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Synthesis, Crystal Structure, and Properties of an Azido-Bridged 1D Nickel Hexaazamacrocyclic Complex[1]

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Abstract—A new complex of $[Ni(C_{15}H_{32}N_6)(N_3)]ClO_4 \cdot H_2O$ was obtained by the reaction of macrocyclic precursor complex $[Ni(C_{15}H_{32}N_6)]ClO_4$ with sodium azide in water solution, and characterized by EA, IR, PXRD and single-crystal X-ray diffraction (CIF file CCDC no. 930570). Single X-ray diffraction analysis reveals that the central nickel(II) ion displays six-coordinate octahedral coordination geometry by coordination with four nitrogen atoms of macrocyclic ligand and two nitrogen atoms of N_3^- ligand. In this complex, each $\mu_{1,3}$-N_3^- binds two nickel(II) ions, resulting a 1D chain. Magnetic measurements have been performed on the complex, showing strong antiferromagnetic coupling interaction within the metal center.

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INTRODUCTION

Macrocyclic complexes of transition metal ions, which used as building blocks to construct macrocyclic polymers with bridging ligands, have been the subject of growing interest due to their intriguing network topologies and potential applications in magnetism, luminescence, catalysis, etc. [1–5]. To date, most of these complexes contain tetraaza macrocyclic ligands, whereas the studies of macrocyclic complexes containing six nitrogen atoms are relatively rare [6]. Recently, we have been interested in employing those hexaazamacrocyclic complexes as building blocks to construct macrocyclic coordinated polymers [7–9]. To extend the framework, we selected carboxylic acid organic ligand and Prussian Blue analogues as preferred ligands [10–12]. By contrast, the examples of azido-bridged azamacrocyclic complexes are limited. On the other hand, the azido group is a versatile bridging ligand, which can coordinate two nickel ions in various fashions [13]. Consequently, in this paper, we present an azido-bridged 1D nickel hexaazamacrocyclic complex $[Ni(C_{15}H_{32}N_6)(N_3)]ClO_4 \cdot H_2O$ (**I**), which shows strong antiferromagnetic coupling interaction within the metal center.

EXPERIMENTAL

Material and methods. All reagents were purchased commercially and used without further purification. The precursor complex $[Ni(C_{15}H_{32}N_6)]ClO_4$ was prepared as described [6]. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Vario ELIII CHNS/O elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet Avatar 370 Fourier Transform Infrared spectrometer. X-ray powder diffraction (XRPD) patterns were recorded on a Shimadzu D/MAX-3BX diffractometer with CuK_α radiation.

Synthesis of complex I. A H_2O solution (10 mL) of $[Ni(C_{15}H_{32}N_6)]ClO_4$ (0.150 g, 0.3 mmol) was added to a H_2O solution (10 mL) of NaN_3 (0.019 g, 0.3 mmol). The resulting solution was filtrated and kept at ambient temperature for a week to give purple needle-like crystals suitable for the X-ray structural analysis. The yield was 80% based on NaN_3.

For $C_{15}H_{34}N_9O_5ClNi$			
anal. calcd., %:	C, 35.13;	H, 6.29;	N, 24.59.
Found, %:	C, 35.00;	H, 6.66;	N, 24.47.

IR (KBr; ν, cm^{-1}): 3420 s, 2058 s (N_3^-), 1640 s, 1462 m, 1265 m, 1114 s, 621 m.

Caution! The metal macrocyclic ligands containing perchlorate anions maybe potentially explosive, and should be carefully handled.

X-ray structure determination. Single crystal X-ray diffraction data for the complex was collected on a Bruker Apex CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 293 K. Absorption correction was applied using a multi-scan technique with the Bruker SADABS package [14]. The structure was solved by Direct Methods and SHELXL-97 [15] and refined by full-matrix least-squares on F^2 [16]. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at

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[1] The article is published in the original.

Table 1. Crystallographic data and structural refinement details of complex **I**

Parameter	Value
M	512.66
Crystal size, mm	0.30 × 0.29 × 0.28
Crystal system	Monoclinic
Space group	$P2_1$
a, Å	6.415(3)
b, Å	14.456(6)
c, Å	11.653(5)
β, deg	90.556(6)
V, Å^3	1080.6(8)
Z	2
ρ_{calcd}, g cm^{-3}	1.576
μ(MoK_α), mm^{-1}	1.070
F(000)	540
Limiting indices	$-8 \le h \le 7$, $18 \le k \le 9$, $14 \le l \le 14$
Reflections measured	6204
Reflections unique	3100
R_{int}	0.0664
$R(F)/wR(F^2)$* (all data)	0.0675/0.1540
GOOF (F^2)*	0.997
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	1.025 and –0.948
Flack	0.55(4)

* GOOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obc} - n_{param})]^{1/2}$; $R_1 = \|F_o| - F_c\|/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

