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Tetranuclear nickel(II) complexes with genuine μ_3-1,1,3 and μ_4-1,1,3,3 azide bridges

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Received (in Cambridge, UK) 20th November 2002, Accepted 11th February 2003
First published as an Advance Article on the web 25th February 2003

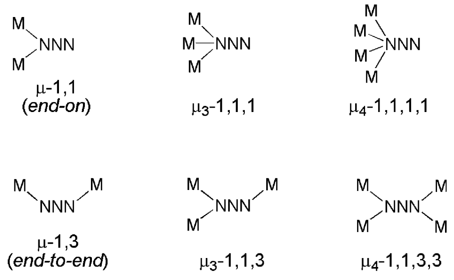
Unique tetranickel(II) complexes have been synthesized which incorporate genuine μ_3-1,1,3 or μ_4-1,1,3,3 bridging azido ligands. Identification of two distinct isomeric μ_4-1,1,3,3 binding modes confirms the structural flexibility of the quadruply bridging azide.

The flexidentate azide ion is one of the most versatile ligands and provides coordination compounds of great structural variety. Current impetus comes from, *inter alia*, the field of molecular magnetism, where azido bridges efficiently mediate different kinds of magnetic coupling depending on their mode of coordination.[1] In particular, a variety of molecular architectures for di- and polynuclear nickel(II) azido complexes have been discovered.[2–5] The common azide bridging modes are μ-1,1 (*end-on*, Scheme 1) which usually entails ferromagnetic coupling, and μ-1,3 (*end-to-end)* which gives rise to antiferromagnetic behavior.[1,2] In view of the increasing interest in high-nuclearity complexes and 2D- or 3D-polymeric coordination networks, azide binding modes that link more than two metal ions are highly desirable. However, examples for the triply or quadruply bridging modes have remained scarce. μ_3-1,1,1 azide is mainly found in some cubane-type structures,[3,6] while the μ_3-1,1,3 mode has only been observed in a few polymeric systems where at least one of the M–N distances is very long (semi-coordinative).[5,7] Recently, genuine μ_4-1,1,1,1 azide binding in molecular complexes has been reported.[8] In contrast, the μ_4-1,1,3,3 mode is restricted to a very few polymeric structures, again showing some semi-coordinative M–N distances.[9] Azide ions surrounded by six Ag^+ have been found in the layer-type framework of $AgN_3{\cdot}AgNO_3$.[10] Here we report novel molecular tetranickel(II) complexes that feature genuine μ_3-1,1,3 and μ_4-1,1,3,3 azide coordination, including two distinct isomeric forms of the μ_4-1,1,3,3 azide bridge.

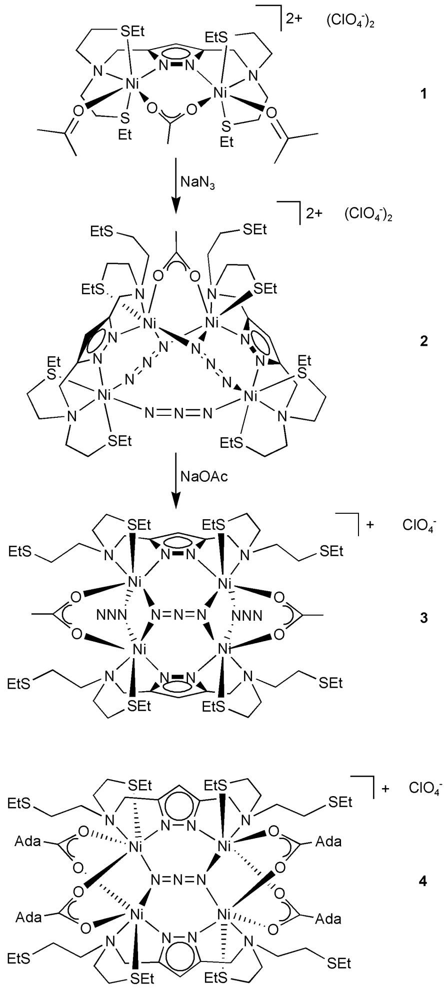
Pyrazolate-based bimetallic complexes with accessible coordination sites can serve as building blocks for the assembly of polynuclear compounds or 1D extended chains with alternating bridges.[11] Following this strategy, we set out to link dinickel entities $[LNi_2(OAc)]^{2+}$ *via* replacement of the labile acetone ligands in **1**[12] (Scheme 2) by potentially bridging azide ions. Unexpectedly however, treatment of a solution of **1** with NaN_3 led to a complete reshuffling of all azide and acetate ligands, giving the Ni_4 complex **2** in good yield.† The tetranuclear nature of **2** was indicated by FD mass spectrum which shows a prominent signal at m/z = 1474 characteristic of the ion $[L_2Ni_4(N_3)_3(OAc)(ClO_4)]^+$. A detailed picture of its molecular structure was provided by X-ray crystallography.‡ The unique central Ni_4 core of **2** is depicted in Fig. 1.

