



Synthesis and magnetic properties of a series of 3d/4f/3d heterometallic trinuclear complexes incorporating *in situ* ligand formation

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ARTICLE INFO

Article history:

Available online 31 January 2012

Dedicated to Prof. Jon Zubieta on the occasion of his 65th birthday.

Keywords:

X-ray crystal structures
Magnetism
Lanthanoids
Transition metal
Metal cluster

ABSTRACT

The dicyanonitrosomethanide (dcnm) ligand undergoes an *in situ* transition metal promoted nucleophilic addition of methanol to a nitrile group to form cyano(imino(methoxy)methyl)nitrosomethanide (cmnm) in the formation of the 3d/4f heterometallic complexes (Me₄N)[{Ni(cmnm)₃Ln(cmnm)₂}] (**1Ln**; **1Ln** = **1La**, **1Ce**, **1Pr**, **1Nd**, **1Sm**). A change in the counter-ions of the metal and ligand salts employed under alternate reaction conditions results in the formation of (Et₄N)₂[{Ni(cmnm)₃Ln(dcnm)₂}(ClO₄)] (**2Ln**; **2Ln** = **2La**, **2Ce**), in which unreacted dcnm ligands are coordinated to the central lanthanoid. In both types of complexes three cmnm ligands chelate to a nickel metal centre to form a [Ni(cmnm)₃] metallo-ligand. Two of these metallo-ligands are then bound to a central lanthanoid via the nitroso oxygen atoms, resulting in a trinuclear complex in which each nickel cation is connected to the lanthanoid by three bridging nitroso groups. Variable temperature magnetic susceptibilities on these {Ni(S = 1), Ln(^f to ^{f⁵}), Ni(S = 1)} spin systems reveal very weak to zero Ln–Ni or Ni–Ni exchange coupling with the thermal depopulation between Stark levels on the Ln centres being of similar magnitude, and the Ni₂Ce and Ni₂Pr cases giving strongest evidence for exchange coupling.

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1. Introduction

The synthesis of heterometallic complexes and coordination polymers incorporating lanthanoids and transition metals has become a key focus in magnetochemistry [1,2]. Of particular interest are single molecule magnets (SMMs) [3–6] – discrete complexes that can retain their magnetisation below a certain temperature after a magnetic field is removed, with possible future applications as qubits in quantum computing [7]. Previously the majority of work in this field has focused upon complexes containing transition metals such as iron [8] and manganese [9–13], although monometallic complexes containing the lanthanoid dysprosium have also been shown to exhibit SMM like behaviour [14–19].

There are now, however, numerous reports of 3d/4f complexes exhibiting SMM behaviour, with the high spin and anisotropy of certain lanthanoids warranting their inclusion in complexes as these properties are critical to forming SMMs [20–34]. This is exemplified by the high nuclearity complexes Cu₆Dy₃ [23], Dy₄Mn₁₁ [32], Dy₆Mn₆ [31] and Dy₈Mn₉ [35] which contain a significant lanthanoid component. Thus there is considerable interest in new 3d/4f heterometallic

complexes with different superexchange pathways that will allow us to further probe the magnetic interactions between the metal centres. Only very recently have 3d/4f/3d trinuclear clusters, M^{II}LnM^{II}, been found to display SMM properties [20,22,36,37], including a NiDyNi example [36], but heterometallic oximate M–N–O–M'-bridged species, related to the present nitroso-bridged systems, are thus far restricted to {3d3d'3d} exchange-coupled species. Few, if any, of these complexes display SMM properties [37], with one NiTbNi compound showing magnetism akin to that described here and with no SMM features [38].

