

Increasing the crystallisation temperature to access new spin clusters: conversion of $[\text{Ni}_8(\text{cit})_6(\text{OH})_2(\text{H}_2\text{O})_2]^{10-}$ to $[\text{Ni}_8(\text{cit})_6(\text{OH})_2]^{10-}$

Mark Murrie,^{*a} Daniel Biner,^a Helen Stöckli-Evans^b and Hans U. Güdel^a

^a *Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, 3000 Bern 9, Switzerland.*

E-mail: mark.murrie@iac.unibe.ch; Fax: (+41) 31-631-4399; Tel: (+41) 31-631-4253

^b *Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, 2000 Neuchâtel, Switzerland*

Received (in Cambridge, UK) 23rd October 2002, Accepted 21st November 2002

First published as an Advance Article on the web 10th December 2002

The role of temperature in the formation of high nuclearity nickel(II) citrate spin clusters is explored, revealing how changes in structure and hence magnetic properties can be triggered through desolvation and ligand reorganisation.

The possibility of using discrete transition metal complexes as nanomagnets¹ continues to fuel the synthesis and magnetic study of high nuclearity spin clusters.² Typical synthetic routes to spin clusters culminate in crystallisation of the reaction product from solution at ambient temperature. High reaction temperatures have been employed in the synthesis of chromium(III) clusters,^{3,4} and ligand ‘melts’ have also been used to good effect as reaction solvents.⁵ However, even in these rare examples, the crystallisation step is carried out at room temperature,^{3,5} or by slowly cooling a superheated solution.⁴

We have developed a synthetic approach to nickel(II) spin clusters, using the ligand citrate.⁶ Previously, we reported a heptanuclear nickel(II) complex in which the predominantly ferromagnetic exchange is mediated by citrate, leading to a high-spin $S = 7$ ground state. To investigate further the potential of assembling high-spin molecules using citrate, and as part of a study into the role of the different reaction parameters, we have begun to explore the effect of temperature. Herein, we illustrate how changes in the structure and hence the magnetic properties of nickel(II) citrate clusters, can be triggered by synthesis and crystallisation at elevated temperature.

Slow evaporation of a basic aqueous solution containing nickel(II) sulfate, citric acid and tetramethylammonium hydroxide (*ca.* 1:1:3.6) at ambient temperature produces $(\text{NMe}_4)_{10}[\text{Ni}_8(\text{cit})_6(\text{OH})_2(\text{H}_2\text{O})_2]$ **1**, $\{\text{H}_4\text{cit} = \text{C}(\text{OH})(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})_2\}$.[†] This compound differs to that previously reported by Strouse *et al.* in both the crystal packing of the octanuclear clusters, and in the number of lattice water molecules.⁷ The structure consists of two distorted nickel(II) tetrahedra related by a centre of inversion (Fig. 1a).[‡] The tetrahedra are capped by three tridentate groups: one μ_3 -hydroxide (bridging Ni1–Ni2–Ni4) and two μ_3 -alkoxide groups from two of the three independent citrate ligands (bridging Ni2–Ni3–Ni4 and Ni1–Ni2–Ni3). The carboxylate groups of these two citrate ligands are monodentate. The third citrate ligand caps Ni4 through one β -CO₂[−] group and the α -CO₂[−] group. The second β -CO₂[−] group displays a 1,1,3 bridging motif (to Ni1, Ni1' and Ni2'), thus providing an exchange pathway between the two nickel(II) tetrahedra. The final citrate alkoxide is μ_2 -bridging (Ni1–Ni4) while a H₂O ligand completes the coordination at Ni3, which displays approximate square pyramidal geometry.

Crystallisation of the reaction mixture at 50 °C instead of ambient temperature produces $(\text{NMe}_4)_{10}[\text{Ni}_8(\text{cit})_6(\text{OH})_2]$ **2**,[‡] which contains a double-cubane structure (Fig. 1b).[‡] Compound **2** is the doubly-dehydrated analogue of **1**, and thus is structurally related. However, a comparison of the two structures reveals a series of fascinating differences. The citrate ligand which bridges four metal centres in **1**, now bridges five metal centres in **2**. The citrate μ_2 -alkoxide group in **1** becomes μ_3 -bridging in **2** (Fig. 2), thus closing the open edge of the cubane (for **1**, Ni1–Ni3 = 3.65 Å; for **2**, Ni1–Ni3 = 3.14 Å); in doing so, this ligand has changed its conformation from

