Versatility of the Azido Bridging Ligand in the First Two Examples of Ferro–Antiferromagnetic Alternating Nickel(II) Chains

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A one-pot reaction of $Ni(ClO_4)_2 \cdot 6H_2O$, *N,N*-dimethylethylenediamine (dmen) or 2-aminoethylpyridine (aep) and NaN_3 affords the two $[Ni(dmen)(\mu\text{-}N_3)_2]_n$ **1** and $[Ni(aep)(\mu\text{-}N_3)_2]_n$ **2** chains with unprecedented alternating end-on and end-to-end bridging loops perpendicular to one another; magnetic susceptibility measurements indicate that they are the first two ferro–antiferromagnetic alternating chains of Ni^{II}.

There is growing interest in molecular-based magnets.[1] The study of multi-atom bridged polynuclear metal complexes is an important area in this regard, primarily for understanding the mechanism of magnetic interactions[2] propagated among paramagnetic ions. Recently,[3–8] we have studied magneto-structural correlations of μ-azidonickel(II) complexes using different amines as blocking ligands. The most remarkable species obtained to date are the neutral polymeric $[Ni(diamine)(\mu\text{-}N_3)_2]_n$ compounds: double end-on (EO) bridged one-dimensional systems,[4b] a single end-to-end (EE) and triple EO alternating bridged one-dimensional complex[7] and a bidimensional sheet[8] with alternating single EE and double EO bridges. The wide range of magnetic behaviour arising from the changes in versatile bridging motifs was explained in terms of subtle changes in structural factors correlated with appropriate basic orbital mechanisms:[9] a ferromagnetic (F) coupling with EO coordination mode, an antiferromagnetic (AF) interaction in the case of EE coordination mode and the net global antiferromagnetism[7] and/or canting phenomenon[8] from combined EE and EO coordination linkings. In this communication we report the synthesis, crystal structure and preliminary magnetic study of two polynuclear one-dimensional complexes $[Ni(dmen)(\mu\text{-}N_3)_2]_n$ **1** (dmen = *N,N*-dimethylethylenediamine) and $[Ni(aep)(\mu\text{-}N_3)_2]_n$ **2** (aep = 2-aminoethylpyridine) which are the first two examples of dibridged nickel(II) alternating EO and EE chains.

The one-dimensional polymers were easily obtained in almost quantitative yield by treating an aqueous solution (25 ml) of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.74 g, 2 mmol) with 0.18 g (2 mmol) of dmen or 0.27 g (2 mmol) of aep. After filtration an aqueous solution of NaN_3 (0.26 g, 4 mmol) was added. Slow evaporation at room temperature provides X-ray quality green monocrystals.

Single-crystal X-ray structure determination of **1** and **2** (Figs. 1 and 2) established that they are similar but also show significant differences.† Both structures consist of distorted nickel octahedra linked by two types of azido bridge in alternation: EO and EE. The EE and EO bridges are propagated with a mutual perpendicular alignment producing a net one-dimensional chain. The Ni–N(azido) bond distances are characteristic of bridging azido nickel(II) complexes.[3–8] The main difference between the complexes is in the EE $[Ni(\mu\text{-}N_3)_2Ni]$ fragment: in **1** the two azido bridging ligands form a plane:‡ the dihedral angle between this mean $(N_3)_2$ plane and the two nickel atoms is almost zero, the displacement of each Ni^{II} from this $(N_3)_2$ plane being 0.069 Å.§ In **2** the structure of this $[Ni(\mu\text{-}N_3)_2Ni]$ fragment is not planar. The N(3)Ni(2)N(6)N(5)N(4) atoms form a plane while N(2), N(1) and Ni(1) are clearly separated from this plane. The distance to the mean plane are: Ni(1)–plane 1.32 Å and N(1)–plane 1.62 Å. Other possible differences between **1** and **2** are less important: the Ni–N–Ni angle in the EO fragment is 98° for **1** and 99° for **2**, which are slightly lower than those (102–104°) reported for other F dinuclear or monodimensional nickel(II) complexes,[4] but much higher (*ca.* 25°) than that found for the AF triple EO bridge system.[7]

Repetitive susceptibility measurements (300–4 K) for **1** show (Fig. 3) that below 300 K the molar magnetic susceptibility increases slightly, to reach a broad maximum near 230 K, then decreases continuously down to 30 K and from 30 to 4 K there is an increasing trend.¶ The position of the maximum is the nearest to room temperature reported so far for any nickel(II) azido complex.‖ The same measurements for **2** gave different results: below 300 K the molar magnetic susceptibility increases to reach a broad maximum near 20 K and for 20 to 4 K

