# New Unexpected Coordination Mode of Azide acting as a Bridging Ligand between Nickel(II) Ions. Synthesis, Crystal Structure and Magnetic Properties of $[Ni(N_3)_2(2,2\text{-dimethylpropane-1,3-diamine})]_n$, and Infinite Bidimensional Polymer

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The reaction between aqueous solutions of $Ni(ClO_4)_2$, $NaN_3$ and 2,2-dimethylpropane-1,3-diamine (dmpd) gives blue crystals of the title compound which presents the $N_3^-$ in a new coordination mode (end-to-end with respect to two $Ni^{II}$ and end-on to another $Ni^{II}$), the crystal structure of which reveals a new infinite bidimensional sheet with anomalous magnetic behaviour at low temperature.

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$N_3^-$ is a versatile ligand which can coordinate two metal ions in two different ways: end-to-end and end-on, both possibilities being structurally well characterized for nickel(II)[1–5] and copper(II)[6–9] cations. There is a remarkable difference in the magnetic behaviour of the two coordination modes: in the first case the coupling is always antiferromagnetic, whereas the second is always ferromagnetic.[6] Kahn and coworkers[10] have studied exhaustively the interaction between copper(II) ions through the azide bridge from a theoretical point of view (even with *ab initio* calculations on model systems), emphasising the role of spin polarization in the magnetic exchange process, which can explain this behaviour.

In contrast with the abundant number of $Cu^{II}$ complexes studied, there were relatively few similar $Ni^{II}$ complexes which were only dinuclear. For this reason we have undertaken the synthesis and characterization of new polynuclear systems with $Ni^{II}$ and azido bridge. With this aim, we have recently reported the first 1D nickel–azido complex,[11] in which double and single azido bridges alternate in the chain; on the other hand, we have also reported the first antiferromagnetic $Ni^{II}$ chains with end-to-end azido bridges.[12,13] Here we report the synthesis, crystal structure and preliminary magnetic properties of the first 2D polynuclear $Ni^{II}$ complex, in which the bridging azido groups have a new and unexpected coordination mode.

To an aqueous solution of $Ni(ClO_4)_2$ (1.89 g, 1 mmol) and dmpd (0.51 g, 1 mmol), an aqueous solution of $NaN_3$ (0.65 g,

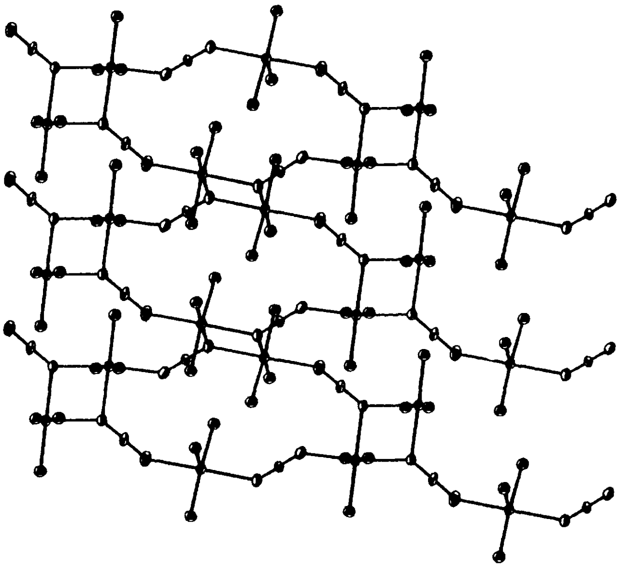

Fig. 1 View of the one layer in $[Ni(N_3)_2(dmpd)]_n$

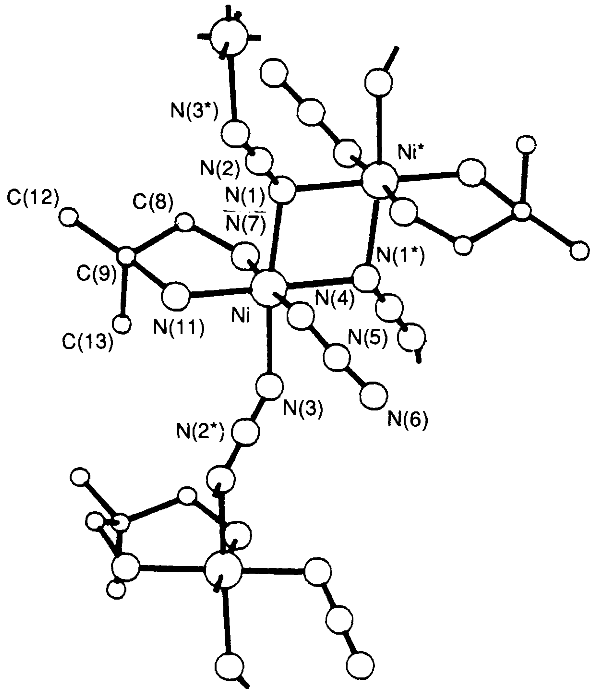

**Fig. 2** The chemical unit of $[Ni(N_3)_2(dmpd)]_n$. Selected bond distances (Å) and angles (°): Ni-N(1) 2.177(4), Ni-N(1*) 2.209(4), Ni-N(3) 2.188(5), Ni-N(4) 2.062(5), Ni-N(7) 2.053(5), Ni-N(11) 2.052(5), N(2)-N(1) 1.181(6), N(2)-N(3*) 1.154(6), N(5)-N(4) 1.191(7), N(6)-N(5) 1.165(7); N(1)-Ni-N(1*) 81.9(2), Ni-N(1)-Ni* 98.1(4), Ni-N(1)-N(2) 124.2(4), Ni-N(3)-N(2*) 138.8(4)