extended in **1**, to rotated in **2**. Furthermore, the β -CO₂[−] group of this ligand, which is capping Ni4 in **1** is capping Ni3 in **2**. Hence the position of the 5-coordinate nickel(II) differs from **1** (Ni3) to **2** (Ni2). Conformational changes in the remaining two independent citrate ligands are also seen. Compound **2** represents the first reported example of this structural motif for a transition metal cluster ligated by oxygen donors, but resembles a sulfur bridged $\{\text{Fe}_6\text{Mo}_2\}$ double-cubane cluster.⁸ In contrast, a compound containing a face-sharing $\{\text{Ni}_6(\text{OH})_6\}$ double-cubane, $[\text{Ni}_6(\text{OH})_6\{\text{Ni}(\text{mhp})_3\}_5(\text{Hmhp})(\text{H}_2\text{O})_2\text{Cl}]$, has been reported for nickel(II).⁹

A comparison of the magnetic properties of **1** and **2** is shown in Fig. 3, revealing that the two octanuclear compounds display different magnetic behaviour at low temperature. In the high temperature regime (300–30 K), χT for both compounds increases as the temperature is lowered due to predominantly ferromagnetic interactions. χT continues to increase for **1**, reaching 17.3 cm³ mol^{−1} K at 1.8 K. For **2**, χT decreases from 12.4 cm³ mol^{−1} K at 26 K, to 7.96 cm³ mol^{−1} K at 1.8 K. Magnetisation measurements were performed at 1.8 K, where $M/N\mu_B$ at 5 T = 12.3 for **1** and 8.5 for **2** (Fig. 4).§

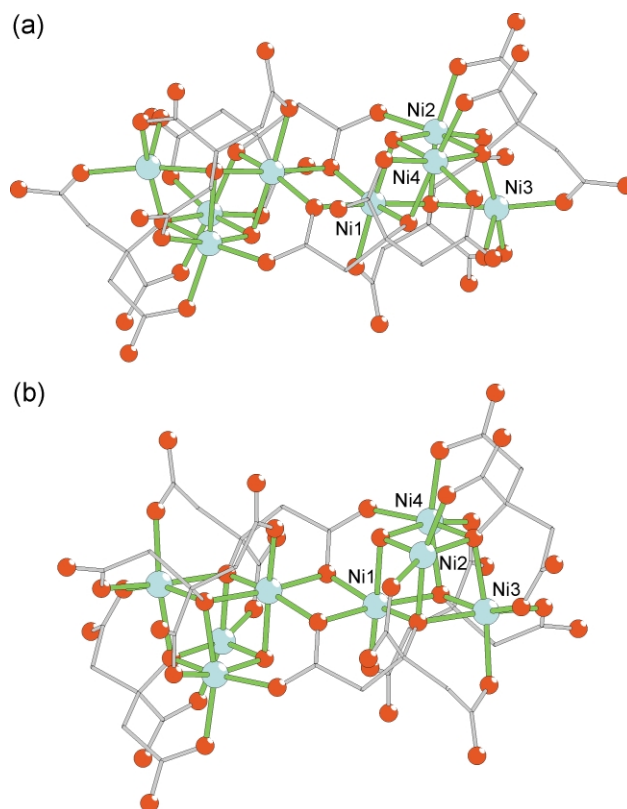


Fig. 1 The structure of the anions in **1** and **2** (Ni, blue; O, red; C, grey lines; H atoms omitted for clarity). (a) For **1**, bond length ranges: Ni–O 1.98–2.14 Å. Ni...Ni distances: 2.88 to 3.65 Å. Bond angle ranges: Ni–O–Ni 86.4–122.5°. (b) For **2**, bond length ranges: Ni–O 1.96 to 2.16 Å. Ni...Ni distances: 2.84 to 3.27 Å. Bond angle ranges: Ni–O–Ni 85.8 to 103.5°.