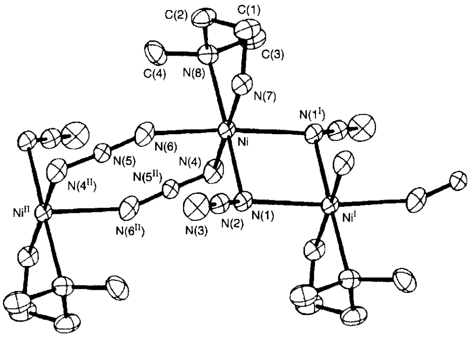

Fig. 1 Crystal structure of $[Ni(dmen)(\mu\text{-}N_3)_2]_n$ **1**. Selected bond distances (Å) and angles (°): Ni–N(1) 2.152(2), Ni–N(1^{I}) 2.114(2), Ni–N(4) 2.096(2), Ni–N(6) 2.115(2), Ni–N(7) 2.062(2), Ni–N(8) 2.171(2), N(1)–N(2) 1.201(2), N(2)–N(3) 1.151(2), N(4)–N(5^{II}) 1.183(2), N(5)–N(6) 1.164(2), Ni···Ni^{I} 3.224(1), Ni···Ni^{II} 5.180(1); Ni–N(1)–Ni^{I} 98.18(6), Ni–N(4)–N(5^{II}) 121.10(12), Ni–N(6)–N(5) 139.37(12), N(6)–N(5)–N(4^{II}) 175.3(2), Ni–N(1)–N(2) 114.54(12), N(1)–Ni–N(1^{I}) 81.82(6), N(4)–Ni–N(6) 94.75(6), N(7)–Ni–N(8) 83.77(7), N(8)–Ni–N(1^{I}) 100.42(6).

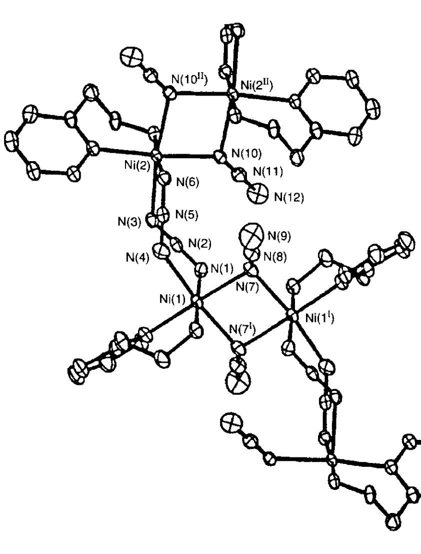

Fig. 2 Crystal structure of $[Ni(aep)(\mu\text{-}N_3)_2]_n$ **2**. Selected bond distances (Å) and angles (°): Ni(1)–N(13) 2.084(3), Ni(1)–N(7) 2.147(3), Ni(1)–N(4) 2.132(3), Ni(1)–N(1) 2.138(3), Ni(2)–N(3) 2.138(3), Ni(2)–N(6) 2.146(3), Ni(2)–N(10) 2.137(3), Ni(2)–N(15) 2.070(3), N(13)–Ni(1)–N(7) 90.66(12), N(4)–Ni(1)–N(1) 90.44(11), N(13)–Ni(1)–N(7) 89.66, N(7^{I})–Ni(1)–N(7) 81.76, Ni(1^{I})–N(7)–Ni(1) 98.24(11), Ni(2)–N(10)–N(2) 99.45(11).

there is an increasing trend.¶ To explain the magnetic behaviour of **1** and **2** we must assume two J values (an alternating chain): J_1 for the EE coordination and J_2 for the EO coordination. According to the molecular structures and literature data, J_1 must be negative[3] (AF) and J_2 must be positive[4] (F). In **1** the χ_M maximum near room temperature indicates strong global AF behaviour. The geometry of the EE part (torsion angle near zero) suggests a strong J_1 AF coupling. On the other hand, in **2** the maximum in the susceptibility curve at very low temperature indicates low AF coupling. The deviation from the planar geometry reduces the overlap between magnetic orbitals, as previously reported[3,10] in other similar nickel(II) complexes, creating small AF coupling.

The bridging angle (98–99°) in EO frames close to but lower than most[4] of the reported values (103–104°) leads us to state small J_2 F coupling. Thus a F–AF alternating $S = 1$ chain is present in these compounds, which represents the first $S = 1$ alternating systems reported in the literature. If we take into consideration the formula for an F–AF copper(II) chain ($S = 1/2$), recently reported,[11] we realize that when AF interactions are dominant, this behaviour exhibits little sensitivity to the F exchange value.

