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Synthesis and characterization of one-dimensional nickel(II) macrocyclic complexes with bridging organic ligands

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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 1,3,5-benzenetricarboxylate (BTC), 1,4-benzenedicarboxylate (BDC) and 2,5-pyridinedicarboxylate (PDC) in CHCl₃/water solution yield the one-dimensional nickel(II) complexes $[Ni(L)]_3[BTC]_2 \cdot 8H_2O$ (1), $[Ni(L)(BDC)] \cdot 2H_2O$ (2) and $[Ni(L)(PDC)] \cdot H_2O$ (3). The structures were characterized by X-ray crystallography, magnetic susceptibility and thermogravimetry. Complex 1 reveals a geometrically symmetric core with a {4/6} coordination number set. The geometry around the four-coordinate Ni(3) is depicted as square planar, while the coordination geometry around the Ni(1) and Ni(2) ions is a tetragonally distorted octahedron in the direction of the chain. The crystal structures of the chain compounds 2 and 3 show an elongated octahedral *trans* arrangement about each nickel(II) ion. The magnetic behavior of all three compounds exhibits weak intrachain antiferromagnetic interactions with J values of -1.13 cm⁻¹ for 1, -1.37 cm⁻¹ for 2 and -1.47 cm⁻¹ for 3. Compounds 1–3 thermally decompose to form the same products. The identities of the decomposition products are discussed. The hydrogen-bonding interaction in compounds 1–3 plays a significant role in aligning the molecules and the polymer strands in the crystalline solids. © 2001 Published by Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Nickel(II) complexes; Macrocycle; Organic ligands; Chain complexes

1. Introduction

The self-assembly and self-organization of infinite metal complexes with specific network topologies have been of great interest due to their potential for supramolecular chemistry and crystal engineering [1,2]. Cooperative intermolecular interactions such as coordination bonds, hydrogen bonds, and $\pi - \pi$ stacking provide supramolecular assemblies through the creation of one-dimensional and multi-dimensional networks [3]. Recently, Atwood et al. [4] reported the crystal struc-[M(terephthalate)(4-picoline)₂(H₂O)₂]·2(4of tures [M(terephthalate)(pyridine)₂(H₂O)₂]· picoline) and $2(\text{pyridine}) \cdot 2(\text{H}_2\text{O}) \text{ (M} = \text{Co}^{2+}, \text{Ni}^{2+}) \text{ which assemble}$ in the solid state to form one-dimensional coordination polymers. Fujita et al. unprecedentedly observed the appearance of quite different network patterns from almost the same crystallographic molecules. Upon complexation with $Cd(NO_3)_2$, the ligand N,N'-diphenyl-1,4phenylenediamine [5] gave an infinite molecular ladder, whilst fluorination of this ligand [6] afforded an infinite molecular brick, despite the very similar unit crystal structures of these complexes. However, macrocyclic complexes have seldom been used as building blocks in the construction of multidimensional networks [7]. The multidentate macrocycle 1,3,5-benzenetricarboxylate (BTC) is a good candidate for a molecular building block because of its rigidity and stability in the resulting porous framework. In polymeric structures containing 1,3,5-benzenetricarboxylate (BTC³⁻), several factors influence the specific framework structure that is formed. For example [7a], the two-dimensional network $[Ni(L)]_3[BTC]_2 \cdot 18H_2O$ (L = 1, 8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane) results in a brick wall structure, whilst a honeycomb structure is obtained

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for $[Ni(L)]_3[BTC]_2 \cdot 18H_2O \cdot 2C_5H_5N$. The different molecular topologies in these complexes arose from the different coordination modes of the BTC^{3-} anion.

In the present study, we report the preparation, crystal structures and chemical properties of the one-dimensional structures $[Ni(L)]_3[BTC]_2 \cdot 8H_2O$ (1), $[Ni(L)(BDC)] \cdot 2H_2O$ (2) and $[Ni(L)(PDC)] \cdot H_2O$ (3) $(BTC^{3-} = 1,3,5$ -benzenetricarboxylate, $BDC^{2-} = 1,4$ -benzenedicarboxylate, $PDC^{2-} = 2,5$ -pyridinedicarboxylate, L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo- $[14,4,0^{1.18},0^{7.12}]$ docosane). We also found that intermolecular hydrogen bonds in all compounds expand the one-dimensional chain structures into two-dimensional networks.

