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A novel triruthenium metal string complex with naphthylridylamide ligand: Synthesis, structure, magnetism, and molecular conductance



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ABSTRACT

A triruthenium metal string, $[Ru_3(npa)_4(NCS)_2][PF_6]$ (1), supported by naphthylridylamide (npa) ligands was successfully synthesized and is reported in this work. X-ray single crystal analysis shows that compound 1 exhibits a nonlinear $[Ru_3]^{7+}$ backbone ($\angle = 170.26(3)^\circ$) with long Ru–Ru bond lengths (2.3554(8) Å). The long Ru–Ru distances observed for 1 decrease the Ru–Ru interactions and electric conductance. Magnetic measurements indicate that compound 1 is in a S = 1/2 state. DFT calculations suggest that this unpaired electron occupies the π^* orbital which is stabilized by π -acid NCS⁻ ligands and thus weakening the Ru–Ru π interaction.

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Metal string complexes possessing a 1D transition metal framework are of great interests because electrons can transport through these molecules, and metal string complexes are expected to exhibit the wire-like behavior and function as nano-wires [1]. Because of this potential application, metal string complexes have attracted considerable attention from scientists in the field of molecular electronics [2]. Generally, the approach used to synthesize metal string complexes is by oligopyridylamine ligands (Scheme 1). After deprotonation of oligopyridylamine ligands, the resulting oligopyridylamide can provide enough negative charges to stabilize the central positive 1D metal core. A series of metal string complexes supported by these oligopyridylamine ligands have been synthesized and reported over the past two decades [3]. In 2006, for the first time, our group attempted to develop oligonaphthylridylamine ligands for synthesis of metal string complexes [4a]. Since oligonaphthylridylamide ligands are less anionic than oligopyridylamide ligands with same length, the new metal string complexes tended to form a reduced mix-valent metal core, which significantly enhances the electric conductance [4]. Because of this exciting result, our strategy for developing novel metal string complexes shifted to focus on the oligonaphthylridylamine ligands. More and more metal string complexes supported by various oligonaphthylridylamine ligands are being designed and synthesized [4,5]. Although oligonaphthylridylamide-supported metal strings are the rising stars in the field, it should be noted that currently reported examples of 1D metal chains of have mainly consisted of first row transition metal ions. Considering that heavier transition metal ions (4d and 5d) may show different physical characters, it is important to extend studies of oligonaphthylridylamide-supported metal strings to the heavier transition metal ions. In view of this consideration, here we report the preparation, crystal structure, magnetism, electrochemistry and electric conductance of the naphthylridylamide supported triruthenium string, [Ru₃(npa)₄(NCS)₂][PF₆] (1).

Compound **1** was prepared from the reaction of 2-naphthyridylphenylamine (Hnpa) and Ru₂(OAc)₄Cl in the presence of *t*-BuOK and NaSCN, followed by stirring with excess KPF₆ (Scheme 2) [6]. The crystal structure of **1** is depicted in Fig. 1, and selected bond lengths are reported in Fig. 2 [7]. Compound **1** shows a non-linear [Ru₃]⁷⁺ core ($\angle = 170.26(3)^{\circ}$), which is helically wrapped by four npa⁻ ligands. The coordination environment of three ruthenium ions is distorted octahedron. The four npa⁻ ligands in **1** adopt a (3,1) arrangement. Due to different steric hindrances between phenyl groups and axial NCS⁻ ligands at the two terminals, the two NCS⁻ ligands



Scheme 1. Oligopyridylamine ligands.

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Scheme 2. Synthesis of Hnpa and 1.

bond to Ru ions with linear and bent coordination modes, respectively. The Ru–Ru distances in **1** are 2.3462(8) and 2.3646(8) Å respectively, which are longer than that of the $[Ru_3(dpa)_4Cl]^+$ analog (**2**, 2.2911(6) Å) [8]. It should be noted that the bite angle (N-N-N) of supported ligands has direct influence on the metal–metal distances [9]. Compared with the bite angle in **2** (~171.6°), the larger bite angle in **1** (~175.5°) resulted from the rigidity of npa leading to the elongation of Ru–Ru distances in **1**.