2 mmol) was added with constant stirring. The solution was left undisturbed for several days and good blue crystals were collected, filtered and washed with cold water. X-Ray crystallographic analysis of this material revealed an infinite 2D $[Ni(N_3)_2(dmpd)]$ neutral framework.†

This infinite layer is represented in Fig. 1. In this sheet each $Ni^{II}$ is octahedrally coordinated by the two nitrogen atoms of the amine ligand, one $N_3^-$ terminal ligand and three other bridging $N_3^-$ shared by three $Ni^{II}$, giving a total stoichiometry of $[Ni(N_3)(N_3)_{3/3}(dmpd)]$. As can be seen in Fig. 2, each bridging azido ligand coordinates two $Ni^{II}$ ions in an end-on mode but, at the same time, this same azido ligand coordinates the neighbouring $Ni^{II}$ ion in an end-to-end mode. Consequently, in each layer there are $Ni_2(N_3)_2$ units linked together by the bridging azides. Four of these units create a type of metallomacrocycle which is repeated throughout the layer (Fig. 1). This is the first time this type of coordination has been reported in $Ni^{II}$ complexes which opens a new approach in magneto-structural correlations, since, according to the Kahn theory,[10] there are two $Ni^{II}$ ions coupled in a ferromagnetic way (end-on $N_3^-$) and two pairs of $Ni^{II}$ ions coupled in antiferromagnetic way (end-to-end $N_3^-$).

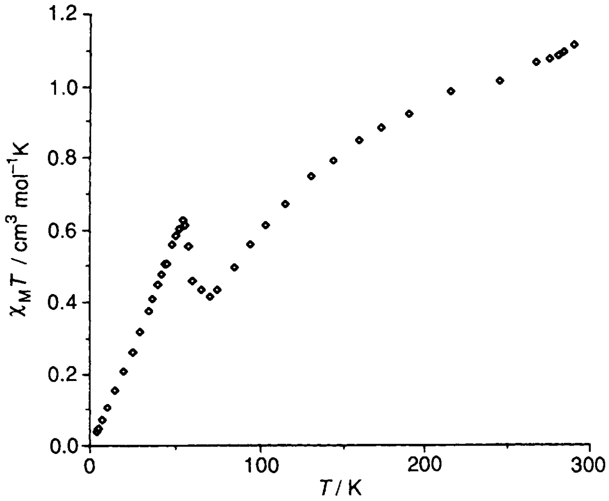

**Fig. 3** Plot of the $\chi_M T$ *vs.* $T$ for $[Ni(N_3)_2(dmpd)]_n$

Preliminary, but repetitive, susceptibility measurements are anomalous (Fig. 3) because from room temperature down to 60 K there is a clear decrease in $\chi_M T$ values, indicating strong antiferromagnetic coupling, but at *ca.* 60 K there is an abrupt change from 0.4 to 0.6 cm$^3$ mol$^{-1}$ K which may indicate a rearrangement in the layers giving a long-order cooperative (canting) phenomenon.[14] Further studies are necessary to clarify this unexpected behaviour.

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† *Crystal data* for $[Ni(N_3)_2(dmpd)]$: $C_5H_{14}N_8Ni$. $M_r$ = 244.93, monoclinic, space group $P2_1/c$, $a$ = 12.649(3), $b$ = 7.031(2), $c$ = 12.114(3), $\beta$ = 112.39(2)°, $V$ = 996.1(8) Å$^3$, $D_c$ = 1.633 mg mm$^{-3}$, $Z$ = 4, $F(000)$ = 512.0, $\lambda$Mo-K$\alpha$ = 0.71069 Å, $\mu$(Mo-K$\alpha$) = 19.21 cm$^{-1}$, $T$ = 298 K. Crystal dimensions: 0.1 × 0.1 × 0.2 mm. Philips PW-1100 diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($8 < \theta < 12°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo-K$\alpha$ radiation using the $\omega$-scan technique. 1533 reflections were measured in the range $2 < \theta < 25$. 1352 of which were assumed as observed applying the condition $I > 2.5\sigma(I)$. Lorentz-polarization but not absorption corrections were made. The structure was solved by Patterson synthesis, using SHELXS computer program and refined by full-matrix least-squares method, with the SHELX76 computer program. The function minimized was $\Sigma\, w\, ||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.057|F_o|^2]^{-1}$. $f$, $f'$ and $f''$ were taken from international tables of X-ray crystallography. The position of all hydrogen atoms was located from a difference synthesis and refined with an overall isotropic temperature factor $R$ = 0.059 ($R_w$ = 0.059). Number of defined parameters was 170. Max. shift/esd = 0.1. Max. and min. peaks in final difference synthesis was 0.4 and −0.4 e Å$^{-3}$, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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