2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The macrocycle L and $[Ni(L)]Cl_2 \cdot 2H_2O$ were prepared according to the literature method [8]. IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer using KBr pellets. UV-Vis diffuse reflectance spectra were recorded with a Shimadzu UV2401 PC/DRS spectrophotometer. Magnetic susceptibility data on powder samples were collected in the temperature range 2-300 K in an applied field of 1 T with the use of a Quantum Design MPMS7 SQUID magnetometer. The diamagnetic corrections were estimated from Pascal's constants. Differential thermal analysis and thermogravimetric analysis were performed using a TGA 2050 Thermogravimetric Analyzer in flowing nitrogen at a heating rate of 10°C min⁻¹. High-resolution fast atom bombardment mass spectrometry (FAB MS) were performed by using a Jeol JMS-HA 110A/110A instrument. Elemental analyses were carried out by the Korea Research Institute of Chemical Technology, Taejon, Korea.

2.2. Synthesis of $[(NiL)_3(BTC)_2] \cdot 8H_2O$ (1)

A chloroform solution (20 ml) of $[Ni(L)]Cl_2 \cdot 2H_2O$ (502 mg, 1 mmol) was allowed to diffuse into an aqueous solution (5 ml) of Na₃BTC (276 mg, 1 mmol) in a test tube for several days. A quantity of pink crystals formed at the CHCl₃/water interface. Crystals were collected by filtration and washed with diethyl ether, giving a yield of 62%. *Anal.* Found: C, 49.7; H, 8.5; N, 8.8. Calc. for C₇₈H₁₅₈N₁₂Ni₃O₂₈: C, 49.6; H, 8.4; N, 8.9%. IR (KBr, cm⁻¹): 3411(s), 3352(s), 3053(s), 2929(s), 1624(s), 1558(s), 1446(m), 1430(s), 1363(s), 1306(w), 1273(w), 1188(w), 1093(s), 1050(m), 1019(m), 996(w), 952(w), 914(w), 806(m), 768(m), 726(s), 620(m). UV–Vis (diffuse reflectance spectrum, λ_{max}): 523 nm. FAB MS (m/z): 1888 (M^+).

2.3. Synthesis of $[Ni(L)(BDC)] \cdot 2H_2O$ (2)

This compound was prepared as pink crystals in a reaction similar to that of 1, using Na₂BDC (186 mg, 1 mmol) instead of Na₃BTC. Yield: 63%. *Anal.* Found: C, 56.4; H, 8.2; N, 9.5. Calc. for C₂₈H₄₈N₄NiO₆: C, 56.5; H, 8.1; N, 9.4%. IR (KBr, cm⁻¹): 3421(s), 3257(m), 3147(m), 2930(s), 1613(s), 1570(s), 1431(m), 1372(s), 1304(m), 1154(m), 1110(s), 1062(m), 1014(m), 994(m), 948(m), 898(m), 813(s), 749(s), 638(w), 503(w). UV–Vis (diffuse reflectance spectrum, λ_{max}): 524 nm. FAB MS (m/z): 595 (M^+).

2.4. Synthesis of $[Ni(L)(PDC)] \cdot H_2O$ (3)

This compound was prepared as pink crystals in a reaction similar to that of 1, using Na₂PDC (187 mg, 1 mmol) instead of Na₃BTC. Yield: 53%. *Anal.* Found: C, 56.1; H, 7.8; N, 12.1. Calc. for C₂₇H₄₅N₅NiO₅: C, 56.1; H, 7.8; N, 12.1%. IR (KBr, cm⁻¹): 3536(s), 3259(m), 3157(m), 2933(s), 2878(m), 1590(s), 1467(w), 1428(w), 1389(s), 1348(s), 1306(m), 1155(m), 1112(s), 1068(m), 1018(m), 995(m), 950(m), 902(m), 815(s), 764(m), 502(w). UV–Vis (diffuse reflectance spectrum, λ_{max}): 518 nm. FAB MS (m/z): 578 (M^+).

