



Dicyanonitrosomethanide and Carbamoylcyanonitrosomethanide: Heterofunctionalised Anionic Ligands for the Formation of 3d/4f Bimetallic Coordination Polymers and Complexes

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Abstract. The two-dimensional heterobimetallic coordination network $\{[\text{Na}(\text{H}_2\text{O})_3][\text{Ce}(\text{dcnm})_4(\text{H}_2\text{O})_4]\}$ (dcnm = dicyanonitrosomethanide) was obtained from an aqueous reaction of $\text{Na}(\text{dcnm})$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. The structure contains $\mu_2\text{-}\eta^2\text{-}\eta^1$ nitroso-bridged Ce-Na pairs. These heterometallic units are joined through non-chelating dcnm ligands, via nitrile-Na and O-Ce interactions, to produce (4,4) sheets. The transition metal promoted *in situ* nucleophilic addition of water to dcnm results in the formation of carbamoylcyanonitrosomethanide (ccnm) which is included in the trinuclear 3d/4f heterobimetallic complex $[\{\text{Gd}(\text{OH})(\text{ccnm})_2(\text{H}_2\text{O})_4\}_2\text{Mn}^{\text{III}}](\text{ClO}_4)_3 \cdot 2(18\text{-crown-6})$, which formed from an aqueous reaction of $\text{Gd}(\text{dcnm})_3$, $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 18-crown-6. The ccnm ligands display a $\mu_2\text{-}\eta^2(\text{O}_{\text{carbamoyl}}, \text{N}_{\text{nitroso}})\text{Gd}:\eta^1(\text{O}_{\text{nitroso}})\text{Mn}$ coordination mode, with the 18-crown-6 molecules residing in the lattice acting as hydrogen bond acceptors to aqua and ccnm ligands, resulting in the formation of (4,4) sheets.

Keywords: Heterobimetallic; Dicyanonitrosomethanide; Self Assembly; Hydrogen bonding

Introduction

The polynitrile anions dicyanamide and tricyanomethanide are widely recognised for their ability to form coordination polymers of varying dimensionalities, which may often display interesting magnetic properties such as long range ferromagnetic coupling.¹ However, the homofunctionalised nature of these ligands may create difficulties in forming complexes which incorporate different metal types, as the nitrile groups will preferentially coordinate to specific metals, creating only homometallic systems. In order to overcome these synthetic challenges, related heterofunctionalised ligands such as dicyanonitrosomethanide (dcnm)² and carbamoyldicyanomethanide (cdm),³ offer a means of utilising functional groups that target specific metal types, creating bimetallic systems. In addition to the rich variety of coordination modes offered by the dcnm ligand,^{4,5,6,7,8,9,10} it has also shown a propensity to undergo the *in situ* transition metal promoted nucleophilic addition of water,¹¹ protic solvents^{12,13} or amines¹⁴ to a nitrile group, giving rise to a diverse range of derivative

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¹¹ H. Köhler, B. Seifert, *Z. Anorg. Alleg. Chemie* **1970**, 379, 1.

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ligands (Figure 1). The acid catalysed addition of amines and alcohols to dicyanonitrosomethanide is also known, although this reaction pathway results in the protonation of the nitroso functional group, forming an oxime.¹⁵

