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Axial extension of trinickel string complex by 1,4-benzenedicarboxylate: synthesis, structure, and magnetism of $\{[\text{Ni}_3(\text{dpa})_4(1,4\text{-bdc})] \cdot 0.5\text{H}_2\text{O}\}_n$

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Axial extension of trinickel string complex by 1,4-benzenedicarboxylate: synthesis, structure, and magnetism of $\{[\text{Ni}_3(\text{dpa})_4(1,4\text{-bdc})] \cdot 0.5\text{H}_2\text{O}\}_n$

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The reaction of $[\text{Ni}_3(\text{dpa})_4(\text{ClO}_4)_2]$ with 1,4-benzenedicarboxylate through diffusion of layered-solution led to the precipitation of **1**, $\{[\text{Ni}_3(\text{dpa})_4(1,4\text{-bdc})] \cdot 0.5\text{H}_2\text{O}\}_n$, where dpa^- is 2,2'-dipyridylamido anion, which was characterized by IR, elemental analysis, MS, fluorescence spectrum, TG analysis, and magnetic measurement. Extension of the metal string complex by assembly of $[\text{Ni}_3(\text{dpa})_4]^{2+}$ and $1,4\text{-bdc}^{2-}$ gives a 1-D polymeric structure, in which the axial $1,4\text{-bdc}^{2-}$ influences the $\text{Ni} \cdots \text{Ni}$ distances, fluorescence emission, and magnetism.

Keywords: Metal string complex; Axial extension; Crystal structure; Magnetic property; Synthesis

1. Introduction

Metal string complexes have received attention due to their potential applications as molecular wires and in catalysis [1–3]. The length of metal string complexes can be tuned in two ways: (1) making longer polypyridylamine ligands synthesize polynuclear complexes and (2) axial extension of metal complexes. The trinickel complexes, for example $[\text{Ni}_3(\text{dpa})_4\text{Cl}_2]$, are the prototypes for understanding structural, electronic, and chemical properties of longer metal complexes [4, 5]. Polymeric complexes with trinickel units are sparse; CSD search (CSD, Version 5.31-Aug 2010) only gave three 1-D polymeric structures with $[\text{Ni}_3(\text{dpa})_4]^{2+}$ [6]; 1,4-Benzenedicarboxylate ($1,4\text{-bdc}^{2-}$) is widely used in the construction of MOF polymeric complexes [7–11]. Here, we present the synthesis, structure, and properties of a 1-D polymeric linear complex with $[\text{Ni}_3(\text{dpa})_4]^{2+}$ and $1,4\text{-bdc}^{2-}$, $\{[\text{Ni}_3(\text{dpa})_4(1,4\text{-bdc})] \cdot 0.5\text{H}_2\text{O}\}_n$ (**1**).

2. Experimental

2.1. Materials and instruments

Chemicals (except 2,2'-dipyridylamine) and solvents were purchased from commercial sources and used as received. The 2,2'-dipyridylamine (Hdpa), $[\text{Ni}_3(\text{dpa})_4\text{Cl}_2]$, and

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$[\text{Ni}_3(\text{dpa})_4(\text{ClO}_4)_2]$ were prepared as described in our previous studies [12, 13]. The IR spectrum was recorded on a Nicolet Nexus 470 spectrophotometer from 400 to 4000 cm^{-1} in a KBr pellet. Elemental analyses (C, H, and N) were carried out on a ThermoFinnigan Flash EA1112. Thermogravimetric analysis (TGA) was carried out using a Delta Series TA-SDT Q600 in N_2 between room temperature and 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ using Al_2O_3 crucibles. Fluorescence was carried out on a powder sample at room temperature using a Shimadzu RF-50 spectrometer. Molar magnetic susceptibilities were recorded from 2 to 300 K on a SQUID system with a 3000 gauss external magnetic field. MS (FAB) was determined by a Thermo MAT 95 XP.

