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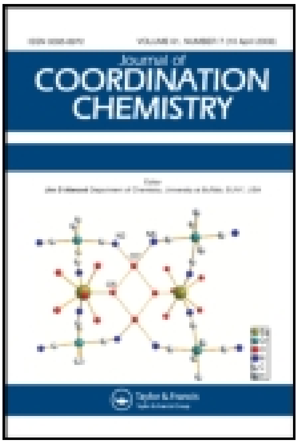

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Synthesis and characterization of a dinuclear (Hedta)Ru(III) complex

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Synthesis and characterization of a dinuclear (Hedta)Ru(III) complex

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A ruthenium(III) complex containing ethylenediaminetetraacetate (edta), $[\{Ru(Hedta)\}_2(Pyz)] \cdot 8H_2O$ (**1**) (Pyz = pyrazine), has been synthesized by the reaction between $K[Ru(Hedta)Cl] \cdot 1.5H_2O$ and pyrazine. The structure of the complex was determined by single X-ray diffraction. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.293(9)$ Å, $b = 10.575(14)$ Å, $c = 12.742(16)$ Å, $\alpha = 104.044(19)^\circ$, $\beta = 91.893(19)^\circ$, $\gamma = 93.35(2)^\circ$, $Z = 1$. The product was also characterized by IR, UV-Vis, EPR spectrum and magnetic techniques.

Keywords: Ruthenium(III) complex; Pyrazine; Magnetic techniques

1. Introduction

Considerable attention has been devoted to the chemistry of ruthenium due to its fascinating redox, photophysical, and photochemical properties [1–3], especially the polyaminopolycarboxylate complexes of Ru(II), Ru(III) is also of interest due to biochemical importance and catalytic activity in oxidation reactions [4]. Increasing attention has been devoted to Ru(edta) complexes because of their stronger affinity to bridging N-heterocyclic ligands, which can be used to design binuclear complexes [5]. Many ruthenium(III)–edta complexes of N-heterocycles have been reported, but few such ruthenium(III)–edta complexes have been structurally characterized [6]. We have selected pyrazine as ligand, which is a representative of bridging ligands in view of its construction of infinite frameworks.

We report herein the synthesis and X-ray structure of $[\{Ru(Hedta)\}_2(Pyz)] \cdot 8H_2O$, obtained by the reaction of $K[Ru(Hedta)Cl] \cdot 1.5H_2O$ and pyrazine, and we also investigate the magnetic and other properties of the complex.

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2. Experimental

2.1. *Physical measurements*

C, H, N analyses were carried out with a Perkin-Elmer analyzer, model 240. Electronic spectra were recorded with a Shimadzu UV-2101PC spectrophotometer in the 200–2000 nm range at room temperature. FT-IR spectra were recorded with KBr pellets from 4000 to 400 cm^{-1} with a Bio-Rad FTS 135 spectrometer. The ESR spectrum was recorded on a JES-FEIXG ESR spectrophotometer at X-band frequency.

2.2. *Starting materials*

$\mathrm{K[Ru(Hedta)Cl]\cdot 1.5H_2O}$ was prepared as described [5]. Pyrazine was reagent grade and used without purification.

2.3. *Synthesis of* $[\{\mathrm{Ru(Hedta)}\}_2(\mathrm{Pyz})]\cdot 8\mathrm{H_2O}$ *(1)*

A methanol solution (10 mL) of Pyz (8 mg, 0.1 mmol) was added to an aqueous solution (10 mL) of $\mathrm{K[Ru(Hedta)Cl]\cdot 1.5H_2O}$ (98 mg, 0.2 mmol); the resulting solution was stirred for 15 min at room temperature and then filtered. Orange single crystals suitable for X-ray diffraction were obtained in several days by slow evaporation of filtrate. Elemental analysis (%) for $\mathrm{C_{24}H_{46}N_6O_{24}Ru_2}$ (Fw. 1004.81): Anal. Calcd (%): C, 28.69; H, 4.61; N, 8.36. Found (%): C, 28.78; H, 4.58; N, 8.39. IR spectrum in KBr, selected bands, cm^{-1}, 3420 s, ν(O–H); 1652 s, ν_{as}(C=O); 1287 m, ν_s(C=O).

2.4. *X-ray analysis*

2.4.1. X-ray crystallographic study. All measurements were made on a Bruker SMART diffractometer equipped with a graphite monochromator and Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares. Hydrogens were added geometrically and refined by mixed method. All calculations were performed using SHELX-97 program.