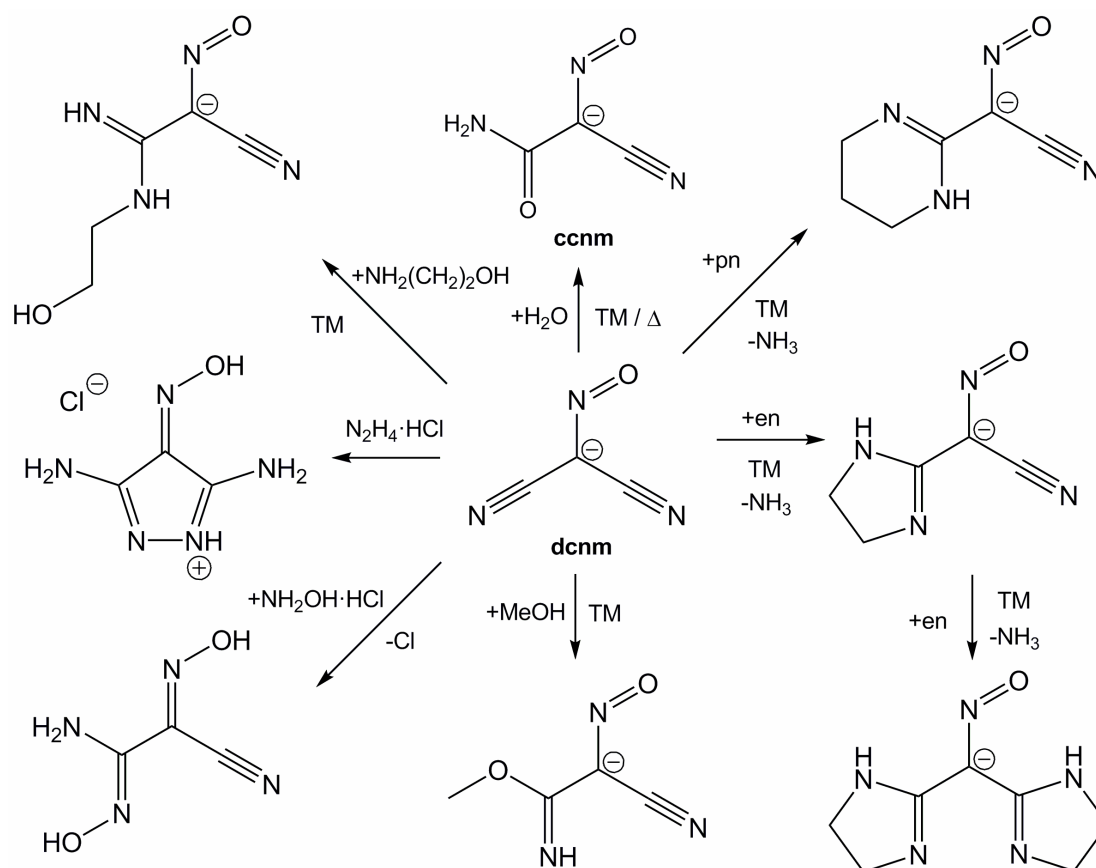


Figure 1. Ligands resulting from nucleophilic addition to dcnm; TM = transition metal.

The addition of water or methanol to the dcnm ligand results in the formation of carbamoylcyanonitrosomethanide (ccnm) and cyano(imino(methoxy)methyl)nitrosomethanide (cmnm), respectively. These ligands have demonstrated versatility in forming complexes of varying nuclearity, with the ccnm ligand being incorporated into polycarbonatolanthanoidate clusters known as ‘lanthaballs’, $[\text{Ln}_{13}(\text{H}_2\text{O})_6(\text{phen})_{18}(\text{ccnm})_6(\text{CO}_3)_{14}]\cdot\text{Cl}_3\cdot\text{CO}_3$,¹⁶ while the cmnm ligand can be found in the antiferromagnetically coupled trinuclear $[\text{Mn}_3(\text{cmnm})_3](\text{NO}_3)\cdot 2\text{H}_2\text{O}$ ¹⁷ or the solvothermally synthesised, ferromagnetically coupled, coordination polymer $[\text{Cu}(\text{cmnm})_2]$.¹⁸ Despite the potential offered by these ligands in forming heterobimetallic complexes, to the best of our knowledge only one such complex exists, $[\text{Na}(\text{H}_2\text{O})_6][\text{Ni}_2\text{Na}(\text{ccnm})_6]$.¹⁹ In this complex the ccnm displays a $\mu_2\text{-}\eta^2(\text{O}_{\text{carbamoyl}}, \text{N}_{\text{nitroso}})\text{Ni}:\eta^1(\text{O}_{\text{nitroso}})\text{Na}$ coordination mode, demonstrating the potential of this ligand system for further heterobimetallic application. Herein we report the crystal structures of the first heterobimetallic coordination polymer and discrete $3d/4f$ bimetallic complex to incorporate the dcnm and ccnm ligands, respectively.

¹³ A. S. R. Chesman, D. R. Turner, B. Moubaraki, K. S. Murray, G. B. Deacon, S. R. Batten, *Eur. J. Inorg. Chem.*, **2009**, in press.

¹⁴ A. S. R. Chesman, D. R. Turner, G. B. Deacon, S. R. Batten, *Chem. Asian J.* **2009**, *4*, 761.

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¹⁸ A. S. R. Chesman, D. R. Turner, D. J. Price, B. Moubaraki, K. S. Murray, G. B. Deacon, S. R. Batten, *Chem. Commun.* **2007**, 3541.

¹⁹ N. N. Gerasimchuk, N. K. Dalley, *J. Coord. Chem.* **2004**, *57*, 1431.