The tetranuclear units consist of two LNi_2 fragments that are connected by three azido ligands in an unusual fashion and are additionally held together by a single bridging acetate. Two of the azido ligands are found in the rare μ_3-1,1,3 mode, while the third exhibits *end-to-end* binding between Ni2 and Ni4. All Ni–N_{azide} bond lengths lie in the usual range of 2.05–2.15 Å. While the *end-to-end* azido bridge is symmetric (d(N13–N14) = 1.172(3) Å, d(N14–N15) = 1.174(3) Å), the μ_3-1,1,3 bridges display pronounced asymmetry (d(N10–N11) = 1.194(3)/d(N17–N18) = 1.202(3) Å *versus* d(N11–N12) = 1.168(3)/d(N16–N17) = 1.165(3) Å).

All nickel(II) ions in **2** are six-coordinate, which leaves two of the thioether side arms of the pyrazolate ligands dangling (Scheme 2). Upon treatment with additional acetate, two more



Scheme 1 Azide bridging modes.



Scheme 2

DOI: 10.1039/b211486k

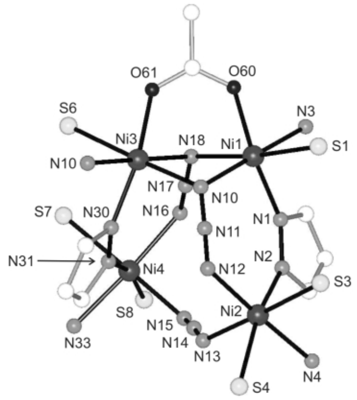


Fig. 1 Structure of the central tetranuclear core of **2**. Selected atom distances [Å]: Ni1–N10 2.118(2), Ni1–N18 2.150(2), Ni2–N12 2.115(3), Ni2–N13 2.058(3), Ni3–N10 2.146(2), Ni4–N15 2.070(2), Ni4–N16 2.098(2), N10–N11 1.194(3), N11–N12 1.168(3), N13–N14 1.172(3), N14–N15 1.174(3), N16–N17 1.165(3), N17–N18 1.202(3), Ni1···Ni2 4.479, Ni1···Ni3 3.151, Ni3···Ni4 4.461, Ni2···Ni4 5.493, Ni1···Ni4 5.499, Ni2···Ni3 5.419.

thioether donors dissociate and the cage structure of **2** is opened to give complex **3** (which can also be obtained directly from the components). Its composition is confirmed by FAB mass spectrometry which shows the expected signal for $[L_2Ni_4(N_3)_3(OAc)_2]^+$ at m/z = 1434. In **3**, the four Ni ions form a rectangle where the long edges are spanned by the pyrazolate and each short edge is spanned by an acetate and a μ-1,1 azide. The remaining azide caps the rectangle as a μ_4-1,1,3,3 bridging ligand (Fig. 2). X-Ray crystallography clearly establishes the structure of the Ni_4 core of **3** and reveals almost symmetric coordination of the central azide cap, but the poor quality of the structural data (due to disorder in the dangling thioether side arms and disorder of the ClO_4^- counteranion) precludes a more detailed analysis.

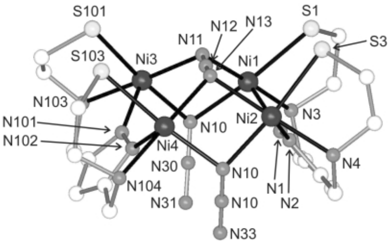


Fig. 2 Structure of the central tetranuclear core of **3**.

