into a suitable solvent and crystallisation.[5] Although these results demonstrate the possibilities of higher temperature routes, they lack the advantages of solution chemistry, most importantly the direct crystallisation of products. We were inspired by the pioneering work of Zubieta and co-workers in the hydrothermal synthesis of high-nuclearity, high-valent (alkoxo)polyoxovanadates and -molybdates[6] to investigate the use of solvothermal techniques in the synthesis of large paramagnetic clusters of the 1st row transition metal ions. This Microreview summarises the important literature to date, and highlights some of our early successes in this area demonstrating the applicability of these techniques in cluster chemistry of metals across the 1st row, with examples of vanadium(III), chromium(III), manganese(II/III), iron(III) and nickel(II) chemistry, including some of the highest spin ground state molecules known.

Solvothermal Synthesis

Hydrothermal or, more generally, solvothermal techniques involve heating a reaction mixture in a sealed vessel such that reaction temperatures greater than the boiling point of the solvent can be reached (typically between 100 and 250 °C in hydrothermal chemistry), typically under autogenous pressure. [Note that some authors reserve the term hydro(solvo)thermal to refer to supercritical conditions – in this work we merely imply heating beyond the boiling point.] Superheated solvents exhibit (i) reduced viscosity (and therefore enhanced diffusion of chemical species) and (ii) very different solubilising properties (e.g. the dielectric constant of water decreases rapidly with increasing temperature)[7] compared to ambient conditions. These factors can lead to very different chemistry. For example, (ii) can lead to otherwise insoluble reagents being solubilised (which can be exploited to overcome solubility differences between metal salts and ligands), and (i) can lead to enhanced crystal growth from reaction solutions. Furthermore, the temperature regime available in solvothermal techniques, intermediate between low-temperature solution chemistry and high-temperature solid-state chemistry, can favour the formation of metastable kinetic products rather than the thermodynamic products (e.g. metal oxides) favoured at higher temperatures. All these features of hydrothermal chemistry have long been exploited in materials chemistry, e.g. in the preparation of zeolites, and there are several excellent reviews in this area.[7,8] More recently, these techniques have been employed extensively in the synthesis of coordination polymers (or metalorganic frameworks),[9] including magnetic materials.[10]

However, there is much less literature on the solvothermal synthesis of *discrete molecular clusters*, despite the fact that all the above advantages are equally applicable. In particular, the propensity to crystallise products direct from reaction solution is invaluable because product identification in cluster chemistry relies almost entirely on single-crystal X-ray diffraction given the complexity, and unpredictability,[11] of the materials being formed. The literature on solvothermal cluster synthesis is dominated by Zubieta's systematic exploration of the hydrothermal synthesis of polyoxo/alkoxovanadates,[6] although there is also a significant body of work involving metal chalcogenide clusters.[12] Zubieta's work highlights another important advantage of solvothermal conditions for cluster synthesis. From a very simple set of reagents – for example, a source of vanadium(III) (V_2O_3) and vanadium(V) [V_2O_5 or $(NH_4)VO_3$], a bridging ligand (tri- or tetraalcohol, which are readily deprotonated to alkoxides), and a mineraliser salt and source of counterion (alkylammonium halide salt) in superheated water (150–210 °C) – a vast array of vanadium(IV/V) clusters can be formed: for example, $[V_6O_7\{EtC(CH_2O)_3\}_4]^{2-}$ (based on a V_6 octahedron, see Figure 1),[13] $[V_{10}O_{16}\{EtC(CH_2O)_3\}_4]^{2-/4-}$, $[V_{10}O_{13}\{EtC(CH_2O)_3\}_5]^-$ (based on V_{10} edge-sharing bioctahedra),[14] and $[V_{16}O_{20}\{CH_2(OH)C(CH_2O)_3\}_8(H_2O)_4]$,[15] amongst many others. Thus, because solvothermal conditions facilitate the isolation of metastable species, the nature of the product (nuclearity, oxidation states, topology) is very sensitive to the specific reaction conditions and there is a vast "parameter space" to explore over and above the obvious variables of reagents and solvent, viz. stoichiometery, temperature, pressure, pH, mineralisers, fill volume of the reaction vessel, etc. O'Hare has also recently highlighted this in hydrothermal syntheses of uranyl-based coordination polymers.[9c]

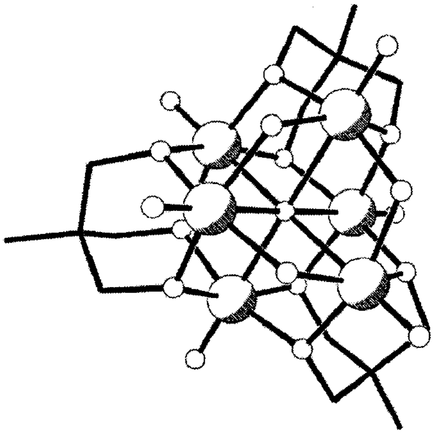

Figure 1. Structure of Zubieta's $[V_6O_7\{MeC(CH_2O)_3\}_4]^{2-}$ anion, after ref.[13]; scheme: V (large shaded circles), O (small open), C (connectivity only), H omitted for clarity

