The first one-dimensional coordination polymer containing O–H···F–Ni hydrogen bonding: crystal structure of $[Ni_3(dpa)_4F_2][Ni_3(dpa)_4(H_2O)_2](BF_4)_2 \cdot 2CH_3OH$

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Abstract

The one-dimensional coordination polymer, $[Ni_3(dpa)_4F_2][Ni_3(dpa)_4(H_2O)_2](BF_4)_2 \cdot 2CH_3OH$ (dpa⁻ = bis(2-pyridyl)amido ligand), has been constructed. The title complex crystallizes in the triclinic system, space group P1̄, with $a = 11.5966(1)$, $b = 19.5609(2)$, $c = 20.1509(2)$ Å, $\alpha = 79.5672(4)$, $\beta = 75.4196(4)$, $\gamma = 76.2199(5)°$, $Z = 2$. The rare type hydrogen bonding of O–H···F–Ni links the two kinds of the trinickel metal string complexes as building blocks.
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1. Introduction

In the past decade, the trinuclear metal string complexes of various metal centers (Ni [1–3], Cu [4,5], Cr [6–9], Co [10–12], Ru [13], Rh [13]) with bis(2-pyridyl)amido ligand (dpa⁻ anion) have been extensively investigated. The longer linear oligo-nuclear metal string complexes with four [14], five [15–17], seven [14,18] and nine [19] metal centers have been developed by our group. These complexes have the potential to be applied in the molecular metal wire, which drive us to investigate further. On other hand, all of these metal string complexes can act as the building blocks or 'supramolecular synthons' because they have two easily replaced axial ligands. These complexes will become a new type of character in supramolecular chemistry. From the simplest metal string complexes, $[M_3(\mu_3\text{-dpa})_4Cl_2]$ (M = Ni(II), Cr(II) and Co(II)), to the long metal string complexes, a series of substitution reactions in the axial positions using various anions (for example, N_3^-, SCN⁻)

have been carried out. Some one-dimensional coordination polymers have been achieved in which the trinuclear metal string complexes are linked by the different axial ligands as a bridging ligand [3].

Hydrogen bonding is the most reliable directional interaction in supramolecular construction [20–22]. There are many papers related to the hydrogen bonding in organic system. However, the research on assembling the coordination polymer by hydrogen bonding is quite young and some confusable comparison with organic molecules systems. The main problem comes from the typical atoms that form the hydrogen bonding are also good resources for the ligand to coordinate with metal ions. Thus, we are interested in the coordination polymers assembled by the hydrogen bonding. Here, we reported the first one-dimensional coordination polymer containing rare type hydrogen bonding of O–H···F–Ni.

2. Experimental

The $Ni_3(dpa)_4Cl_2$ were synthesized according to the literature [3]. Solvents were purified and were freshly distilled before using.

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2.1. Synthesis of $[Ni_3(dpa)_4F_2][Ni_3(dpa)_4(H_2O)_2](BF_4)_2 \cdot 2CH_3OH$

A methanol solution (2 ml) of $AgBF_4$ (32.12 mg, 0.165 mmol) was added to a methanol solution (20 ml) of $Ni_3(dpa)_4Cl_2$ (50 mg, 0.055 mmol) with stirring for 24 h at room temperature. There are white precipitates, which are AgCl, in the reaction solution. The filtrate (A) from this reaction mixture will be used in the next step. Other hands, a methanol solution (2 ml) of $AgBF_4$ (21.41 mg, 0.110 mmol) was slowly added to a methanol solution (20 ml) of $Ni_3(dpa)_4Cl_2$ (50 mg, 0.055 mmol) with stirring for 5 h at room temperature and then filtered the reaction mixture and reduced the volume of the filtrate to 5 ml. Following then, 10 ml distilling water was added into the filtrate (B) and stirred for 3 h at 70 °C. Mixing the A and B gives the dark purple solution. The dark purple single crystals suitable for X-ray analysis were obtained by evaporating this solution very slowly. The yield is 70%. *Anal. Calc.* for $C_{82}H_{76}B_2F_{10}N_{24}Ni_6O_4$: C, 48.62%; H, 3.78%; N, 16.60%. Found: C, 48.58%; H, 3.72%; N, 16.65%.