The temperature dependence of effective magnetic moment (μ_{eff}) of **1** is shown in Fig. 3. The μ_{eff} is 2.09 B.M. at 300 K, which is close to the spin-only value of one unpaired electron (1.73 B.M.). With decreasing temperature, the μ_{eff} decreases slowly resulting from a

weak intermolecular antiferromagnetic interaction. The EPR spectrum recorded at 4 K for **1** is coincident with the feature of the s = 1/2 spin state, which supports the magnetism (Fig. 3, inset). Single point spin-unrestricted DFT calculation was performed on complex **1** based on its X-ray structure [10]. The DFT calculation suggests that compound **1** possesses a $\sigma^2 \pi^4 \delta^2 \pi^4_{hb} \delta^2_{hb} \pi^{*3}$ electronic configuration (Fig. S2), which shows stabilized π^* orbitals in compared with those of **2** ($\sigma^2 \pi^4 \delta^2 \pi^4_{hb} \delta^2_{hb} \delta^{*2} \sigma^1_{hb}$). This stabilization of π^* orbitals of **1** may be attributed to the weakening of Ru π -bonds resulting from the lengthening of Ru–Ru distances (Scheme 3). Moreover, the degenerated π^* orbitals are asymmetrically occupied by three π^* electrons, which may also be the cause of non-linear geometry.



Fig. 1. The ORTEP of the cationic part for [Ru₃(npa)₄(NCS)₂][PF₆]·(Me₂CO)₂·(Et₂O)₂ (1). Thermal ellipsoids are drawn at the 40% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.



Fig. 2. Selected interatomic distances observed for 1.



Fig. 3. Temperature-dependent magnetic effective moment (\bigcirc) for compound 1. Inset: Powder X-band EPR spectrum for 1 at 4 K.



 $[Ru_3(npa)_4(NCS)_2]^+$ $[Ru_3(dpa)_4Cl_2]^+$

Scheme 3. Electronic configurations of $[Ru_3(npa)_4(NCS)_2]^+$ (left) and $[Ru_3(dpa)_4Cl_2]^+$ (right). The π -acid ligands NCS⁻ in $[Ru_3(npa)_4(NCS)_2]^+$ stabilize the π^* orbitals and the π -base ligands Cl⁻ in $[Ru_3(dpa)_4Cl_2]^+$ destabilize the π^* orbitals.



Fig. 5. Cyclic voltammogram of compound 1 in CH_2Cl_2 containing 0.1 M TBAP with scan rate =100 mV s $^{-1}$.

The single molecular conductance of **1** was measured by the scanning tunneling microscopy (STM) break-junction method (Fig. 4) [11]. Fig. 4a shows a typical conductance trace. The vertical axis is plotted in units of G_0 (~(12.9 k Ω)⁻¹), defined as the conductance quantum of a gold nanowire with a cross-section of a single atom. The conductance value changed in a stepwise fashion as the STM tip was pulled away from the substrate. Each stepwise drop, as the distance of the substrate from the tip increases, indicates the loss of a molecule from the tipsubstrate junction. The histogram of counts from more than one thousand traces shows local maxima at conductance values which are integer multiples of a fundamental one, suggesting that the number of molecules in the junctions was one, two and so forth. The conductance of this $[Ru_3]^{7+}$ complex is $6.9 \times 10^{-4} G_0$ (18.7 M Ω), which is less conductive than $[Ru_3(dpa)_4(NCS)_2]^+$ $(10.2 \times 10^{-3} G_0)$ [12]. The decreased conductance may be attributed to the elongation of the distance between Ru ions weakening their interactions.

It is well-known that Ru ions exhibit various oxidation states from +2 to +8 [13]. Therefore, the cyclic voltammogram of compound **1** shows multiple redox processes (Fig. 5). Compound **1** displays three redox couples at -0.39, +0.09, and +0.9 V, corresponding to $[Ru_3(npa)_4(NCS)_2]^0/[Ru_3(npa)_4(NCS)_2]^-$, $[Ru_3(npa)_4(NCS)_2]^0$, $[Ru_3(npa)_4(NCS)_2]^2+/[Ru_3(npa)_4(NCS)_2]^1$, respectively. These three reversible redox couples suggest that the reduced and oxidized products of **1** may be isolated by performing suitable methods in the ambient condition.