There is now a very large amount of literature on hydrothermally prepared polyoxometallate clusters of the vanadium group – in addition to Zubieta's alkoxide-based work (reviewed in detail elsewhere),[6] there are many polyoxovanadates exploiting inorganic (borate, phosphonate, arsenate, germanate) templates,[16] and several heterometallic vanadate/molybdates[17] and tungstates.[18] (Alkoxo)polyoxovanadate[19] and -molybdate[20] clusters-of-clusters with nuclearities up to 18 and 42, respectively, have also been prepared by hydrothermally induced condensation of smaller, preformed clusters.

All this work is based on vanadium and molybdenum in the +4 or +5 oxidation state, and even in the fully reduced M^{IV} forms these clusters only have one unpaired electron per metal centre. In our work, where we are targeting very high spin ground state clusters, we require transition-metal ions with several unpaired electrons; thus, we are utilising later transition ions or lower oxidation states of the early transition metals. There are very few solvothermally prepared clusters with later transition ions, but there are a few important examples. Secondary metals − Co^{II}, Mn^{II}, Cu^{II} and Zn^{II} − have been introduced into polyoxovanadates and -molybdates.[21] More significantly in the context of this article, Zubieta has recently extended his poly(alkoxide) work to Fe^{III} in $[\{Fe(OH)(MeCN)_2\}Fe_6OCl_6\{CH_2(OH)C(CH_2O)_3\}_4]$ (based on a face-capped Fe_6 octahedron), $[Fe_{10}O_2Cl_8\{EtC(CH_2O)_3\}_6]$ and the heterometallic $[(VO)_2Fe_8O_2Cl_6\{EtC(CH_2O)_3\}_6]$ (both structurally related to the edge-sharing bioctahedral V_{10} clusters, above) all synthesised from mixtures of $FeCl_2$, V_2O_5 and tri- or tetra-alcohol ligand in MeCN at 120−150 °C.[22] In addition, two hexametallic Co^{II} clusters have been reported by solvothermal routes: Wood et al. prepared the Co_6 ring $[Co_6\{O_3PCH_2N(CH_2CO_2)_2\}_6]^{12-}$ from the potassium salt of the ligand and $Co(NO_3)_2$ in MeOH at 200 °C,[23] while Ōkawa's $[Co_6(OH)_2(phenylcinnamate)_{10}]$ is prepared from the organic acid, $Co(NO_3)_2$ and base in water at 170 °C.[24] It is perhaps significant that several of these latter examples use organic solvents rather than water, as these less polar solvents have been suggested to favour formation of clusters rather than infinite solids under solvothermal conditions,[23] presumably due to the effectively limitless source of O^{2-}/OH^- available in hydrothermal synthesis favouring the formation of polymers.[23]

Our Work

Our rationale was to use the simple triangular clusters $[M_3O(O_2CR)_6L_3]^{n+}$ (Figure 2) as our source of metal ion, in superheated alcohols as solvent and source of bridging ligand. The "basic metal carboxylates"[25] have several advantages as precursors: (i) they are small clusters themselves, (ii) they are known for the 1st row transition metals from vanadium to cobalt, (iii) homovalent M^{III}_3 (n = 1) and heterovalent $M^{III}_2M^{II}$ (n = 0) triangles are available for V, Mn, and Fe, (iv) heterometallic triangles are known, (v) they can be prepared with a wide range of carboxylates and terminal ligands (L), (vi) the central oxide and bridging carboxylates provide sources of ligands with several potential bridging modes. Hence, these simple metal triangles have been used extensively as precursors to higher nuclearity clusters, particularly with manganese and iron by "conventional" synthetic methods (for example, Mn12 derivatives can be prepared by oxidation of $[Mn_3O(O_2CR)_6L_3]^+$),[1a] and with chromium(III) by high-temperature solid-state routes.[5] There is much less literature[21c,22,23,26] on solvothermal synthesis with alcohols than with water. However, in addition to (perhaps) favouring cluster formation (see above), alcohols obviously provide a source of alkoxide that can bridge in μ_2 and μ_3 modes, thus providing further scope for extensive metal aggregation.