Results and Discussion

The reaction of Na(dcnm) with $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in methanol afforded upon evaporation to dryness a small number of pale yellow crystals of the complex $\{[\text{Na}(\text{H}_2\text{O})_3][\text{Ce}(\text{dcnm})_4(\text{H}_2\text{O})_4]\}$ (**1**), sufficient in quantity for only infra-red spectroscopy and single crystal X-ray diffraction analysis. The compound crystallises in the non-centrosymmetric orthorhombic space group $Aba2$. The asymmetric unit contains one half of a unique Ce atom, one half of a unique Na atom, two unique dcnm ligands (type I and II, Figure 2a), and four unique aqua ligands (two of which bind to Ce, and two of which bind to Na). The repeating chemical unit of the structure is $\{[\text{Na}(\text{H}_2\text{O})_3][\text{Ce}(\text{dcnm})_4(\text{H}_2\text{O})_4]\}$, consisting of a $[\text{Ce}(\text{dcnm})_4(\text{H}_2\text{O})_4]^-$ unit which is charged-balanced by a partially hydrated sodium ion (Figure 2a). The cerium atom is 10-coordinate with two η^2 -chelating type I dcnm ligands, two O-donor type II dcnm ligands, and four water molecules in the coordination sphere. The coordination geometry of the cerium atom can be described as square-antiprismatic if the chelating ligands are viewed as being monodentate from the N=O midpoint. The chelating nitroso group is unusual for the dcnm ligand, although we have previously observed this coordination mode with rare-earths in structures of the form $(\text{R}_4\text{N})_3[\text{Ln}(\text{dcnm})_6]$.⁵ The chelation in the current study is not as symmetrical as that observed in the $[\text{Ln}(\text{dcnm})_6]^{3-}$ systems, with the difference between the Ce–O and Ce–N bond lengths being 0.242(11) Å, compared to less than 0.05 Å in the discrete $[\text{Ce}(\text{dcnm})_6]^{3-}$ complexes.⁵ The chelating type I dcnm ligand is also involved in a bridging interaction to the sodium ion through the oxygen atom, making the full coordination mode of the ligand $\mu_2:\eta^2(\text{O},\text{N})\text{Ce}-\eta^1(\text{O})\text{Na}$. The oxygen atom is situated almost centrally between the cerium and sodium atoms with bond lengths of 2.497(5) and 2.389(6) Å, respectively. The sodium atom is 7-coordinate with interactions to two type I dcnm oxygen atoms, two type II dcnm nitrogen atoms and three aqua ligands, and adopts a distorted mono-capped trigonal-prismatic coordination geometry (Figure 2b).

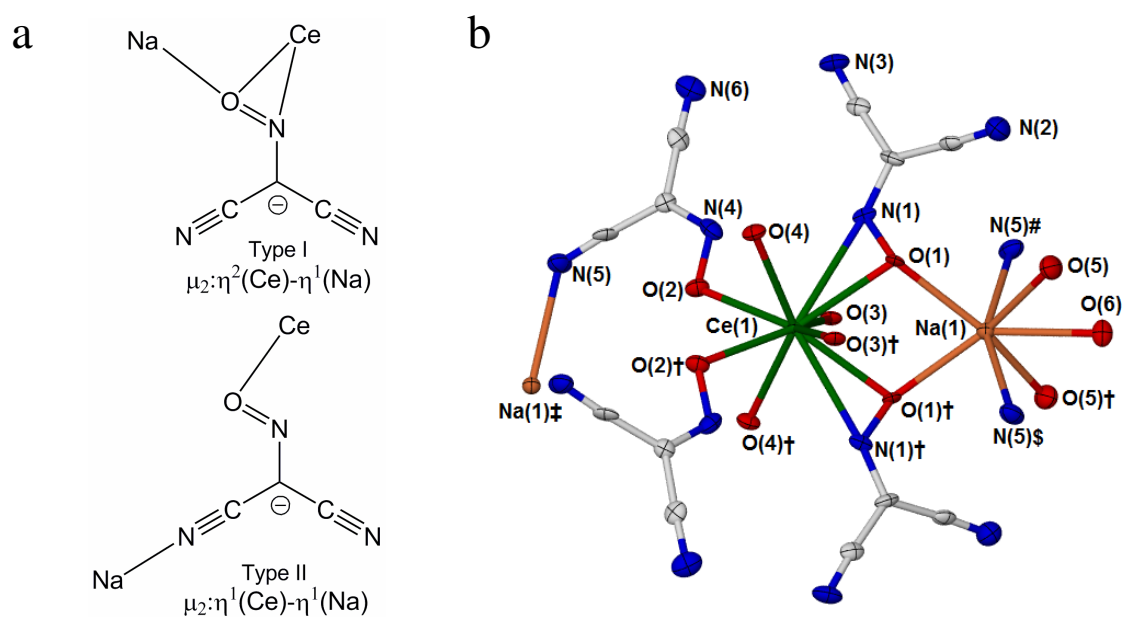


Figure 2. (a) The different coordination modes of the two unique dcnm ligands. (b) A portion of the $\{[\text{Na}(\text{H}_2\text{O})_3][\text{Ce}(\text{dcnm})_4(\text{H}_2\text{O})_4]\}$ coordination polymer with the coordination sphere of the sodium completed by bridging nitrile nitrogen atoms, ellipsoids displayed at 50 % probability. Symmetry elements used: † = $1 - x, 1 - y, z$; ‡ = $\frac{1}{2} - x, y, z - \frac{1}{2}$; # = $\frac{1}{2} - x, y, \frac{1}{2} + z$; \$ = $x - \frac{1}{2}, 1 - y, \frac{1}{2} + z$. Selected bond lengths and angles are listed in Table 1.

Table 1. Selected bond lengths (Å) and angles (°) for **1**.^a

Ce(1)–O(1)	2.497(5)	Ce(1)–O(2)	2.455(5)
Ce(1)–N(1)	2.739(6)	Ce(1)···N(4)	3.108(5)
Ce(1)–O(3)	2.608(4)	Ce(1)–O(4)	2.593(5)
Na(1)–O(1)	2.389(6)	Na(1)–N(5)	2.587(6)
Na(1)–O(5)	2.303(6)	Na(1)–O(6)	2.398(12)
Ce(1)···Na(1)	3.919(4)	O(1)–N(1)	1.313(7)
Ce(1)–O(1)–N(1)	86.0(4)	Ce(1)–O(1)–Na(1)	106.6(2)
O(3)···N(3)%	2.849(6)	O(4)···N(6)*	2.871(6)

^a Symmetry elements used: % = $\frac{1}{2} + x, \frac{1}{2} - y, z$; * = $x - \frac{1}{2}, \frac{1}{2} - y, z$.