2.5. X-ray crystallography

[Ni(L)]₃[BTC]₂·8H₂O Crystals of (1), [Ni(L)(BDC)]·2H₂O (2) and [Ni(L)(PDC)]·H₂O (3) were used for data collection. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda =$ 0.71069 A) at room temperature. Accurate cell parameters and an orientation matrix were determined from the least-squares fit of 25 reflections. An asymmetric unit of intensity data was collected in the ω -2 θ scan mode. The intensity data were corrected for Lorentz and polarization effects. Empirical absorption correction (ψ -scan) was applied. The crystal parameters and details of the data collections and refinement for 1-3are listed in Table 1. The structures were solved by direct methods and successive cycles of difference Fourier maps followed by least-squares refinements [9]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and allowed to ride upon the appropriate carbon and nitrogen atoms and all their parameters were fixed. The crystallographic data of 1-3 are summarized in Table 1 and the selected bond distances and angles in Tables 2 - 4.

| Table 1 | |
|-----------------------|--|
| Crystallographic data | |

| | 1 | 2 | 3 |
|--|--|---|---|
| Empirical formula | C ₇₈ H ₁₅₈ N ₁₂ Ni ₃ O ₂₈ | C ₂₈ H ₄₈ N ₄ NiO ₆ | C ₂₇ H ₄₅ N ₅ NiO ₅ |
| Formula weight | 1888.29 | 595.41 | 578.39 |
| Temperature (K) | 291 | 293 | 293 |
| Wavelength (Å) | 0.71069 | 0.71069 | 0.71069 |
| Crystal system | Triclinic | Triclinic | Monoclinic |
| Space group | $P\overline{1}$ | $P\overline{1}$ | P21 |
| Unit cell dimensions | | | |
| a (Å) | 9.473(2) | 8.860(2) | 11.442(3) |
| $b(\mathbf{A})$ | 16.403(2) | 9.777(2) | 13.754(2) |
| $c(\dot{A})$ | 16.831(2) | 10.178(2) | 9.994(1) |
| α (°) | 68.26(1) | 66.17(2) | |
| β (°) | 85.16(1) | 65.74(2) | 115.75(2) |
| γ (°) | 79.52(2) | 76.25(2) | |
| $V(Å^3)$ | 2388.3(6) | 732.5(2) | 1416.6(5) |
| Z | 1 | 1 | 2 |
| D_{calc} (Mg m ⁻³) | 1.313 | 1.350 | 1.356 |
| Absorption coefficient (mm^{-1}) | 0.664 | 0.709 | 0.730 |
| F(000) | 1018 | 320 | 620 |
| Crystal size (mm) | $0.59 \times 0.36 \times 0.26$ | $0.23 \times 0.13 \times 0.10$ | $0.40 \times 0.17 \times 0.07$ |
| θ range for data collection (°) | 2.19-24.97 | 2.29-24.97 | 2.26-24.97 |
| Index ranges | $-11 \le h \le 11, -18 \le k \le 19,$ | $-9 \le h \le 10, -10 \le k \le 11,$ | $-13 \le h \le 12, \ 0 \le k \le 16,$ |
| - | $0 \le l \le 19$ | $0 \le l \le 12$ | $0 \le l \le 11$ |
| Reflections collected | 7776 | 2540 | 2763 |
| Independent reflections | 7492 ($R_{\rm int} = 0.0727$) | 2390 $(R_{int} = 0.0381)$ | 2607 ($R_{\rm int} = 0.0307$) |
| Absorption correction | Empirical | Empirical | Empirical |
| Max./min. transmission | 0.829 and 0.582 | 0.917 and 0.085 | 0.948 and 0.463 |
| Refinement method | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 |
| Data/restraints/parameters | 7492/0/547 | 2390/0/178 | 2607/1/343 |
| Goodness-of-fit on F^2 | 1.015 | 1.124 | 1.030 |
| Final R indices $(I > 2\sigma(I))$ | $R_1^{a} = 0.0704, wR_2^{b} = 0.2242$ | $R_1 = 0.0540, \ wR_2 = 0.1189$ | $R_1 = 0.0504, wR_2 = 0.1141$ |
| R indices (all data) | $R_1 = 0.0969, wR_2 = 0.2404$ | $R_1 = 0.0758, wR_2 = 0.1240$ | $R_1 = 0.1042, wR_2 = 0.1399$ |
| Largest difference peak and hole (e $Å^{-3}$) | 1.529 and -0.920 | 0.603 and -0.890 | 0.428 and -0.300 |