1.2 times U_{eq} of the parent atoms (1.5 times for methyl groups). A solvent water molecule was observed in the crystal structure, however, its hydrogen atoms could not be localized. The compound crystallized in the non-centrosymmetric space group $P2_1$. However, the value of the Flack parameter indicated a racemic twin, and hence the refinement was proceeded with the TWIN and BASF instructions in SHELXL, converging to a final Flack parameter of 0.55(4). Consequently, the absolute configuration of the asymmetric unit was established (N(1S), N(2R), N(3R), N(4S) and C(8R)), but also the 'inverse' structure is almost equally present in the crystal. Details of the crystal parameters, data collection and refinement are summarized in Table 1. Selected bond lengths and bond angles are collected in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 930570; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The molecular structure of the complex is presented in Fig. 1 together with an atomic labeling scheme. The crystal structure of complex consists of a independent $[Ni(C_{15}H_{32}N_6)]^{2+}$ unit, one N_3^-, ClO_4^- ion and one water molecule. The framework of $[Ni(C_{15}H_{32}N_6)]^{2+}$ was firstly reported by S. Sujatha et al. in 2009 and no any other papers report on this cation involved into the coordination polymer. X-ray structural analysis shows that the nickel atom is coordinated by two secondary and two tertiary amines of the macrocycle ligand and two nitrogen atoms of the azido ligands. The Ni–N bond distances in NiN_4 plane range from 2.046 to 2.115 Å, and the average of the four distances is 2.079 Å, which is comparable to those of other Ni(II) complexes of tetraaza macrocyclic ligands [6–13]. The NNiN angles (93.1° and 94.0°) of the six-membered chelate ring are much larger than the NNiN angles (86.2° and 86.7°) of the five-membered chelate ring, as is usual [7]. The axial Ni–N(azido) distances of 2.212 Å and 2.188 Å are longer than the equatorial Ni–N bonds, which indicate the nickel(II) ion adopts an axially elongated octahedral geometry. The axial Ni–N(7) bond and Ni–N(9) bond are not perfectly perpendicular to the NiN_4 plane with the NNiN angles from 86.4° to 94.1°. In this complex, each N_3^- binds two nickel (II) ions in end-to-end fashion ($\mu_{1,3}$) into a 1D chain along the [100] direction (Fig. 2). Moreover, these chains are cross-linked along xy direction by the hydrogen bonds to give rise to 3D architecture, which further stabilize this supramolecular network (Table 3). In our previous work [7], we reported a mononuclear complex *trans*-$[Ni(Hhto)(N_3)_2]$ (Hto = 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane). In the complex *trans*-$[Ni(hto)(N_3)_2]$, azido acts as a monodendate ligand, exhibiting a 0D complex. Hence, with a slight difference of macrocyclic ligand, two complexs possess entirely different structures. The comparison of them demonstrates that the different ligand plays a crucial role in the formation of their final architectures.

The simulated and experimental PXRD patterns of complex were obtained at room temperature. Their peak positions are in good consistency with each other, indicating the phase purity of the solid. The differences in intensity may be due to the preferred orientation of the powder samples. A single very strong band at 2058 cm^{-1} in complex was assigned to (N_3^-) stretching of the coordinated azido ligand at the nickel center.

The measurements on temperature dependence of the magnetic susceptibility at 2–300 K in a field of

Table 2. Selected bondl engths and angles for complex **I**

Bond	*d*, Å	Bond	*d*, Å
N(4)–Ni(1)	2.046(6)	N(2)–Ni(1)	2.115(6)
N(1)–Ni(1)	2.099(8)	N(7)–Ni(1)	2.212(6)
N(3)–Ni(1)	2.055(9)	Ni(1)–N(9)	2.188(6)
Angle	ω, deg	Angle	ω, deg
N(4)Ni(1)N(3)	86.2(4)	N(3)Ni(1)N(9)	89.8(3)
N(4)Ni(1)N(1)	93.1(3)	N(1)Ni(1)N(9)	91.2(3)
N(3)Ni(1)N(1)	178.8(3)	N(2)Ni(1)N(9)	89.9(2)
N(4)Ni(1)N(2)	179.6(4)	N(4)Ni(1)N(7)	86.4(3)
N(3)Ni(1)N(2)	94.0(4)	N(3)Ni(1)N(7)	86.9(3)
N(1)Ni(1)N(2)	86.7(4)	N(1)Ni(1)N(7)	92.1(3)
N(4)Ni(1)N(9)	89.7(3)	N(2)Ni(1)N(7)	94.1(2)
N(9)Ni(1)N(7)	175.0(3)		

Table 3. Geometric parameters of hydrogen bonds for complex **I***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(4)–H(3N)···O(3)[a]	0.95(11)	2.40(11)	3.342(10)	171(8)
N(3)–H(4N)···N(9)[b]	0.81(6)	2.56(7)	2.997(13)	115(6)
N(3)–H(4N)···O(1*w*)[c]	0.81(6)	2.65(7)	3.160(13)	123(6)

* Symmetry codes: [a] $-x + 1, y + 1/2, -z + 1$; [b] $x + 1, y, z$; [c] $-x + 2, y - 1/2, -z + 1$.