When using adamantyl carboxylate instead of acetate, the related tetranuclear species **4** could be isolated. In contrast to **3**, complex **4** contains double carboxylate bridges at both short edges of the Ni_4 arrangement, but it also features a μ_4-1,1,3,3 azido ligand (Fig. 3). The N–N–N unit is rather symmetric (d(N9–N10) = 1.172(7)/d(N10–N11) = 1.161(7) Å) and all $Ni–N_{azide}$ distances are found in the narrow range 2.021–2.034 Å. However, the binding situation of the μ_4-1,1,3,3 azido ligands in **3** and **4** is completely different: in **3**, the $Ni–N_3–Ni$ entities are almost planar with respect to the *end-to-end* linkages, while in **4** it is the *end-on* bridged Ni ions that are in plane with the N_3^- ligand (torsion angle between the Ni1/N9/Ni3 and Ni2/N11/Ni4 planes: ~53°). These distinct geometric characteristics indicate considerable structural flexibility of a μ_4-bridging azide, and hence such a μ_4-azide promises to be a versatile building block for the assembly of high-nuclearity complexes.

In the IR spectra, the $\nu_{as}(N_3)$ stretches are found at 2042(s)/2081(vs)/2092(sh) for **2**, 2043(s)/2074(vs)/2079(sh) for **3** and 2128(s) cm^{-1} for **4**, *i.e.* in the typical region for bridging azide. A more detailed investigation of these unique tetranickel complexes—including their spectroscopic and magnetic properties—is currently in progress.

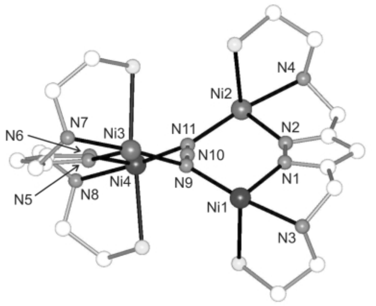


Fig. 3 Structure of the central tetranuclear core of **4**. Selected atom distances [(] and angles [°]: Ni1–N9 2.023(5), Ni2–N11 2.034(5), Ni3–N9 2.021(5), Ni4–N11 2.022(5), N9–N10 1.172(7), N10–N11 1.161(7), Ni1···Ni2 4.521(1), Ni1···Ni3 3.577(1), Ni3···Ni4 4.508(1), Ni2···Ni4 3.583(1).

Funding of this work by the DFG (priority program 1137 'Molecular Magnetism') is gratefully acknowledged.

Notes and references

† Elemental analysis for **2**: calc. for $C_{44}H_{85}Cl_2N_{17}Ni_4O_{10}S_8$·0.75acetone (found): C 34.33 (34.20), H 5.58 (5.42), N 14.72 (14.87%); for **3**: calc. for $C_{46}H_{88}ClN_{17}Ni_4O_8S_8$ (found): C 36.02 (35.42), H 5.78 (5.73), N 15.52 (15.07%).

‡ Crystal data for **2**: $C_{44}H_{85}Cl_2N_{17}Ni_4O_{10}S_8$·0.75acetone, M = 1618.0, monoclinic, $P2(1)/c$, a = 21.140(4), b = 16.348(3), c = 22.316(5) Å, β = 113.59(3)°, V = 7068(2) Å^3, T = 200 K, Z = 4, ρ_{calc} = 1.521 g cm^{-3}, μ(Mo-K$_\alpha$) = 1.424 mm^{-1}, 18801 unique reflections (R_{int} = 0.045), 12291 observed [$I > 2\sigma(I)$], 887 parameters, largest diff. peak 0.97 e Å^{-3}, final $R1[I > 2\sigma(I)]$ = 0.042, $wR2$ = 0.117, goodness of fit on F^2 = 1.043, CCDC 149456. For **4**: $C_{86}H_{142}ClN_{11}Ni_4O_{12}S_8$, M = 2048.9, monoclinic, $P2_1$, a = 16.391(2), b = 16.515(2), c = 18.416(2) Å, β = 103.902(2)°, V = 4839(1) Å^3, T = 106 K, Z = 2, ρ_{calc} = 1.406 g cm^{-3}, μ(Mo-K$_\alpha$) = 1.029 mm^{-1}, 14795 unique reflections (R_{int} = 0.057), 11505 observed [$I > 2\sigma(I)$], 1115 parameters, largest diff. peak −1.04 e Å^{-3}, final $R1[I > 2\sigma(I)]$ = 0.051, $wR2$ = 0.135, goodness of fit on F^2 = 1.036, CCDC 198560. See http://www.rsc.org/suppdata/cc/b2/b211486k/ for crystallographic files in CIF or other electronic format.

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