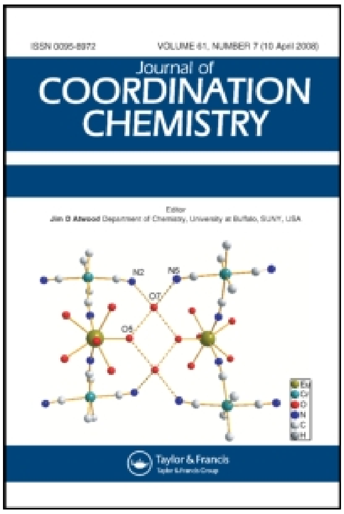

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Influence of axial ligands and anions on the Ni-Ni distances in trinickel string complexes: synthesis, structure, and properties of $[Ni_3(dpa)_4(CH_3CN)_2] \cdot (ClO_4)_2 \cdot (CH_3CN) \cdot H_2O$

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Influence of axial ligands and anions on the Ni–Ni distances in trinickel string complexes: synthesis, structure, and properties of $[Ni_3(dpa)_4(CH_3CN)_2]\cdot(ClO_4)_2\cdot(CH_3CN)\cdot H_2O$

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A cation–anion metal string complex with neutral axial ligands, $[Ni_3(dpa)_4(CH_3CN)_2]\cdot(ClO_4)_2\cdot(CH_3CN)\cdot H_2O$ (**1**) where dpa^- is 2,2′-dipyridylamine anion, was synthesized and characterized by elemental analysis, IR, fluorescence, UV, and CV spectroscopic methods, and single crystal X-ray analysis. The Ni–Ni distances in **1** are longer than those in $[Ni_3(dpa)_4(CH_3CN)_2]\cdot(PF_6)_2\cdot 3.14CH_3CN$ (**2**) and $[Ni_3(dpa)_4F_2]\cdot[Ni_3(dpa)_4(H_2O)_2]\cdot(BF_4)_2\cdot 2CH_3OH$, indicating that the counter anions affect the Ni–Ni distances of trinickel string complexes. Compared with $Ni_3(dpa)_4Cl_2$ and $Ni_3(dpa)_4(ClO_4)_2$, **1** also has different fluorescence, UV, and CV properties. Therefore, this study clearly indicates that ligands and counter anions largely influence the structures and properties of trinickel string complexes.

Keywords: Trinickel string complex; Metal string complex; Cyclic voltammetric property; Axial substitution; Neutral ligand

1. Introduction

Trinuclear metal string complexes with 2,2′-dipyridylamine (Hdpa) ligands have received considerable attention due to their potential applications in the areas of molecule-based magnetism [1, 2], electronics [3], and photochemistry [4]. Most reported trinickel string complexes have anionic axial ligands, such as Cl^-, SCN^-, CN^-, etc. [5–15]. CSD search (Version 5.31, February 2010) only gave one complex with two terminal neutral ligands, $[Ni_3(dpa)_4(CH_3CN)_2]\cdot(PF_6)_2\cdot 3.14CH_3CN$ (**2**) [16], one complex with one neutral terminal ligand and one weakly coordinated $PF_6{}^-$, $Ni_3(dpa)_4(CH_3CN)(PF_6)_2\cdot 2CH_2Cl_2$ (**3**) [17], and one complex containing $[Ni_3(dpa)_4(H_2O)_2]^{2+}$ which has two terminal neutral ligands, $[Ni_3(dpa)_4F_2]\cdot[Ni_3(dpa)_4(H_2O)_2]\cdot(BF_4)_2\cdot 2CH_3OH$ (**4**) [18]. The axial ligands, counter anions, and solvents can influence the structures of trinickel string complexes, and their properties can be tuned by such axial modifications. Therefore, investigation of trinickel string complexes with neutral axial ligands is important to tune functional properties. To further investigate the structures and properties of trinickel string complexes with

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neutral axial ligands, we prepared a new complex with two axial neutral ligands, $[Ni_3(dpa)_4(CH_3CN)_2]\cdot(ClO_4)_2\cdot(CH_3CN)\cdot H_2O$ (**1**). Comparison of **1**–**4**, $Ni_3(dpa)_4Cl_2$, and $Ni_3(dpa)_4(ClO_4)_2$ gives diverse Ni–Ni distances, different cyclic voltammetric (CV), and UV properties, indicating neutral axial ligands and counter anions influence structures and properties.

