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Self-assembly of 1D coordination polymers from nickel(II) tetraaza macrocycle and carboxylate ligands

Ki-Young Choi *, Ki-Jeong Kim

Department of Chemistry Education, Kongju National University, Kongju 314-701, Republic of Korea

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Abstract

Reactions of $[Ni(L)]Cl_2 \cdot 2H_2O$ (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$]docosane) with isophthalic acid (H_2isoph) and 1,3,5-cyclohexanetricarboxylic acid (H_3chtc) yield the 1D nickel(II) complexes $\{[Ni(L)(isoph)] \cdot 3H_2O\}_n$ (**1**) and $\{[Ni(L)(H\text{-}chtc)] \cdot H_2O\}_n$ (**2**). The structures were characterized by X-ray crystallography, spectroscopic and magnetic susceptibility. The crystal structures of the 1D chain compounds **1** and **2** show an elongated distorted octahedron about each nickel(II) ion. The magnetic behavior of two compounds exhibits weak intrachain antiferromagnetic interaction with J values of $-0.93\ cm^{-1}$ for **1** and $-1.28\ cm^{-1}$ for **2**. The electronic spectra of the complexes are significantly affected by the nature of the carboxylate ligands.
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Keywords: Crystal structures; Nickel(II) complexes; Tetraaza macrocycle; 1D chain complexes; Antiferromagnetic coupling; Octahedral complexes

1. Introduction

Self-assembled coordination polymers of metal ions and multidentate organic ligands have been of great interest due to their potential for supramolecular materials [1–6], which exhibit novel properties such as porosity [7,8], magnetism [9–11] and non-linear optical behavior [12,13]. The benzoic acid-based ligands such as terephthalate (tp) and 1,3,5-benzenetricarboxylate (btc) are good candidates for the construction of multidimensional coordination polymers because of their rigidity and stability in the resulting porous framework. The construction of these structures can be influenced by the choice of the metal and organic ligand species, metal-to-ligand ratio, solvent system, and inorganic counterion [14–16]. For example, one-dimensional nickel(II) complexes $[Ni(L)(tp)] \cdot 2H_2O$ (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$]-docosane; tp = terephthalate) and $[Ni(L)(pdc)] \cdot H_2O$ (pdc = 2,5-pyridinedicarboxylate) [17] show distorted octahedral geometries and reveal weak antiferromagentic interactions, which are assembled by square-planar nickel(II) macrocyclic complex and aromatic carboxylate ligands. However, two-dimensional polymers with distorted octahedral environments $[Ni(bhct)]_3[btc]_2 \cdot 18H_2O$ and $[Ni(bhct)]_3[btc]_2 \cdot 18H_2O \cdot 2C_5H_5N$ (bhct = 1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane) [18] exhibit weak antiferromagnetic couplings and reveal the brick wall and honeycomb structures, respectively. The different molecular topologies in these complexes may be due to the different coordination modes of the btc ligand.

In order to better understand some aspects of nickel(II) complexes of tetraaza macrocycle with the carboxylate ligands, we report the structures, spectroscopic and magnetic properties of 1D nickel(II) complexes $\{[Ni(L)(isoph)] \cdot 3H_2O\}_n$ (**1**) (isoph = isophthalate) and $\{[Ni(L)(H\text{-}chtc)] \cdot H_2O\}_n$ (**2**) (H-chtc = cyclohexane-1-carboxylic acid-3,5-dicarboxylate).

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* Corresponding author. Tel.: +82 41 850 8284; fax: +82 41 850 8347.
E-mail address: kychoi@kongju.ac.kr (K.-Y. Choi).

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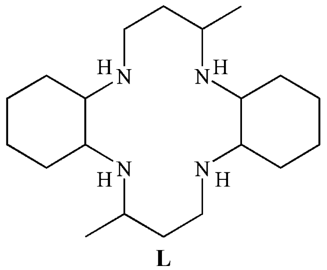

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2. Experimental

2.1. Materials and physical methods

All chemicals used in syntheses were of reagent grade and were used without further purification. The macrocycle 3,14-dimethyl-2,6,13,17-tetraazatricyclo[$14,4,0^{1.18},0^{7.12}$]docosane (L) and [Ni(L)]$Cl_2 \cdot 2H_2O$ were prepared according to the literature methods [19,20]. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. The solution electronic and diffuse reflectance spectra were obtained on a Jasco V-550 spectrophotometer. Magnetic susceptibility data were collected in the temperature range 5.0–300 K in an applied field of 1.0 T with the use of a Quantum Design MPMS7 SQUID magnetometer. The diamagnetic corrections were calculated from Pascal's constants. Elemental analyses (C, H, N) were performed on a Perkin–Elmer CHN-2400 analyzer.