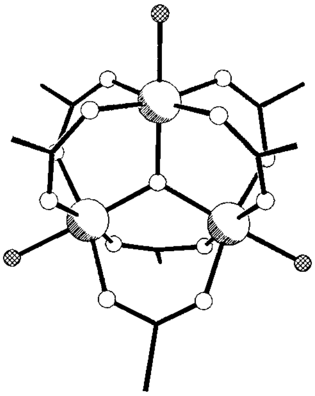

Figure 2. Structure of $[M_3O(O_2CMe)_3L_3]^{+/0}$; scheme: M (large shaded circles), terminal ligands L (cross-hatched circle), others as in Figure 1

Our first efforts employed this simple reaction system of metal triangle in alcohols with no additional source of bridging ligand. For example, reaction of $[Cr_3O(O_2CMe)_6(H_2O)_3]Cl$ in MeOH or EtOH at 200 °C yields the decametallic clusters $[Cr_{10}(OR)_{20}(O_2CMe)_{10}]$, which have a cyclic structure with respect to the metal ions where neighbouring ions are bridged by a μ_2-acetate and two μ_2-alkoxides (Figure 3).[27] Thus, in this example extensive bridging of metal ions has occurred, utilising ligands from both the metal precursor and deprotonated solvent as we had hoped. Furthermore, otherwise identical reactions under reflux only give recrystallised versions of the starting triangle (although Bino has reported that refluxing $[Cr_3O(O_2CMe)_6(H_2O)_3]Cl$ in H_2O yields the octametallic $[Cr_8(OH)_{12}(O_2CMe)_{12}]$)[28]. Therefore, the superheated conditions have allowed us to overcome the kinetic inertness of the Cr^{III} ion to form larger clusters. Alternative routes to Cr^{III} clusters have also been by high temperatures for this reason. For example, heating $[Cr_3O(O_2CCMe_3)_6(H_2O)_3]NO_3$ in the solid state at 300 °C, followed by extraction with and crystallisation from *n*PrOH, gives $[Cr_{12}O_9(OH)_3(O_2CCMe_3)_{15}]$,[5] and refluxing $[Cr_3O(O_2CMe)_6(H_2O)_3]Cl$ in a high-boiling solvent, PhCN at 188 °C, in the presence of 2,2′-bipyridine (bipy) gives the butterfly tetramers $[Cr_4O_2(O_2CMe)_7(bipy)_2]Cl$.[29]

The magnetic properties of the $[Cr_{10}(OR)_{20}(O_2CMe)_{10}]$ clusters are highly unusual.[27] $[Cr_{10}(OEt)_{20}(O_2CMe)_{10}]$ is weakly antiferromagnetically coupled (J = −0.9 cm^{-1}), leading to an S = 0 ground state. This is the norm for paramagnetic "molecular wheels" in the literature, albeit the magnitude of $|J|$ is small compared to other (octametallic) Cr^{III} examples.[3] However, $[Cr_{10}(OMe)_{20}(O_2CMe)_{10}]$ is weakly ferromagnetically coupled (J = +4.5 cm^{-1}). The logical consequence of this is an S = 15 ground state, which

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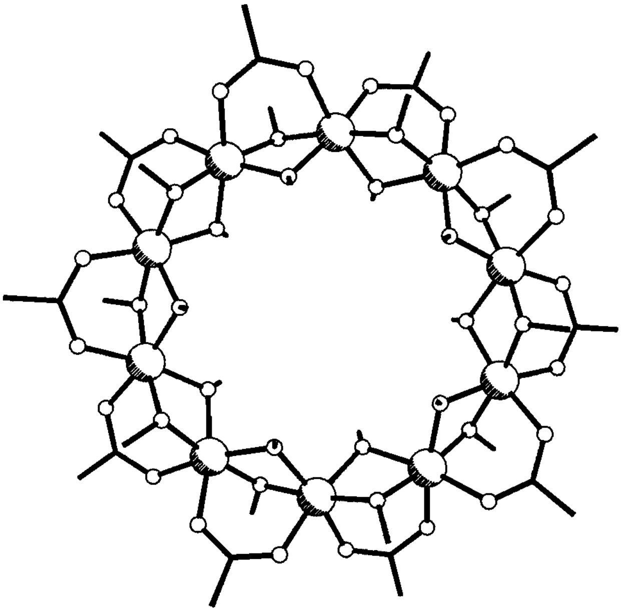