2. Experimental

2.1. *Materials*

All chemicals (except 2,2′-dipyridylamine) and solvents were purchased from commercial sources and used as received. The 2,2′-dipyridylamine (Hdpa) and $Ni_3(dpa)_4Cl_2$ were prepared according to the literature and described in our previous study [19].

2.2. *Physical measurements*

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. The electronic spectrum was measured on a SPECORD 2000 UV-Vis spectrophotometer in CH_2Cl_2 at room temperature. Fluorescence was carried out on a powder sample at room temperature using a Shimadzu RF-50 spectrometer. Electrochemistry was carried out on a CHI 600C potentiostat. Cyclic voltammograms were measured by a homemade three-electrode cell which was assembled with a BAS glassy carbon disc ($0.07\,cm^2$) as the working electrode, a platinum plate ($12\,cm^2$) as the auxiliary electrode, and a homemade Ag/AgCl (saturated) reference electrode. These electrodes were separately arranged by placing in a L-tube filled with electrolyte solution. Potentials are reported *versus* Ag/AgCl (saturated) and referenced to the ferrocene–ferrocenium ($[Cp_2Fe]/[Cp_2Fe]^+$) couple which occurs at $E_{1/2} = +0.54\,V$ *versus* Ag/AgCl (saturated). The values of $E_{1/2}$ are taken as $(E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively.

2.3. *Synthesis*

2.3.1. Synthesis of $Ni_3(dpa)_4(ClO_4)_2$. A mixture of 5 mL of MeOH solution containing $AgClO_4$ (0.486 g, 2.0 mmol) and 20 mL of CH_2Cl_2 solution containing $[Ni_3(dpa)_4Cl_2]$ (0.928 g, 1.0 mmol) was stirred for 2 h, then filtered. The solvent of the filtrate was removed under vacuum, and the remaining dark purple solid was recrystallized with ether and CH_2Cl_2, and dried under vacuum. The complex was confirmed by mass spectrum and elemental analysis.

2.3.2. Synthesis of $[Ni_3(dpa)_4(CH_3CN)_2]\cdot(ClO_4)_2\cdot(CH_3CN)\cdot H_2O$ (1). A solution of CH_2Cl_2 (30 mL) containing $[Ni_3(dpa)_4(ClO_4)_2]$ (0.106 g, 0.1 mmol) was added to 10 mL of CH_3CN and stirred for 2 days, and then filtered. The filtration was saturated by ether atmosphere. After 2 days, dark purple block-shaped crystals had formed. Anal. Calcd for $C_{46}H_{43}Cl_2N_{15}Ni_3O_9$: C, 46.16%; H, 3.62%; N, 17.55%. Found: C, 46.56%; H, 3.97%; N, 17.02%. IR (KBr, cm^{-1}): 3449 m, 1604 m, 1550 w, 1469 s, 1425 s, 1358 m, 1313 w, 1284 w, 1243 w, 1154 m, 1119 m, 1086 m, 1014 w, 894 w, 764 w, 740 w, 624 w, 519 w, 427 w.

2.4. *X-ray crystallographic determination*

The single crystal of **1** was mounted on the tip of a fiber and data collection was performed on a Bruker SMART diffractometer equipped with a CCD area detector. The structure was solved by direct methods and successive Fourier syntheses. Full-matrix least squares refinements on F^2 were carried out using SHELXL-97 package [20] in the WinGX Suite, version 1.64 [21]. All non-hydrogen atoms were anisotropically refined. Hydrogens on carbons were placed in idealized positions and refined as riding, with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The water was disordered over two positions and hydrogens on this disordered water were not added. The molecular drawings were helped by ORTEP-III for Windows [22]. Detailed crystal data and structure refinements for **1** are listed in table 1.

