# Dalton Communications

## Unusual Magnetic and Structural One-dimensional Nickel(II) Azido Systems

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The complexes of general formula $[Ni(L)(N_3)][ClO_4]$ (L is *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane or 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene), have been characterized by X-ray crystallography; both are chains in which the nickel(II)–tetraammine fragment is bridged by one μ-azido ligand in *trans* arrangement, showing unusual magnetic and/or crystallographic properties; preliminary magnetic susceptibility data indicate strong antiferromagnetic coupling.

The single end-to-end azido bridge presents exceptional ability to generate interesting one-dimensional systems from structural and magnetic points of view. Assuming a *trans* geometry around each nickel(II) ion, azido bridges present two local Ni–N–N angles and two Ni–N distances. By combining the high coordination flexibility of this ligand with the inherent symmetry properties of a chain, we can expect at least two uniform (**I**, **II**) and two alternate (**III**, **IV**) magnetic systems.

**I** No inversion centre or $C_2$ on Ni or $N_b$ atoms: one $J$ and $g$.

$-Ni-N_a-N_b-N_c-Ni-N_a-N_b-N_c-Ni-N_a-N_b-N_c-$

**II** Two inversion centres or $C_2$ on Ni and $N_b$: one $J$ and $g$.

$-Ni-N_a-N_b-N_a-Ni-N_a-N_b-N_a-Ni-N_a-N_b-N_a-$

**III** One inversion centre or $C_2$ on $N_b$ ($N_d$): two $J$, $J'$ and one $g$.

$-Ni-N_a-N_b-N_a-Ni-N_c-N_d-N_c-Ni-N_a-N_b-N_a-$

**IV** One inversion centre or $C_2$ on Ni (Ni*): one $J$ and two $g$, $g'$.

$-Ni-N_a-N_b-N_c-Ni^*-N_c-N_b-N_a-Ni-N_a-N_b-N_c-$

The first nickel(II)–single-azido chains were recently reported by us[1,2] and correspond to type **I**. Following this research, we now present two new one-dimensional compounds: $[\{NiL^1(\mu\text{-}N_3)\}_n][ClO_4]_n$ **1** and $[\{NiL^2(\mu\text{-}N_3)\}_n][ClO_4]_n$ **2** in which $L^1$ is *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and $L^2$ is 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene. Complex **1** contains two different chains of type **I** and type **II** in the same unit cell (Fig. 1) and **2** is an unambiguously alternating chain of type **III** (Fig. 2).†

The two compounds were obtained according to the general procedure reported in ref. 1. Slow evaporation of the corresponding solutions gives the violet **1** and brown **2** as well formed crystals.

The local co-ordination of the nickel(II) ion is similar in both compounds: the nickel atom shows an octahedral arrangement, with the nickel and the four N-macrocycle atoms placed in the same plane and two azido ligands co-ordinated in *trans* fashion. Each azido group links adjacent nickel ions in end-to-end coordination, giving a one-dimensional compound. The perchlorate anions are placed in the interchain space and no hydrogen bonds are present between the chains and perchlorate anions.

In compound **1** the chains lie along the [001] direction but two different isomeric chains (A and B, Fig. 3) are present in the

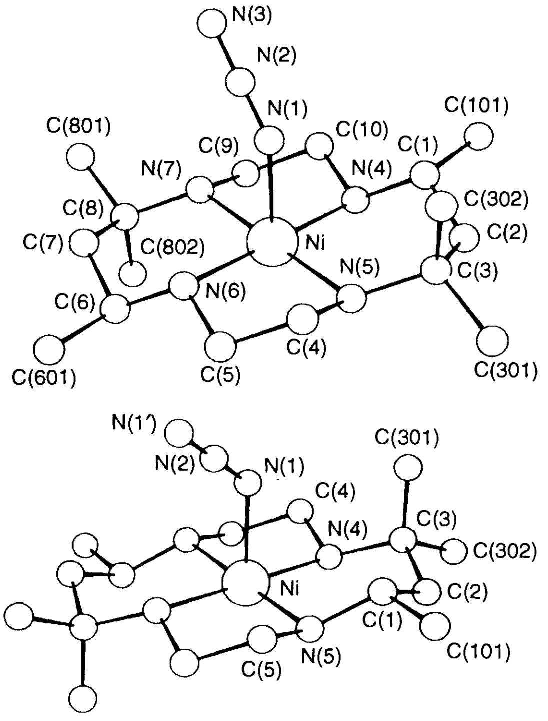

**Fig. 1** Structure of a monomeric unit of chain A (above) and B (below) in $[\{NiL^1(\mu\text{-}N_3)\}_n][ClO_4]_n$ **1** with atom labelling scheme. Main bond parameters: chain A, Ni–N(1) 2.188(5), Ni–N(3') 2.170(4) Å, Ni–N(1)–N(2) 128.5(4), Ni–N(3')–N(2') 130.7(4)°; chain B, Ni–N(1) 2.170(4) Å, Ni–N(1)–N(2) 131.4(3)°