Figure 3. X-ray structure of a molecule of $[Cr_{10}(OMe)_{20}(O_2CMe)_{10}]$; scheme: Cr (large shaded circles), others as in Figure 1

is the highest know for a Cr-based cluster, and among the highest for any metal ion.[30] We have recently confirmed this by inelastic neutron scattering (INS) measurements on $[Cr_{10}(OCD_3)_{20}(O_2CCD_3)_{10}]$,[31] prepared by reaction of $[Cr_3O(O_2CCD_3)_6(H_2O)_3]NO_3$ in CD_3OD at 200 °C. The simplicity of the solvothermal route and the high yield (60−80%) of these clusters is vital in preparing the gram-scale quantities of per-deuterated complex required for INS studies at reasonable cost. This remarkable change from an $S = 0$ to an $S = 15$ ground state by changing the alkoxide bridge is simply a consequence of a small shift in J (ca. 6 cm^{-1}) that happens to cross $J = 0$. The small decrease in the antiferromagnetic contribution to J on changing from OEt to OMe is rationalisable in terms of the decrease in electron density at the bridging atom and consequent poorer overlap of magnetic orbitals, and similar shifts in J have been observed in Cr^{III} dimers.[32] We have now prepared a large family of these compounds $[Cr_{10}(OR)_{20}(O_2CR')_{10}]$ (R′ = Me, Et, $CCMe_3$; R = Me, Et) by the same route, and for each R′ the R = Me species are less antiferromagnetically coupled than the R = Et ones, including a second ferromagnetically coupled example, $[Cr_{10}(OMe)_{20}(O_2CCMe_3)_{10}]$.[31]

The analogous Fe^{III} wheels are known, the first known example being Lippard's $[Fe_{10}(OMe)_{20}(O_2CCH_2Cl)_{10}]$ "ferric wheel",[33] and can be prepared under much more facile conditions reflecting the greater kinetic lability of the ferric ion. Under solvothermal conditions we have only prepared insoluble powders from $[Fe_3O(O_2CMe)_3L_3]X$ in alcohols. Similar results have been reported by others from reactions under reflux − continuous extraction of this mixture is one of the routes to isolating the parent ferric wheel $[Fe_{10}(OMe)_{20}(O_2CMe)_{10}]$.[34] Nevertheless, the isolation of $[M_{10}(OR)_{20}(O_2CR')_{10}]$ with Fe^{III} and Cr^{III} indicates that this should be a stable molecule for a range of M^{III} ions, and indeed we have recently prepared the dark-green V^{III} analogue $[V_{10}(OMe)_{20}(O_2CMe)_{10}]$ by reaction of $[V_3O(O_2CMe)_6(pyridine)_3][ReO_4]$ (we have been exploring perrhenate as a non-explosive analogue of perchlorate) in MeOH at 150 °C (equivalent reactions under reflux only give pale-yellow powders).[35] There is very little V^{III} cluster chemistry in the literature because of the readily oxidisable nature of this ion, and $[V_{10}(OMe)_{20}(O_2CMe)_{10}]$ is the highest nuclearity example reported to date. Here we have exploited the reducing nature of alcohols under solvothermal conditions to stabilise the V^{III} ion − others have used this effect to reduce V^{V} precursors to make V^{IV} clusters,[36] and V^{III} coordination polymers have also been prepared from VCl_3 under hydrothermal conditions.[37] Similar reactions of $[V_3O(O_2CR')_6L_3]^+$ with carboxylates other than acetate in superheated ROH lead to the formation of the octametallic V^{III} rings $[V_8(OH)_4(OR)_8(O_2CR')_{12}]$ with alternate $(\mu_2\text{-}OH)(\mu_2\text{-}O_2CR')_2$ and $(\mu_2\text{-}OR)_2(\mu_2\text{-}O_2CR')$ bridging (Figure 4) − this is in contrast to the analogous Cr^{III} chemistry where the decametallic wheel is always formed.[35,38] V^{III} clusters are an appealing goal since some V^{III} dimers exhibit very strong ferromagnetic coupling[39] and if this could be introduced into larger clusters it would generate the well-isolated, large spin states necessary for SMM behaviour. Although both the eight and ten-membered V^{III} wheels are antiferromagnetically coupled, the establishment of a reliable synthetic route to high-nuclearity V^{III} clusters is an important step forward.

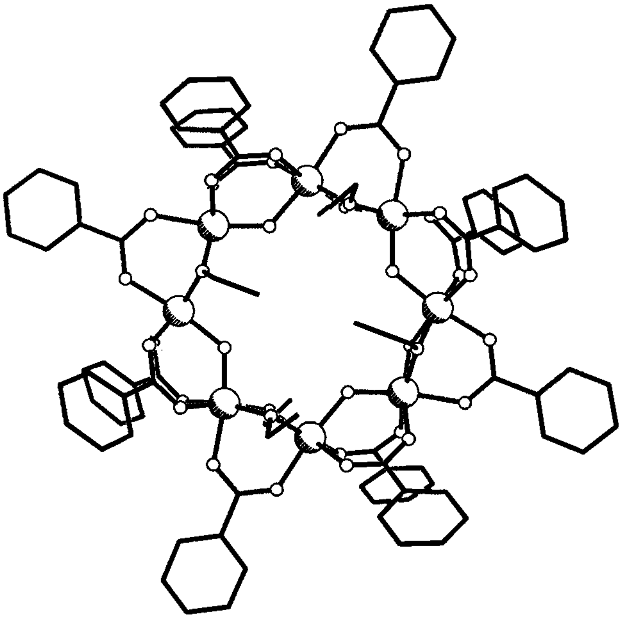

Figure 4. X-ray structure of a molecule of $[V_8(OH)_4(OEt)_8(O_2CPh)_{12}]$; scheme: V (large shaded circles), others as in Figure 1

