

Hydrothermal Synthesis, Structure, and Magnetic Properties of a Three-dimensional Polymeric Ni^{II} Complex, [Ni(bpp)(NIP)(H₂O)]_n (bpp = 1,3-di(4-pyridyl)propane, NIP = 5-nitroisophthalate)

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Abstract. A three-dimensional polymeric Ni^{II} complex, [Ni(bpp)(NIP)(H₂O)]_n (bpp = 1,3-di(4-pyridyl)propane and NIP = 5-nitroisophthalate), has been synthesized and characterized. The coordination number of the nickel atom is six (NiN₂O₄) and the coordination environment around the Ni^{II} atom may be described as a distorted octahedron in which two nitrogen atoms of “bpp” ligand occupy the *cis* positions. The effective magnetic moment for this

complex indicate that the interactions between two Ni^{II} atoms through the effective exchange media are antiferromagnetic. Self-assembly of these compounds in the solid state via π - π -stacking interactions is discussed.

Keywords: Nickel; 5-Nitroisophthalate; 1,3-Di(4-pyridyl)propane; Three-dimensional polymer; Magnetic properties

The design of crystal structures and control of molecular arrangements of coordination polymers has attracted much attention in recent years [1–10]. The metal-organic coordination polymers of 1,3-di(4-pyridyl)propane (bpp) have attracted continuous attention in recent years [11–13]. This is a flexible ligand and it has three different conformations, TT, TG and GG (Figure 1). The polytypic 5-nitroisophthalate (NIP) anion is also an interesting ligand, with both carboxylate and nitro groups available as coordinating groups. The incorporation of the flexible ligand such as “bpp” and the polytypic ligand such as “NIP” in the design and preparation of new coordination polymers is of considerable interest for potential application in control of the properties of metal-organic coordination polymers. In this paper, we report the synthesis, structure and magnetic properties of a 3D polymeric Ni^{II} complex of 1,3-di(4-pyridyl)propane (bpp) and 5-nitroisophthalate (NIP) ligands, [Ni(bpp)(NIP)(H₂O)]_n.

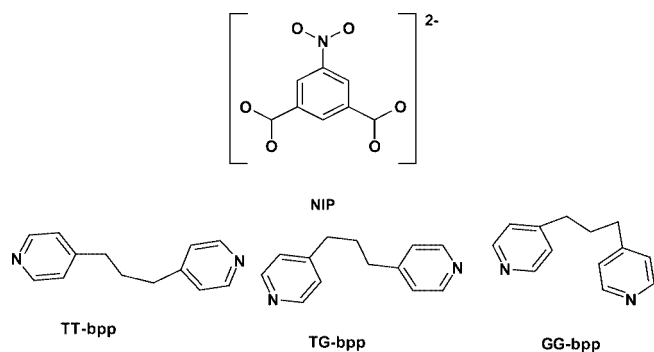


Fig. 1 The general structure of the “NIP” ligand and different conformations of “bpp”.

Experimental Section

Infrared spectra were measured on a Perkin Elmer 2000 system in the range 4000–400 cm⁻¹ with KBr disk technique. C, H and N were analyzed using a Carlo-Erba 1112 Elemental Analyzer. Variable-temperature magnetic susceptibilities were determined with a crystalline sample in the temperature 2–300 K on a Quantum Design MPMS SQUID magnetometer at 2T. The field dependent magnetizations were measured at 2K in the field range 1–50 T. Corrections were applied for diamagnetism calculated from Pascal constants. Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$, where χ_M is the magnetic susceptibility per formula unit. Crystallographic measurements of a singly crystal of dimensions 0.28 x 0.12 x 0.09 mm were made at 298(2) K on a Bruker APEX area-detector diffractometer. The intensity data were collected within the range $1.66^\circ \leq \theta \leq 26.00^\circ$ using graphite monochromated MoK α radiation (λ 0.71073 Å). Accurate unit-cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. The intensities of 22463 unique reflections were collected, from which 4150 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 . The positions of the H-atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each H-atom was assigned an isotropic thermal parameter. R and R_w with goodness of fit on F^2 1.369 are 0.1275 and 0.2325. The reason for the relatively high values of the R factors is the poor quality of the crystal.

Preparation of [Ni(bpp)(NIP)(H₂O)]_n

Nickel(II) acetate tetrahydrate (0.5 mmol), 5-nitroisophthalic acid (0.5 mmol) and 1,3-di(4-pyridyl)propane (0.5 mmol) were placed in a 30 ml, Teflon-lined, stainless-steel Parr bomb together with water (20 ml). The bomb was heated at 423K for six days. The bomb was cooled slowly to room temperature to furnish green crystals. Yield: 0.125g, 52 %, (Found: C: 52.13, H: 3.97, N: 8.59; calculated for C₂₁H₁₉N₃NiO₇; C: 52.05, H: 3.92, N: 8.67 %).