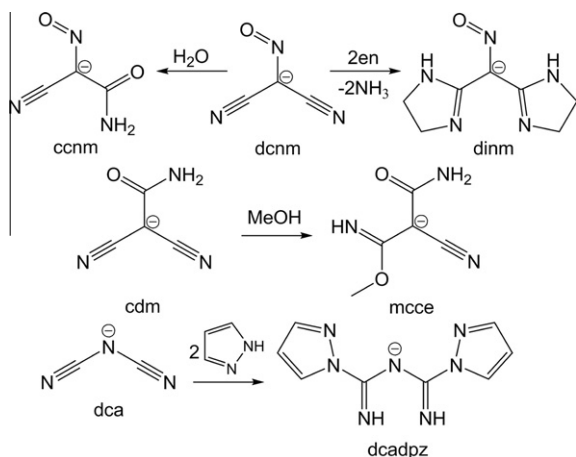
The transition metal promoted nucleophilic addition to pseudohalide ligands is established as a recognised means of *in situ* ligand formation [39,40]. This synthetic route has predominantly resulted in mononuclear complexes although recent progress has moved towards making complexes of increasing nuclearity [41]. The addition of methanol to a nitrile group of dcnm to form cyano(imino(methoxy)methyl)nitrosomethanide (cmnm) facilitated the formation of the trinuclear cluster [Mn^{II}₂Mn^{III}(cmnm)](NO₃), while the addition of water resulted in carbamoylcyanonitrosomethanide (ccnm) which was incorporated into the 'butterfly' complex (Me₄N)₂[Mn₄O₂(ccnm)₄(H₂O)₆(MeCN)₂](NO₃)₄ [42]. This motif was also observed in the mixed ligand heterometallic cluster [Ln^{III}₂Mn^{III}O₂(ccnm)₆(dcnm)₂(H₂O)₂] (Ln = Gd, Tb, Er) (Scheme 1) [43].

The formation of polynuclear complexes by ligands derived from nucleophilic addition to dcnm is not restricted to simple alcohol addition products. Addition of two equivalents of diaminoethane (en) to

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Scheme 1. Ligands resulting from the transition metal promoted nucleophilic addition to pseudohalides.

dcnm and subsequent cyclisation gives diimidazolynitrosomethanide (dinm), which is included in $[\{\text{Cu}(\text{dinm})(\text{en})\}_2\text{en}](\text{ClO}_4)_2$ [44], while the dianionic amidocarbonyl(cyano)nitrosomethanide (acnm) is contained in the strongly antiferromagnetically coupled $[\text{Cu}_3(\text{acnm})_2(\text{dmae})_2(\text{H}_2\text{O})_2]$ ($\text{dmae} = N,N$ -dimethylaminoethoxide) [45]. The formation of clusters from *in situ* generated ligands also extends to related pseudohalide systems, with methanol addition to cdm (carbamoyldicyanomethanide) forming methyl 2-carbamoyl-2-cyanoethanimidate (mcce) in the cluster based polymer $[\text{Fe}_{10}\text{O}_4(\text{MeO})_{14}\text{Cl}_4(\text{mcce})_4]$ [46], while the addition of two pyrazoles to dicyanamide (dca) gives di(pyrazolecarbimido)aminato (dcadpz) in $[\text{Cu}_3(\text{dcadpz})_2(\text{pz})_2(\text{ClO}_4)_2]$ ($\text{pz} = \text{pyrazole}$) (Scheme 1) [47,48].

While derivatives of dcnm, dca and cdm have proven to be viable ligands to facilitate cluster formation, dca and the related tricyanomethanide (tcm) have also garnered attention for their ability to form magnetically coupled pathways between metal centres [49]. This property has been observed to extend to the derivatives of these pseudohalides, with a highlight being the solvothermally synthesised ferromagnetically coupled $[\text{Cu}(\text{cmnm})_2]$ [50]. The heterofunctionalised nature of addition products of dcnm make them ideal for selective coordination between lanthanoid and transition metals, thus encouraging for the formation of heterometallic clusters with magnetic coupling.

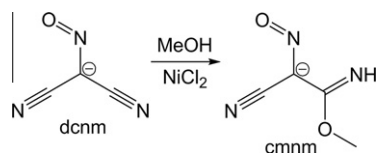
Herein, we report the synthesis and structure of a series of heterotrimeric lanthanoid/nickel(II) clusters, NiLnNi , incorporating the cmnm ligand and discuss the resulting magnetic properties of these $d^8f^0d^8$ combinations, where $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$. It has, unfortunately, not been possible to isolate the heavier lanthanide derivatives from Gd onwards.

2. Results and discussion

2.1. Synthesis and structure

Reactions of $(\text{Me}_4\text{N})(\text{dcnm})$ with nickel chloride and the respective lanthanoid chloride in methanol yielded complexes of the type $(\text{Me}_4\text{N})\{[\text{Ni}(\text{cmnm})_3]\}_2\text{Ln}(\text{cmnm})_2$ (**1Ln**; **1Ln** = **1La**, **1Ce**, **1Pr**, **1Nd**, **1Sm**). The cmnm ligand formation results from the transition metal promoted nucleophilic addition of methanol to a nitrile group of dcnm (Scheme 2) [50]. It is unlikely that the lanthanoid metal promoted the nucleophilic addition as a series of anions, $[\text{Ln}(\text{dcnm})_6]^{3-}$ ($\text{Ln} = \text{La} - \text{Nd}, \text{Sm}, \text{Gd}$) [51,52], were synthesised in methanol and no evidence of cmnm formation was observed.

