Na$_3$Ru$_2$(hedp)$_2$·4H$_2$O: A mixed valent diruthenium diphosphonate with three-dimensional structure

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Abstract

Hydrothermal treatment of RuCl$_3$, hedpH$_4$ [hedp = 1-hydroxyethylidenediphosphonate, CH$_3$C(OH)(PO$_3$)$_2$] and NaOH at 180 °C gives a mixed valence diruthenium(II,III) compound Na$_3$Ru$_2$(hedp)$_2$·4H$_2$O (**1**). In this compound, the paddlewheel diruthenium units of Ru$_2$(hedp)$_2^{3-}$ are cross-linked into a square-grid layer. The layers are further connected through {NaO$_6$} octahedra, forming a three-dimensional framework structure. Crystal data: monoclinic, space group *C2/c*, *a* = 19.285(5), *b* = 9.528(3), *c* = 10.050(3) Å, *β* = 96.499(5), *V* = 1834.8(9) Å^3, *Z* = 4. Ferromagnetic interactions are mediated between the Ru$_2$(hedp)$_2^{3-}$ dimers within the layer.
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1. Introduction

In recent years, the design and syntheses of extended networks with novel topologies is of great interest owing to their potential for many applications [1]. The utility of metal-metal bonded dinuclear complexes, which bear unique structural and physical properties, in the assembly of these network structures provides a new area of supramolecular chemistry. Particular attention has been paid to the paramagnetic diruthenium units such as Ru$_2$(O$_2$CR)$_4^{n+}$ ($n = 1, 0$) [2]. The mixed-valent Ru$_2$(O$_2$CR)$_4^+$ cation is of special interest because it has a $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$ electronic configuration. The π^* and δ^* orbitals are nearly degenerate, resulting in a high-spin $S = 3/2$ ground state [3]. By combining diruthenium tetracarboxylates with inorganic or organic bridging ligands, many compounds with chain structures [4] and a few compounds with two- and three-dimensional structures [5,6] have been obtained.

Compared with the researches involving diruthenium tetracarboxylates, those concerning diruthenium phosphonates are rare. Based on 1-hydroxyethylidenediphosphonate [CH$_3$-C(OH)(PO$_3$)$_2$, hedp], we have synthesized complexes Na$_4$Ru$_2$-(hedp)$_2$X·16H$_2$O (X = Cl, Br) and Na$_7$[Ru$_2$(hedp)$_2$Fe(CN)$_6$]·24H$_2$O with one-dimensional structures [7], and compound (NH$_4$)$_3$Ru$_2$(hedp)$_2$·2H$_2$O with a two-dimensional structure [8]. All possess a mixed-valent paddlewheel core of Ru$_2$(hedp)$_2^{3-}$, similar to that of Ru$_2$(O$_2$CR)$_4^+$. In this paper we report the hydrothermal synthesis of a new diruthenium phosphonate with a 3D framework structure, namely, Na$_3$Ru$_2$(hedp)$_2$·4H$_2$O (**1**).
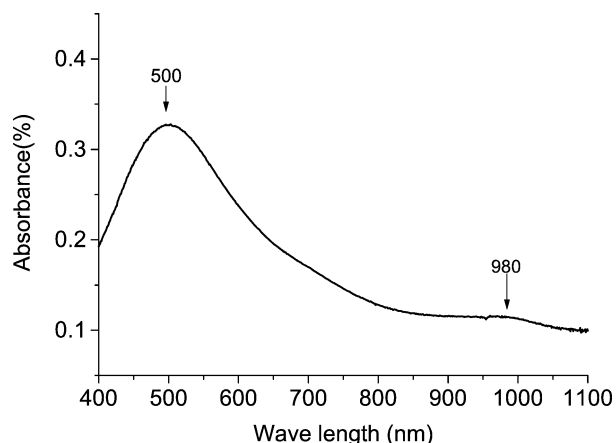
2. Experimental

2.1. Materials and methods

All the starting materials were of reagent quality and were obtained from commercial sources without further purification. Elemental analysis was performed on a Perkin Elmer 240C elemental analyzer. IR spectrum was obtained as a KBr disk on a VECTOR 22 spectrometer. Thermal analysis was performed in nitrogen with a heating rate of 20 °C/min on a TGA-DTA V1.1 TA Inst 2100 instrument. Variable-temperature magnetic susceptibility data were obtained on polycrystalline sample (26.68 mg) from 2 to 300 K in a magnetic field of 2 kOe using a Quantum Design SQUID magnetometer.

Fig. 1. UV–vis spectrum of compound **1**.