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

Formula	$C_{46}H_{43}Cl_2N_{15}Ni_3O_9$
Molecular weight	1196.93
Temperature (K)	295 ± 2
Crystal color/shape	Dark purple/block
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	13.3953(4)
b	24.1132(7)
c	16.7534(5)
α	90
β	101.150(1)
γ	90
Volume (Å^3), Z	5309.3(3), 4
Calculated density, D (g cm^{-3})	1.497
Absorption coefficient, μ (mm^{-1})	1.221
$F(000)$	2448
Crystal size (mm^3)	0.14 × 0.23 × 0.35
θ range for data collection (°)	1.7–25.0
Measured reflections	22,803
Unique reflections	8872
Observed reflections	5483
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.075$, $wR_2 = 0.201$
R indices (all data)	$R_1 = 0.120$, $wR_2 = 0.225$
Number of variables	689
Goodness-of-fit	1.293
Largest difference peak and hole (e Å^{-3})	0.953 and –0.943

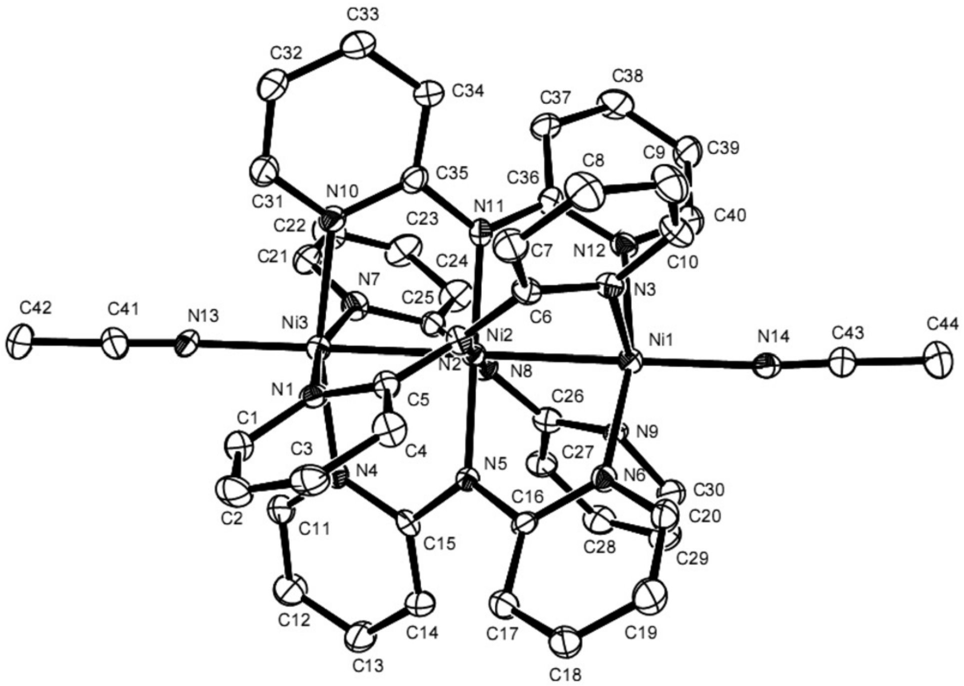

Figure 1. The structure of $[Ni_3(dpa)_4(CH_3CN)_2]^{2+}$ in **1**. Hydrogens are omitted for clarity.

3. Results and discussion

3.1. *Synthesis*

Trinickel string complexes with non-chloride axial ligands, in general, were synthesized from axial replacement of $[Ni_3(dpa)_4Cl_2]$. Replacement of chloride by other anions is somewhat difficult; therefore, silver salts are used to remove the chlorides. In our synthetic procedure, we used the $AgClO_4$ salt, introducing ClO_4^-, which has weak coordination ability; therefore, CH_3CN replaces ClO_4^- to coordinate nickel ions.