In the molecular structures of the trinuclear clusters, the two nickel octahedral metal centres are each coordinated by three cmnm ligands



Scheme 2. The addition of methanol to dcnm, resulting in the cmnm ligand.

which chelate through the nitrogen atoms of the nitroso and imine groups, to form a $[\text{Ni}(\text{cmnm})_3]^-$ moiety (Fig. 1). This moiety is similar to the previously reported *in situ* generated $[\text{Mn}^{\text{II}}(\text{cmnm})_3]$ metalloligand in the trinuclear complex $[\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}(\text{cmnm})_6](\text{NO}_3)$ [42], as well as the $[\text{Ni}(\text{ccnm})_3]^-$ moiety contained in the $[\text{Na}(\text{H}_2\text{O})_6][\text{Na}(\text{Ni}(\text{ccnm})_3)_2]$ trinuclear complex, although in that instance the ligand was not generated *in situ* [53]. The bite angle of the chelating cmnm ligands is significantly less than 90° , giving the metal centre a distorted octahedral geometry (Table 1).

The two symmetry related $[\text{Ni}(\text{cmnm})_3]^-$ metalloligands cap either side of the central lanthanoid metal, which lies on a 2-fold axis, to form the overall trinuclear complex, resulting in the cmnm ligand having an $\mu_2\text{-}\eta^2(\text{N},\text{N}')\text{Ni}:\eta^1(\text{O})\text{Ln}$ coordination mode (Fig. 2). Due to the influence of the lanthanoid contraction the lengths of the three unique coordination bonds from the oxygen atoms to the lanthanoid metal centre decrease across the lanthanoid series (Table 2) except between 1Ce and 1Pr. The bond lengths between the nickel and nitrogen atoms do not show a comparable change across the series (Table S1, Supplementary Information). The coordination sphere of the central 10 coordinate lanthanoid is completed by two cmnm ligands exhibiting an η^2 coordination mode through the nitroso group. If each chelating cmnm ligand is viewed as a single coordinating entity, with the midpoint between the nitrogen and oxygen atoms of the nitroso group taken as the point of attachment, the lanthanoid has a slightly distorted square anti-prismatic geometry. The cmnm ligand coordinating to only the lanthanoid atom participates in an intramolecular hydrogen bond, with the imine group acting as a hydrogen bond donor to the oxygen atom of the nitroso group of an adjacent cmnm ligand (Fig. 2).

The nitroso group which chelates to the lanthanoid atom coordinates in an asymmetric fashion, with the oxygen atom closer to the oxophilic lanthanoid atom than the nitrogen atom. The difference in these bond lengths across the series is within the small range of $0.196(5) \text{ \AA}$ (**1La**) to $0.210(6) \text{ \AA}$ (**1Ce**). The asymmetry in this chelation is similar to the bonding observed in the homoleptic trianionic complexes $[\text{Ln}(\text{ccnm})_6]^{3-}$ [51], where steric crowding

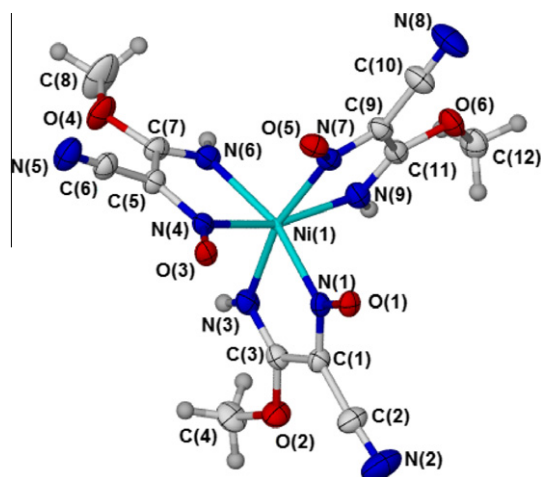


Fig. 1. The $[\text{Ni}(\text{cmnm})_3]^-$ metalloligand from the crystal structure of **1La**·5MeOH, ellipsoids shown at 50% probability.

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