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

3. Results and discussion

3.1. Description of the structures

An ORTEP diagram of [(NiL)₃(BTC)₂]·8H₂O (1) with the atomic numbering scheme is shown in Fig. 1(a). The compound 1 contains a mixture of polymeric and monomeric ions. An inversion center exists on the central nickel(II) ion. The complex has a geometrically symmetric core with a $\{4/6\}$ coordination number set. The geometry around the four-coordinate Ni(3) is depicted as square planar with four secondary amines of the macrocycle, while the coordination geometry around the Ni(1) and Ni(2) ions is a tetragonally distorted octahedron in which each nickel ion is coordinated by four secondary amines of the macrocycle and by two carboxylate oxygen atoms of the BTC ligands. The two Ni-N₄ (secondary amines) distances $(Ni(1)-N_{av} = 2.077(4) \text{ and } Ni(2)-N_{av} = 2.057(4) \text{ Å}) \text{ are}$ shorter than the two Ni-O (carboxylate oxygens) dis-

tances (Ni(1)-O(1) = 2.193(4))and Ni(2) - O(3) =2.163(4) Å), giving an axially elongated octahedron in the one-dimensional chain direction. The average Ni(3)–N bond distance of 1.988(4) Å is in the normal range for Ni-N (secondary amines) bond distances of square-planar nickel(II) complexes with 14-membered tetraaza macrocycles [8b,10]. Two nickel(II) macrocyclic complexes (Ni(1) and Ni(2)) are bridged by the BTC^{3 –} unit with a separation of 11.347(3) Å, whereas the Ni(1)...Ni(3) and Ni(2)...Ni(3) distances between the two complexes and uncoordinated Ni(3) complex are 9.302(1) and 10.097(2) Å, respectively. The coordination of the benzenetricarboxylato bridge is slightly asymmetrical; the two Ni(1)-O(1)-C(35)and Ni(2)-O(3)-C(31) angles are 132.8(4) and 134.9(4)°, the larger angle corresponding to the shorter bond distance. The dihedral angles (α) between the plane of the carboxylate group and benzene ring involving Ni(1) and Ni(2) are 20.0 and 1.7°. Moreover, the dihedral angles (β) between the plane of the carboxylate group

and NiN₂O₂ plane involving Ni(1) and Ni(2) are 10.6 and 9.5°, respectively. The free carbonyl oxygen atoms of BTC form hydrogen bonds with the secondary amines of the macrocycle (O(2)¹...N(2) 2.846(7) Å, 163.0° and O(4)²...N(3) 2.910(8) Å, 154.6°. The water molecules also forms hydrogen bonds with the secondary amine of the macrocycle (OW(4)³...N(1) 3.117(9) Å, 167.0° with carboxylate oxygen atoms (OW(4)...O(2) 2.722(8) Å and OW(5)...O(5) 2.760(9) Å) and with the other water inclusions (OW(1)...OW(2) 2.861(6) Å, OW(1)...OW(3) 2.859(6) Å,