The overall polymeric structure takes the form of infinite 2D sheets with a (4,4) topology (Figure 3). The dinuclear $[\text{NaCe}(\text{dcnm})_4(\text{H}_2\text{O})_7]$ moieties act as 4-connecting nodes, with each connected to four others by the type II dcnm ligands, which bridge between the Ce atoms (O-bound) and Na atoms (nitrile N-bound). Alternatively, the sheets could also be described as having (6,3) topology, with Ce and Na both acting as 3-connecting nodes, and the links provided by either double type I dcnm bridges, or single type II dcnm bridges. The sheets propagate parallel to the *ac*-plane.

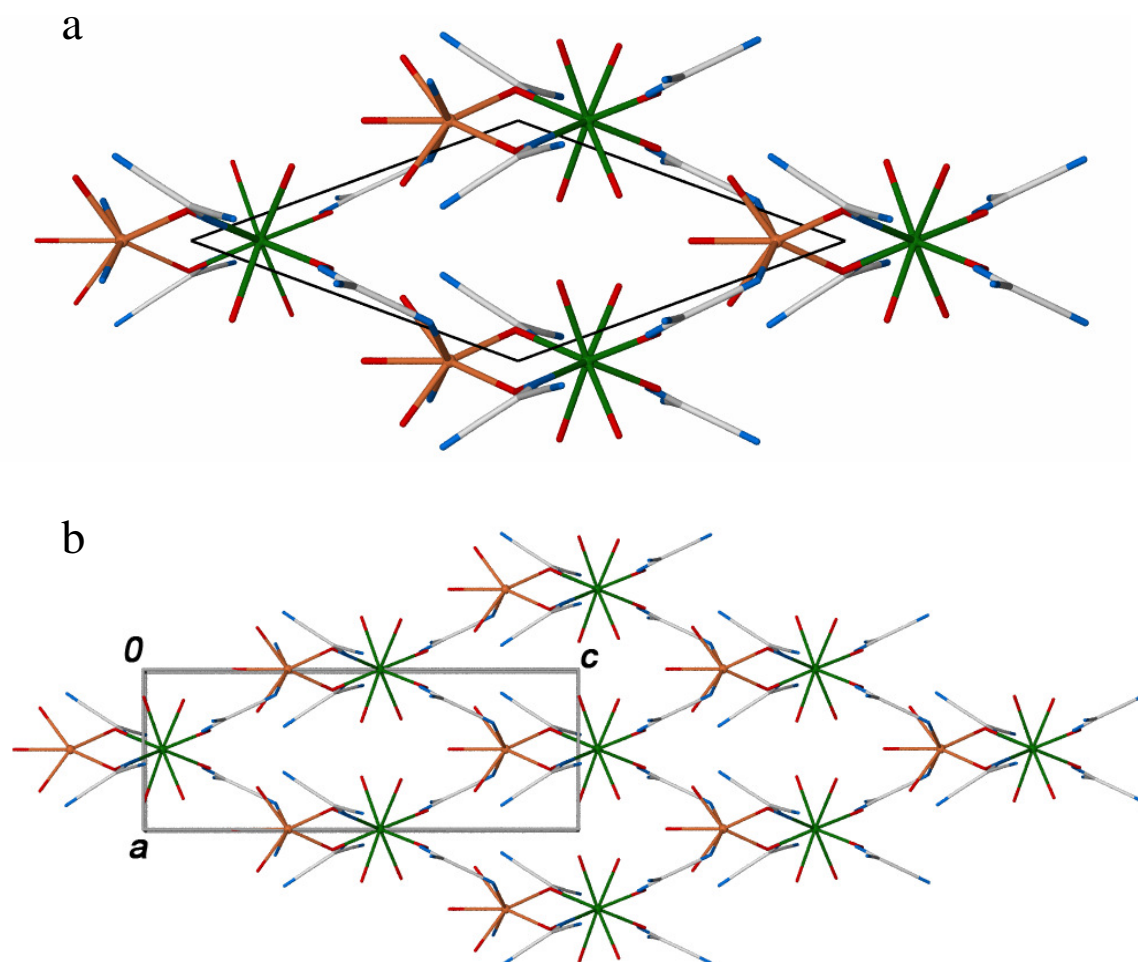


Figure 3. (a) The Na/Ce units act as the 4-connecting nodes in the (4,4) network. (b) One (4,4) sheet as viewed looking down the *b*-axis.