In conclusion we assume that the EE part is always AF (large or small depending on the torsion angle); in the EO part, a clear tendency is observed: when the Ni–N–Ni angle is near 103°, J is positive and close to 30 cm^{-1};[4] when the angle is 84°, J is negative (AF coupling);[7] when is 98–99° (as in the present case), J is also positive, but certainly lower than at 103°. The recent magneto-structural correlations by Thompson and co-workers for azido-bridged copper adds strength to these arguments relating to bond angles which infer that a small F coupling is operating.[12]

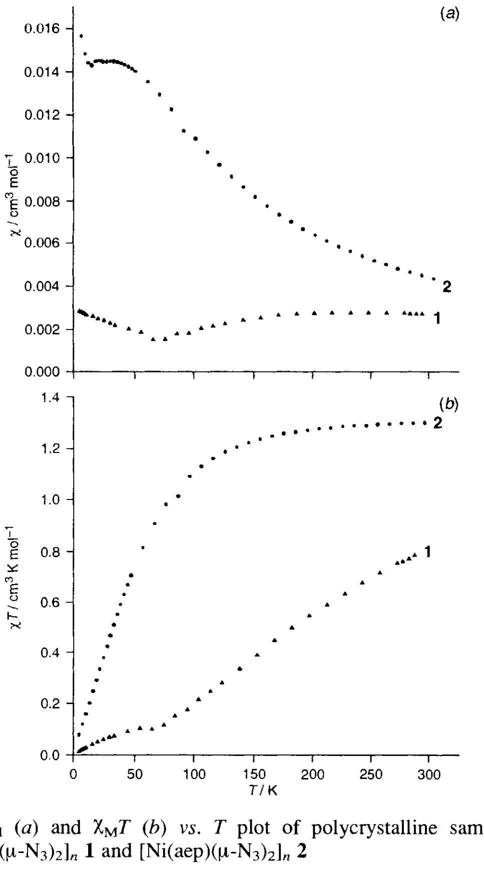

Fig. 3 χ_M (*a*) and $\chi_M T$ (*b*) *vs.* T plot of polycrystalline samples of $[Ni(dmen)(\mu\text{-}N_3)_2]_n$ **1** and $[Ni(aep)(\mu\text{-}N_3)_2]_n$ **2**

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Footnotes

† *X-Ray crystal structure analyses*: Enraf-Nonius CAD4 diffractometer. Mo-Kα radiation. $\lambda = 0.71069$ Å, graphite monochromator, 293 K. Lorentz-polarization and absorption corrections. Data collection, solution and refinement: ω–2θ, standard Patterson methods with SHELXS computer program, refinement: SHELXS93 computer program. For **1**, $C_4H_{12}N_8Ni$, $M = 230.93$, monoclinic, space group $P2_1/n$, $a = 10.569(2)$, $b = 7.331(4)$, $c = 12.907(8)$ Å, $\beta = 111.32(10)°$, $U = 931.6(5)$ Å^3. $Z = 4$, $D_c = 1.646$ g cm^{-3}, $\mu = 20.53$ cm^{-1}. Air-stable moisture-insensitive green prisms, crystal size $0.1 \times 0.1 \times 0.2$ mm. 2815 reflections were measured in the range $2.14 < \theta < 29.99°$, 2714 of which were non-equivalent by symmetry [R_{int}(on I) = 0.025]. 2324 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. The extinction coefficient was 0.016. 153 parameters. $R(F_o) = 0.033$, $R_w(|F_o|^2) = 0.089$. For **2**, $C_7H_{10}N_8Ni$, $M = 264.94$, monoclinic, space group $P2_1/c$, $a = 12.299(5)$, $b = 14.307(2)$, $c = 12.604(3)$ Å, $\beta = 106.1(10)°$, $U = 2124.1(10)$ Å^3. $Z = 4$, $D_c = 1.657$ g cm,$^{-3}$, $\mu = 18.13$ cm^{-1}. Air-stable moisture-insensitive green prisms, crystal size $0.1 \times 0.1 \times 0.2$ mm. 6170 reflections were measured in the range $1.73 < \theta < 29.99°$, 6119 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. The extinction coefficient was 0.00004; 324 parameters. $R(F_o) = 0.031$, $R_w(|F_o|^2) = 0.093$. Atomic coordinates, bond lengths and angles, and thermal parameters for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ This $(N_3)_2$ planar structure is characteristic of all polynuclear complexes with double EE azido bridges. Only in one case is this planarity not observed: the double-bridged moiety in the $-(Ni-(N_3)_2-Ni-N_3-)_n$ alternating chain, in which the two azido bridging ligands are crossed: R. Vicente, A. Escuer, J. Ribas and X. Solans, *Inorg. Chem.*, 1992, **31**, 1726.

§ In the reported dinuclear complexes with two EE azido bridges, the dihedral $Ni(N_3)_2Ni$ angle varies from 3° ($J = -114.5$ cm^{-1}) to 45.0° ($J = -4.6$ cm^{-1}). These values are gathered in ref. 3.

¶ This increasing trend is due to small canting phenomena as shown in preliminary magnetization measurements.

|| In the reported uniform one-dimensional complexes with one azido as bridging ligand the maximum in χ_M *vs.* T varies from 4 K (small antiferromagnetism) to 180 K ($J = -100$ cm^{-1}).

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