This simple reaction fails with Mn^{III} for the very reason that it works for V^{III}. The Mn^{III} ions in $[Mn_3O(O_2CR)L_3]X$ (X = anion) are reduced to Mn^{II} in superheated alcohol solutions and only pale-pink solutions are formed. However, by changing to a more inert solvent we have shown that solvothermal techniques are also applicable to manganese cluster synthesis. For example, reaction of the mixed-valent $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$ (py = pyridine) in MeCN at 100 °C gives the hexametallic $[Mn_6O_2(O_2CPh)_{12}(py)_2]$.[40] In contrast to the alcohol-based reactions above, there is very little rearrangement of the precursor, simply a dimerisation of triangle with loss of terminal ligands. The $\{Mn_6O_2\}^{12+}$ core (Figure 5) consists of two planar $\{Mn_3O\}^{6+}$ units linked by four μ_3-carboxylates. Christou has previously shown that the same precursor can undergo thermally induced aggregation by reflux in a relatively high-boiling solvent (PhCN at 188 °C) to give an alternative hexametallic species, $[Mn_6O_2(O_2CPh)_{10}(py)_4]$, based on an edge-sharing bitetrahedral $\{Mn_6O_2\}^{10+}$ core.[41] This higher temperature, but non-solvothermal, reaction has led to more substantial rearrangement, and reduction, of the precursor − the related cluster $[Mn_6O_2(O_2CCMe_3)_{10}(HO_2CCMe_3)_4]$ has also been prepared by reflux in other relatively high-boiling solvents (toluene at 110 °C, dioxane at 100 °C).[42] This illustrates the importance of the temperature regime in cluster formation, and therefore the advantages of the greater range of this parameter in a wider range of solvents afforded by the solvothermal methodology. In this example we have prepared a product of the same nuclearity as higher temperature, non-sovothermal reactions, but with different metal topology and oxidation states. This leads to very different magnetic behaviour − $[Mn_6O_2(O_2CPh)_{10}(py)_4]$ has an $S = 0$ ground state, while $[Mn_6O_2(O_2CPh)_{12}(py)_2]$ has $S = 3$ (the parent monomer has an $S = 3/2$ ground state, so this can be considered as a simple ferromagnetic coupling of the two "halves" in the hexametallic cluster).[40]

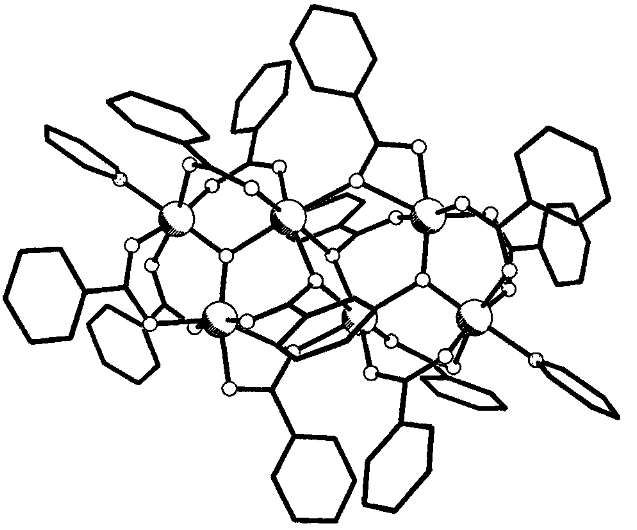

Figure 5. X-ray structure of a molecule of $[Mn_6O_2(O_2CPh)_{12}(py)_2]$; scheme: Mn (large shaded circles), others as in Figure 1