Only two of the nitrile groups per $[\text{NaCe}(\text{dcnm})_4(\text{H}_2\text{O})_7]$ unit (out of a total of eight) are involved in coordinative bonding to metal atoms. Although the hydrogen atoms of the aqua ligands could not be crystallographically located, the interatomic distances between the nitrogen atom of one nitrile group of each of the two unique dcnm ligands and the oxygen atoms of two coordinated water molecules are suggestive of hydrogen bonding (Table 1). The remaining nitrile substituents not participating in any coordinative or hydrogen bonding are directed parallel to the 2D sheets of the (4,4)-network.

An aqueous solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, 18-crown-6 and $\text{Gd}(\text{dcnm})_3$ was allowed to evaporate to dryness, yielding a small number of crystals of the complex $[\{\text{Gd}(\text{OH})(\text{ccnm})_2(\text{H}_2\text{O})_4\}_2\text{Mn}^{\text{III}}](\text{ClO}_4)_3 \cdot 2(18\text{-crown-6})$ (**2**), insufficient in quantity for additional analysis. The ccnm ligand results from the manganese ions promoting the nucleophilic addition of water to a nitrile group of dcnm to form a carbamoyl group, as has been observed with other transition metals.^{12,13} The product crystallises in the monoclinic space group *C2/c*, with the asymmetric unit containing one unique half of the $[\{\text{Gd}(\text{OH})(\text{ccnm})_2(\text{H}_2\text{O})_4\}_2\text{Mn}^{\text{III}}]^{3+}$ complex, one 18-crown-6 molecule, one complete and one half occupancy perchlorate anion and several partial occupancy water molecules disordered throughout the lattice. The $[\{\text{Gd}(\text{OH})(\text{ccnm})_2(\text{H}_2\text{O})_4\}_2\text{Mn}^{\text{III}}]^{3+}$ complex consists of two $[\text{Gd}(\text{OH})(\text{ccnm})_2(\text{H}_2\text{O})_4]$ moieties which bridge through the hydroxide group and the nitroso groups of the two

ccnm ligands to the central manganese atom. The ccnm ligands chelate to the gadolinium atom via the oxygen and nitrogen atoms of the carbamoyl and nitroso groups, respectively, resulting in a $\mu_2\text{-}\eta^2(\text{O}_{\text{carbamoyl}}, \text{N}_{\text{nitroso}})\text{Gd}:\eta^1(\text{O}_{\text{nitroso}})\text{Mn}$ coordination mode. The two unique ccnm ligands coordinate in a *cis* fashion to one face of the metal centre, with the four aqua ligands and the bridging hydroxide group coordinating on the opposite side of the metal centre (Figure 4, Table 2).

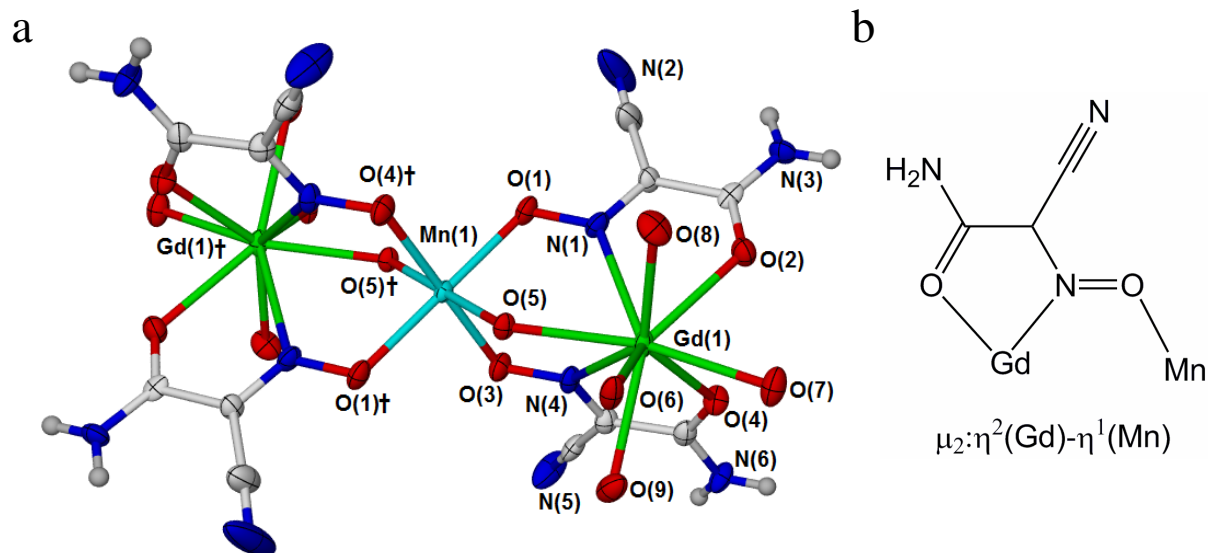


Figure 4. (a) The $[\{\text{Gd}(\text{OH})(\text{ccnm})_2(\text{H}_2\text{O})_4\}_2\text{Mn}]^{3+}$ complex. Ellipsoids shown at 50 % probability, symmetry element used: $\dagger = \frac{1}{2} - x, \frac{1}{2} - y, -z$. (b) The coordination mode of the ccnm ligand.