Table 2

Selected bond lengths (Å) and angles (°) for $[(NiL)_3(BTC)_2]\cdot 8H_2O$ (1) a

| Ni(1)–N(1) | 2.092(5) | O(1)-C(35) | 1.242(7) |
|------------------------------|-----------|------------------|-----------|
| Ni(1)–N(2) | 2.062(5) | O(2)-C(35) | 1.233(7) |
| Ni(1)–O(1) | 2.193(4) | O(3)–C(31) | 1.230(7) |
| Ni(2)-N(3) | 2.027(5) | O(4)–C(31) | 1.265(7) |
| Ni(2)–N(4) | 2.087(5) | O(5)–C(38) | 1.182(7) |
| Ni(2)-O(3) | 2.163(4) | O(6)–C(38) | 1.310(8) |
| Ni(3)-N(5) | 1.951(5) | Ni(2)Ni(3) | 10.099(2) |
| Ni(3)–N(6) | 2.024(5) | Ni(1)Ni(3) | 9.302(1) |
| Ni(1)Ni(2) | 11.347(2) | | |
| N(1)-Ni(1)-N(2) | 82.4(2) | Ni(2)-O(3)-C(31) | 134.9(4) |
| N(1)-Ni(1)-N(2) ^b | 97.6(2) | O(1)-C(35)-O(2) | 128.0(6) |
| O(1)-Ni(1)-N(1) | 87.75(18) | O(1)-C(35)-C(34) | 117.1(6) |
| O(1)-Ni(1)-N(2) | 90.9(2) | O(2)-C(35)-C(34) | 114.9(6) |
| N(3)-Ni(2)-N(4) | 80.9(2) | O(3)-C(31)-O(4) | 126.5(6) |
| N(3)-Ni(2)-N(4) ° | 99.1(2) | O(3)-C(31)-C(32) | 117.6(6) |
| O(3)-Ni(2)-N(3) | 88.2(2) | O(4)-C(31)-C(32) | 115.9(5) |
| O(3)-Ni(2)-N(4) | 82.0(2) | O(5)-C(38)-O(6) | 120.2(7) |
| N(5)-Ni(3)-N(6) | 94.5(2) | O(5)-C(38)-C(37) | 125.4(6) |
| N(5)-Ni(3)-N(6) ^d | 85.5(2) | O(6)-C(38)-C(37) | 113.9(6) |
| Ni(1)-O(1)-C(35) | 132.8(4) | | |

| ^a Symmetry transform | nations used | to generate | equivalent | atoms. |
|---------------------------------|--------------|-------------|------------|--------|
| $^{b}-r - v + 1 - z + 1$ | 1 | | | |

 $x^{-x}, -y+1, -z+1.$ $x^{-x}-x+2, -y, -z+1.$

d - x + 1, -y + 1, -z.

Table 3 Selected bond lengths (Å) and angles (°) for $[Ni(L)(BDC)]\cdot 2H_2O$ (2) a

| Ni–N(1) | 2.053(4) | O(1)-C(11) | 1.235(5) |
|----------------|----------|-------------------|-----------|
| N1-N(2) | 2.080(4) | O(2) - C(11) | 1.257(5) |
| Ni-O(1) | 2.116(3) | NiNi ^b | 11.528(3) |
| N(1)-Ni-N(2) | 84.5(2) | Ni-O(1)-C(11) | 136.1(3) |
| N(1)–Ni–N(2) ° | 95.5(2) | O(1)-C(11)-O(2) | 127.0(5) |
| O(1)-Ni-N(1) | 88.2(1) | O(1)-C(11)-C(12) | 117.5(4) |
| O(1)-Ni-N(2) | 83.2(1) | O(2)-C(11)-C(12) | 115.3(4) |
| | | | |

^a Symmetry transformations used to generate equivalent atoms.

 $^{b}-x, -y+1, -z+1.$

 $^{c}-x+1, -y, -z+1.$

³ Symmetry code: -x + 1, -y + 1, -z + 1.

Table 4

Selected bond lengths (Å) and angles (°) for [Ni(L)(PDC)]·H₂O (3) ^a

| Ni–N(1) | 2.031(13) | O(1)–C(21) | 1.263(14) |
|----------------------------|-----------|----------------------------|-----------|
| Ni–N(2) | 2.066(16) | O(2)–C(21) | 1.244(16) |
| Ni-N(3) | 2.129(16) | O(3)–C(27) | 1.254(15) |
| Ni–N(4) | 2.088(13) | O(4)–C(27) | 1.229(17) |
| Ni-O(1) | 2.137(10) | NiNi ^b | 11.465(4) |
| Ni-O(3) ^b | 2.121(9) | | |
| N(1)-Ni-N(2) | 86.3(6) | O(3) ^b -Ni-N(2) | 84.7(5) |
| N(1)-Ni-N(3) | 97.7(6) | O(3) ^b –Ni–N(3) | 95.7(5) |
| N(1)-Ni-N(4) | 178.7(10) | O(3) ^b –Ni–N(4) | 92.6(4) |
| N(2)-Ni-N(3) | 176.0(7) | O(1)-Ni-O(3) ^b | 179.4(7) |
| N(2)-Ni-N(4) | 94.9(6) | Ni-O(1)-C(21) | 135.0(10) |
| N(3)-Ni-N(4) | 81.1(7) | Ni °-O(3)-C(27) | 134.7(9) |
| O(1)-Ni-N(1) | 92.4(4) | O(1)-C(21)-O(2) | 125.9(13) |
| O(1)-Ni-N(2) | 94.8(6) | O(1)-C(21)-C(22) | 112.8(13) |
| O(1)-Ni-N(3) | 84.7(5) | O(3)-C(27)-O(4) | 124.9(13) |
| O(1)-Ni-N(4) | 87.1(4) | O(3)-C(27)-C(24) | 117.7(13) |
| O(3) ^b –Ni–N(1) | 87.9(4) | | |
| | | | |

