

High-nuclearity homometallic iron and nickel clusters: Fe₂₂ and Ni₂₄ complexes from the use of *N*-methyldiethanolamine

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Received (in Cambridge, UK) 1st June 2005, Accepted 11th July 2005

First published as an Advance Article on the web 3rd August 2005

DOI: 10.1039/b507748f

The use of *N*-methyldiethanolamine (mdaH₂) in reactions with Fe(III) and Ni(II) sources has led to Fe₂₂ and Ni₂₄ products; the clusters are the highest and second-highest, respectively, homometallic clusters for these metals to date, and possess *S* = 0 and *S* = 6 ground states, respectively.

There are various reasons for the current interest by groups around the world in the synthesis and study of high nuclearity 3d molecular metal clusters. Among these is the search for various nuclearity oxide-bridged metal clusters to model M_x sites in biomolecules, including understanding the growth of the core of the ferritin protein, and synthesis of the Mn site of water oxidation within the photosynthetic apparatus of green plants and cyanobacteria.¹ In addition, high nuclearity 3d metal clusters often display interesting and occasionally novel magnetic properties, including high ground state spin values, currently up to *S* = 51/2, and single-molecule magnetism behaviour.² The latter results when a molecule possesses both a large ground state spin and a significant magnetic anisotropy of the Ising (or easy axis) type, as reflected in a negative zero-field splitting parameter (*D*). Crucial to such efforts and others is the continuing development of new synthetic procedures to high nuclearity species. However, there is no obvious and guaranteed route to such species. Much work over many years has been invested in exploring different strategies, and there are now several empirically established approaches to a variety of species. Among these is the use of hydrolysis and alcoholysis reactions. In Mn and Fe chemistry, for example, alcoholysis in the presence of carboxylate groups, with or without chelating ligands, has proven to be a very useful method for obtaining both oxo and hydroxo-containing clusters.^{3,4} Another approach is to use chelates containing alcohol groups, since alkoxides are good bridging groups and thus foster formation of polynuclear products.⁵

Our efforts with alcohol-containing chelates have mainly concentrated to date on Mn chemistry, but we have now extended such reactions to Fe and Ni chemistry. In the present work, we have been investigating the use of *N*-methyldiethanolamine (mdaH₂) and its analogues for the synthesis of transition metal clusters and can report some interesting developments. The mdaH₂ group has been used previously by Saalfrank, who reported the hexanuclear [Fe₆Cl₆(mda)₆] complexes,⁶ but we and others⁷ suspected there might be a number of high nuclearity Fe_x species accessible and have therefore been investigating its reactions with Fe(III) sources under a variety of conditions.

The reaction between FeCl₃, NaO₂CMe and mdaH₂ in a 1 : 3 : 1 molar ratio in EtOH gave an orange solution and a white

precipitate. The solution was filtered and the filtrate left undisturbed for one week in a sealed flask. Pale orange, plate-like crystals slowly formed, together with some white powder. Recrystallization from CH₂Cl₂/Et₂O gave orange crystals of [Fe₂₂O₁₄(OH)₃(O₂CMe)₂₁(mda)₆](ClO₄)₂·4H₂O·4EtOH·4Et₂O (**1**) in 20% overall yield.†

The structure‡ of **1** (Fig. 1) is unprecedented and consists of 22 Fe(III) ions arranged in three sub-units; this is the largest homometallic Fe cluster to date. There is a central [Fe₄(μ₃-OH)₂(μ₄-O)₂]⁶⁺ cubane (Fig. 2, bottom), whose hydroxide O atoms are O32 and O34, to which are attached two penta-coordinated Fe(III) ions, Fe9 and Fe14. This resultant Fe₆ sub-unit is sandwiched between two identical Fe₈ units (Fig. 2, top), the linkages being *via* oxide bridges. With the exception of Fe9 and Fe14, all Fe atoms have distorted octahedral geometry. The complete [Fe₂₂]²⁺ cation would have virtual twofold symmetry except that there is an interesting asymmetry in the centre, best seen in Fig. 2 (bottom), with the Fe9/Fe10 pair bridged by the third hydroxide ion (O28) whereas the corresponding Fe13/Fe14 pair on the other side is bridged by an acetate group in the same *syn, syn* η¹:η¹:μ-mode as the other acetate groups.