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) for **2**.^a

Gd(1)–N(1)	2.604(5)	Gd(1)⋯Mn(1)	3.7427(3)
Gd(1)–O(2)	2.418(5)	Mn(1)–O(3)	2.070(5)
Gd(1)–N(4)	2.643(6)	Mn(1)–O(5)	1.882(5)
Gd(1)–O(4)	2.436(5)	Gd(1)–O(5)–Mn(1)	125.0(2)
Gd(1)–O(5)	2.331(5)	N(1)–Gd(1)–O(2)	63.2(2)
Gd(1)–O(6)	2.446(5)	N(4)–Gd(1)–O(4)	62.4(2)
Gd(1)–O(7)	2.417(5)	O(1)–Mn(1)–O(3)	89.6(2)
Gd(1)–O(8)	2.414(5)	O(1)–Mn(1)–O(5)	90.3(2)
Gd(1)–O(9)	2.456(5)	O(1)–Mn(1)–O(3)†	90.4(2)

^a Symmetry element used: $\dagger = \frac{1}{2} - x, \frac{1}{2} - y, -z$.

The coordination geometry of the 9-coordinate gadolinium atoms can be best described as monocapped square antiprismatic with the central manganese atom having an octahedral geometry. The 3+ oxidation state of manganese is confirmed by bond valence sum calculations and is also supported by the charge balancing of the complex.

Although hydrogen atoms of the aqua ligands could not be located by X-ray crystallography, the bond lengths and the angle between two oxygen atoms of the 18-crown-6 molecule and the water molecule coordinated to the gadolinium atom in the capping position of the monocapped square antiprismatic are strongly suggestive of hydrogen bonding ($\text{O}(6)\cdots\text{O}(13) = 3.000(7)$, $\text{O}(6)\cdots\text{O}(13)\cdots\text{O}(10) = 109.8(2)$). The hydroxide which bridges the manganese and gadolinium metal centres is orientated so it also acts as a hydrogen bond donor to the same 18-crown-6 molecule. Additionally, the carbamoyl group of one unique ccnm ligand also forms hydrogen bonds to an adjacent 18-crown-6 molecule (Figure 5, Table 3). Each $[\{\text{Gd}(\text{OH})(\text{ccnm})_2(\text{H}_2\text{O})_4\}_2\text{Mn}^{\text{III}}]^{3+} \cdot 2(18\text{-crown-6})$ hydrogen bonded unit forms hydrogen bonds to four other equivalent units, resulting in the formation of a hydrogen bonded (4,4) network. Vacant crown molecules have previously been observed to act as versatile hydrogen bond acceptors, with numerous examples of aqua ligands hydrogen bonding to 12-crown-4,²⁰ 15-crown-5,^{21,22} and 18-crown-6²³ to form 1D chains. The carbamoyl group

²⁰ P. C. Junk, M. K. Smith, J. W. Steed, *Polyhedron* **2001**, *20*, 2979.

²¹ P. C. Junk, B. Moubarki, K. S. Murray, *Polyhedron* **2007**, *26*, 237.

of the unique ccnm ligand which is not participating in hydrogen bonding to the 18-crown-6 molecule acts as a hydrogen bond donor to the full occupancy perchlorate anion and a water molecule residing in the lattice (Table 3).

