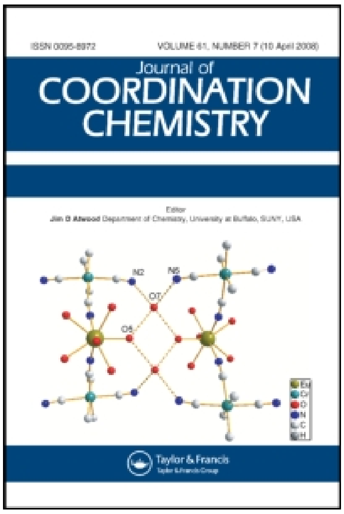

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Synthesis and characterization of a mononuclear ruthenium(III) triazole complex

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Synthesis and characterization of a mononuclear ruthenium(III) triazole complex

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A mononuclear ruthenium(III) complex containing ethylenediaminetetraacetate (edta), $[Ru(Hedta)(Htrz)] \cdot 4H_2O$ (**1**) (Htrz = 1H-1,2,4-triazole), has been synthesized and the structure was determined by single-crystal X-ray diffraction. The complex crystallizes in the triclinic space group $P\bar{1}$, with the unit cell parameters $a = 7.212(3)$ Å, $b = 9.873(4)$ Å, $c = 13.806(6)$ Å, $\alpha = 91.945(6)^\circ$, $\beta = 100.078(6)^\circ$, $\gamma = 97.230(7)$ and $Z = 2$. The complex was also characterized by elemental analysis, IR, UV–Vis and ESR spectra. Cyclic voltammetry for the complex shows a ruthenium(III)/ruthenium(IV) oxidation and a ruthenium(III)/ruthenium(II) reduction within the range of −1.5–0.5 V. Magnetic susceptibility data give an effective moment of 1.81 B.M. at room temperature.

Keywords: Ruthenium(III) complex; Triazole; Cyclic voltammetry; Paramagnetic

1. Introduction

Increasing attention has been devoted to Ru(edta) type complexes because of their biochemical importance and catalytic activity in oxidation reactions [1–6]. The chemistry of Ru(edta) type complexes of N heterocyclic ligands have been receiving serious attention largely because of their affinity to bridging N heterocyclic ligands [7–9]. Among these N heterocyclic compounds, we have selected 1H-1,2,4-triazole as ligand; it has diverse coordination geometries binding to metal ions with the 2-position of "pyrazole" type, while the 4-position is of "imidazole" type (scheme 1) [10, 11].

We report herein the synthesis and the X-ray structure of $[Ru(Hedta)(Htrz)] \cdot 4H_2O$ (**1**), which is obtained by reaction of $K[Ru(Hedta)Cl] \cdot 1.5H_2O$ with 1H-1,2,4-triazole, and we also investigate the spectroscopic and magnetic properties of the complex.

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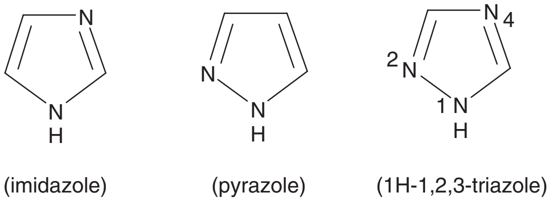

Scheme 1. Diverse coordination geometries of 1H-1,2,4-triazole.

2. Experimental

2.1. *Physical measurements*

C, H and N elemental 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. The FT-IR spectra were recorded with KBr pellets in the range 4000–400 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*

$K[Ru(Hedta)Cl] \cdot 1.5H_2O$ was prepared as described [5]. 1H-1,2,4-triazole and silver nitrate were reagent grade and used without purification.

2.3. *Synthesis of [Ru(Hedta)(Htrz)] • 4H$_2$O*

An aqueous solution (15 mL) of $K[Ru(Hedta)Cl] \cdot 1.5H_2O$ (98 mg, 0.2 mmol) and $AgNO_3$ (33 mg, 0.2 mmol) was stirred at room temperature for ten minutes. The white precipitate, AgCl, was removed by filtration, and to the filtrate 10 mL methanol solution of Htrz (14 mg, 0.2 mmol) was added, and stirring continued for another five minutes. The resulting solution was filtered and left to stand at room temperature. Orange single crystals suitable for X-ray diffraction were obtained in several days by slow evaporation. Elemental analysis (%) for $C_{12}H_{24}N_5O_{12}Ru$ (Fw. 531.43): Anal. Calcd: C, 27.12; H, 4.55; N, 13.18. Found: C, 27.18; H, 4.61; N, 13.25. IR spectrum in KBr, selected bands, cm^{-1}, 3127 vs, ν(N–H); 1654 s, ν_{as}(C=O); 1313 m, ν_s(C=O).