In conclusion, the triruthenium metal string supported by naphthylridylamide ligands was successfully synthesized and studied in this work. Because of the large bite angle resulting from the rigidity of the npa⁻ ligand, compound **1** exhibits longer Ru–Ru distances than



Fig. 4. Single-molecule conductance of $[Ru_3(npa)_4(NCS)_2]^+$ as measured by STM break-junction at a bias of 50 mV. The conductance of a single $[Ru_3(npa)_4(NCS)_2]^+$ is $6.9 \times 10^{-4} G_0 (R = 18.7 M\Omega)$. (a) Typical conductance-distance traces acquired by stretching the molecular junction with arbitrary x axis offsets. (b) The conductance histogram is obtained from more than 1000 measurements, and plotted by using 540 bins for the range presented.

those of [Ru₃(dpa)₄Cl]⁺. This longer Ru–Ru distance decreases the electron transport through the central triruthenium framework. Although the conductivity of **1** is lower than those of dpa-supported triruthenium analogs, the rich-redox property of **1** suggests that complex **1** with various oxidation states may be generated by applying suitable oxidization or reduction potential. Since variation in oxidation state of metal string complexes may significantly change their electric conductance, complex **1** may have potential application as an electrically-controlled molecular switch. Further studies extending the scope of this work are currently being undertaken by our group.

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Appendix A. Supplementary data

CCDC 946659 contains the supplementary crystallographic data for this article. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac. uk/data_request/cif. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.10.009.

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- [6] Ligand Hnpa (111 mg, 0.5 mmol), excess Ru₂(OAC)₄Cl (178 mg, 0.375 mmol) and naphthalene (40 g) were placed in an Erlenmeyer flask under argon atmosphere. The mixture was heated to 180 °C for 30 min, and then raised to 220 °C. A solution of t-BuOK (56 mg, 0.5 mmol) in *n*-BuOH (5 mL) was added dropwise. After 180 min, excess NaSCN was introduced into the flask and the reaction was continued for another 60 min. After the mixture was cooled to 80 °C, *n*-hexane (100 mL) was added and the precipitate was filtered. The solid was extracted with CH₂Cl₂ (200 mL). The mixture was dissolved in CH₂Cl₂, and then the potassium hexafluorophosphate was added and stirred for 30 min. The mixture was filtered and the solvent were removed by a rotary evaporator. Then purified through silica gel and eluted with acetone and CH₂Cl₂. The crude material was dissolved in CH₂Cl₂, and then the potassium hexafluorophosphate was added and stirred for 30 min. The mixture was filtered and the solvent were removed by a rotary evaporator. Crystallization from acetone and diethyl ether afforded 15 mg of dark green crystal (yield 10 %). MS(FAB): *m/z*: 1302 [Ru₃(npa)₄(NCS)₂]⁺, 1244 [Ru₃(npa)₄(NCS)]⁺, 1184 [Ru₃(npa)₄]⁺; elemental analysis calcd (%) for [Ru₃(npa)₄(NCS)][PF₆]: C 48.20, H 2.79, N 13.57; found: C 48.22, H 2.91, N 13.74; IR (KBr): $\hat{v} = 2044$, 1617, 1589, 1552, 1484, 1425, 1382, 1328, 1211, 1151, 844, 698, 555 cm⁻¹. UV/vis (CH₂Cl₂) λ_{max}/nm (ϵ /10⁴ M⁻¹ cm⁻¹): 239 (7.8), 352 (2.9), 450_{broad} (1.3), 597_{broad} (0.8).
- [7] The chosen crystals were mounted on a glass fiber, and the X-Ray crystallographic data were collected at 150 K on a NONIUS Kappa CCD diffractometer installed with monochromated Mo-K α radiation, $\lambda = 0.71073$ Å. Cell parameters were retrieved and refined by using DENZO-SMN software on all observed reflections. Absorption correlations were applied with SORTAV program. The structure was solved by direct method with SHELX-97 program and refined by full-matrix least squares on F^2 values. Hydrogen atoms were fixed at calculated positions and refined using a riding mode. All DFIX restrains are used to model disordered PF₆ anion and the cocrystallized acetone molecules. The disordered PF₆ anion was modeled as a pair of rigid octahedron, with 70 % and 30 % occupancy respectively. And one of the acetone molecules was also disordered. Crystal data for 1 (deep green crystal): Cr₂₂H₇₂ F₆N₁₄O₄PRu₃S₂, Mr = 1709.74, monoclinic, space group *P*2₁/n, a = 17.2886(4) Å, b = 24.3132(6) Å, c = 17.6177(4) Å, $\beta = 91.518(2)$ °, V = 7402.8(3) Å³, Z = 4, D_{calcd} = 1.534 g/cm³, $\mu = 0.0755$ mm⁻¹, $R_1 = 0.0596$, $wR_2 = 0.1426$, GOF = 1.004 ($I > 2\sigma(I)$). The functions minimized during least-squares cycles where $R_1 = \Sigma$] $F_0 F_c |/\Sigma|F_0|$; $wR_2 = [\Sigmaw|F_0^2 F_c^2|^2\Sigmaw(F_0^4)]$.
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