2.2. Synthesis of $\{[\text{Ni}_3(\text{dpa})_4(1,4\text{-bdc})] \cdot 0.5\text{H}_2\text{O}\}_n$ (**1**)

Complex **1** was synthesized using a three-layered solution technique in a slender tube of 0.8 cm diameter. The bottom layer was 5 mL of a 0.015 mol L^{-1} aqueous solution containing sodium hydrogen 1,4-benzenedicarboxylate $[\text{Na}(1,4\text{-Hbdc})]$, the middle layer 10 mL of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ with a volume ratio of 2:3, and the upper layer 5 mL of methanol solution containing 0.0075 mol L^{-1} $[\text{Ni}_3(\text{dpa})_4(\text{ClO}_4)_2]$. After 40 days, suitable dark purple crystals for X-ray analysis were obtained. Calcd for $\text{C}_{96}\text{H}_{74}\text{N}_{24}\text{O}_9\text{Ni}_6$: C, 55.97; H, 3.62; and N, 16.32%. Found: C, 55.45; H, 3.73; and N, 16.13%. IR (KBr, cm^{-1}): 3448 s, 1604 s, 1593 s, 1550 w, 1468 s, 1459 s, 1425 s, 1358 m, 1312 w, 1285 w, 1243 w, 1154 m, 1122 m, 1109 w, 1014 m, 893 w, 765 m, 741 m, 641 w, 624 w, 518 w, and 426 w. MS(FAB), m/z : 1022 ($[\text{Ni}_3(\text{dpa})_4(\text{bdc})]^+$). Complex **1** is insoluble in common organic solvents and water and has high thermal stability with the desolvated material decomposing at 330°C .

2.3. X-ray crystallographic determination

Data collection for the single crystal of **1** was performed on a Bruker SMART diffractometer equipped with a CCD area detector. The structure was initially solved by direct methods and successive Fourier syntheses. Full-matrix least-squares refinements on F^2 were carried out using SHELXL-97 [14] in the WinGX Suite with version 1.64 [15]. All non-hydrogen atoms were anisotropically refined. Hydrogens on carbons were placed in idealized positions and refined as riding, with $\text{C-H} = 0.93\text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Hydrogens on water were not added. The molecular drawings were prepared by ORTEP-III for Windows [16] and Mercury software. Details of crystal data and structure refinements for **1** are listed in table 1 and bond lengths and angles in table 2.

3. Results and discussion

3.1. Crystal structure

The asymmetric unit of **1** is shown in figures 1 and 2. The molecular structure of **1** is a 1-D linear polymeric chain (figure 3) where each $1,4\text{-bdc}^{2-}$ bridges two trinickel cores. In the trinickel core, the linear trinickel string is wrapped by four syn-type dpa^- ligands. Each terminal Ni is five-coordinate to four N donors from four dpa^- and one oxygen from one $1,4\text{-bdc}^{2-}$, while the inner Ni is square planar defined by four nitrogens of

Table 1. Crystallographic data and refinement parameters for **1**.

Empirical Formula	C ₉₆ H ₇₄ N ₂₄ Ni ₆ O ₉
Mr	2060.05
Temperature (K)	295 ± 2
Crystal color/shape	Dark purple/block
Space group	Triclinic, <i>P</i> 1
Unit cell dimensions (Å, °)	
<i>a</i>	11.5024(3)
<i>b</i>	11.8679(3)
<i>c</i>	17.5565(5)
α	75.445(1)
β	79.966(1)
γ	87.282(1)
Volume (Å ³), <i>Z</i>	2284.21(11), 1
Calculated density (g cm ⁻³)	1.498
Absorption coefficient (mm ⁻¹)	1.284
<i>F</i> (000)	1058
Measured reflections	31358
Unique reflections	8071
Observed reflections	6843
Crystal size (mm ³)	0.17 × 0.20 × 0.24
θ range for data collection (°)	1.8–25.1
Goodness-of-fit on <i>F</i> ²	1.098
<i>R</i> ₁ and <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.036, 0.111
<i>R</i> ₁ and <i>wR</i> ₂ (all data)	0.045, 0.137
Number of variables	613

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Ni1–Ni2	2.4245(5)	Ni2–Ni3	2.4240(4)
Ni1–N1	2.078(3)	Ni1–N4	2.077(3)
Ni2–N7	2.111(3)	Ni1–N10	2.095(3)
Ni1–O1	1.998(2)	Ni2–N2	1.896(3)
Ni2–N5	1.882(2)	Ni2–N8	1.894(3)
Ni2–N11	1.892(2)	Ni3–N3	2.101(3)
Ni3–N6	2.090(3)	Ni3–N9	2.109(3)
Ni3–N12	2.104(3)	Ni3–O4 ⁱ	2.017(2)
N1–Ni1–N4	93.05(11)	N1–Ni1–N7	163.24(10)
N1–Ni1–N10	86.68(11)	N1–Ni1–O1	103.47(11)
N4–Ni1–N7	88.16(11)	N4–Ni1–N10	164.58(10)
N4–Ni1–O1	100.35(11)	N7–Ni1–N10	87.76(11)
N7–Ni1–O1	92.72(10)	N10–Ni1–O1	94.69(10)
N2–Ni2–N5	89.82(11)	N2–Ni2–N8	179.50(11)
N2–Ni2–N11	91.09(12)	N5–Ni2–N8	89.70(11)
N5–Ni2–N11	179.03(12)	N8–Ni2–N11	89.39(12)
N3–Ni3–N6	89.43(10)	N3–Ni3–N9	162.68(10)
N3–Ni3–N12	88.30(10)	N3–Ni3–O4 ⁱ	92.24(9)
N6–Ni3–N9	90.11(10)	N6–Ni3–N12	163.54(9)
N6–Ni3–O4 ⁱ	99.43(10)	N9–Ni3–N12	87.26(10)
N9–Ni3–O4 ⁱ	104.91(10)	N12–Ni3–O4 ⁱ	96.95(10)
Ni1–Ni2–Ni3	179.44(2)		