^a Symmetry transformations used to generate equivalent atoms. ^b x-1, y, z-1.

 $^{c}x+1, y, z+1.$

OW(1)...OW(8)¹ 2.532(3) Å, OW(2)...OW(3) 2.870(7) Å, OW(4)...OW(5)² 2.963(9) Å, and OW(6)...OW(7) 2.718(11) Å). Interestingly, the secondary amines N(5) and N(6) of the macrocycle found in the lattice form hydrogen bonds to an adjacent polymeric chain via carboxylate oxygens O(5) and O(6) of the uncoordinated BTC ligand, which gives rise to a two-dimensional hydrogen-bonded network (O(5)...N(5) 3.149(9) Å, 128.4°, O(5)...N(6) 3.234(8) Å, 127.9° and O(6)...N(6) 2.781(8) Å, 177.0°) (Fig. 1(b)).

An ORTEP drawing of $[Ni(L)(BDC)] \cdot 2H_2O$ (2) with the atomic numbering scheme is shown in Fig. 2(a). The crystal structure of **2** has cationic $[Ni(L)]^{2+}$ units, BDC^{2-} anion, and water molecules. The complex has an inversion center at the midpoint of the benzene ring of the BDC²⁻ ligand. In the chain structure, the nickel(II) ion exists in a distorted octahedral coordination environment in which the macrocycle and two trans BDC ligands have assembled around the metal center. Therefore, one-dimensional coordination polymers have formed. The Ni...Ni' distance across the polymer backbone is 11.528(3) Å, whereas the closest Ni...Ni' distance between neighboring strands is 10.898(3) Å. The average Ni-N distance of 2.067(3) Å is shorter than the axial Ni-O(1) distance of 2.116(3) Å, indicating the axially elongated octahedron is in the chain direction. The axial Ni-O(1) bond is not perpendicular NiN₄ plane with N(1)–Ni–O(1) and to the N(2)-Ni-O(1) angles of 88.2(1) and 83.2(1)°, respectively. The Ni–O(1)–C(11) angle and C(11)–O(1) distance relative to the BDC ligand are 136.1(3)° and 1.235(5) Å, respectively. The values of the dihedral angles (α and β) for this structure are 5.6 and 7.3°, respectively. Interestingly, the one-dimensional chain in

¹ Symmetry code: -x, -y + 1, -z + 1.

² Symmetry code: -x + 2, -y, -z + 1.



Fig. 1. (a) An ORTEP drawing of $[(NiL)_3(BTC)_2]$ ·8H₂O (1) with the atomic numbering scheme (30% probability ellipsoids shown). (b) Crystal packing of 1, showing the intermolecular hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity.

2 is linked by hydrogen bonds involving the carboxylate oxygen atoms of BDC ligand and the secondary amines of the macrocycle (O(1)...N(2) 2.785(5) Å, 107.5°, O(1)⁴...N(1) 2.995(5) Å, 100.6° and O(2)⁴...N(1) 2.932(5) Å, 153.6°. The water molecule found in the

lattice also forms hydrogen bonds with the carboxylate oxygens of a BDC ion (OW...O(2) 2.883(5) Å and OW⁵...O(2) 2.900(6) Å. This interaction, as shown in Fig. 2(b), gives rise to a two-dimensional hydrogenbonded network.

⁴ Symmetry code: -x + 1, -y, -z + 1.

⁵ Symmetry code: -x + 1, -y + 1, -z.