For **1**, both magnetic susceptibility and magnetisation data are consistent with an $S = 6$ ground state, with the rise in χT at low temperature due to thermal depopulation of excited spin states (for an isotropic $S = 6$ ground state and $g = 2.2$: χT calculated = $25.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$; M_{sat} calculated = 13.2). For **2**, the value of χT at around 20 K is consistent with an $S = 4$

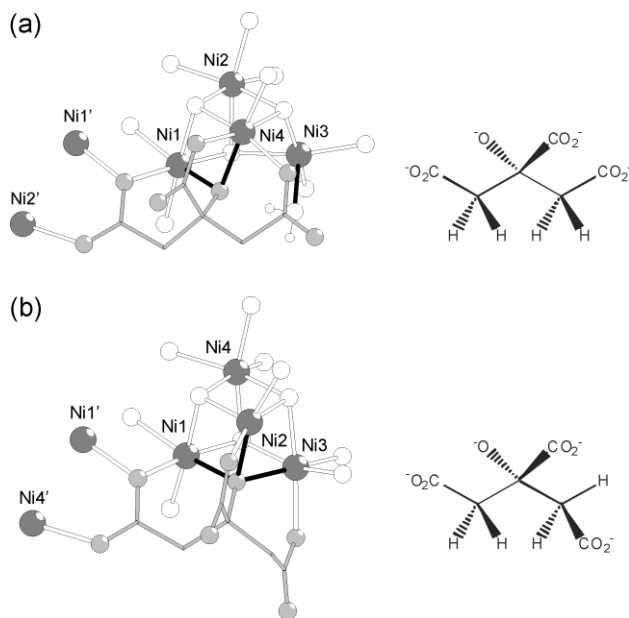


Fig. 2 (a) Coordination of the citrate ligand containing the μ_2 -alkoxide in **1** (citrate extended conformation) and (b) the μ_3 -alkoxide in **2** (citrate rotated conformation).

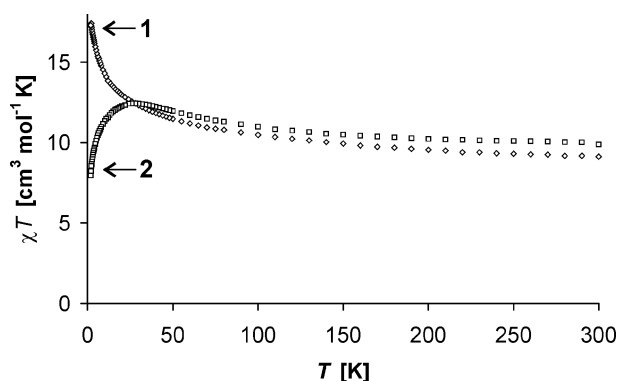


Fig. 3 Magnetic susceptibility (χT vs. T) of **1** (open diamonds) and **2** (open squares).

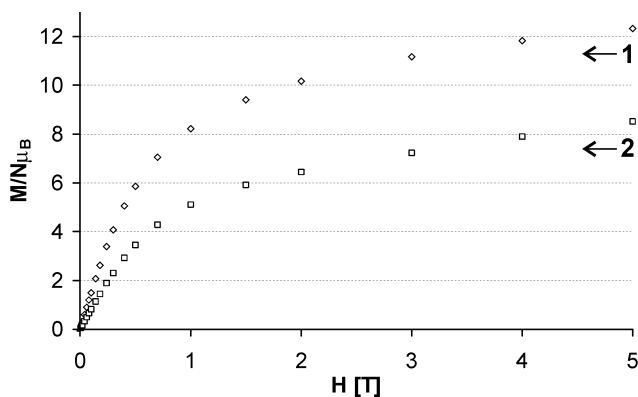


Fig. 4 Field dependence of the magnetisation at 1.8 K of **1** (open diamonds) and **2** (open squares).

ground state (for an isotropic $S = 4$ ground state and $g = 2.2$: χT calculated = $12.1 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). The drop in χT below 20 K is attributed to anisotropy, resulting in a zero-field splitting within the $S = 4$ ground state. The magnetisation data suggest an $S = 4$ ground state (for $S = 4$ and $g = 2.2$: M_{sat} calculated = 8.8) and indicate the presence of low-lying excited states with $S > 4$. Inspection of the bridging angles in these compounds reveals the presence of competing ferro- and antiferromagnetic exchange interactions (Ni–O–Ni angles for **1**, 86.4 – 122.5° ; for **2**, 85.8 to 103.5°). This situation is consistent with spin ground states lying between $S = 0$ (all antiferro-) and 8 (all ferro-).