Symmetry code, *i*: 1 + *x*, 1 + *y*, *z*.

four dpa⁻. The axial ligand can influence the Ni–Ni distances; Ni–Ni distances [2.4245(5) and 2.4240(4) Å] in **1** are shorter than those in [Ni₃(dpa)₄Cl₂ · 2CH₂Cl₂] [17], but longer than those in [Ni₃(dpa)₄(CH₃CN)₂](ClO₄)₂(CH₃CN)(H₂O) with two neutral axial ligands [18], indicating that axial ligands influence the structural parameters. The Ni–O distances [1.998(2) and 2.017(2) Å] are shorter than those in [Ni₃(dpa)₄(NO₃)₂]

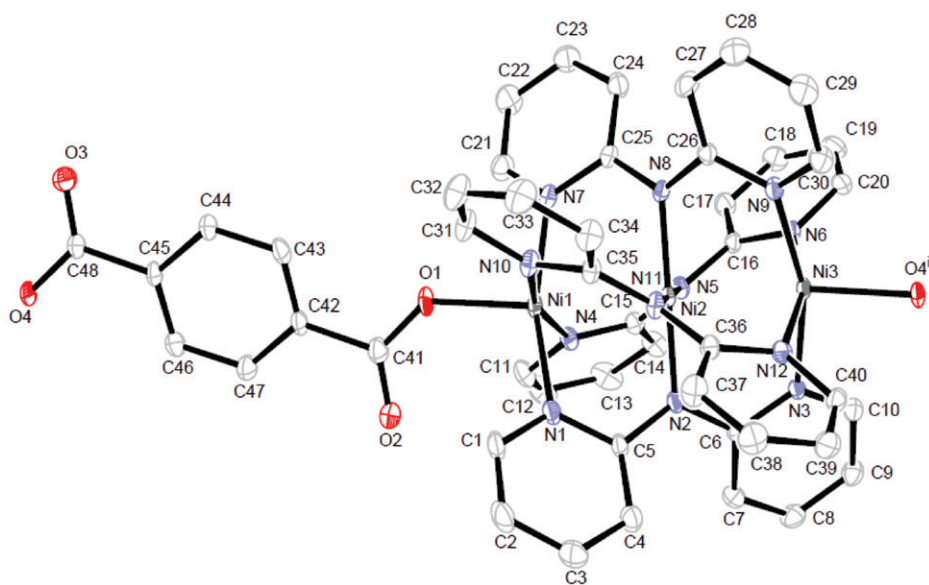


Figure 1. ORTEP of the molecular structure of **1**. Hydrogens and water are omitted for clarity. Symmetry code, *i*: 1 + *x*, 1 + *y*, *z*.