2.4. *X-ray analysis*

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) source. The structure was solved by direct methods and refined by full-matrix least-squares. Hydrogen atoms were added geometrically and refined by mixed method. All calculations were performed using SHELX-97.

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

Empirical formula	$C_{12}H_{24}N_5O_{12}Ru$
Formula weight	531.43
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.212(3)
b	9.873(4)
c	13.806(6)
α	91.945(6)
β	100.078(6)
γ	97.230(7)
V (Å^3)	958.6(7)
Z	2
D_{Calcd} (Mg m^{-3})	1.841
μ (mm^{-1})	0.893
$F(000)$	542
Crystal size (mm)^3	$0.20 \times 0.18 \times 0.14$
θ range for data collection (°)	1.50–25.01
Limiting indices	$-5 \leq h \leq 8$, $-11 \leq k \leq 9$, $-16 \leq l \leq 16$
Reflections collected	4967
Unique reflections	3368 [$R_{\mathrm{int}} = 0.0190$]
Goodness-of-fit on F^2	1.141
R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0286$, $wR_2 = 0.0779$
R_1, wR_2 (all data)	$R_1 = 0.0328$, $wR_2 = 0.0891$

3. Results and discussion

3.1. *X-ray diffraction studies*

Crystallographic data and processing parameters for analysis of **1** are summarized in table 1. The coordination environment is shown in figure 1; selected bond lengths and angles are listed in table 2. The ruthenium center coordinates with Hedta which is a pentadentate, trianionic ligand with a free carboxylate arm, and the sixth coordination position is occupied by N(3) from monodentate triazole. The Ru is coordinated by two deprotonated nitrogens [N(2) and N(3)] and two oxygens [O(1) and O(5)] from carboxylato groups in the equatorial plane and with two axial positions occupied by N(1) and O(7). The central Ru atom is displaced about 0.0153 Å from the equatorial mean plane. The structural analysis shows that the geometry of the RuO3N3 coordination polyhedra is appreciably elongated octahedral. The Ru–O(carboxylate) bond lengths, Ru(1)–O(5), Ru(1)–O(7), Ru(1)–O(1), are of 1.985(3), 2.007(3) and 2.053(3) Å, similar to those for the *trans* carboxylato groups in (Hedta)Ru(III) complexes reported [5, 12, 13]. The bond lengths of Ru–N(Hedta), Ru(1)–N(1) and Ru(1)–N(2) are of 2.139(3) and 2.061(3) Å. The coordination of triazole to ruthenium via N(3) with bond length of 2.079(3) Å is slightly longer than that of (Htrz)[$RuCl_4(Htrz)_2$] at 2.0627(10) Å and 2.0733(10) Å [11], but shorter than those of [Ph_3PCH_2Ph] [*trans*-$RuCl_4$(Htrz)(DMSO)] and [$(Ph_3P)_2N$][*trans*-$RuCl_4$(Htrz)(DMSO)] at 2.1207(17) and 2.1042(12) Å [14].

In this complex, 1,2,4-triazole is similar in geometry to imidazole, which is observed in most other complexes containing triazole as well as overwhelmingly in

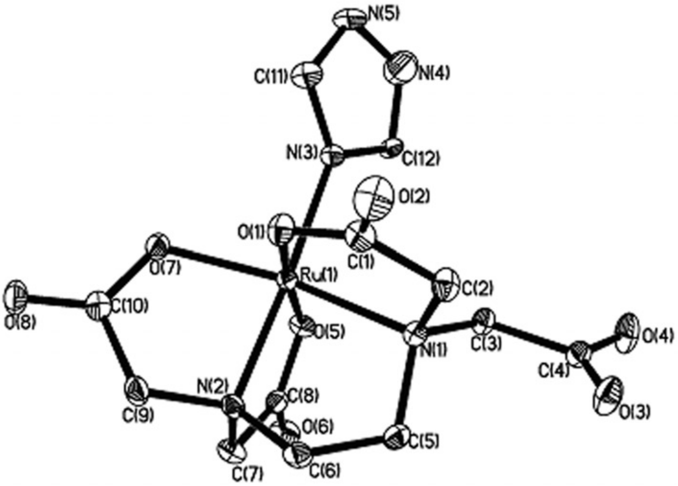

Figure 1. Molecular structure of **1** (hydrogen atoms omitted for clarity).

Table 2. Selected bond lengths [Å] and angles [°] for **1**.