Fig. 2. (a) An ORTEP drawing of $[Ni(L)(BDC)] \cdot 2H_2O$ (2) with the atomic numbering scheme (30% probability ellipsoids shown). (b) Crystal packing of 2, showing the intermolecular hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity.

An ORTEP drawing of $[Ni(L)(PDC)] \cdot H_2O(3)$ with the atomic numbering scheme is shown in Fig. 3(a). The nickel atom occupies a distorted octahedral coordination environment in which the macrocycle, two water molecules and two trans PDC²⁻ ions have assembled around each nickel center. Consequently, a one-dimensional coordination polymer has formed. Each nickel atom is coordinated by one macrocycle two PDC ligands. The intramolecular Ni...Ni' distance is 11.465(4) A, whereas the shorter intermolecular Ni...Ni' distance is 8.947(3) Å. The average Ni–N distance of 2.079(7) Å is somewhat shorter than the two Ni-O distances (PDC) (Ni–O(1) = 2.137(10) and Ni–O(3)⁶ = 2.121(9) Å), which is similar to that observed in 2. Furthermore, the axial Ni-O (BDC) linkage is bent slightly off the perpendicular to the NiN₄ plane by $2.1-5.7^{\circ}$. The Ni-O(1)-C(21) and $Ni^{7}-O(3)-C(27)$ angles and C(21)-O(1) and C(27)-O(3) distances relative to the PDC ligand are 135.0(10)-134.7(9)° and 1.263(14) - 1.254(15) Å, respectively. The values of the dihedral angles (α and β) for **3** are 2.8, 3.6° and 5.7, 11.6°, respectively. The secondary amines of the macrocycle forms hydrogen bonds with carboxylate oxygens

3.2. Spectroscopic properties

The electronic diffuse reflectance spectra of the compounds exhibit maximum absorptions at 523 nm for 1, 524 nm for 2 and 518 nm for 3, which are characteristic chromophores for the nickel(II) ion coordinated with N₄O₂ donors [11]. However, all compounds dissolve in water and decompose into the original building block [Ni(L)]Cl₂·2H₂O, which is identified by the UV–Vis spectra showing the characteristic chromophore ($\lambda_{max} = 463$ nm) [8].

of the PDC ligand (N(1)...O(2) 2.926(15) Å, 156.1°, N(2)...O(3)⁸ 2.822(18) Å, 105.9°, N(3)...O(1) 2.874(19) Å, 107.7° and N(4)...O(4)⁸ 2.908(16) Å, 151.4°. Furthermore, the water molecule OW(2) is linked to the uncoordinated PDC oxygen atoms O(2) and O(4) through hydrogen bonds (OW(2)...O(2) 2.954(15) Å and OW(2)...O(4)⁹ 2.851(14) Å, to form the two-dimensional hydrogen-bond system (Fig. 3(b)).

⁶ symmetry code: x-1, y, z-1.

⁷ symmetry code: x + 1, y, z + 1.

⁸ Symmetry code: x-1, y, z-1.

⁹ Symmetry code: x, y, z-1.

3.3. Magnetic properties

The temperature dependency of the magnetic susceptibilities (χ_m) and the effective magnetic moments (μ_{eff}) per nickel(II) ion for the compounds **1**–**3** are shown in Fig. 4(a–c). The room temperature magnetic moments (μ_B) are 2.89 for **1**, 3.19 for **2**, and 2.88 for **3**. For all compounds the μ_{eff} values gradually decrease with decreasing temperature, suggesting the presence of an antiferromagnetic interaction between the nickel(II) centers. The χ_m data are interpreted using the isotropic nickel(II) chain spin Hamiltonian (S = 1 and $H_{chain} =$ $-J\Sigma S_i \cdot S_{i+1}$) and fitted to Eq. (1) by neglecting zerofield splitting and the Haldane gap effect [2a,12].

$$\chi_{\rm m} = \frac{N\beta^2 g^2 S(S+1)}{3kT} \frac{(1+\mu)}{(1+\mu)}$$

where $\mu = \operatorname{coth}\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right]$ (1)

The results of the best-fit are summarized in Table 5 together with some structural data. It can be seen that the magnetic interaction is very weak $(J \le -2 \text{ cm}^{-1})$. The weak coupling observed may be due to the large intramolecular Ni...Ni distance ($\ge 11.3 \text{ Å}$). The intraand intermolecular Ni...Ni distances and the values of the dihedral angles (α and β) are included in Table 5. Given that the intramolecular Ni...Ni distances are

practically constant in this series and that the values of the α dihedral angle do not follow the expected trend, these factors may not play a significant role. However, the values of the β dihedral angle of these complexes does slightly decrease with increasing antiferromagnetic coupling. Although the intermolecular Ni...Ni distances vary from 8.9 to 10.9 Å, the values of J are insensitive to it indicating that the weak magnetic coupling observed is of intramolecular nature.