3. Results and discussion

3.1. *X-ray diffraction studies*

Crystallographic data and processing parameters for structural analysis of **1** are summarized in table 1. The coordination environment of **1** is shown in figure 1; selected bond lengths and angles are listed in table 2. In **1**, each ruthenium is coordinated with Hedta as a pentadentate, trianionic ligand with a free carboxylate arm, and the sixth coordination position is occupied by nitrogen from bridging pyrazine. Thus Ru(1) is coordinated by N(1) and N(3) and two oxygens from carboxylates [O(3) and O(5)] in the equatorial plane, and N(2) and O(1) in axial positions. The Ru–O(carboxylate) bond lengths, Ru(1)–O(1), Ru(1)–O(3), Ru(1)–O(5), are 2.003(3), 1.977(2), and

Table 1. Crystal and refinement data for **1**.

Empirical formula	$C_{24}H_{46}N_6O_{24}Ru_2$
Formula weight	1004.81
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.293(9)
b	10.575(14)
c	12.742(16)
α	104.044(19)
β	91.893(19)
γ	93.35(2)
Volume (Å^3), Z	951(2), 1
Calculated density D_{calcd} (Mg m^{-3})	1.755
μ (mm^{-1})	0.892
$F(000)$	512
Crystal size (mm^3)	0.34 × 0.28 × 0.16
Goodness-of-fit on F^2	1.141
Limiting indices	$-8 \le h \le 7$; $-12 \le k \le 9$; $-15 \le l \le 14$
R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0261$, $wR_2 = 0.0670$
R_1, wR_2 (all data)	$R_1 = 0.0297$, $wR_2 = 0.0699$

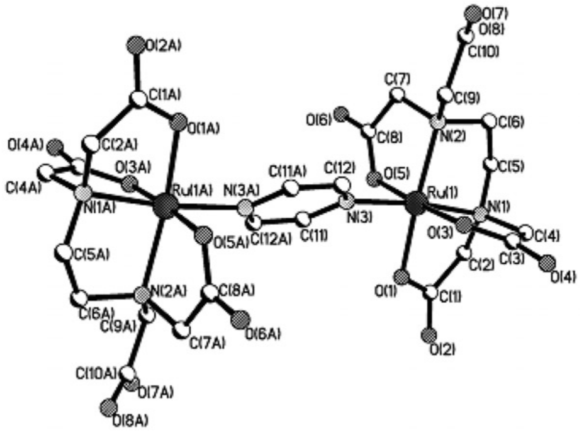

Figure 1. Perspective view of **1** showing the atom numbering; hydrogens are omitted for clarity.

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

Ru(1)–O(1)	2.003(3)	Ru(1)–O(3)	1.977(2)
Ru(1)–O(5)	2.026(3)	Ru(1)–N(1)	2.052(3)
Ru(1)–N(3)	2.071(3)	Ru(1)–N(2)	2.142(3)
O(3)–Ru(1)–O(1)	92.54(12)	O(3)–Ru(1)–O(5)	176.37(8)
O(1)–Ru(1)–O(5)	90.65(12)	O(3)–Ru(1)–N(1)	85.07(12)
O(1)–Ru(1)–N(1)	83.43(11)	O(5)–Ru(1)–N(1)	93.57(12)
O(3)–Ru(1)–N(3)	93.90(12)	O(1)–Ru(1)–N(3)	90.05(10)
O(5)–Ru(1)–N(3)	87.83(12)	N(1)–Ru(1)–N(3)	173.34(9)
O(3)–Ru(1)–N(2)	96.26(12)	O(1)–Ru(1)–N(2)	165.27(9)
O(5)–Ru(1)–N(2)	80.26(12)	N(1)–Ru(1)–N(2)	85.57(11)
N(3)–Ru(1)–N(2)	101.09(11)	C(1)–O(1)–Ru(1)	113.7(2)
C(3)–O(3)–Ru(1)	115.29(18)	C(8)–O(5)–Ru(1)	117.3(2)

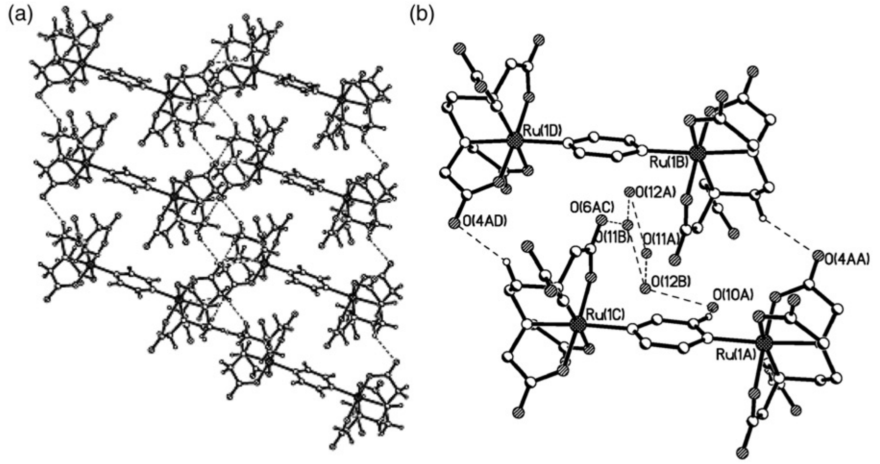

Figure 2. (a) 2-D structures of **1** through strong H-bonding and (b) a cyclic water tetramer located in the cavity of the 2-D structures.