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† Crystal data. $[\{NiL^1(\mu\text{-}N_3)\}_n][ClO_4]_n$ **1**: $M = 480.64$ (per monomeric unit), orthorhombic, space group *Pnab*, $a = 12.134(3)$, $b = 16.107(4)$, $c = 34.527(7)$ Å, $U = 6748(5)$ Å$^3$, $\lambda$(Mo-K$\alpha$) = 0.710 69 Å, $Z = 12$, $D_c = 1.419$ g cm$^{-3}$, $F(000) = 3048.0$, $\mu$(Mo-K$\alpha$) = 10.17 cm$^{-1}$, $R = 0.065$, $R' = 0.070$ for 4292 reflections with $I > 2.5\sigma(I)$ collected on an Enraf-Nonius CAD4 diffractometer, $\theta$–$2\theta$ scan, $2 \leqslant \theta \leqslant 30°$. $[\{NiL^2(\mu\text{-}N_3)\}_n][ClO_4]_n$ **2**: $M = 426.55$ (per monomeric unit), orthorhombic, space group *F2dd*, $a = 33.943(6)$, $b = 15.230(3)$, $c = 15.198(3)$ Å, $U = 7857(5)$ Å$^3$, $\lambda$(Mo-K$\alpha$) = 0.710 69 Å, $Z = 16$, $D_c = 1.442$ g cm$^{-3}$, $F(000) = 3584.0$, $\mu$(Mo-K$\alpha$) = 11.54 cm$^{-1}$, $R = 0.035$, $R' = 0.037$ for 813 reflections with $I > 2.5\sigma(I)$ collected on a Philips PW-1100 diffractometer, $\theta$–$2\theta$ scan, $2 \leqslant \theta \leqslant 30°$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

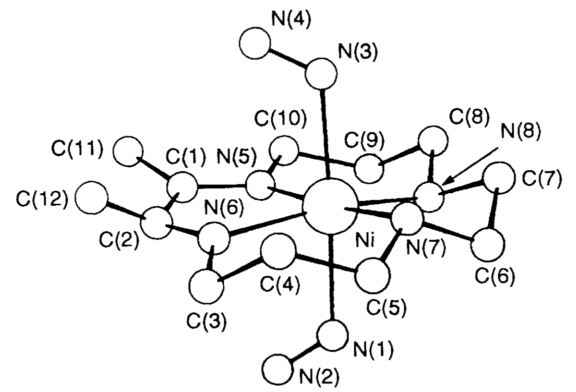

**Fig. 2** Structure of a monomeric unit in $[\{NiL^2(\mu\text{-}N_3)\}_n][ClO_4]_n$ **2** with atom labelling scheme. Main bond parameters: Ni–N(1) 2.143(11), Ni–N(3) 2.158(11) Å, Ni–N(1)–N(2) 122.9(8), Ni–N(3)–N(4) 116.5(8)°

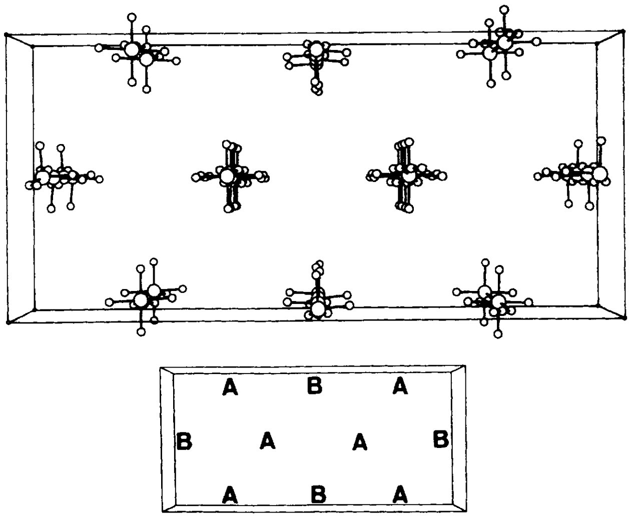

**Fig. 3** Perspective view along the [001] axis of the nickel–nitrogen skeleton of **1**. The lower diagram shows the extremely unusual coexistence of two isomeric chains, of type **I** and **II**