2 kOe were investigated on a Quantum Design SQUID susceptometer. They are shown in the form of $\chi_m T$ versus T curve, and the χ_m^{-1} versus T curve (Fig. 3). The observed $\chi_m T$ value per Ni unit at 300 K is 0.96 emu K mol^{-1} close to the spin-only value (1.0 emu K mol^{-1}) for one magnetically isolated Ni^{2+} ions with $S = 1$, $g = 2.0$ [1]. As temperature decreases, the $\chi_m T$ product decreases gradually to nearly zero, 0.022 emu K mol^{-1} at 2 K. These features are indicative of an overall antiferromagnetic behavior, alike most Ni complexes containing azido linkers with EE bridging modes. Fitting χ_m^{-1} versus T to the Curie–Weiss law ($\chi_m = C/(T - \theta)$) gives a Curie constant $C =$ 0.91 emu K mol^{-1} and $\theta = -29.02$ K at the range of 50 to 300 K ($R = 0.99$). This behavior proves the presence of strong antiferromagnetic coupling interaction within the metal center in this complex.

According the isotropic exchange Hamiltonian $H = -2JS_{\mathrm{Ni1}}S_{\mathrm{Ni1\#}}$, where J is the coupling interaction within the nickel(II) ions via the N_3^- ligand, the magnetic susceptibility can be expressed by equation $\chi_m = (N\beta^2g^2/KT)(2 + A\alpha + B\alpha^2)/(3 + C\alpha + D\alpha^2 + E\alpha^3)$ [13, 17], where N is the Avogadro's number, β is Bohr magneton, g is the Lande gvalue, J is the exchange integral, and K is the Bohzmann's constant, in which $A = 0.0194$, $B = 0.777$, $C = 4.346$, $D = 3.232$, and $E = 5.834$, and $\alpha = /J/KT$. A good agreement with the experimental data in the range 50–200 K has been obtained from the following parameters: $J = -20.01$ cm^{-1}, $g = 2.07$. This result shows the presence

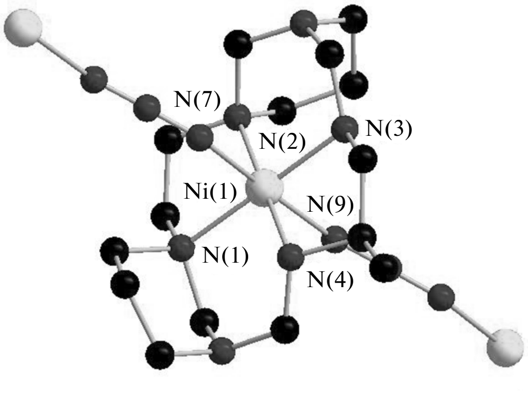

Fig. 1. Diagram of molecular (water molecule and ClO_4^- ions are omitted for clarity).

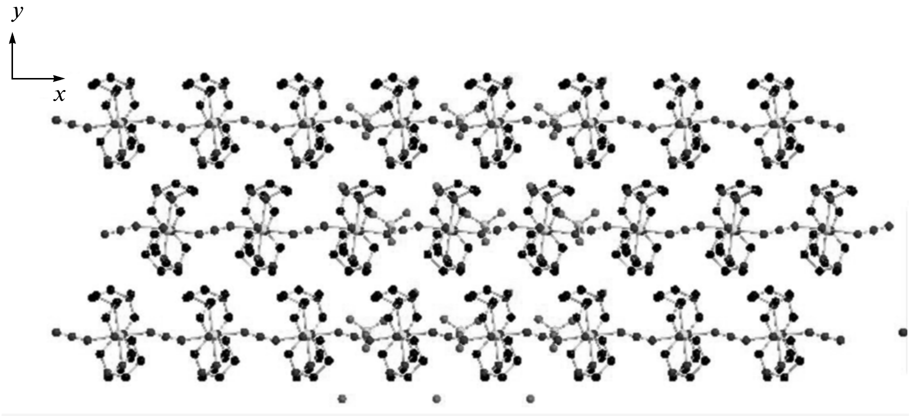

Fig. 2. 1D chains in complex **I**.