By changing one parameter only, namely temperature, we have been able to study its role in the synthesis of nickel(II) citrate clusters. We find that synthesis at elevated temperature promotes dehydration and ligand rearrangement, triggering structural changes that are directly responsible for the different magnetic properties of **1** and **2** observed at the lowest temperatures. We are currently exploring further the role of temperature in the synthesis of transition metal citrate complexes, and hope that these studies will provide valuable insight into the assembly of spin clusters and single molecule magnets.

We thank the Swiss National Science Foundation (NRP47 ‘Supramolecular Functional Materials’) and the European Community (Fifth Framework Programme MOLNANOMAG HPRN-CT-1999-00012) for funding.

Notes and references

† Satisfactory elemental analyses were obtained for **1** and **2**.

‡ Crystal data for **1**·4H₂O: C₇₆H₂₄₂N₁₀Ni₈O₉₂, $M = 3238.48$, triclinic, space group $P\bar{1}$, $a = 12.7400(9)$, $b = 16.1927(11)$, $c = 19.6657(14)$ Å, $\alpha = 101.970(8)$, $\beta = 98.544(9)$, $\gamma = 111.854(8)^\circ$, $V = 3567.8(4)$ Å³, $Z = 1$, $T = 153(2)$ K, $\mu(\text{Mo-K}\alpha) = 1.143 \text{ mm}^{-1}$, 28203 reflections measured, 12902 unique ($R_{\text{int}} = 0.0550$) which were used in all calculations. The final $R_1(F^2)$ was 0.0445 (observed data), $wR_2 = 0.1284$ (all data). For **2**·24H₂O: C₇₆H₁₉₄N₁₀Ni₈O₆₈, $M = 2811.13$, triclinic, space group $P\bar{1}$, $a = 13.9785(10)$, $b = 19.1426(14)$, $c = 24.6570(19)$ Å, $\alpha = 79.703(9)$, $\beta = 87.441(9)$, $\gamma = 70.468(8)^\circ$, $V = 6117.2(8)$ Å³, $Z = 2$, $T = 153(2)$ K, $\mu(\text{Mo-K}\alpha) = 1.307 \text{ mm}^{-1}$, 47845 reflections measured, 22174 unique ($R_{\text{int}} = 0.0944$) which were used in all calculations. The final $R_1(F^2)$ was 0.0642 (observed data), $wR_2 = 0.1708$ (all data). Structures were solved by direct methods using the programme SHELXS-97. The refinement and all further calculations were carried out using SHELXL-97. CCDC 196103 and 196104. See <http://www.rsc.org/suppdata/cc/b2/b210327c/> for crystallographic data in CIF or other electronic format.

§ Powder magnetic susceptibility measurements between 300 and 1.8 K were performed using a Quantum Design MPMS-XL SQUID magnetometer in a field of 100 G. Samples were sealed in gelatine capsules and diamagnetic corrections applied for both sample and holder.

- R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141; R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804.
- G. Aromí, S. Bhaduri, P. Artús, K. Folting and G. Christou, *Inorg. Chem.*, 2002, **41**, 805; M. Murugesu, C. E. Anson and A. K. Powell, *Chem. Commun.*, 2002, 1054; A. L. Dearden, S. Parsons and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2001, **40**, 151.
- I. M. Atkinson, C. Benelli, M. Murrell, S. Parsons and R. E. P. Winpenny, *Chem. Commun.*, 1999, 285.
- E. J. L. McInnes, C. Anson, A. K. Powell, A. J. Thompson, S. Poussereau and R. Sessoli, *Chem. Commun.*, 2001, 89.
- A. J. Blake, C. M. Grant, S. Parsons, J. M. Rawson and R. E. P. Winpenny, *J. Chem. Soc. Chem. Commun.*, 1994, 2363.
- M. Murrell, H. Stoeckli-Evans and H. U. Güdel, *Angew. Chem., Int. Ed.*, 2001, **40**, 1957.
- J. Strouse, S. W. Layten and C. E. Strouse, *J. Am. Chem. Soc.*, 1977, **99**, 562.
- K. D. Demadis and D. Coucouvanis, *Inorg. Chem.*, 1994, **33**, 4195.
- E. K. Brechin, W. Clegg, M. Murrell, S. Parsons, S. J. Teat and R. E. P. Winpenny, *J. Am. Chem. Soc.*, 1998, **120**, 7365.