3.2. *Structure*

Complex **1** consists of a cation, $[Ni_3(dpa)_4(CH_3CN)_2]^{2+}$, two anions, one CH_3CN, and one water. Thermal ellipsoid drawing of the cation of **1** is shown in figure 1, and selected bond lengths and angles are listed in table 2. The cation $[Ni_3(dpa)_4(CH_3CN)_2]^{2+}$ is linear (figure 2) with the trinickel chain helically wrapped by four syn-type dpa^- ligands. The terminal sites of $[Ni_3(dpa)_4]^{2+}$ are occupied by two CH_3CN. Each dpa^- coordinates to three Ni ions. The total length for the cation is 14.01 Å. The pyridine rings of dpa^- are twisted with dihedral angles of 51.8(3)° for N1/C1–C5 and N3/C6–C10, 52.9(3)° for N4/C11–C15 and N6/C16–C20, 55.9(2)° for N7/C21–C25 and N9/C26–C30, and 55.4(3)° for N10/C31–C35 and N12/C36–C40. In **1**, the Ni$\cdots$Ni separations are 2.3983(12) Å for Ni1–Ni2 and 2.4047(12) Å for Ni2–Ni3, subtly longer

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

Ni1–Ni2	2.3983(12)	Ni2–Ni3	2.4047(12)
Ni1–N3	2.080(5)	Ni1–N6	2.090(5)
Ni1–N9	2.094(5)	Ni1–N12	2.104(5)
Ni2–N2	1.887(5)	Ni2–N5	1.908(5)
Ni2–N8	1.894(5)	Ni2–N11	1.886(5)
Ni3–N1	2.098(5)	Ni3–N4	2.079(5)
Ni3–N7	2.097(6)	Ni3–N10	2.081(5)
Ni1–N14	2.058(7)	Ni3–N13	2.056(7)
N3–Ni1–N6	88.8(2)	N3–Ni1–N9	165.1(2)
N3–Ni1–N12	88.7(2)	N3–Ni1–N14	96.0(2)
N6–Ni1–N9	87.9(2)	N6–Ni1–N12	166.5(2)
N6–Ni1–N14	96.8(2)	N9–Ni1–N12	91.1(2)
N9–Ni1–N14	98.9(2)	N12–Ni1–N14	96.7(2)
N2–Ni2–N5	89.4(2)	N2–Ni2–N8	179.1(2)
N2–Ni2–N11	91.0(2)	N5–Ni2–N8	90.3(2)
N5–Ni2–N11	179.5(2)	N8–Ni2–N11	89.3(2)
N1–Ni3–N4	87.7(2)	N1–Ni3–N7	165.9(2)
N1–Ni3–N10	90.3(2)	N1–Ni3–N13	97.1(2)
N4–Ni3–N7	90.2(2)	N4–Ni3–N10	166.3(2)
N4–Ni3–N13	96.9(2)	N7–Ni3–N10	88.4(2)
N7–Ni3–N13	97.0(2)	N10–Ni3–N13	96.8(2)
Ni1–Ni2–Ni3	179.91(5)		