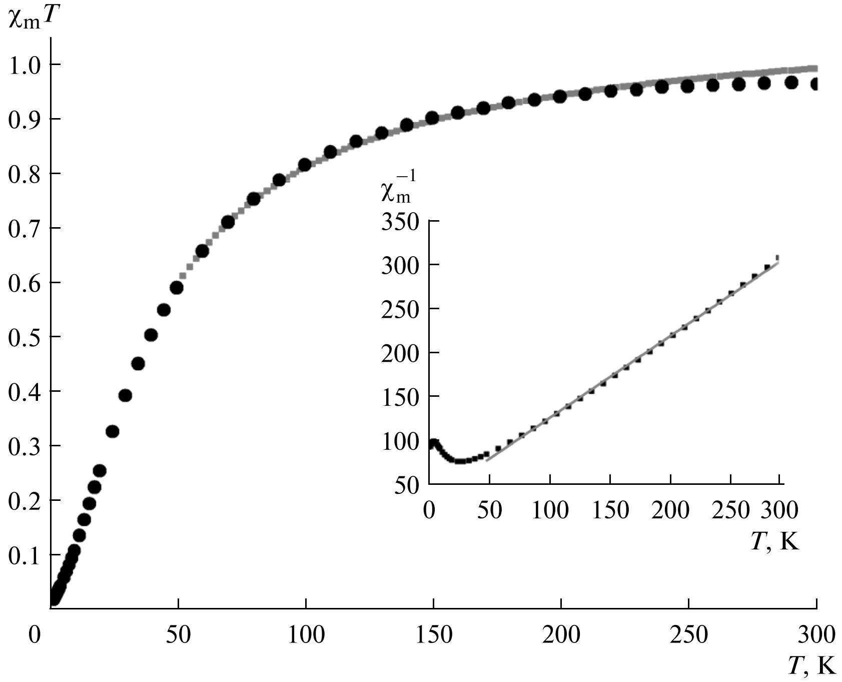

Fig. 3. Temperature dependence of $\chi_m T$ and χ_m^{-1} for compound **I** and the dotted line the fit to the Curie–Weiss law; the solid line represents the theoretical values and the dotted line the fitting.

of strong antiferromagnetic interaction between metal centers.

In conclusion, we have obtained a new complex of $[Ni(C_{15}H_{32}N_6)(N_3)]ClO_4 \cdot H_2O$ by the reaction of macrocyclic precursor complex $[Ni(C_{15}H_{32}N_6)]ClO_4$ with sodium nitride in water solution, and the crystal structure was determined. The combination of our previous work demonstrates that the different macrocyclic ligand play a crucial role in the formation of their final architectures. Variable-temperature magnetic susceptibility indicates there is a strong antiferromagnetic interaction exist in this Ni(II) complex.

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REFERENCES

1. El Fallah, M.S., Escuer, A., Vicente, R., et al., *Inorg. Chim. Acta*, 2003, vol. 344, p. 133.
2. Choi, K.Y., Chun, K.M., Lee, K.C., and Kim, J., *Polyhedron*, 2002, vol. 21, p. 1913.

3. Wagner, F., Mocella, M.T., D'Aniello, M.J., Jr., et al., *J. Am. Chem. Soc.,* 1974, vol. 96, p. 2625.
4. Morohashi, N., Narumi, F., Nobuhiko, H., et al., *Chem. Rev.*, 2006, vol. 106, p. 5291.
5. Ni, Z.H., Kou, H.Z., Zhao, H.Y., et al., *Inorg. Chem.*, 2005, vol. 44, p. 2050.
6. Sujatha, S., Balasubramanian, S., and Varghese, B., *Polyhedron*, 2009, vol. 28, p. 3723.
7. Tao, B., Jiang, X., Li, X.W., et al., *J. Mol. Struct.*, 2011, vol. 1003, p. 111.
8. Jiang, X., Tao, B., Xia, H., and Liao, G.Y., *CrystEngComm*, 2012, vol. 14, p. 3271.
9. Tao, B., Jiang, X., Xia, H., and Cheng, H.F., *J. Mol. Struct.,* 2012, vol. 1011, p. 15.
10. Kou, H.Z., Zhou, B.C., Si, S.F., and Wang, R.J., *Eur. J. Inorg. Chem.*, 2004, vol. 2004, p. 401.
11. Meng, X.R., Zhong, D.C., Jiang, L., et al., *Cryst. Growth Des.,* 2011, vol. 11, p. 2020.
12. Park, H.J. and Suh, M.P., *CrystEngComm*, 2012, vol. 14, p. 2748.
13. Escuer, A., Vicente, R., Ribas, J., et al., *Inorg. Chem.*, 1993, vol. 32, p. 1033.
14. *SMART and SADABS*, Madison (WI, USA): Bruker AXS Inc., 2001.
15. Sheldrick, G.M., *SHELXL-97, Program for the Solution of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
16. Sheldrick, G.M., *SHELXL-97, Program for the Refinement of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
17. Kahn, O., *Molecular Magnetism*, New York: VCH, 1993.