The central [Fe^{III}₄O₂(OH)₂] cubane is a very rare unit at this oxidation level. Some Fe/O cubanes with Fe^{II} or mixed Fe^{II/III}

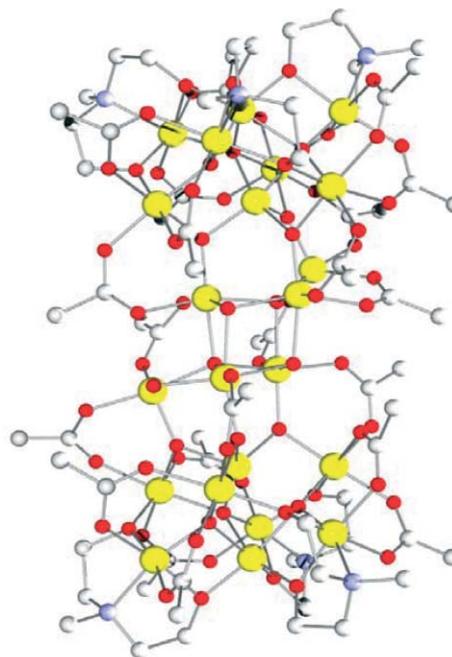


Fig. 1 Pov-Ray representation of complex **1**: Fe yellow; O red; N blue.

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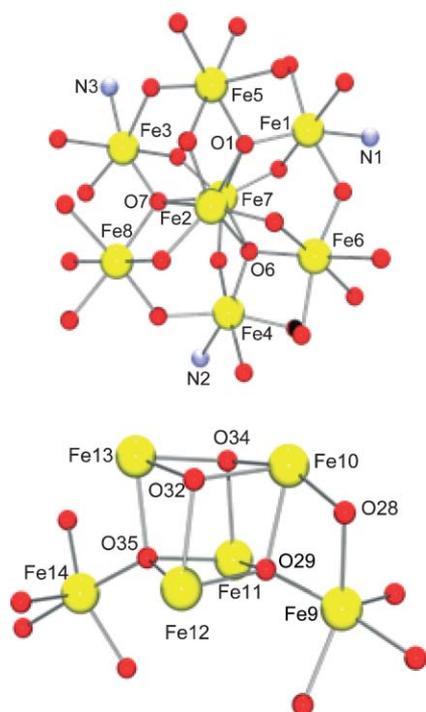


Fig. 2 Pov-Ray representation of the types of sub-units within complex **1**: (top) the Fe_8 unit at each end of the molecule; and (bottom) the central Fe_6 unit.

cores are known, but there is only one $\text{Fe}^{\text{III}}_4\text{O}_4$ cubane in the literature.⁸ Similarly, the end Fe_8 units have only once been previously observed. These have a three-blade propeller topology with the Fe_2/Fe_7 vector being the axle, and they are bridged by three $\mu_4\text{-O}^{2-}$ ions O1, O6 and O7, which also connect to the Fe_1/Fe_5 , Fe_4/Fe_6 and Fe_3/Fe_8 blades, respectively. Additional O atom bridges between Fe_2 pairs are provided by the alkoxide arms of mda^{2-} groups, which bind in a $\eta^2:\eta^1:\eta^2:\mu_3$ fashion. This Fe_8 propeller structure is overall very similar to that of $[\text{Fe}_8\text{O}_3(\text{O}_2\text{CPh})_9(\text{tea})(\text{teaH})_3]$ (teaH_3 is triethanolamine).⁹

Complex **1** is soluble in many organic solvents and was subjected to a variety of reactivity studies. These included reactions with bases to see if deprotonation of the bridging hydroxide ions might trigger a nuclearity change, but in those cases where we were able to isolate a clean product, this turned out to be the starting material. Similarly, many changes to the reaction ratios and solvent were made, but again complex **1** was the only product identified. It thus appears that this complex represents a particularly thermodynamically stable compound.