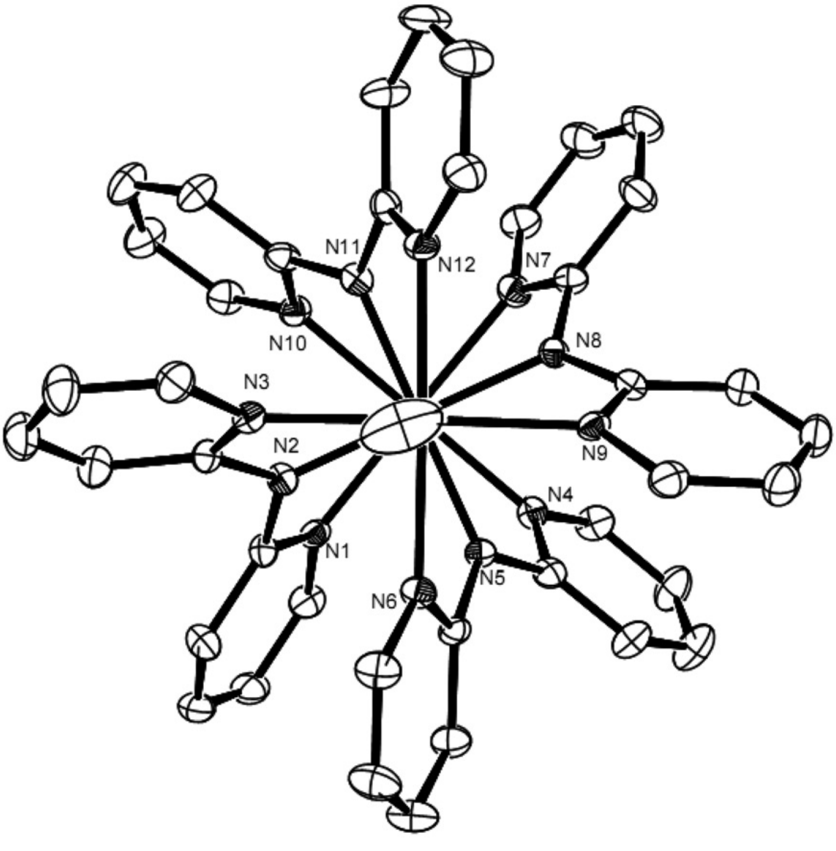

Figure 2. View down the Ni–Ni–Ni direction for the cation of $[Ni_3(dpa)_4(CH_3CN)_2]^{2+}$ in **1**.

than the corresponding distances in $[Ni_3(dpa)_4(CH_3CN)_2]\cdot(PF_6)_2\cdot 3.14CH_3CN$ (**2**) [2.371(2) and 2.376(2) Å] [16], but significantly shorter than those in $Ni_3(dpa)_4Cl_2\cdot 2CH_2Cl_2$ in which the average Ni–Ni distance is 2.4303 Å [23], indicating that the counter anions affect structural parameters.

The nitrogens from dpa^- are nearly square planar around each Ni(II) in **1** and the average Ni–N lengths are 2.092 and 2.089 Å for the two outer nickels, and 1.894 Å for the inner nickel. The Ni–N bond lengths clearly indicate the low-spin state for central Ni and high-spin states for terminal Ni [6]. These Ni–N distances are similar to related values in $[Ni_3(dpa)_4Cl_2]\cdot$solvent [2.0975 and 2.0885 Å for outer and 1.89125 Å for inner] [23], but a little longer than those in **2** [2.0780 and 2.0795 Å for outer and 1.8815 Å for inner]. $[Ni_3(dpa)_4F_2]\cdot[Ni_3(dpa)_4(H_2O)_2](BF_4)_2\cdot 2CH_3OH$ also contains $[Ni_3(dpa)_4(H_2O)_2]^{2+}$ with neutral axial ligands and the average Ni–Ni distance is 2.391 Å, slightly shorter than those in **1**.

Distortion of the square-pyramidal for terminal Ni is strongly related to the Ni–Ni distances, measured by the *d* value, which can be defined as the distance from Ni to the center of the idealized square base given by four dpa^- nitrogens. The *d* values for Ni bonded to CH_3CN axial ligands are 0.258(3) Å for Ni1 and 0.253(3) Å for Ni3, rather longer than those in **2** [0.242 and 0.235 Å]. For comparison, the calculated *d* values for Ni away from the square planes are 0.289 and 0.278 Å in $Ni_3(dpa)_4Cl_2$ [16], 0.238 Å in $[Ni_3(depa)_4(CH_3CN)_2]$ [5], 0.239 Å in $[Ni_3(dpa)_4(CH_3CN)](PF_6)_2\cdot 2CH_2Cl_2]$ [17], and 0.103 Å for $[Ni_3(depa)_4](PF_6)_3$ [16]. These data strongly imply the connection between the *d* values and the bonding strength of axial ligands to the outer Ni. The larger *d* values for terminal Ni away from the square plane, the longer the Ni–Ni distances.