2.2. Synthesis of $\{[Ni(L)(isoph)] \cdot 3H_2O\}_n$ (**1**)

An aqueous solution (10 ml) of [Ni(L)]$Cl_2 \cdot 2\,H_2O$ (251 mg, 0.5 mmol) was added to an aqueous solution (10 ml) of sodium isophthalate (105 mg, 0.5 mmol) and the mixture was stirred for 30 min at room temperature. The solution was filtered and left at room temperature until the violet crystals formed. The product was recrystallized from a hot water/acetonitrile (1:1 v/v, 10 ml) mixture. Yield: 65%. *Anal.* Calc. for $C_{28}H_{50}N_4NiO_7$: C, 54.82; H, 8.22; N, 9.13. Found: C, 54.93; H, 8.31; N, 9.04%. IR (KBr, cm^{-1}): ν(NH) 3210, ν_{as}(COO) 1717, 1606, 1560, ν_{sym}(COO) 1425, 1381.

2.3. Syntheses of $\{[Ni(L)(H\text{-}chtc)] \cdot H_2O\}_n$ (**2**)

This compound was prepared as violet crystals in a reaction similar to that of **1**, using sodium 1,3,5-cyclohexanetricarboxylate (140 mg, 0.5 mmol) instead of sodium isophthalate. Yield: 68%. *Anal.* Calc. for $C_{29}H_{52}N_4NiO_7$: C, 55.51; H, 8.35; N, 8.93. Found: C, 55.42; H, 8.43; N, 8.86%. IR (KBr, cm^{-1}): ν(OH) 3405, ν(NH) 3205, ν_{as}(COO) 1690, 1560, ν_{sym}(COO) 1449, 1394.

2.4. X-ray crystal structure analysis

Intensity data collected on a Bruker SMART 1000 CCD (**1**) and an Enraf-Nonius CAD4 (**2**) diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Accurate cell parameters and an orientation matrix were determined by the least-squares fit of 25 reflections. The intensity data were collected by the ω-2θ technique and corrected for Lorentz and polarization effects. An empirical absorption correction was applied with the SADABS program [21] for **1** and φ-scan [22] for **2**. The structure was solved by direct methods [23] and the least-squares refinement of the structure was performed by the SHELXL-97 program [24]. All atoms except for all hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions, allowing them to ride on their parent C or N atoms with $U_{iso}(H) = 1.2U_{eq}$(C or N). For **1**, the

Table 1
Crystallographic data

	1	**2**
Empirical formula	$C_{28}H_{50}N_4NiO_7$	$C_{29}H_{52}N_4NiO_7$
Formula weight	613.43	627.46
Temperature (K)	293(2)	293(2)
Crystal color/habit	violet/plate	violet/prism
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	16.0642(11)	9.9995(18)
b (Å)	19.6800(13)	12.755(2)
c (Å)	10.1155(7)	12.8119(18)
α (°)		93.00(2)
β (°)	103.717(2)	102.16(2)
γ (°)		106.77(2)
V (Å^3)	3106.7(4)	1518.3(4)
Z	4	2
D_{calc} (Mg m^{-3})	1.312	1.372
Absorption coefficient (mm^{-1})	0.673	0.690
$F(000)$	1320	676
Crystal size (mm)	0.22 × 0.11 × 0.07	0.20 × 0.10 × 0.10
θ Range (°)	1.30 to 28.31	1.64 to 24.98
Limiting indices	$-9 \leqslant h \leqslant 21$, $-26 \leqslant k \leqslant 25$, $-13 \leqslant l \leqslant 12$	$-11 \leqslant h \leqslant 11$, $-15 \leqslant k \leqslant 15$, $-1 \leqslant l \leqslant 15$
Reflection collected/unique (R_{int})	22688/7713 (0.0603)	6112/5326 (0.1011)
Absorption correction	SADABS	φ-scan
Maximum and minimum transmission	0.9553 and 0.6541	0.9331 and 0.7569
Data/restraints/parameters	7713/0/387	5326/0/388
Goodness-of-fit on F^2	0.932	0.955
Final R indices ($I > 2\sigma(I)$)	$R_1^a = 0.0545$, $wR_2^b = 0.1379$	$R_1 = 0.0797$, $wR_2 = 0.1404$
R indices (all data)	$R_1 = 0.1218$, $wR_2 = 0.1902$	$R_1 = 0.2871$, $wR_2 = 0.1923$
Largest difference in peak and hole (e Å^{-3})	0.597 and −0.574	0.449 and −0.822

[a] $R_1 = \|F_o| - |F_c\|/\sum|F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.