The use of mdaH_2 in reactions with $\text{Ni}(\text{II})$ reagents was also explored under a variety of conditions. The reaction of $\text{Ni}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ with mdaH_2 in a 3 : 1 molar ratio in $\text{EtOH}/\text{acetic acid}$ (1 : 2 v/v) gave a lime solution. Layering of this solution with Et_2O and slow mixing by diffusion slowly led to the formation of lime, plate crystals of $[\text{Ni}_{24}(\text{O}_2\text{CMe})_{42}(\text{mdaH})_6(\text{EtOH})_6] \cdot 12\text{H}_2\text{O} \cdot 6\text{MeCO}_2\text{H} \cdot 12\text{EtOH} \cdot 12\text{Et}_2\text{O}$ (**2**) in 24% yield. The structure is shown in Fig. 3, together with the cell asymmetric unit, $[\text{Ni}_4(\text{O}_2\text{CMe})_7(\text{mdaH})(\text{EtOH})]$. The complex consists of a Ni_{18} loop to which are connected six additional $\text{Ni}(\text{II})$ atoms (Ni1). All Ni atoms are distorted octahedral, and the loop has a chair-like conformation. The mono-deprotonated $\eta^1:\eta^1:\eta^3:\mu_3\text{-mdaH}^-$

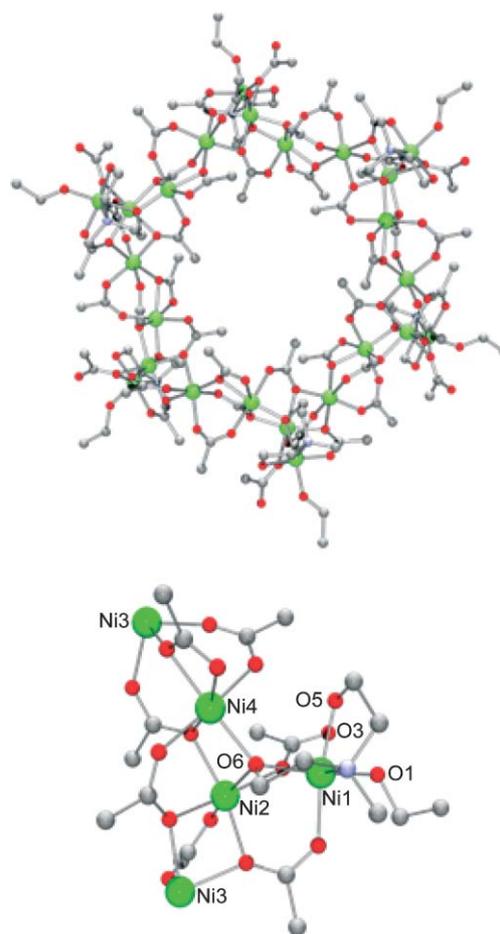


Fig. 3 ORTEP representation of complex **2** and its asymmetric unit.

groups chelate the external Ni1 atoms, with their protonated alcohol arm (O5) bound terminally to Ni1 , and their deprotonated alkoxide arm (O6) triply bridging $\text{Ni1}/\text{Ni2}/\text{Ni4}$. Additional bridges between Ni atoms are provided by acetate groups in various coordination modes: mono-atomically bridging $\text{Ni1}/\text{Ni3}$, with the unbound O atom (O3) forming a weak hydrogen bond with the OH of the terminal EtOH molecule on Ni1 ($\text{O3} \cdots \text{O1} = 3.1 \text{ \AA}$); the common *syn, syn*, $\eta^1:\eta^1:\mu$ mode bridging $\text{Ni2}/\text{Ni3}$ and $\text{Ni3}/\text{Ni4}$; rarer *syn, syn, anti*, $\eta^1:\eta^2:\mu_3$ bridging $\text{Ni1}/\text{Ni2}/\text{Ni3}$, $\text{Ni2}/\text{Ni4}/\text{Ni3}$ and $\text{Ni3}/\text{Ni2}/\text{Ni4}$; and *syn, syn, anti*, $\eta^1:\eta^2:\mu$ bridging between $\text{Ni3}/\text{Ni4}$. The central Ni_{18} loop within **2** is the biggest Ni loop to date,^{10,11} and only $[\text{Ni}_{34}\text{Se}_{22}(\text{PPh}_3)_{10}]$ is a higher-nuclearity homometallic Ni cluster of any structure.¹²

The magnetic susceptibilities (χ_M) of **1** and **2** (see Fig. 4) were measured on microcrystalline samples in a 0.1 tesla field in the 5.00–300 K temperature range. $\chi_M T$ for **1** decreases steadily with decreasing temperature from $33.33 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K to $0.97 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 5.00 K, suggesting an $S = 0$ spin ground state, consistent with the expected antiferromagnetic coupling between $\text{Fe}(\text{III})$ ions.

