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Magnetic properties and structure of a new one-dimensional azido-bridged nickel(II) coordination polymer

Xiao-li Yu [a], Wan-sheng You [a,*], Xin Guo [a], Lan-cui Zhang [a], Yan Xu [a], Zhen-gang Sun [a], Rodolphe Clérac [b,*]

[a] *Institute of Chemistry for Functionalized Materials, Faculty of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, Liaoning 116029, People's Republic of China*

[b] *Université Bordeaux 1; CNRS, Centre de Recherche Paul Pascal-UPR8641, 115 avenue du Dr. A. Schweitzer, 33600 Pessac, France*

A new one-dimensional nickel(II) coordination polymer with azido-bridge, $[Ni(dpa)(N_3)_2] \cdot H_2O$ **1** (where dpa is the 2,2′-dipyridylamine ligand) has been synthesized and crystal structure was determined by single-crystal X-ray diffraction. Complex **1** exhibits a zigzag chain structural arrangement, and the hexa-coordinated Ni(II) ion exhibits a distorted octahedral coordination sphere. The chains topologies are built via three EO and one EE azido bridges. The study of the magnetic properties reveals dominating antiferromagnetic interactions between Ni(II) ions through the EE bridges.

Keywords: Coordination polymer; Magnetic properties; Azide; Ni(II) complex

Investigation of the structural and magnetic properties of polynuclear molecules and coordination polymers is a fascinating subject, for understanding the magneto-structural correlations in molecular systems [1,2]. In recent years, low-dimensional polymers (one or two-dimensional) have been synthesized and characterized to develop new functional molecule-based materials [3,4].

The azide anion is an excellent ligand to build low-dimensional coordination polymers [5–8]. It is so versatile that μ-1, 1 (end-on, EO), μ-1, 3 (end-to-end, EE), μ-1, 1, 3 and other modes are allowed [9,23,10]. The simultaneous presence of more than one of these coordination modes in the same complex is not rare, increasing the connectivity possibilities and the possible final structural architectures [11]. The most important aspect of these azido-bridged complexes is the variety of the magnetic exchange interaction that they can mediate. The magnetic exchange between transition metal ions through an azido bridge can be ferro- (F) or antiferromagnetic (AF), depending on the bridging mode and bonding parameters [12–14]. The versatility of the azide anion in term of structural motifs and magnetic interactions generates a variety of magnetic behaviors, which may be difficult to achieve with other bridging ligands [15]. Examples of Ni(II)/azido based systems gradually appear over the past years. Molecular [16–18], one- [17b, 19–21], two- [22] and three- [23] dimensional Ni(II)/azido compounds have been discovered. Quite generally, the bridging azido ligand adopting a single EE mode [16,17,19,20] leads to antiferromagnetic interaction between Ni(II) centers. On the other hand, single or double EO mode [18, 21–23] mediates ferromagnetic interactions.

In this paper, we report the synthesis [24] and structure of a new 1D azido-bridged Ni(II) complex with 2,2′-dipyridylamine (dpa), $[Ni(dpa)(N_3)_2] \cdot H_2O$ **1**. The complex structure was characterized by IR spectroscopic techniques, single-crystal X-ray diffraction [25] and magnetic

* Corresponding authors. Tel.: +86 41182156658; fax: +86 41182156858 (W.-S. You).

E-mail address: wsyou@lnnu.edu.cn (W.-s. You).

measurements [26]. This complex consists of Ni(II) ions connected by alternating three EO and one EE azido bridges inducing dominant antiferromagnetic interactions.

The IR spectra of complex **1** exhibits characteristic $\nu_{as}(N_3)$ bands in the 2000–2100 cm^{-1} region. The occurrence of two sharp and strong bands, observed at 2078.9 and 2051.3 cm^{-1}, indicates the presence of two different azido groups [27]. The band of higher frequency is attributable to the EO bridge, and other is due to the EE bridge [21]. Furthermore, the IR spectra of complex **1** features the bands characteristic of the 2,2′-dipyridylamine molecule, seen in the stretching and bending modes of the C–C and C–N bonds in the ranges between ca. 1641–1432 and 1235–770 cm^{-1} respectively.