In the examples above we have taken very simple reaction systems involving only a triangular precursor and a solvent. We are now starting to explore analogous reactions but with additional ligands with potential for extensive metal bridging and possible structure-directing properties. For example, we have already shown that reaction of M^{III} acetate triangles in methanol leads to formation of $[M_{10}(OMe)_{20}(O_2CMe)_{10}]$ wheels. If we add an additional ligand which competes with the alkoxides, we should prevent formation of the metal wheels and thus force the formation of clusters of different shape and size. For example, reaction of $[Fe_3O(O_2CMe)_6(H_2O)_3]Cl$ in MeOH at 100 °C, in the presence of benzotriazole (btaH), yields the tetradecametallic Fe^{III} cluster $[Fe_{14}(bta)_6O_6(OMe)_{18}Cl_6]$ (Figure 6).[43] The structure is based on a hexa-capped hexagonal bipyramid of Fe^{III} ions with the caps on alternate faces (Figure 7). The bta^- ligands coordinate in their maximal μ_3-mode to form two $\{Fe_4(bta)_3\}$ moieties (Figure 6b) which sandwich a central Fe_6 ring, bridged by 18 μ_2-methoxides and six μ_4-oxides. The $\{M_4(bta)_3\}$ fragment is well known in M^{II} chemistry in the centred tetrahedral clusters $[M_5(bta)_6(diketonate)_4]$;[44] thus, its formation here is not unexpected and in this case has capped the growth of the iron oxide/alkoxide cluster. However, the absence of carboxylate in the structure is totally unexpected. As with all the reactions above, the product is crystallised directly from the reaction solution. The equivalent reaction under reflux gives only solutions from which we have failed to crystallise any cluster products.

$[Fe_{14}(bta)_6O_6(OMe)_{18}Cl_6]$ has one of the largest ground state spins yet observed, with initial magnetisation data suggesting $S = 23$ but possibly as high as 25.[43] This higher value can be easily rationalised from competing *anti*ferromagnetic interactions within the cluster: the relative magnitude of the four chemically distinct nearest-neighbour exchange pathways, via μ_2-O(Me) and/or μ_4-O, can be predicted on the basis of the Fe−O−Fe angles (Figure 7). The Fe(apex)−Fe(face cap) (J_1) and Fe(apex)−Fe(ring) (J_3) interactions are expected to be the most antiferromagnetic because of the largest angles, and therefore dominate over the much weaker antiferromagnetic Fe(face cap)−Fe(ring) (J_2) and Fe(ring)−Fe(ring) (J_4) interactions. This would lead to a very simple spin structure in the ground state with the two apical iron ions of the bipyramid "spin up" and all other ions "spin down". Conventional fitting of the experimental magnetic susceptibility data to a spin Hamiltonian to derive the four distinct J values is not possible for this system of 14 $S = 5/2$ spins. However, density functional theory calculations in tandem with Monte Carlo simulations of the experimental magnetic data to estimate the J values supports this simple model with values of $J_1 = -22$ cm^{-1}, $J_2 = -8.7$ cm^{-1}, $J_3 = -29.7$ cm^{-1} and $J_4 = -3.7$ cm^{-1}.[45] Scheme 1 summarises the clusters prepared above from simple $[M_3O(O_2CR)_6L_3]X$ precursors.

Finally, we give an example of the solvothermal synthesis of a late transition ion cluster, namely nickel(II). The typically large zero-field splitting of Ni^{II} makes this ion a promising building block for SMMs.[46] Since Ni^{II} cannot form M_3 triangles, we have used simple $[Ni(diketonate)_2]$ monomers as our precursors − these are known to form heterocubane $[Ni_4(OR)_4(diketonate)_4]$ species in alcohols under

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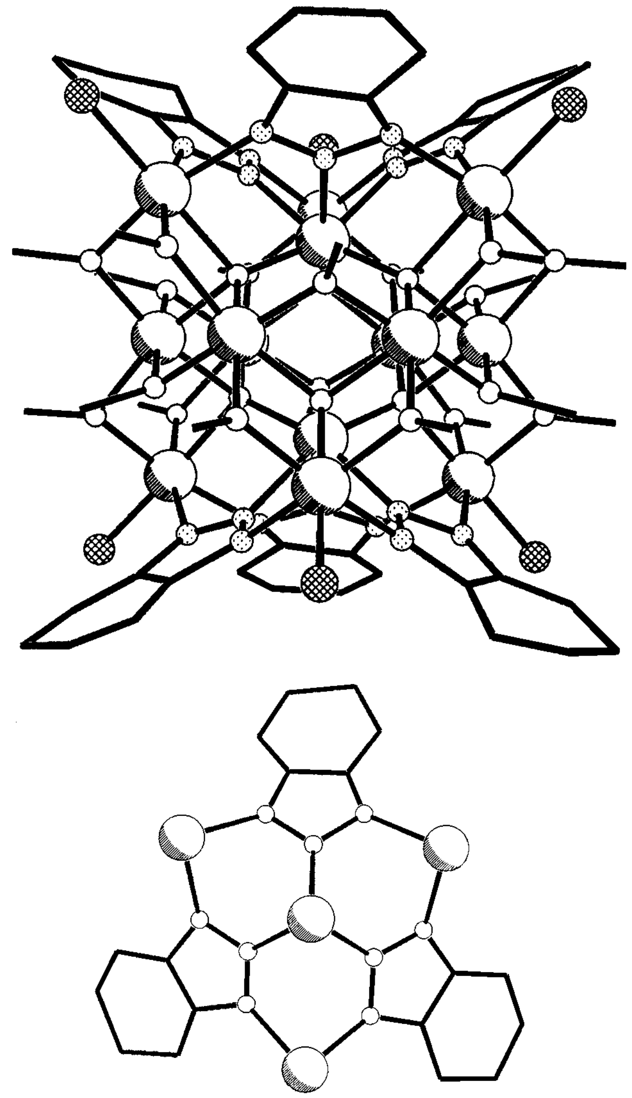