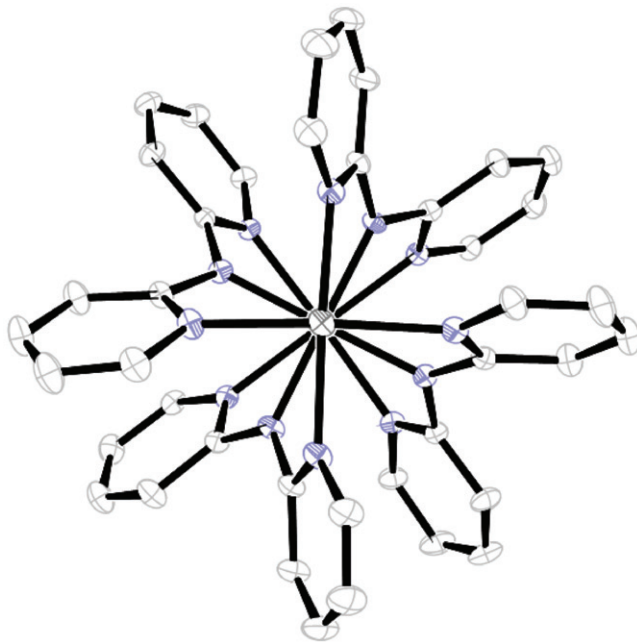
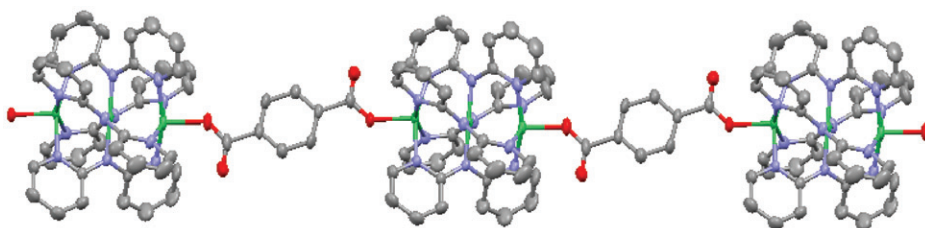
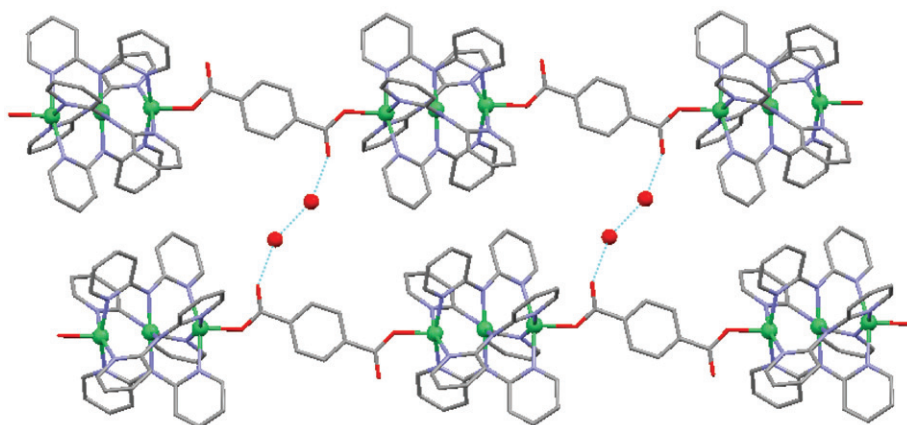


Figure 2. View of the $[\text{Ni}_3(\text{dpa})_4]^{2+}$ unit along Ni_3 axis.

Figure 3. View of the 1-D chain for **1**.Figure 4. View of the 1-D ladder hydrogen-bonding chain for **1**.

[19], but similar to those in trinickel complexes with metalloporphyrins [20]. The average $\text{Ni}_{\text{outer}}\text{-N}$ bond lengths are 2.090(3) Å for Ni1–N and 2.101(3) Å for Ni3–N, and the average Ni2–N is 1.891(3) Å, consistent with the high-spin states for terminal Ni and a low-spin state for central Ni [5, 17, 21–23]. The distance from the Ni to the center of the idealized square base from four dpa^- donors can be related to the Ni \cdots Ni distances in previous references [24]. In **1**, the values for Ni bonded to O axial atoms are 0.288(1) Å for Ni1 and 0.308(1) Å for Ni3, respectively, longer than those in $[\text{Ni}_3(\text{dpa})_4\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2]$ [17], but the Ni \cdots Ni distances in $[\text{Ni}_3(\text{dpa})_4\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2]$ are longer than those in **1**.

Each $1,4\text{-bdc}^{2-}$ is bis-monodentate to Ni and two carboxylates are coplanar with the benzyl ring. The uncoordinated carboxylate oxygens are far away from Ni and capable of forming hydrogen bonds with lattice water. These hydrogen bonds generate a ladder 1-D chain (figure 4) with a total potential solvent-accessible area volume of 128.1 Å³ in **1** (figure 5) [25]. Abundant C–H \cdots π interactions between 1-D polymeric chains are observed. As a result, hydrogen bonds and C–H \cdots π interactions provide additional structural stability.