2.2. Crystal structure determination

A dark purple crystal ($0.12 \times 0.12 \times 0.05$ mm^3) was mounted on a glass capillary. Data collection was carried out on a Siemens SMART diffractometer with a CCD detector with Mo K$_\alpha$ radiation ($\lambda = 0.71079$ Å) at 150 K. The θ range for data collection was from 2.11° to 27.50°. The completeness to 2θ was 99.9%. An absorption correction was applied with the maximum and minimum transmission factors of 0.949 and 0.900, respectively. Crystal data for $C_{82}H_{76}B_2F_{10}N_{24}Ni_6O_4$ (see also supplementary materials): $M_w = 2025.55$, triclinic, space group P$\bar{1}$, $Z = 2$, $a = 11.5966(1)$, $b = 19.5609(2)$, $c = 20.1509(2)$ Å, $\alpha = 79.5672(4)$, $\beta = 75.4196(4)$, $\gamma = 76.2199(5)°$, $V = 4260.67$ Å^3, $d_{calcd.} = 1.579$ g m^{-3} ($\mu = 1.387$ mm^{-1}). The structure was solved by the direct methods with the SHELXTL 97 program [23]. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically based on F^2. Some of hydrogen atoms were placed in their geometrically generated positions and other hydrogen atoms were located from the different Fourier map and refined isotropically. The R_{int} is 0.0393 for 19 560 independent reflections and $R1$ is 0.0560 ($wR2 = 0.1471$) for 13 071 reflections with $I > 2\sigma(I)$.

3. Results and discussion

One building block in the title complex is a neutral species $[Ni_3(\mu_3\text{-dpa})_4F_2]$, in which F$^-$ ion comes from the decomposition of BF_4^- anion [6]. The other is $[Ni_3(\mu_3\text{-dpa})_4(H_2O)_2]^{2+}$ cations (Fig. 1(a)). It is the first

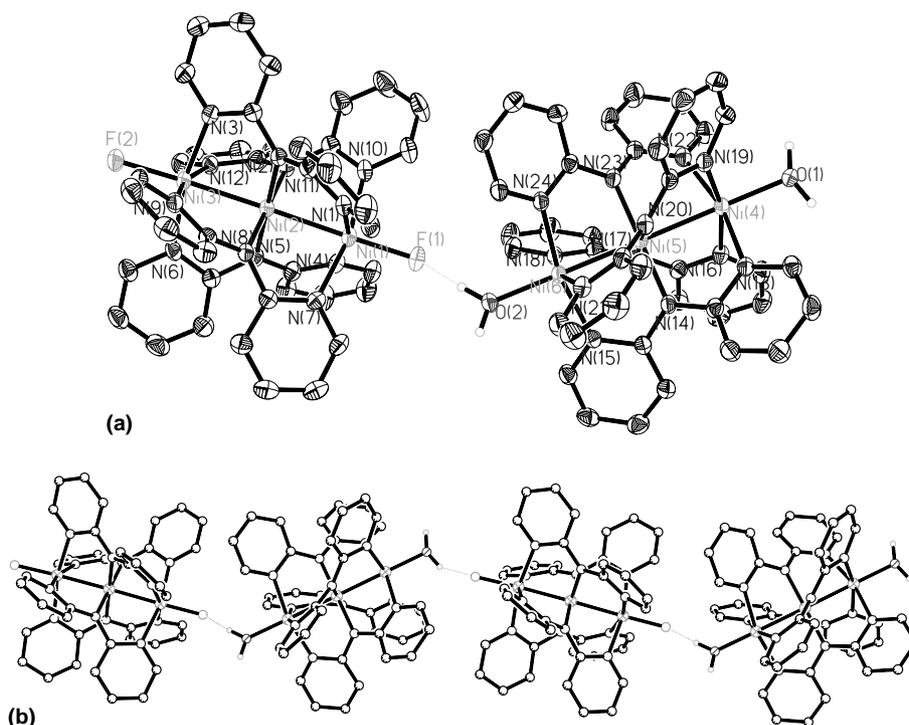Fig. 1. (a) The molecular structure of the $[Ni_3(dpa)_4F_2][Ni_3(dpa)_4(H_2O)_2](BF_4)_2 \cdot 2CH_3OH$ as 50% probability ellipsoids. (b) The picture of O–H$\cdots$F–Ni hydrogen bonding along the one-dimensional chain of the title complex. F1$\cdots$H2 = 1.568 Å, O2–H2$\cdots$F1 172.4°, H2$\cdots$F1–Ni1 153.5°; F2$\cdots$H1A = 1.656 Å, O1A–H1A$\cdots$F2 147.2°, H1A$\cdots$F2–Ni3 170.5°. The anions, solvent water molecules and hydrogen atoms are omitted for clarity in both pictures.