For **2**, $\chi_M T$ decreases steadily from $36.77 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K to $24.26 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 5.00 K, indicating both ferro- and antiferromagnetic interactions within the molecule and a significant resultant ground state spin. The latter was determined by two methods, fitting of dc magnetization vs. field (H) and temperature (T) data, and ac susceptibility measurements.

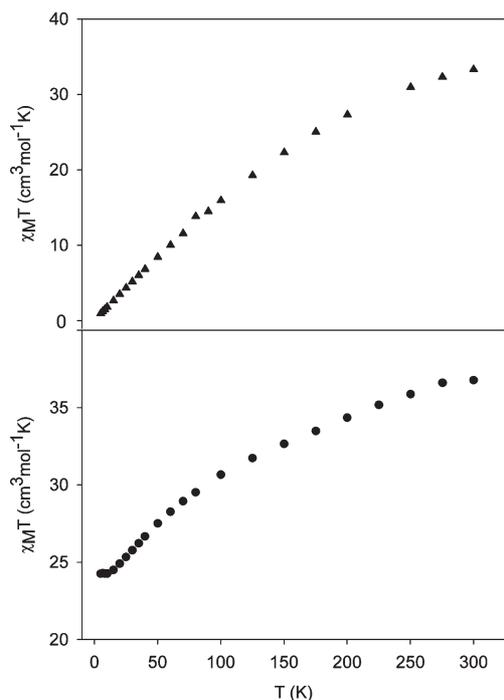


Fig. 4 Plot of $\chi_M T$ vs. T for complexes **1** (top) and **2** (bottom).

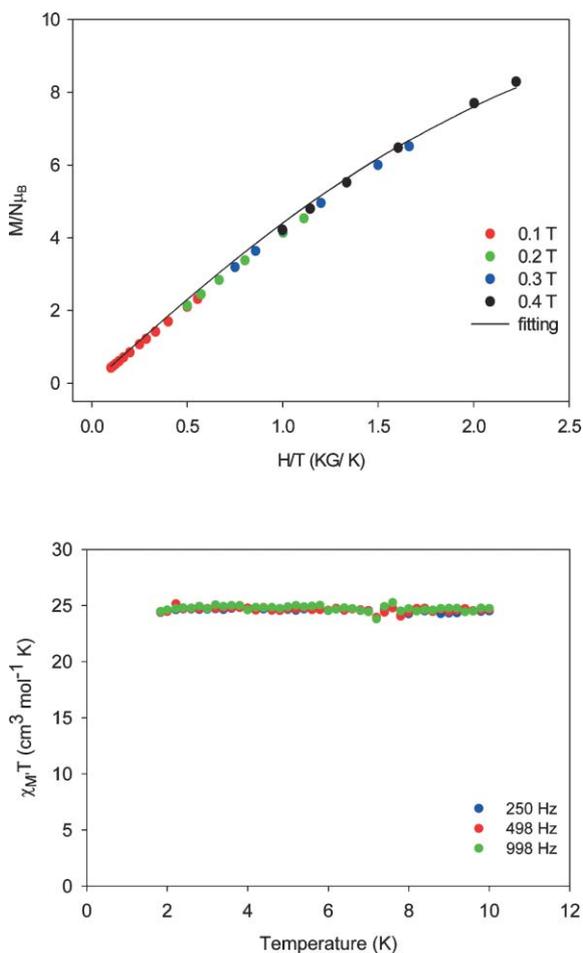


Fig. 5 Reduced magnetization data (top) and ac magnetic susceptibility data (bottom) for complex **2**.

The ground-state spin was determined by fits of dc magnetization (M) data collected in the 1.8–10 K and 0.1–0.4 T ranges: the fits are shown in Fig. 5 (top). Two good fits were obtained, depending on the sign of D : $S = 6$, $g = 2.23$, $D = -0.0047 \text{ cm}^{-1}$, and $S = 6$, $g = 2.26$, $D = 0.0045 \text{ cm}^{-1}$. A root-mean-square error surface of the fit shows that the fit with positive D is superior, suggesting this to be the true sign of D , but confirmation must await EPR studies on **2**. When data collected at fields higher than 0.5 T were used to try to reach saturation, the fits were poor, suggesting excited states with $S \gg 6$ are stabilized by the applied field and become populated even at these low temperatures.