2.2. Synthesis of $Na_3Ru_2(hedp)_2 \cdot 4H_2O$ (**1**)

A mixture of $RuCl_3 \cdot 3.5H_2O$ (0.38 mmol, 0.1015 g), $hedpH_4 \cdot H_2O$ (1.50 mmol, 0.3367 g) in 4 mL of H_2O, adjusted to pH = 4.70 with 1M NaOH, was kept in a Teflon-lined autoclave at 180 °C for 4 days. After slow cooling to room temperature, brown-red block crystals were collected as a monophasic material, as judged by the powder X-ray diffraction pattern. Yield: 0.1302 g (97% based on Ru). Anal. found (calcd) for $C_4H_{17}O_{18}P_4Na_3Ru_2$: C, 6.54 (6.42); H, 1.74 (2.15)%. IR (KBr, cm^{-1}): 3513(br, s), 3378(br, s), 1671(m), 1618(m), 1458(m), 1192(s), 1157(m), 1110(vs), 1050(m), 988(m), 958(s), 950(s), 791(s), 730(m), 695(m), 580(s), 568(s), 509(m), 449(m). Thermal analysis shows that the weight loss in the temperature range 20–220 °C is 10.7%, slightly higher than the calculated value for the release of four water molecules (9.6%). The weight loss above 400 °C is due to the decomposition of the organophosphonate ligand and the collapse of the lattice structure. The final product was not characterized. The infrared spectrum exhibits a series of bands in the 1000–1157 cm^{-1} range, corresponding to the vibrations of phosphonate PO_3 groups. The diffuse reflectance spectrum gives a major band at *ca.* 500 nm and a weak band at *ca.* 980 nm (Fig. 1) which are assigned to the $\pi(Ru–O, Ru_2) \rightarrow \pi^*(Ru_2)$ and $\delta(Ru_2) \rightarrow \delta^*(Ru_2)$ transitions, respectively, in agreement with the mixed-valent nature of the compound [9].

2.3. Crystallographic studies

A single crystal of dimensions $0.24 \times 0.26 \times 0.32$ mm for **1** was selected for indexing and intensity data collection at 293 K on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromatized Mo K_α ($\lambda = 0.71073$ Å) radiation. A hemisphere of data was collected in the θ range 2.13–25.99° using a narrow-frame method with scan widths of 0.30° in ω and exposure time of 10 s/frame. The numbers of measured, unique and observed reflections [$I > 2\sigma(I)$] are 4634, 1785 and 1312 ($R_{int} = 0.040$), respectively. The data were integrated using the Siemens SAINT program [10], with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through

Table 1
Crystallographic data for **1**

Formula	$C_4H_{16}O_{18}P_4Na_3Ru_2$
M	747.16
Crystal system	Monoclinic
Space group	C2/c
a (Å)	19.285(5)
b (Å)	9.528(3)
c (Å)	10.050(3)
β (°)	96.499(5)
V (Å^3)	1834.8(9)
Z	4
D (g cm^{-3})	2.705
$F(000)$	1460
Goodness-of-fit on F^2	1.086
$R1, wR2$ [$I > 2\sigma(I)$][a]	0.0523, 0.0966
$R1, wR2$ (all data)[a]	0.0764, 0.0997
$(\Delta\rho)_{max}, (\Delta\rho)_{min}$ (e Å^{-3})	1.059, −0.841

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
Ru(1)	0.2671(1)	0.2041(1)	0.6074(1)	0.0312(2)
Na(1)	0.3217(1)	−0.3785(3)	0.4069(2)	0.0296(8)
Na(2)	1/2	0.4310(4)	1/4	0.0362(12)
P(1)	0.2959(1)	0.0073(2)	0.3850(2)	0.0278(5)
P(2)	0.3900(1)	0.2572(2)	0.4517(2)	0.0303(6)
O(1)	0.2803(2)	0.0056(5)	0.5327(4)	0.0268(14)
O(1W)	0.4377(2)	−0.3669(5)	0.3435(4)	0.0339(14)
O(2)	0.2434(2)	0.1067(5)	0.3044(4)	0.0262(14)
O(2W)	0.3791(2)	0.4236(5)	0.1259(4)	0.0321(16)
O(3)	0.2937(2)	−0.1396(5)	0.3286(5)	0.0336(17)
O(4)	0.3694(2)	0.2485(5)	0.5979(4)	0.0308(16)
O(5)	0.3320(2)	0.3491(5)	0.3686(4)	0.0313(16)
O(6)	0.4613(2)	0.3125(5)	0.4407(4)	0.0285(14)
O(7)	0.4366(2)	−0.0111(5)	0.4370(5)	0.0400(16)
C(1)	0.3858(4)	0.0702(8)	0.3926(8)	0.042(3)
C(2)	0.4073(4)	0.0772(8)	0.2507(7)	0.038(3)

the detector faceplate. Empirical absorption correction was applied.

The structure was solved by direct method and refined on F^2 by full-matrix least squares using SHELXTL [11]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions (C–H = 0.96 Å, O–H = 0.85 Å). In the final Fourier difference map, the deepest hole was −0.841 e Å^{-3} and the highest peak 1.059 e Å^{-3}. Crystallographic and refinement details are listed in Table 1. The atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3, respectively.

3. Results and discussion

3.1. Synthesis

In a previous communication, we reported the hydrothermal synthesis of compound $(NH_4)_3Ru_2(hedp)_2 \cdot 2H_2O$ [8] where the NH_4^+ cations occupy the spaces within and between the layers of $\{Ru_2(hedp)_2\}_n^{3n-}$. Investigations were then carried