3.2. Fluorescence

The fluorescence spectrum of **1** (figure S1 as Supplementary material) in the solid state was carried out on a powder sample at room temperature with the $\lambda_{\text{ex}} = 220$ nm. Complex **1** displays strong blue emissions at 409 and 470 nm with a red-shift compared

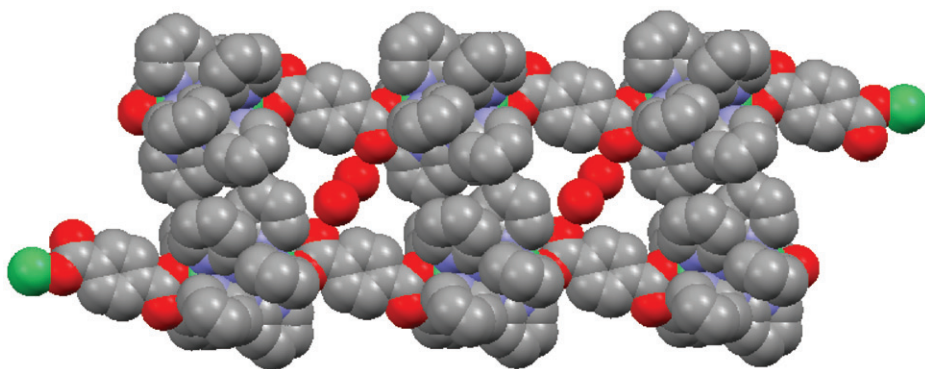


Figure 5. Space-filling view of the 1-D ladder hydrogen-bonding chain for **1**.

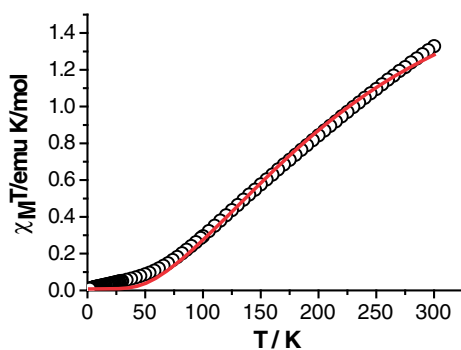


Figure 6. Plot of $\chi_M T$ vs. T for **1**. The solid lines represent least squares fits to the data using equation (1).

to those of $[\text{Ni}_3(\text{dpa})_4\text{Cl}_2]$. These emissions mainly come from dpa^- ligand and can be attributed to ligand-centered $\pi-\pi^*$ transition.

3.3. Magnetism

The magnetism of **1** was studied from 2 to 300 K, with an applied field of 1000 gauss. The plot of $\chi_M T$ versus T is shown in figure 6. At 300 K, the $\chi_M T$ value of $1.3 \text{ emu K mol}^{-1}$ is less than $2.00 \text{ emu K mol}^{-1}$ for two independent $S = 1$ centers, but is in agreement with a five-coordinate Ni. The $\chi_M T$ value gradually decreases as the temperature decreases, towards zero below 50 K, indicating the ground state of a spin state of $S = 0$. The magnetic data were modeled using the approximate equation (1) for fitting the data according to previous reports [26, 27]:

$$\chi_M = (1 - P)C'(2e^{2J/kT} + 10e^{5J/kT})/(1 + 3e^{2j/Kt} + 5e^{6x}) + P(2N_g^2\beta^2/3kT) + N\alpha \quad (1)$$

$$C' = N g^2 \beta^2 / k(T - \theta)$$

Table 3. Least squares fitting parameters of magnetic susceptibility data.

J (cm^{-1})	g	P	θ	$N\alpha$	R
-82.7	2.03	0.00757	0	5.5×10^{-5}	0.9963

where N is Avogadro's number, g the Landé factor, β the Bohr magneton, k the Boltzmann constant, J the coupling constant, T the absolute temperature, θ the Weiss temperature, P the relative content for paramagnetic impurity where spin state $S = 1$ is assumed, and $N\alpha$ the temperature-independent paramagnetism. Least squares fitting gives the best fitting parameters with g of 2.03 and an exchange parameter J of -82.7 cm^{-1} . Other fitting parameters are shown in table 3. Some previous reports showed that the J values depend on the nature of the axial ligands. Longer Ni...Ni distances lead to more negative J value [28]. Such a fact is not true for **1** because the Ni...Ni distances are similar in **1** and $[\text{Ni}_3(\text{dpa})_4(\text{AnCOO})_2]$ [28], while their J values are significantly different.

4. Conclusion

The 1-D polymeric complex $\{[\text{Ni}_3(\text{dpa})_4(1,4\text{-bdc})] \cdot 0.5\text{H}_2\text{O}\}_n$ with 1,4-benzenedicarboxylate was synthesized and the axial extension results in some differences: (1) the axial 1,4-bdc²⁻ influences the Ni...Ni distances; (2) in **1**, the displacements from the square plane are not closely related to the Ni...Ni distances, which has been established in references; and (3) the J value is not simply related to Ni...Ni distances.

Supplementary material

CCDC-788066 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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