In order to independently confirm the ground state, the influence of the applied dc field was removed completely by carrying out ac susceptibility measurements in the 1.8–10 K range with a 3.5 G ac field oscillating at frequencies in the 50–1500 Hz range. The in-phase (χ_M') signal (Fig. 5, bottom) is temperature-independent in this temperature range at $\sim 25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, giving $S = 6$ and $g \approx 2.2$, in satisfying agreement with the dc fit parameters.

In conclusion, the use of mdaH₂ has led to two particularly high nuclearity Fe and Ni clusters, and this suggests that even larger molecular coordination clusters of these paramagnetic 3d metals may be possible using this or similar synthetic strategies.

This work was supported by the National Science Foundation.

Notes and references

† Vacuum-dried samples of both compounds analysed as solvent-free. Calcd. (found) for **1**: C, 23.72 (23.55); H, 3.65 (3.75); N, 2.31 (2.00%). Calcd. (found) for **2**: C, 28.03 (27.70); H, 4.75 (4.58) N, 1.72 (1.74%).

‡ Crystal data for **1**·4H₂O·4EtOH·4Et₂O: C₉₆H₂₀₂Cl₂Fe₂₂N₆O₉₁, $M_r = 4196.24$, monoclinic, $C2/c$, $a = 29.719(3) \text{ \AA}$, $b = 35.321(4) \text{ \AA}$, $c = 30.651(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 98.367(2)^\circ$, $\gamma = 90^\circ$, $V = 31832(6) \text{ \AA}^3$, $Z = 8$, $T = 173(2) \text{ K}$, $R1 = 0.06807$, $wR2 = 0.1581$ (F^2 , all data), 7571 refl.

§ Crystal data for **2**·12H₂O·6MeCO₂H·12EtOH·12Et₂O: C₂₁₀H₄₇₄N₆Ni₂₄O₁₅₆, $M_r = 6988.99$, cubic, $Ia\bar{3}$, $a = b = c = 38.9497(6) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 59,089.8(16) \text{ \AA}^3$, $Z = 8$, $T = 173(2) \text{ K}$, $R1 = 0.0398$, $wR2 = 0.0976$ (F^2 , all data), 6946 refl. CCDC 274154 and 274155. See <http://dx.doi.org/10.1039/b507748f> for crystallographic data in CIF or other electronic format.

- D. M. Kurtz, *Chem. Rev.*, 1990, **90**, 585; T. M. Lohr, *Iron Carriers and Iron Proteins*, VCH, Weinheim, 1989; A. Mishra, W. Wernsdorfer, K. A. Abboud and G. Christou, *Chem. Commun.*, 2005, 54.
- M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud and G. Christou, *J. Am. Chem. Soc.*, 2004, **126**, 4766.
- A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud and G. Christou, *Angew. Chem. Int. Ed.*, 2004, **43**, 2117.
- C. Cañada-Vilalta, T. A. O'Brien, M. Pink, E. R. Davidson and G. Christou, *Inorg. Chem.*, 2003, **42**, 7819.
- M. Murugesu, W. Wernsdorfer, K. A. Abboud and G. Christou, *Angew. Chem. Int. Ed.*, 2005, **44**, 892; D. Foguet-Albiol, T. A. O'Brien, W. Wernsdorfer, B. Moulton, M. J. Zaworotko, K. A. Abboud and G. Christou, *Angew. Chem. Int. Ed.*, 2005, **44**, 897.
- R. W. Saalfrank, I. Bernt, M. M. Chowdhry, F. Hampel and G. B. M. Vaughan, *Chem. Eur. J.*, 2001, **7**, 2765.
- E. M. Rumberger, L. N. Zakharov, A. L. Rheingold and D. N. Hendrickson, *Inorg. Chem.*, 2004, **43**, 6531.
- R. G. Raptis, I. P. Georgakaki and D. C. R. Hockless, *Angew. Chem. Int. Ed.*, 1999, **38**, 1632.
- M. Murugesu, K. A. Abboud and G. Christou, *Dalton Trans.*, 2003, 4552.
- A. J. Blake, C. M. Grant, S. Parsons, J. M. Rawson and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1994, 2363.
- A. L. Dearden, S. Parsons and R. E. P. Winpenny, *Angew. Chem. Int. Ed.*, 2001, **40**, 152.
- D. Fenske, J. Ohmer and J. Hachgenei, *Angew. Chem. Int. Ed.*, 1985, **24**, 993.