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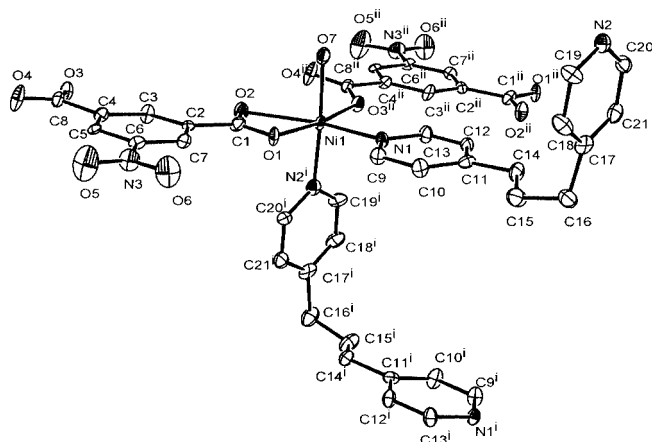


Fig. 2 The coordination sphere of the nickel atom in [Ni(bpp)(NIP)(H₂O)]_n.

Selected bond lengths/Å and bond angles/°: Ni1–O3ⁱⁱ 2.03(5), Ni1–O7 2.08(6), Ni1–N1 2.08(6), Ni1–O1 2.09(5), Ni1–N2ⁱ 2.10(7), Ni1–O2 2.30(6), O3ⁱⁱ–Ni1–O7 87.2(2), O3ⁱⁱ–Ni1–N1 91.8(2), O7–Ni1–N1 91.6(3), O3ⁱⁱ–Ni1–O1 172.6(2), O7–Ni1–O1 88.1(2), N1–Ni1–O1 94.1(2), O3ⁱⁱ–Ni1–N2ⁱ 91.4(3), O7–Ni1–N2ⁱ 175.2(2), N1–Ni1–N2ⁱ 93.1(3), O1–Ni1–N2ⁱ 92.7(3), O3ⁱ–Ni1–O2 114.3(2), O7–Ni1–O2 86.2(2), N1–Ni1–O2 153.6(2), O1–Ni1–O2 59.6(2), N2ⁱ–Ni1–O2 90.2(3).

i: $-x+1/2, y+1/2, -z+1/2$ ii: $x+1/2, y, -z$

IR (cm^{−1}) selected bonds: 3431(s), 3088(m), 2946(w), 1630(vs), 1543(s), 1460(s), 1359(vs), 1223(m), 1079(m), 1023(w), 928(w), 817(m), 790(m) and 725(s).

Results and Discussion

Determination of the structure of the [Ni(bpp)(NIP)(H₂O)]_n by X-ray crystallography showed [14] the complex in the solid state (Fig. 3) to be a polymeric species and is 3D coordination polymer. The nickel atoms are linked by oxygen and nitrogen atoms and can be considered to be six-coordinate with O₄N₂ donor atoms array. The coordination around Ni atom is distorted octahedral and three oxygen atoms of “NIP”, two nitrogen atoms of the “bpp” ligands and one oxygen atom of the water molecule chelate the Ni atom. Two nitrogen atoms from “bpp” ligands are in *cis* position (the N1–Ni1–N2ⁱ angle is 93.1(3)°). The intra-chain Ni^{II}–Ni^{II} distances by “bpp” and “NIP” ligands are 11.18 and 8.87 Å, respectively. Each “NIP” anion acts as a three-dentate ligand, connecting two Ni²⁺ ions. The one of carboxylate groups of the “NIP” ligand act as bidentate and other carboxylate group of this ligand act only as monodentate mode. The oxygen atoms of the nitro group is not coordinated to Ni atoms. This is consistent with the assumption that carboxylate group is the stronger binding ligand than the nitro group (−CO₂[−] > NO₂[−]).

There are three conformations of the “bpp” ligand. This flexible ligand usually assumes TT, TG or GG conformations (Figure 1) with quite different N-to-N distances (within the 6.7–10.1 Å range) [14]. The TT and TG conformations have been fairly widely encountered and such structures tend to pack efficiently, whereas the GG conformations are quite rare in the context of coordination polymers [15–16]. Self-assembly of “bpp” ligand in this complex is the GG conformation type with a N-to-N distance of 8.30 Å (Figure 3).