As shown in Fig. 1, $[Ni(dpa)(N_3)_2] \cdot H_2O$ includes a one-dimensional zig-zag chain consisted of Ni(II) linked alternatively by three EO (end-on) and one EE (end-to-end) bridges. There is only one crystallographically independent Ni(II) ion center. The Ni(II) ion shows distorted octahedral arrangement with two nitrogen atoms from a dpa ligand and four nitrogen atoms from three EO azido bridges and one EE azido bridge. The *cis* N–Ni–N angles range from 78.46(16) to 97.08(14)° and the Ni–N(dpa) distances are 2.052(4) Å and 2.057(4) Å for N1 and N3. The neighboring nickel ions Ni1 and Ni1A are bridged by three EO azido bridges. To the best of our knowledge, few complexes with the three EO azido bridges have been reported so far [28–30]. In the structure, all three N_3^- links are quasi-linear [N4–N5–N6, N7–N8–N9, N10–N11–N12; 179.0(8)°, 177.5(7)°, 179.4(8)°]. The three bridging angles are Ni1–N4–Ni1A, 85.32(19)°, Ni1–N7–Ni1A, 85.32(19)° and Ni1–N10–Ni1A, 86.6(2)°. The three bridging Ni–N(azido) distances are in the range of 2.131(4)–2.172(4) Å. The Ni–Ni separation through the EO bridge is 2.9232(13) Å. The neighboring Ni(II) ions are bridged by one EE azido-bridge with the distance of 6.087 Å. The N13–N14–N13B angle is 180.0(4)°, and the length of Ni1–N13 is 2.109(3) Å. As shown in Fig. 2, the zig-zag chains project along the *b* axis. The dpa molecules in the chains are interpenetrated each other for weak π–π interactions, forming a layer along the *a* axis. The shortest distance between Ni(II) ions in the layer is 8.319 Å.

The susceptibility of complex **1** was measured on a polycrystalline sample from 1.8 to 300 K. The χT vs. T data normalized per one Ni(II) ion are shown in Fig. 3 at 0.1 T. At 300 K, the χT product is 1.1 cm^3 K/mol. This value is in agreement with the presence of one Ni(II) metal ions ($S = 1$, $g = 2$, $C = 1$ cm^3 K/mol). Decreasing the temperature, the χT product at 0.1 T continuously decreases to reach 0.02 cm^3 K/mol at 1.8 K indicating dominant antiferromagnetic interactions between Ni(II) ions and the presence of a singlet ground state.

To model the high temperature behavior of the magnetic susceptibility, a first approach using a simple dinuclear $S = 1$ Heisenberg model considering only the Ni^{II}–Ni^{II}

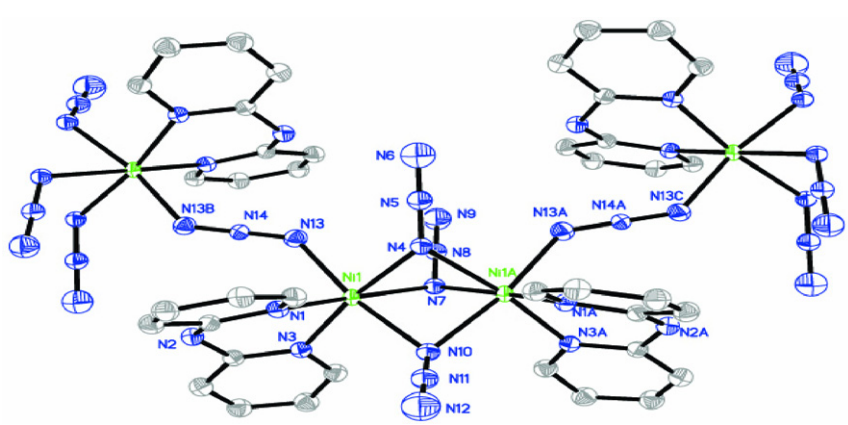

Fig. 1. ORTEP drawing of the chain structure for complex **1** at 30% probability. The H atoms are omitted for the sake of clarity.

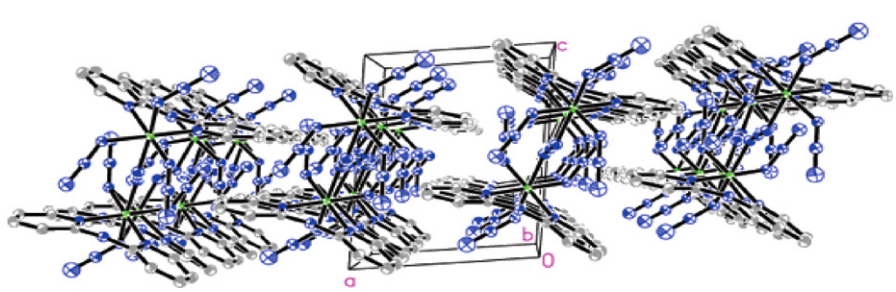

Fig. 2. View of crystal packing of complex **1** along *b*-axis.