The complex has no aromatic interaction due to the helical arrangement, while intense C–H $\cdots\pi$ interaction between C32–H32 and ring 1 with H $\cdots$ ring distance of 2.79 Å [ring 1 contains N1 and C1–C5] occurs. In addition, there is a weak hydrogen bond between ClO_4^- and water. These C–H $\cdots\pi$ and hydrogen bonding interactions enhance the structural stability.

3.3. *Fluorescent analysis*

The fluorescence spectrum of **1** shows emission bands at 411.9, 435.7, 452.7, and 469.9 nm in the solid state at room temperature. The peak at 411.9 nm in **1** is the maximum. These emissions are mainly caused by dpa^- (the emission peaks for 2,2′-dipyridylamine are 407.1, 451.6, and 470.2 nm), and the emission strength of **1** is stronger than those of free Hdpa, $[Ni_3(dpa)_4(Cl)_2]$, and $[Ni_3(dpa)_4(ClO_4)_2]$, indicating axial replacement of anions by neutral ligands enhances the emission.

3.4. *Electrochemical property*

Electrochemical spectra of **1** and $[Ni_3(dpa)_4(ClO_4)_2]$ in CH_2Cl_2 solution with 0.1 mol L^{-1} TBAP as supporting electrolyte are shown in “Supplementary material” and the electrochemical spectrum of $[Ni_3(dpa)_4Cl_2]$ was reported by Cotton [16]. Complex **1** shows a reversible one-electron redox couple with an $E_{1/2}$ of 1.105 V, which is close to the value of 1.205 V in **2** and 1.029 V for $[Ni_3(dpa)_4Cl_2]$ [16], but more positive than that of $[Ni_3(dpa)_4(ClO_4)_2]$. The effect of substitution of axial ClO_4^- in

Table 3. UV-Vis absorption spectral data for **1**, [$Ni_3(dpa)_4Cl_2$], and [$Ni_3(dpa)_4(ClO_4)_2$] in CH_2Cl_2.

Complex	λ_{max} (nm) (ε/dm^3 mol^{-1} cm^{-1})			
1	237(39,088)	253(40,450)	314(363,125)	347(36,038)
[$Ni_3(dpa)_4Cl_2$]	232(49,763)	258(54,825)	321(71,763)	347(65,513)
[$Ni_3(dpa)_4(ClO_4)_2$]	235(46,563)	253(47,638)	317(41,825)	348(45,050)

[$Ni_3(dpa)_4(ClO_4)_2$] and Cl^- in [$Ni_3(dpa)_4(Cl)_2$] by acetonitrile on the values of $E_{1/2}$ is large.

3.5. *Electronic properties*

The UV-Vis properties of **1**, [$Ni_3(dpa)_4Cl_2$], and [$Ni_3(dpa)_4(ClO_4)_2$] were studied in CH_2Cl_2 at room temperature using a SPECORD 2000 UV-Vis spectrophotometer. A comparison of the UV-Vis spectra of these complexes is shown in "Supplementary material" and the spectral data are listed in table 3. There are no obvious shifts among these three complexes in UV-Vis spectra. But it is obvious that the ε values for **1** are slightly weaker than those in [$Ni_3(dpa)_4Cl_2$] and [$Ni_3(dpa)_4(ClO_4)_2$].

4. Conclusion

A new trinickel string complex with two neutral axial ligands was synthesized, only the second example. This complex shows Ni–Ni distances are affected by axial ligands and counter anions. The Ni–Ni distances in **1** with ClO_4^- counter anions are longer than trinickel string complexes with PF_6^- or BF_4^-. Fluorescence, CV and UV spectroscopic data for **1** are different from those of $Ni_3(dpa)_4Cl_2$ and $Ni_3(dpa)_4(ClO_4)_2$, indicating axial replacement by neutral ligands leads to changes of structures and properties. The d values are tightly related to the Ni–Ni distances. This exploration should benefit rational design and synthesis of trinickel string complexes.

Supplementary material

CCDC-774410 contains 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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