2.026(3) Å, similar to those for the *trans* carboxylato groups in (Hedta)Ru(III) complexes [5, 7, 8]. The bond lengths of Ru–N(Hedta), Ru(1)–N(1) and Ru(1)–N(2) are 2.052(3) and 2.142(3) Å. The geometry of the RuO3N3 coordination polyhedron is appreciably elongated octahedral. The distance of nonbonding Ru(1) and Ru(1A) is 6.905 Å.

The structures of neutral dimers are stabilized by intermolecular H-bonding interactions and further extended into 2-D structures (figure 2a). Interestingly, a cyclic water tetramer is perpendicularly located in each cavity of the 2-D structures with O12A ··· O10B, O12A ··· O11A and O12A ··· O11B of 2.842, 2.802 and 2.737 Å (figure 2b), consistent with the data of similar structures reported for other metal complexes [9–11], but are scarcely found for ruthenium complexes. The 2-D structures are connected into 3-D networks also through H-bonding interactions by the water tetramer acting as both hydrogen-bond donors and acceptors (figure 3). Hydrogen-bond data for the complex are listed in table 3 [12].

3.2. *UV-Vis spectra*

The UV-Vis spectrum of **1** in DMSO was measured at room temperature. The electronic spectrum shows two intense absorptions in the UV region at 258 nm ($\varepsilon = 5120$ $(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$) and 307 nm ($\varepsilon = 1723$ $(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$), which can be assigned to ligand-centered π–π* transitions. In addition, there is one relatively weak absorption in the visible region, 736 nm ($\varepsilon = 17.86$ $(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$) [13], assigned to the d–d transition of $^2T_{2g} \rightarrow {}^2A_{2g}$, which has been reported less. In most Ru(III) complexes the UV and visible spectra show only charge-transfer bands [14, 15]. Since, in a d^5 system and especially in ruthenium(III) which has relatively high oxidizing properties, the charge-transfer bands of the type $L_{\pi y} \rightarrow t_{2g}$ are prominent in the low-energy region (495–680 nm) obscuring the weaker bands of d–d transitions [15, 16].

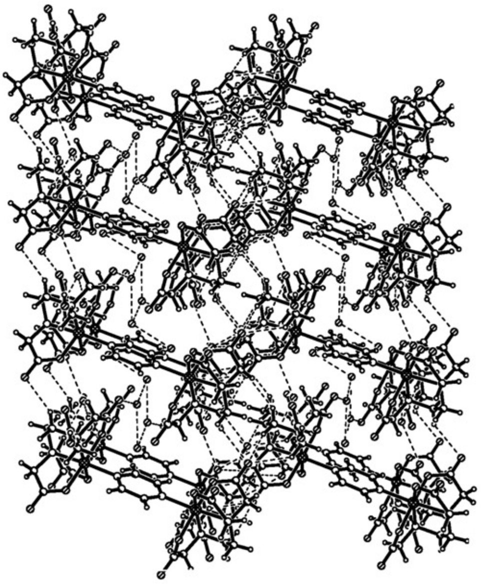

Figure 3. View of the 3-D structure of **1**.

Table 3. Data of hydrogen bonds for **1**.

Bond distances (Å)			Bond angles (°)
O7 ··· O9a	2.594	O7–H7 ··· O9a	168.79
O9 ··· O11	3.177	O9–H9C ··· O10	171.82
O9 ··· O2b	2.821	O9–H9D ··· O2b	172.98
O10 ··· O12b	3.251	O10–H10A ··· O12b	123.40
O12 ··· O10c	2.842	O12–H12B ··· O10	133.73
O10 ··· O12c	2.842	O10–H10A ··· O12c	110.48
O10 ··· O8d	3.090	O10–H10B ··· O8d	114.15
O11 ··· O9	3.177	O11–H11A ··· O9	168.42
O11 ··· O12	2.802	O11–H11B ··· O12	141.84
O12 ··· O11	2.802	O12–H12A ··· O11	137.72

a = [x, $y-1$, z]; b = [$x-1$, y, z]; c = [$-x+1$, $-y+1$, $-z$]; d = [x, $y+1$, z].