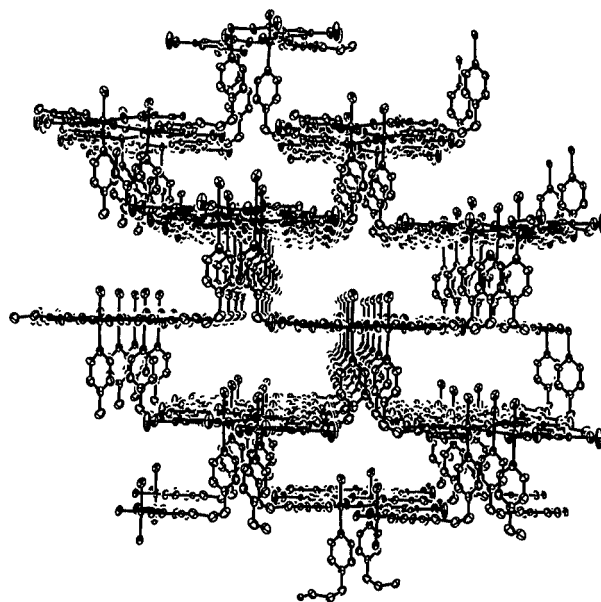


Fig. 3 A view of the [100] layer of the coordination polymer [Ni(bpp)(NIP)(H₂O)]_n.

Table 1 Hydrogen bonds (in Å and °) for [Ni(bpp)(NIP)(H₂O)]_n.

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(7)–H(7B)...O(2) ^v	0.82	2.05	2.763(8)	144.9
O(7)–H(7C)...O(4) ^{vi}	0.81(2)	1.84(3)	2.653(8)	173(11)

v: $-x, -y+2, -z+1$; vi: $-x-1/2, -y+2, z$

The [Ni(bpp)(NIP)(H₂O)]_n is involved in hydrogen bonding. The coordinated water molecule is involved in hydrogen bonding acting as hydrogen-bond acceptors with O atoms of carboxylate group from “NIP” as potential hydrogen-bond donors and the hydrogen bond parameters are given in the Table 1.

There is both face-to-face and edge-to-face π – π stacking [17–19] interactions between aromatic rings belonging to adjacent chains in this network, as shown in Figure 3. The phenyl groups of “NIP” ligands are almost parallel and separated by a distance of about 3.5 Å, close to that of the layers in graphite. Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the face-to-face “ π –stacking” type, rather than “edge-to-face” or “vertex-to-face” types [20–22]. The centroid-centroid distance of phenyl groups is 3.71 Å and angle between the ring normal and the centroid vectors is 18.99°. There is also edge-to-face interactions between the “bpp” ligands and slippage distance is 3.78 Å.

The plot of $\chi_m T$ versus T for the title complex is shown in Figure 4a. The $\chi_m T$ value at 300 K is 0.92 cm³ K mol^{−1}, which decreases smoothly from 300 to 10 K and decreases sharply to reach 0.41 μ_B cm³ K mol^{−1} at 2 K. The μ_{eff} value of per Ni^{II} ion (2.72 μ_B) at room temperature is slightly lower than the spin-only value for Ni^{II} (2.83 μ_B). The data fit the Curie-Weiss law $\chi = C(T - \Theta)^{-1}$, with the parameters of $\Theta = -1.26$ K and $C = 0.925$, indicating that the interactions between two Ni^{II} atoms through the effective exchange media are antiferromagnetic. The M value increases from 0.11 $N\beta$ at 1 T to 1.00 $N\beta$ at 10 T (Figure 4b), consistent with the expected value for an Ni magnetic moments with spin $S_T = 1$. With the increasing of the magnetic field, the M value increases sharply to reach the value of 3.11 $N\beta$ at 50 T, indicating that the spins have

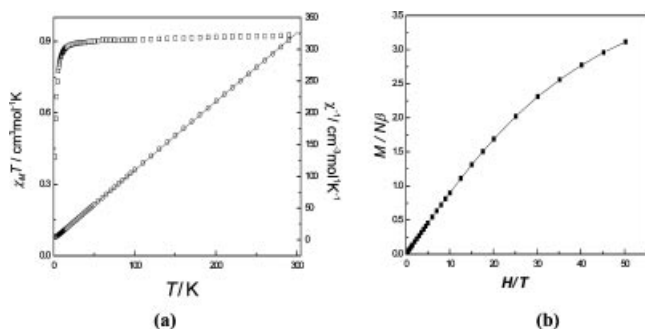


Fig. 4 (a) Plot of $\chi_m T$ at 2T and $\chi_m^{-1} T$ vs T of the complex, (b) Magnetization (solid square) of the complex at 2K as a function of the applied magnetic field (1–50 T).

deviated from the antiferromagnetic coupling and aligned with the applied field.

Supplementary material: Crystallographic data for the structure reported in the paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC-267309. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44–1223/336033; e-mail: deposit@ccdc.cam.ac.uk].

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[14] Crystal Data: $C_{21}H_{19}N_3NiO_7$, M 484.10, orthorhombic, space group Pnna, $a = 16.8886(19)$, $b = 13.9336(16)$, $c = 17.941(2)$ Å, $V = 4221.8(8)$ Å³, D_c ($Z = 8$ f.u.) = 1.523 Mg/m³, $F(000)$ 2000. Specimen: 0.28 x 0.12 x 0.09 mm; $R(wR) = 0.1275$ (0.2325) for 4150 reflections with $I > 2\sigma(I)$.

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