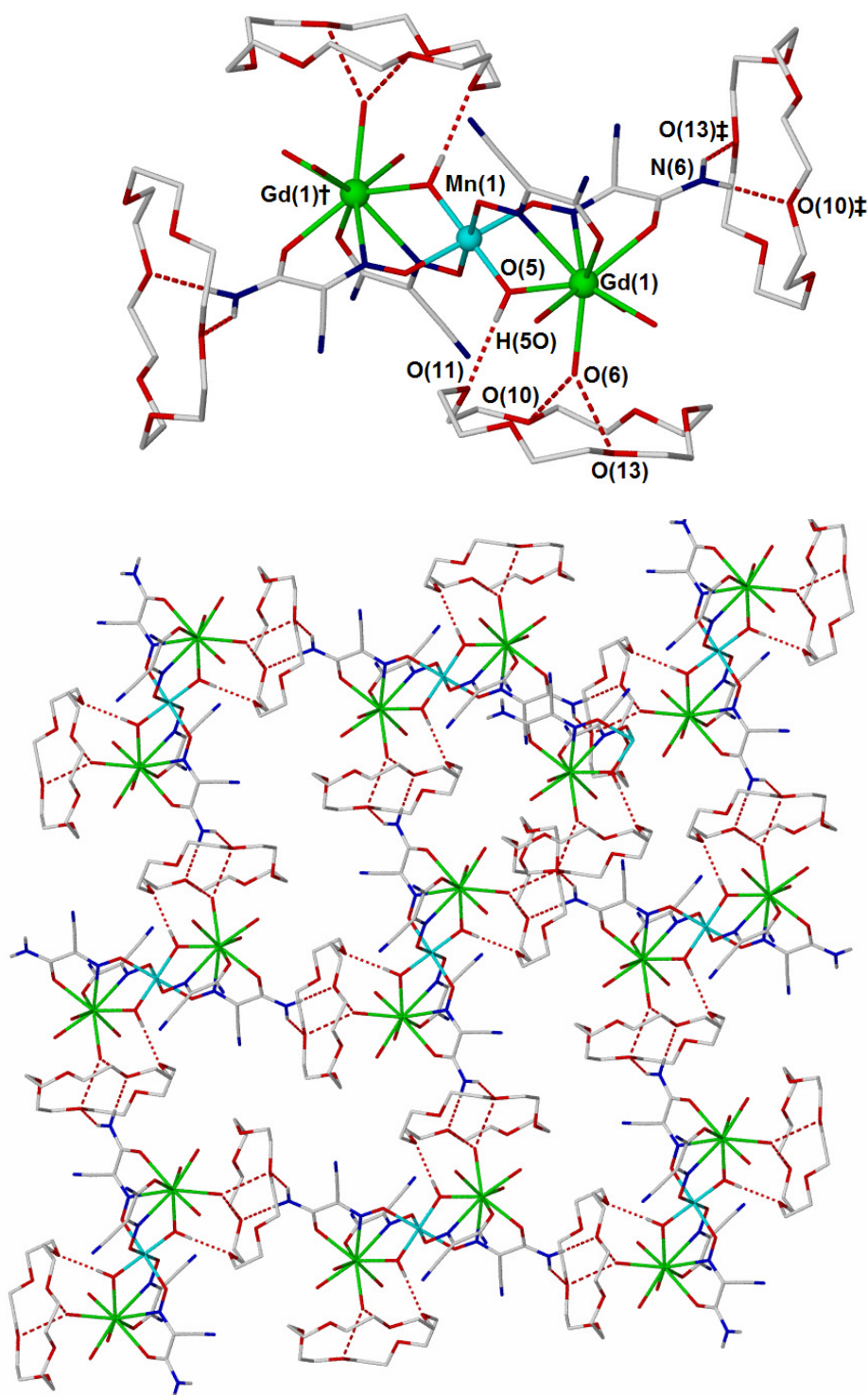


Figure 5. (a) A $[\{Gd(OH)(ccnm)_2(H_2O)_4\}_2Mn]^{3+}$ complex from **2** hydrogen bonding to four adjacent 18-crown-6 molecules. Symmetry elements used: † = $\frac{1}{2} - x, \frac{1}{2} - y, -z$; ‡ = $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. (b) One (4,4) sheet as viewed looking down the crystallographic *a*-axis.

²² J. W. Steed, E. Sakellariou, P. C. Junk, M. K. Smith, *Chem. Eur. J.* **2001**, *7*, 1240.

²³ J. W. Steed, B. J. McCool, P. C. Junk, *J. Chem. Soc., Dalton Trans.* **1998**, 3417.

Table 3. Hydrogen bond lengths and angles in **2**.^a

N(6)···O(10)	2.930(8)	N(6)-H(6A)···O(10)‡	175.2
N(6)···O(13)	3.072(8)	N(6)-H(6B)···O(13)‡	152.1
N(3)···O(19)	2.995(11)	N(3)-H(3A)···O(19)	162.8
N(3)···O(24)	2.872(8)	N(3)-H(3B)···O(24)	146.3
O(6)···O(10)	3.032(7)	O(5)···O(11)	2.858(7)
O(6)···O(13)	3.000(7)	O(6)···O(13)···O(10)	109.8(2)

^a Symmetry elements used: ‡ = $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Conclusion

The heterofunctionalised ligand dcnm and its water addition derivative ccnm have proven to be viable ligands in the formation of bimetallic polynuclear complexes and coordination polymers. The 2D sheet $\{[\text{Na}(\text{H}_2\text{O})_3][\text{Ce}(\text{dcnm})_4(\text{H}_2\text{O})_4]\}$ marks substantial progress towards the formation of 3d/4f pseudohalide based coordination polymers while $\{[\text{Gd}(\text{OH})(\text{ccnm})_2(\text{H}_2\text{O})_4]_2\text{Mn}^{\text{III}}(\text{ClO}_4)_3\}$ demonstrates the ability of this class of ligands to form heterometallic discrete clusters. Future work will focus upon utilising these ligand systems, specifically exploiting the *in situ* nucleophilic addition of alcohols and amines to dcnm, for the formation of coordination polymers of novel connectivity and increasing the nuclearity of the resultant polynuclear clusters with a view to examine the novel magnetic properties that may arise.

Experimental Section

General

All reactions were carried out under aerobic conditions using commercial grade reagents. Ag(dcnm) was synthesised according to literature procedure.² Infrared data were collected using a Perkin Elmer ATR-FTIR spectrometer.

Synthesis

$\{[\text{NaCe}(\text{dcnm})_4(\text{H}_2\text{O})_7]\}$ (**1**)

$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (53 mg, 142 μmol), $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (36 mg, 134 μmol) and $\text{Na}(\text{dcnm})$ (50 mg, 427 μmol) were dissolved in methanol (7 ml) and the reaction solution was allowed to evaporate to dryness over a period of one week, resulting in the formation of several isolated orange crystals of **1** amongst an amorphous precipitate. IR (ATR): $\nu = 3196$ (m, br), 2229 (m), 1620 (vw), 1484 (s), 1414 (m), 1268 (w), 1196 (s), 949 (m) cm^{-1} .