3.3. *EPR spectrum*

The EPR spectrum in solid state at 110 K for **1** showed single isotropic lines with a g value of 2.212. Isotropic lines of this type are observed either due to intramolecular spin exchange which can broaden the lines or from occupancy of the unpaired electron in a degenerate orbital [17]. The nature of the EPR spectrum suggests an octahedral environment around ruthenium and there are no hyperfine interactions with other nuclei present in the complex [15].

3.4. *Magnetic properties*

The temperature dependence of the magnetic susceptibility of **1** was measured from 2 to 300 K (figure 4). The value of its effective magnetic moment at room temperature (300 K)

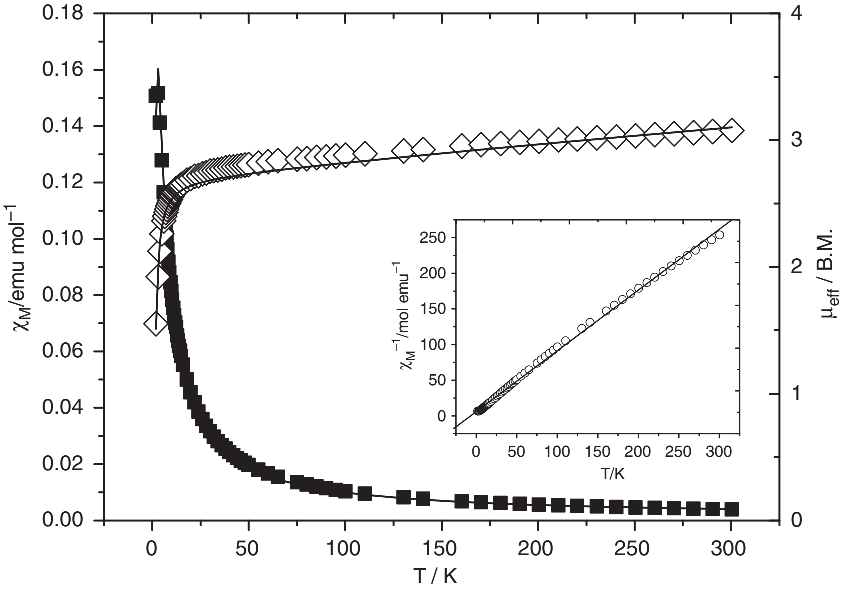

Figure 4. χ_M(■) *vs.* T and μ_{eff}(□) *vs.* T plots for **1**. Inset: $1/\chi_M$(○) *vs.* T for **1**.

is 3.07 B.M. (per dinuclear unit), much higher than the spin-only value (2.45 B.M.) of binuclear low-spin ruthenium system; the result may be attributed to spin–orbit coupling of the ruthenium(III) ions. With decreasing temperature, the effective magnetic moment exhibits a regular decrease, reaching a minimum (1.55 B.M.) at 2 K.

The magnetic susceptibility data were fitted using the following expansion (equation (1)) including the temperature-independent paramagnetism (TIP), the van Vleck equation, which considers a general isotropic exchange spin Hamiltonian $H = -2JS_1S_2$ ($S_1 = S_2 = 1/2$) [18–20].

$$\chi_M = \frac{2Ng^2\beta^2}{3kT}\frac{1}{1+\frac{1}{3}\exp(-2J/kT)} + \mathrm{TIP}. \qquad (1)$$

The parameters obtained are $g = 2.2$, $J = -1.58\,\mathrm{cm}^{-1}$, and $\mathrm{TIP} = 1 \times 10^{-3}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. This g value is consistent with those observed in other dinuclear ruthenium complexes [21]. The low and negative J indicates a very weak intramolecular antiferromagnetic coupling between the unpaired electrons of the Ru(III) centers of each dinuclear molecule. The $1/\chi_M = f(T)$ curve (inset of figure 4) varies linearly and is well-fitted over the experimental temperature region by using the Curie–Weiss law, with $C = 1.17\,\mathrm{emu\,K\,mol}^{-1}$ and $\theta = -6.96\,\mathrm{K}$. The negative value of the Weiss constant also implies the presence of antiferromagnetic interactions between neighboring Ru(III) atoms.

4. Conclusion

We have reported one new diruthenium(III) complex, which is connected into 3-D networks through H-bonding interactions by a water tetramer. This study shows that the $1/\chi_M = f(T)$ curve for the complex fits Curie–Weiss law, implying the presence of antiferromagnetic interactions between neighboring Ru(III) atoms.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with Cambridge Crystallographic Data Center as supplementary publication CCDC No. 251664. Copies of the data can be obtained free of charge on application to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail for inquiry: fileserv@ccdc.cam.ac.uk; E-mail for deposition: deposit@ccdc.cam.ac.uk).

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