Figure 6. (a) X-ray structure of a molecule of $[Fe_{14}(bta)_6O_6(OMe)_{18}Cl_6]$; (b) the $\{Fe_4(bta)_3\}$ fragment; scheme: Fe (large shaded circles), N (dotted), Cl (cross hatched), others as in Figure 1

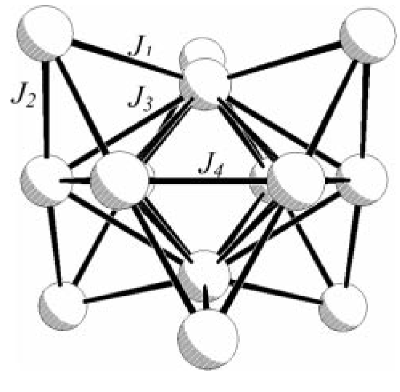
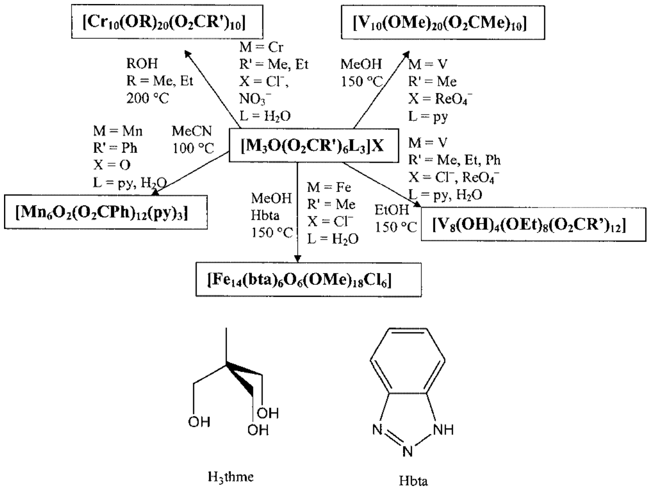


Figure 7. The hexacapped hexagonal-bipyramidal metallic skeleton of $[Fe_{14}(bta)_6O_6(OMe)_{18}Cl_6]$, highlighting the four chemically distinct magnetic exchange interactions



Scheme 1. Summary of clusters prepared solvothermally from $[M_3O(O_2CR)_6L_3]X$ precursors, and structures of the ligands benzotriazole (Hbta) and 1,1,1-tris(hydroxymethyl)ethane (H_3thme)

reflux.[46a] Analogous reactions under solvothermal conditions give identical products. However, in the presence of a competing ligand larger clusters can be obtained. For example, reaction of $[Ni(dbm)_2]$ (Hdbm = dibenzoylmethane) in EtOH at 150 °C with the triol 1,1,1-tris(hydroxymethyl)ethane (H_3thme) gives the decametallic Ni^{II} cluster $[Ni_{10}(O)(thme)_4(dbm)_4(O_2CPh)_2(EtOH)_6]$ (Figure 8a: note the solvothermal conditions have led to the partial degradation of the diketonate to carboxylate − the cluster can be prepared more rationally with carboxylate as an additional reagent).[47] The analogous reaction under reflux gives only heterocubanes − the solvothermal conditions are essential for preventing the formation of this very stable product. The cluster core is a very regular Ni_{10} supertetrahedron, centred on a μ_6-O, where each (near equilateral) triangular Ni_6 face is bound by a single, fully deprotonated $thme^{3-}$ (Figure 8b). The disposition of the three alkoxide arms of $thme^{3-}$, investigated extensively by Zubieta in polyoxovanadate chemistry (see above), is known to favour the formation of triangular M_3 fragments (with each arm μ_2, the ligand overall being μ_3, for example see Figure 1), which can then condense to form larger clusters (hence the preponderance of clusters based on triangular faces with this ligand − octahedral, edge-sharing bioctahedra, etc.).[6] Hence, this could be anticipated with Ni^{II}. However, the formation of the expanded M_6 triangles, allowing formation of the supertetrahedron, is unprecedented. We have also found that other ligands with a potentially similar trigonal arrangement of alcohol groups can form analogous clusters under solvothermal conditions, e.g. *cis,cis*-1,3,5-cyclohexanetriol.[47] The magnetic properties of the Ni_{10} cluster are dominated by the antiferromagnetic exchange interactions across the linear $Ni-\mu_6-O-Ni$ groups. Magnetic ordering phenomena below 20 K prevent full characterisation of the molecular behaviour, which is unfortunate because the supertetrahedral topology should lead to extensive spin frustration effects.