example of water molecules becoming the axial ligand to coordinate with metal string complexes. Fundamentally, water molecules are in competition to coordinate with metal ions in the presence of dpa$^-$ anions. Thus, water molecules should be avoided during the synthesis of metal string complexes. To our knowledge, there are no past reports about water molecules in the crystal structures of the metal string complexes except $[Cr_3(dpa)_4Cl_2]I_3 \cdot THF \cdot 2H_2O$ in which the interstitial water molecules have an adventitious origin [8]. We have successfully introduced water molecules into the trinuclear metal string complexes to meet the requirements of hydrogen bonding research [24]. These results have shown that the $[M_3(\mu_3\text{-dpa})_4]^{2+}$ species are stable in the presence of water molecules.

The skeleton structure of two $[Ni_3(\mu_3\text{-dpa})_4]^{2+}$ units are identical in both species. The Ni–Ni distances of trinickel metal string complexes fall into two ranges depending on the different axial ligands, which are in range of 2.420–2.447 Å and 2.385–2.400 Å. The longest Ni–Ni distance (2.4470(7) Å) and shortest one (2.385(2) Å) have been found in the $[Ni_3(\mu_3\text{-dpa})_4(CN)_2]$ [25] with a strong σ-donor axial ligand and in the $[Ni_3(\mu_3\text{-dpa})_4(\mu_{1,3}\text{-}N_3)](PF_6)$ [3] with the μ-1,3 bridge azide, respectively. The Ni–Ni distances of title complex belong to the latter case. The reason is that the axial ligands in the title complex, F$^-$ and coordinated H_2O ligand, are weak σ-donor ligands. The influence by the σ-donor ability of axial ligand in Ni–Ni distance has also been confirmed by the $[Ni_3(\mu_3\text{-dpa})_4(N_3)_2]$ and $[Ni_3(\mu_3\text{-dpa})_4(\mu_{1,3}\text{-}N_3)](PF_6)$ [3], even by the pentanickel(II) $[Ni_5(\mu_5\text{-tpda})_4X_2]$ complexes [16]. The Ni–N distances in the title complex are divided into two ranges: 2.051(4)–2.103(4) Å for terminal Ni(II) ions and 1.887(3)–1.909(4) Å for the central Ni(II) ions which is consistent with the fact that the two terminal Ni(II) ions

are in a square pyramidal geometry with high-spin ($S = 1$) configuration and the central Ni(II) ion is square planar with low-spin ($S = 0$) configuration.