Ru(1)–O(1)	2.053(3)	Ru(1)–N(1)	2.139(3)
Ru(1)–O(5)	1.985(3)	Ru(1)–N(2)	2.061(3)
Ru(1)–O(7)	2.007(3)	Ru(1)–N(3)	2.079(3)
O(5)–Ru(1)–O(7)	96.80(12)	O(7)–Ru(1)–N(3)	94.09(12)
O(5)–Ru(1)–O(1)	174.64(11)	O(1)–Ru(1)–N(3)	87.69(13)
O(7)–Ru(1)–O(1)	88.45(12)	N(2)–Ru(1)–N(3)	175.73(12)
O(5)–Ru(1)–N(2)	84.67(12)	O(5)–Ru(1)–N(1)	93.71(12)
O(7)–Ru(1)–N(2)	82.61(12)	O(7)–Ru(1)–N(1)	163.61(12)
O(1)–Ru(1)–N(2)	94.91(13)	O(1)–Ru(1)–N(1)	80.93(12)
O(5)–Ru(1)–N(3)	93.05(12)	N(2)–Ru(1)–N(1)	85.89(13)
N(3)–Ru(1)–N(1)	97.88(13)	C(1)O(1)–Ru(1)	116.9(3)

nature [15–17]. Formation of 2-D layers occurs through strong H-bonding interactions involving the triazole ring and carboxylato groups (figure 2). The triazole ring is involved in hydrogen bonds because the ring still carries an active hydrogen bound to nitrogen. In addition, the hydrogens of water take part in hydrogen bonds, involving the carboxylato groups, to connect 2-D layers into 3-D networks (figure 3). The data for hydrogen bonds in the complex are listed in table 3 [18, 19].

3.2. *UV–Vis spectra*

The UV–Vis spectra of **1** in DMSO at room temperature show two intense absorptions in the ultraviolet region at 258 nm ($\varepsilon = 4955\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) and 307 nm ($\varepsilon = 2650\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$), which can be assigned to ligand-to-metal charge-transfer transitions (LMCT). In addition, there is one relatively weak absorption in the visible region, 735 nm ($\varepsilon = 24\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$), assigned to the d–d transition ${}^2T_{2g} \rightarrow {}^2A_{2g}$, which is infrequently reported for Ru(III) complexes [20–22]. In a d^5 system and especially in ruthenium(III) which has relatively high oxidizing properties, charge transfer bands of

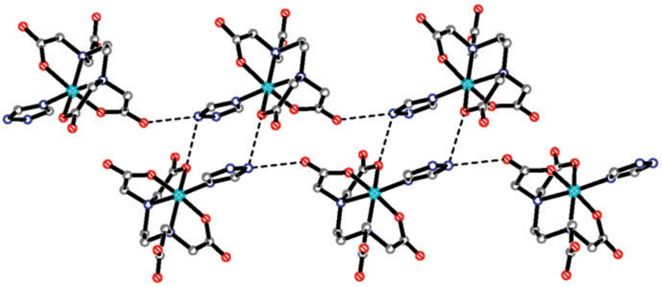

Figure 2. 2-D layers of **1** through strong H-bonding interactions involving the triazole ring and carboxylato groups (hydrogen atoms omitted for clarity).

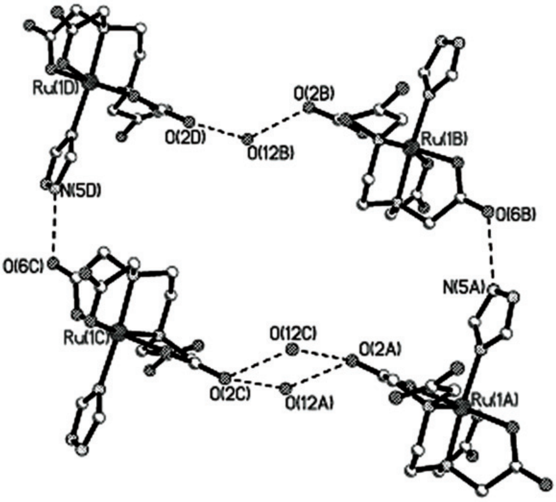

Figure 3. H-bonding interactions of **1** involving water molecules and the carboxylato groups (hydrogen atoms omitted for clarity).

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

Bond distance (Å)		Bond angles (°)	
O4···O9(i)	2.591	O4–H4···O9(i)	170.01
N5···O6(ii)	2.891	N5–H5···O6(ii)	158.98
O9···O10	2.727	O9–H9C···O10	146.03
O9···O11(iii)	2.685	O9–H9D···O11(iii)	158.09
O10···O3(iv)	2.951	O10–H10A···O3(iv)	127.64
O10···O11	3.251	O10–H10A···O11	131.32
O10···O12	2.702	O10–H10B···O12	148.25
O11···O2(v)	2.968	O11–H11A···O2(v)	174.84
O11···O8(vi)	2.783	O11–H11B···O8(vi)	159.41
O12···O2(iv)	2.837	O12–H12A···O2(iv)	176.78
O12···O2(vii)	2.869	O12–H12B···O2(vii)	160.73

Operation codes: (i) = $[-x, -y+1, -z]$; (ii) = $[x, y+1, z]$; (iii) = $[x-1, y, z]$; (iv) = $[-x+1, -y+1, -z]$; (v) = $[x, y-1, z]$; (vi) = $[-x+2, -y+1, -z+1]$; (vii) = $[x-1, y-1, z]$.