$\{[\text{Gd}(\text{ccnm})_2(\text{OH})(\text{H}_2\text{O})_4]_2\text{Mn}(\text{ClO}_4)_3 \cdot 2(18\text{-crown-6}) \cdot 8.4(\text{H}_2\text{O})\}$ (**2**)

Ag(dcnm) (70 mg, 347 μmol) was added to a solution of $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (43 mg, 116 μmol) dissolved in water (4 ml). The reaction solution was stirred while covered from light for one hour and then filtered to remove the precipitate of AgCl. $\text{Mn}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (30 mg, 112 μmol) and 18-crown-6 (31 mg, 117 μmol) were dissolved in the reaction solution which was then allowed to evaporate to dryness, resulting in the formation of several isolated crystals of **2** amongst an amorphous precipitate.

Crystallographic details and data

A single crystal was mounted on fine glass fibres using viscous hydrocarbon oil. Data were collected on a Nonius KappaCCD (**1**) or Bruker X8 Apex II CCD (**2**) diffractometer, both equipped with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The data collection temperature was maintained at 123 K using an open-flow N₂ cryostream. For data collection on a Nonius KappaCCD diffractometer integration was carried out by the program DENZO-SMN and data were corrected for Lorentz-polarisation effects and for absorption using the program SCALEPACK.²⁴ For data collection on a Bruker X8 Apex II diffractometer integration and initial processing was carried out using the SAINT program suite and data was corrected for Lorentz-polarization effects and for absorption.²⁵ The structures were solved by direct methods using SHELXS-97²⁶ followed by successive refinements using full matrix least squares against F^2 using SHELXL-97.²¹ The

²⁴ Z. Otwinowski and W. Minor, *Methods in Enzymology*, Vol. 276, C. W. Carter Jr., R. M. Sweet (Eds.), 99, 307-326, Academic Press, New York, 1997.

²⁵ ApexII, V2.1-0, Bruker AXS Ltd., 2005, Madison, Wisconsin.

²⁶ G. M. Sheldrick, *Acta Crystollogr. A* 2008, **64**, 112.

program X-Seed was used as a graphical SHELX interface.²⁷ X-ray data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif (CCDC 758816 (1), 758817 (2)).

{[NaCe(dcnm)₄(H₂O)₇]} (1): C₁₂H₁₄CeN₁₂NaO₁₁, *M* = 665.46, orange shard, 0.20 × 0.15 × 0.10 mm³, orthorhombic, space group *Aba2* (No. 41), *a* = 6.7903(2), *b* = 19.1564(4), *c* = 18.5410(4) Å, *V* = 2411.77(10) Å³, *Z* = 4, *D_c* = 1.833 g/cm³, *F*₀₀₀ = 1308, 12228 reflections collected, 1436 unique (*R*_{int} = 0.0765). Final *Goof* = 1.077, *R*1 = 0.0379, *wR*2 = 0.0980, *R* indices based on 1224 reflections with *I* > 2σ(*I*) (refinement on *F*²), 169 parameters, 1 restraint. Lp and absorption corrections applied, *μ* = 1.983 mm⁻¹. *μ* = 1.983 mm⁻¹. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the aqua ligands could not be accurately located from the Fourier difference map. The structure was refined as a racemic twin.

[{Gd(ccnm)₂(OH)(H₂O)₄}₂Mn](ClO₄)₃·2(18-crown-6)·8.4(H₂O) (2): C₃₆H_{90.80}Cl₃Gd₂MnN₁₂O_{50.40}, *M* = 1974.20, red shard, 0.20 × 0.10 × 0.10 mm³, monoclinic, space group *C2/c* (No. 15), *a* = 23.7186(7), *b* = 17.4867(6), *c* = 20.0697(5) Å, β = 110.115(2)°, *V* = 7816.4(4) Å³, *Z* = 4, *D_c* = 1.678 g/cm³, *F*₀₀₀ = 3992, 2θ_{max} = 55.0°, 24350 reflections collected, 8948 unique (*R*_{int} = 0.0779). Final *Goof* = 1.028, *R*1 = 0.0579, *wR*2 = 0.1381, *R* indices based on 6036 reflections with *I* > 2σ(*I*) (refinement on *F*²), 513 parameters, 30 restraints. *μ* = 2.047 mm⁻¹. Hydrogen atoms of the carbamoyl group of ccnm were placed in idealised positions and refined using a riding model to the atom to which they are attached. Hydrogen atoms of the aqua ligands could not be accurately located from the Fourier difference map. Lattice molecules with an occupancy below 50 % were refined isotropically. The bond lengths of the perchlorate anions were restrained using the SADI command. The bond length between H(5O) and O(5) restrained using DFIX command. Thermal parameters of O(20) and O(23) lattice parameters restrained using ISOR command.

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²⁷ L.J. Barbour, *J. Supramol. Chem.* 2001, **1**, 189.