cell, in a 2 : 1 ratio, showing different symmetry: the A chain is of type **I** whereas the B chain is the first of type **II** to be observed. This extremely unusual structure implies that the molar susceptibility $\chi_M$ of compound **1** must be expressed as $\chi_M = (2\chi_A + \chi_B)/3$ with two independent $J_A, g_A$ and $J_B, g_B$ sets. Experimental data have been fitted to the Weng[3] equation (spin-Hamiltonian $H = -JS_iS_{i+1}$) up to near the maximum susceptibility value (40 K), and the best fitting parameters obtained are $J_A = -41.1$ and $J_B = -36.4$ cm$^{-1}$ and $R = 4.4 \times 10^{-4}$ by minimizing the function $R = \Sigma(\chi_{M\,calc} - \chi_{M\,obs})^2/\Sigma(\chi_{M\,obs})^2$ (Fig. 4).

From the crystallographic point of view, in compound **2** the chains are parallel and form a set of parallel planes in which the chain direction in each plane is perpendicular to that in the adjacent planes as is shown in Fig. 5, giving a new structural one-dimensional system.

Compound **2** corresponds to a type **III** system, showing inequivalent neighbouring azido bridges, and consequently, the magnetic behaviour of this compound should be interpreted by using two superexchange parameters $J$ and $J'$ with $J' = \alpha J$ in which the alternance parameter[4] $\alpha$ has a value between 0 and 1. The best fitting parameters obtained using the Borras[5] equation, are $J = -101.4$ cm$^{-1}$, $\alpha = 0.82$, $R = 6.2 \times 10^{-5}$, (Fig. 4). This type of compound with local spin $S > \frac{1}{2}$ are rare and, to our knowledge, this is the first magnetic study for an alternate $S = 1$ nickel(II) system.

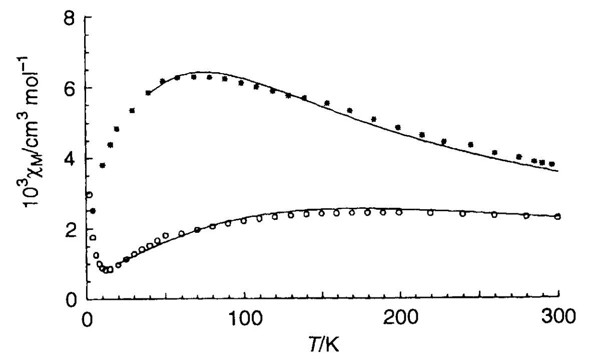

**Fig. 4** Magnetic susceptibility plots $\chi_M$ with the temperature of $[\{NiL^1(\mu\text{-}N_3)\}_n][ClO_4]_n$ (○) and $[\{NiL^2(\mu\text{-}N_3)\}_n][ClO_4]_n$ (✱). Solid lines show the best obtained fit (see text)

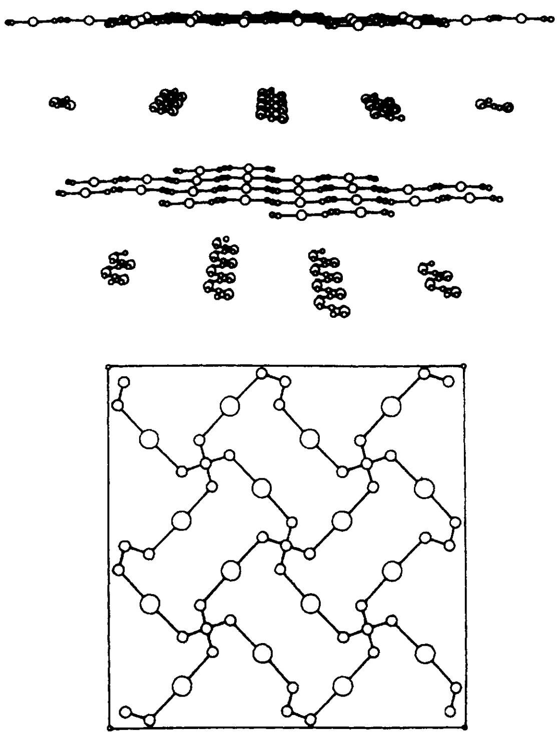

**Fig. 5** Perspective view along the [011] direction (above) and projection along the [100] axis (below) of the nickel–azido skeleton of **2**, showing the exceptional structure of perpendicular chains in neighbouring sublattices

## Acknowledgements

This work was undertaken with the financial support of Direccion General de Investigacion Cientifica y Tecnica grant PB91/0241.

## References

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*Received* 30*th July* 1993; *Communication* 3/04579J