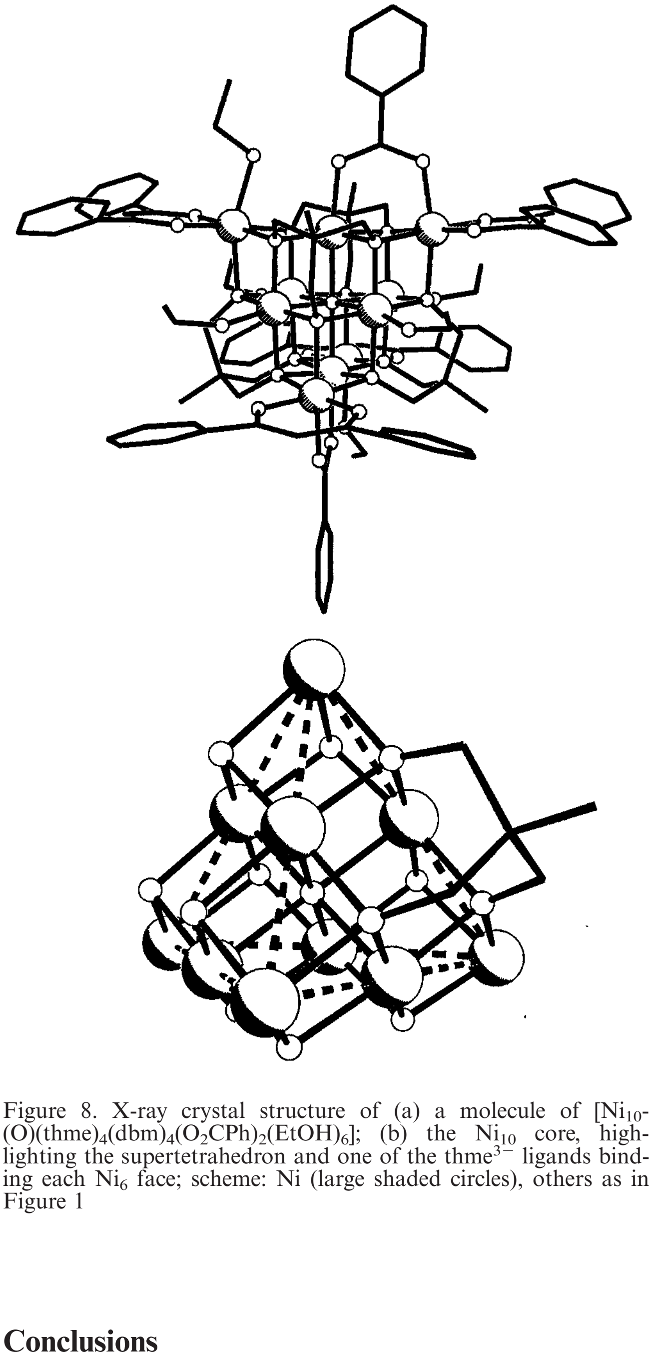


Figure 8. X-ray crystal structure of (a) a molecule of [Ni_{10}-(O)(thme)$_4$(dbm)$_4$(O_2CPh)$_2$(EtOH)$_6$]; (b) the Ni_{10} core, highlighting the supertetrahedron and one of the thme^{3-} ligands binding each Ni_6 face; scheme: Ni (large shaded circles), others as in Figure 1

Conclusions

The work above illustrates some of the advantages of solvothermal synthetic techniques in the synthesis of paramagnetic cluster complexes. In every example above, these products are *only* isolated under solvothermal conditions − under less forcing conditions (ambient or under reflux) either no product is isolated or different products are formed. In addition, in each case the products crystallise directly from the reaction solutions as the only solid product, and in the majority of cases in yields of greater than 50% based on total metal content. Over and above these massive advantages, we also have shown examples of exploiting the solvothermal regime (allowing high-temperature reactions in low-boiling solvents) to overcome the kinetic inertness of Cr^{III}, and to isolate clusters in relatively unusual oxidation states such as V^{III} (exploiting the enhanced reducing nature of alcohols under these conditions). Moreover, several of the clusters we are preparing have interesting magnetic properties including some of the highest ground state spins known. Thus, solvothermal techniques will be an important tool in the synthesis of new SMMs and related materials, alongside the more established synthetic routes.

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