3.4. Thermogravimetric analysis

The compounds 1-3 were heated in the temperature range $30-1000^{\circ}$ C in nitrogen gas (Fig. 5(a-c)). The TGA data for all compounds showed three separate weight losses. For 1, the first weight loss is observed from 30 to 67°C, which is due to the loss of eight water molecules (observed 8.4%, calculated 8.3%). A second weight loss corresponding to the three macrocycles and two BTC ligands (observed 82.1%, calculated 81.6%) is found in the temperature range 309–600°C. A final weight loss is observed above 600°C corresponding to the greenish black residue of NiO (observed 12.2%, calculated 12.9%). For 2, the first weight loss of 6.0%, from 30 to 129°C, corresponds to the loss of the two water molecules (calculated 6.1%). On further heating, 2 lost weight between 274 and 600°C corresponding to



Fig. 3. (a) An ORTEP drawing of [Ni(L)(PDC)]·H₂O (3) with the atomic numbering scheme (30% probability ellipsoids shown). (b) Crystal packing of 3, showing the intermolecular hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity.





Fig. 5. Thermogravimetric plots for (a) 1, (b) 2, and (c) 3.

calculated 84.1%). Further weight loss is observed above 600°C corresponding to the greenish black residue of NiO (observed 10.1%, calculated 10.3%). For compound **3**, the first weight loss occurred from 30 to 124°C, due to the loss of one water molecule (observed

Fig. 4. Plots of χ_m vs $T(\bullet)$ and μ_{eff} vs $T(\bigcirc)$ for (a) 1, (b) 2, and (c) 3. The solid line represents the best fit of the experimental data to Eq. (1).

one macrocycle and one BDC ligand (observed 85.1%,

Table 5 Structural and magnetic data of nickel(II) complexes

| Complex | g | $J (\mathrm{cm}^{-1})$ | $10^5 R^{a}$ | α (°) | β (°) | $d_{\rm intra}$ (Å) | $d_{\rm inter}$ (Å) |
|---|----------------------|-------------------------|-------------------|------------------------------|-------------------------------|----------------------|---------------------|
| [(NiL) ₃ (BTC) ₂]·8H ₂ O (1) [Ni(L)(BDC)]·2H ₂ O (2) [Ni(L)(PDC)]·H ₂ O (3) | 2.13 2.26 2.16 | -1.13 -1.37 -1.47 | 6.4 3.2 4.8 | 1.7, 20.0 5.6 2.8, 3.6 | 9.5, 10.6 7.3 5.7, 11.6 | 11.3 11.5 11.5 | 10.6 10.9 8.9 |

^a $R = [\Sigma(\chi_{obs} - \chi_{calc})^2 / \Sigma \chi_{obs}^2]^{1/2}.$

3.1%, calculated 3.1%). A second weight loss is observed from 325 to 600°C, which is attributed to the release of the one macrocycle and one PDC ligand (observed 81.3%, calculated 81.2%). The final weight loss is completed above 600°C corresponding to the greenish black residue of NiO (observed 12.3%, calculated 12.9%). The second decomposition behaviors for all compounds did not show the mechanisms suggested by Jacobson et al. who reported that the second weight loss of $Co(NCS)_2(H_2O)_2(4,4-bipy)_2$ corresponds to the loss of one ligand molecule from the bridging 4,4-bipy ligands [13]. Unfortunately decomposition processes for all the macrocycle and bridging ligands coordinated to nickel(II) ion happened simultaneously. The formation of NiO also accompanies the decomposition of the BTC, BDC and PDC ligands in the nickel(II) complexes [14].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 147104 for compound 1, 147105 for compound 2, and 147106 for compound 3. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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