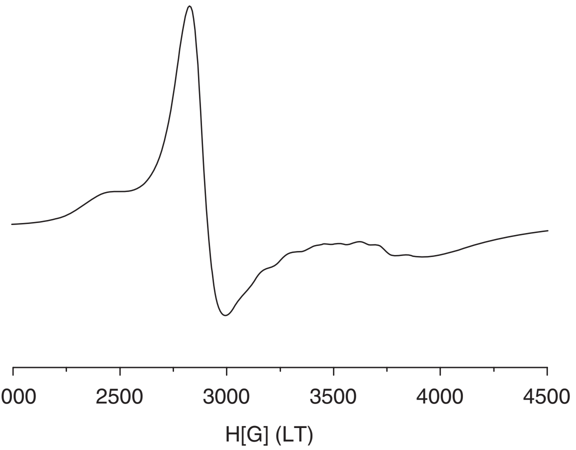

Figure 4. Powder X-band ESR spectrum of **1** at low temperature (110 K).

the type $L_{\pi y} \rightarrow t_{2g}$ are prominent in the low-energy region (495–680 nm), which can obscure the weaker d–d transitions [22, 23].

3.3. *ESR spectra*

ESR spectrum of **1** at X-band microwave frequencies and 110 K is shown in figure 4, with the values of g tensor, $g_1 = 2.756$, $g_2 = 2.351$, $g_3 = 1.720$, average g factor is 2.315 derived from the expression $[1/3(g_1^2 + g_2^2 + g_3^2)]^{1/2}$ [23], which is typical of distorted octahedral Ru(III) species [24]. The ESR spectral data show that **1** is distorted from the ideal octahedral geometry, consistent with the structure determination.

3.4. *Cyclic voltammetric studies*

The cyclic voltammogram of **1** (0.001 M) in DMSO was carried out at a platinum disk working electrode using $[Bu_4N][ClO_4]$ (TBAP, 0.1 M) as supporting electrolyte (perchlorate salts are explosives and should be used with caution) and Ag/AgCl as reference electrode; the result is shown in figure 5. For **1**, two pairs of peaks on the negative potential sides of the cyclic voltammogram correspond to the one-electron oxidation ($Ru^{III} \rightarrow Ru^{IV}$) and reduction ($Ru^{III} \rightarrow Ru^{II}$) steps. Both oxidation ($E_{pc} = -383$ mV, $E_{pa} = -3284$ mV) and reduction processes ($E_{pc} = -3957$ mV, $E_{pa} = -3861$ mV) are reversible with peak-to-peak separation (ΔE_p) values of 99 mV and 97 mV, respectively, characteristic of a single step, one-electron transfer, similar to other ruthenium(III) complexes [21, 25].

3.5. *Magnetic properties*

Complex **1** has an effective magnetic moment of 1.81 B.M. at room temperature, a little higher than expected for the spin-only value of a single-unpaired electron (1.73 B.M.), which is consistent with a paramagnetic low-spin Ru(III) [6, 26].

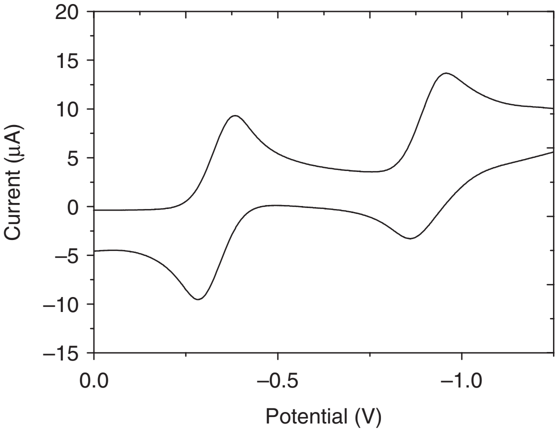

Figure 5. CV diagram of **1** in DMSO ($C = 10^{-4}$ M). Supporting electrolyte: TBAP (0.1 M); Scan rate: 100 mV s^{-1}; all potentials are referred to Ag/AgCl electrode.

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.234620 Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail for inquiry: fileserv@ccdc.cam.ac.uk; Email for deposition: deposit@ccdc.cam.ac.uk).

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