The important structural character of the title complex is that the two building blocks are linked by O–H$\cdots$F hydrogen bond. The detailed O–H$\cdots$F hydrogen bond in the title complex is: F1$\cdots$O2 = 2.458 Å, F1$\cdots$H2 = 1.568 Å, O2–H2$\cdots$F1 172.4°, H2$\cdots$F1–Ni1 153.5°, F2$\cdots$O1A = 2.461Å, F2$\cdots$H1A = 1.656 Å, O1A–H1A$\cdots$F2 147.2°, H1A$\cdots$F2–Ni3 170.5°. Two species are linked asymmetrically by the two types O–H$\cdots$F hydrogen bonds and form the zigzag chain (Fig. 1(b)). The O–H$\cdots$F hydrogen bonding has not been given much attention up until now. Recently, researches on the organic fluorine atoms as hydrogen bonding acceptor are in the process [26–32]. However, no example of coordination polymer containing the O–H$\cdots$F–Ni hydrogen bond can be found in the literatures or CSD. Comparing with O–H$\cdots$F hydrogen bonding in organic system, for example, $HOC(CF_3)_2(4\text{-}Si(i\text{-}Pr)_3\text{-}2, 6\text{-}C_6H_2(CF_3)_2)$ [26], which has the shortest intermolecular O–H$\cdots$F hydrogen bonding to be reported in literature (H$\cdots$F = 2.01 Å; O–H$\cdots$F = 171°), the distance of H$\cdots$F in the title complex is dramatically shorter. It should be mentioned that there is a "unconstrained" connection between the O–H and the F ion in the title complex without the additional, stronger intermolecular hydrogen bonds which are the conventional O–H$\cdots$O, O–H$\cdots$N hydrogen bonding. Obviously, these two situations are quite different. Thus, the O–H$\cdots$F hydrogen bonding can assemble the coordination polymer directly. The bond length of Ni–O (H_2O) is 2.020(3) and 2.026(3) Å, which can match with the Ni–O distance in other complexes with water molecules coordinated with Ni(II) ions (2.085 and 2.055 Å) [32]. No significant changes occur in the Ni–O bond length after formation
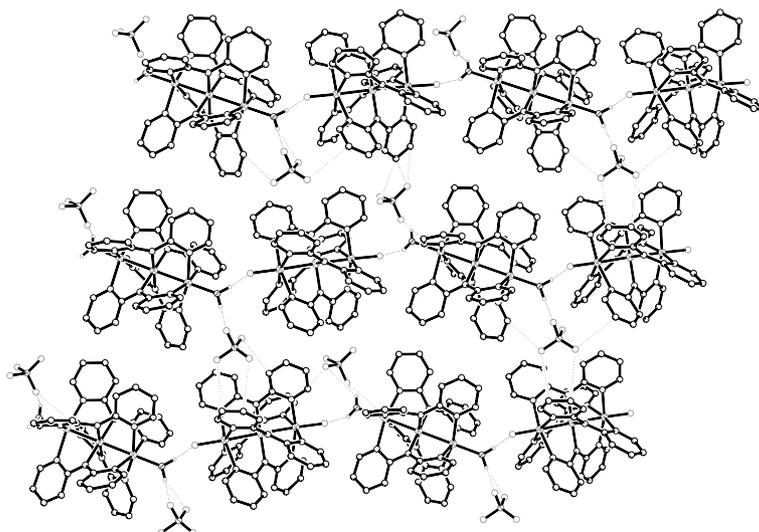

Fig. 2. The picture showing the hydrogen bonding interaction between the chains.

of hydrogen bonding. However, to the best of our knowledge, the crystallography data of Ni(II) coordination complexes with F^- ligand is very scarce. Besides the strong O–H$\cdots$F hydrogen bonding along the chain, the fluoride atoms of BF_4^- anions also form the weak hydrogen bond with another hydrogen atom in the axial H_2O ligand. The distances of F7$\cdots$H2′ and F5$\cdots$H1′ are 1.893 and 1.962 Å, respectively, (F7$\cdots$O2, 2.778 Å, F7$\cdots$H2′–O2, 167.6°; F5$\cdots$O1, 2.768 Å, F5$\cdots$ H1′–O1, 149.1°). The remaining fluoride atoms of BF_4^- anions form weak F$\cdots$H–C hydrogen bonding with the hydrogen atoms of pyridine rings in the dpa$^-$ ligand and assemble the one-dimensional chains into two-dimensional layer structure (Fig. 2) and even three-dimensional hydrogen bond network. They are: F3$\cdots$H77C 2.439 Å, F3$\cdots$C77B, 3.279 Å, F3$\cdots$H77C–C77B 147.3°, F4$\cdots$H68E 2.661Å, F4$\cdots$C68D 3.342 Å, F4$\cdots$H68E–C68D 129.0°. The stereo-hindrance of the chain being wrapped by four all-*syn* type dpa$^-$ ligands may be the reason why the F$\cdots$H hydrogen bond is weak.

In summary, the O–H$\cdots$F hydrogen bonding can play an important role in the direct assembly of coordination polymers, contributing to the supramolecular systems. As mentioned in the beginning of this paper, there are still many problems in coordination polymers assembled by hydrogen bonding. Further investigation is still in process.

Supporting information available. Listing crystallographic parameters in CIF format, atomic coordinates, bond distances and angles, thermal parameters and hydrogen atom positions for the title complex. This material is available free of charge from authors.

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