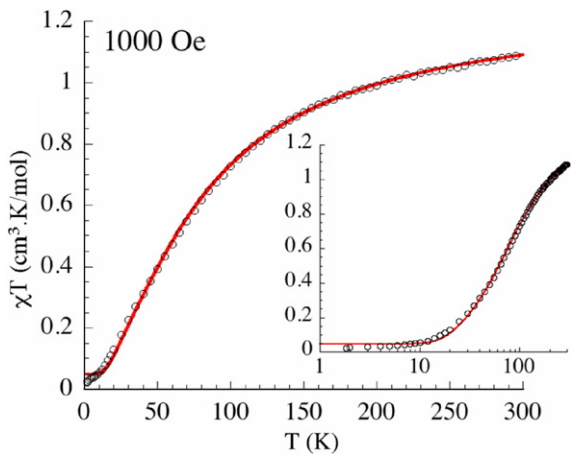

Fig. 3. χT plot for complex **1**. Measurements performed under 1000 Oe between 1.8 and 300 K. The solid line shows the fit of the χT experimental data to the model $S = 1$; inset: Semi-log view of the χT vs. T plot displayed in the main figure.

interactions (J_1) through the EE azido bridge. Indeed, this interaction is likely antiferromagnetic and much stronger than the one mediated by the triple EO azido bridge that is usually ferromagnetic [5,30]. It should be additionally mentioned that calculations performed on double EO bridges between Ni(II) (with Ni–N–Ni angles ranging from 80° to 110°) have revealed that this type of interaction is always of ferromagnetic nature [31]. Therefore, the experimental observation of dominating antiferromagnetic interaction (Fig. 3) strongly suggests that the Ni^{II}–Ni^{II} interaction through the single EE azido bridge clearly dominate the one mediated by the triple EO azido link. In keeping with this structural motif, the Heisenberg spin Hamiltonian can be written as follows: $H = -2J_1 S_{Ni^{II}A} S_{Ni^{II}B}$, where J_1 is the exchange interactions within the dinuclear Ni(II) complex. The application of the van Vleck equation [32] to the Kambe's vector coupling scheme [33], allows a determination of the low field analytical expression of the magnetic susceptibility given in the reference [34]. As shown by Fig. 3, this model was able to reproduce very well the experimental data from 300 K to 1.8 K when an additional paramagnetic contribution is introduced in the model as a Curie component. The best set of parameters found are: $J_1/k_B = -33.4(2)$ K, $g = 2.22(1)$ and $C_{imp} = 0.048$ cm^3 K/mol (4.8% of an $S = 1$ spin). The value of the interaction through the EE azido bridge is in good agreement with previous reports [5]. It is important to mention that the introduction of an additional interaction in the model between Ni(II) through the triple EO azido bridge (i.e. alternating $S = 1$ chain model) did not improve the quality of the fit and leads to unphysical errors on the interaction parameters.

In conclusion, complex **1** possesses an infinite chain motif along the *b*-axis. The azido ions present rare concomitant single EE and triple EO modes between metal ions. Magnetic measurement of **1** indicates the existence of dominating antiferromagnetic interactions between nickel ions through the EE bridge.

Acknowledgements

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Appendix A. Supplementary materials

CCDC 623055 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.08.010.

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[24] A methanol solution (5 ml) containing NaN_3(0.1361 g, 2.09 mmol) and dpa (0.1693 g, 1.00 mmol) were added into 10 ml of water. One millimole of $NiNO_3 \cdot 6H_2O$ (in 5 ml methanol) was added and layered on the top of the first N_3^-/dpa^- solution. After standing for several days, the resulting solution gave green crystal without any other impurity and suitable for X-ray analysis. Yield: ca. 80%. Calcd (found) for $C_{10}H_{11}NiN_9O$ (Fw: 331.99): C, 36.18(36.22); H, 3.34(3.39); N, 37.98(37.94); Ni, 17.68(17.64%).
[25] Crystal structure analysis: The data were collected at 293 K using a SMART APEX II-CCD single crystal X-ray diffractometer (graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXL-97 software. Cell parameters were obtained by the global refinement of the positions of all collected reflections. Empirical absorption correction was applied. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were added theoretically. $C_{10}H_{11}N_9NiO$ (1): crystal size: $0.27 \times 0.18 \times 0.07$ mm^3, monoclinic $P2(1)/m$, a = 8.139(2) Å, b = 14.940(4) Å, c = 10.722(3) Å, $\alpha = 90°$, $\beta = 97.975(4)°$, $\gamma = 90°$, $Z = 4$, $D_{calcd} = 1.697$ Mg/m^3, $R_{int} = 0.0381$. Based on these data, final $R_1 = 0.0619$, w$R_2 = 0.1553$, $F^2 = 1.037$.
[26] The magnetic susceptibility measurements were carried out on polycrystalline samples using a Quantum Design SQUID magnetometer MPMS-XL in the temperature range 1.8–300 K and magnetic fields of −7 to 7 T. Measurements were performed on a polycrystalline sample of 20.72 mg. The magnetic data were corrected for the sample holder. The magnetization as a function of the field at 100 K and χT vs. T data at 1T indicate the absence of ferromagnetic impurities in sample.
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