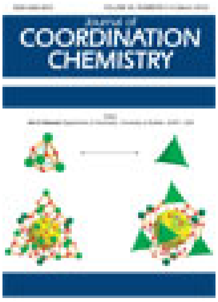

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Synthesis, characterization, spectroscopic study, and catalytic behavior of ruthenium(II) o-phenanthroline complex with dipicolinate

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Synthesis, characterization, spectroscopic study, and catalytic behavior of ruthenium(II) *o*-phenanthroline complex with dipicolinate

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A new dipicolinate complex of Ru(II), *cis*-[Ru(phen)$_2$dipic]$\cdot$9.5H$_2$O (**1**), where dipic is dipicolinate or pyridine-2,6-dicarboxylate and phen is 1,10-phenanthroline, has been synthesized and characterized by elemental analysis, spectroscopic (IR, UV-Vis), cyclic voltammetry, and single-crystal X-ray diffraction. ORTEP drawing of *cis*-[Ru(phen)$_2$dipic]$\cdot$9.5H$_2$O shows that the coordination geometry around Ru(II) is a distorted octahedron. It crystallizes in the triclinic system, with space group $P\bar{1}$, $a = 10.4633(2)$ Å, $b = 13.6332(4)$ Å, $c = 13.6637(4)$ Å, $\alpha = 67.516(3)^\circ$, $\beta = 69.757(2)^\circ$, $\gamma = 77.201(2)^\circ$, $V = 1680.74(8)$ Å^3, $Z = 2$, and $R_{\text{int}} = 0.0311$. In **1**, two phen are bidentate *N*,*N*′ ligands. The Ru(II) in **1** is bonded to dipicolinate through pyridine nitrogen and one oxygen of carboxylate groups, thus pyridine-2,6-dicarboxylate is a bidentate N,O ligand. Efficient and selective oxidation of alcohols with NaIO$_4$ as oxidant was conducted by this complex catalyst in CH$_3$OH/H$_2$O as solvents under air at room temperature.

Keywords: Ruthenium(II); 1,10-Phenanthroline; Dipicolinate; X-ray crystallography; Synthesis

1. Introduction

Pyridinedicarboxylic acids, with isomers, 2,3-, 2,4-, 2,6- etc., have been widely exploited to form 1 : 1 and 1 : 2 metal derivatives which exhibit various structures and interesting properties. Pyridine-2,6-dicarboxylic acid (H$_2$dipic) is an important ligand in inorganic and bioinorganic chemistry, known for its diverse coordination modes, such as monodentate terminal [1], bidentate chelating [2], bidentate bridging [3], and tridentate [2, 4–7]. By closely controlling the coordination environment, backbones with desirable structures and properties can be created. H$_2$dipic is a good chelating,

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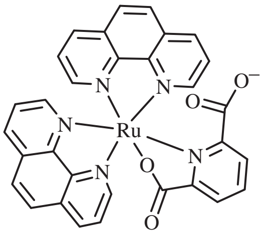


Scheme 1. Structure of the *cis*-[Ru-(phen)$_2$(dipic)].

rigid, amphophilic reagent with low toxicity. Due to its planar nature along with limited steric hindrance, it has potential to be applied to analytical chemistry [8, 9], biochemistry [10–13], catalysis [14], electron transfer [15, 16], and food and plant preservatives [17, 18].

Work on dicarboxylic acids as ligands for ruthenium is meager [19–22]. Dipicolinate complexes have been used as electron carriers in some biological model systems [23] and as specific molecular tools in DNA cleavage [24]. The ability to design molecules which are capable of targeting specific DNA sites offers attractive possibilities in developing both pharmaceuticals and tools for biotechnology [25, 26]. Water soluble and photophysically active polypyridyl ruthenium(II) complexes provide useful tools to probe drug-DNA interaction [27]. The ligands or the metal in these complexes can be substituted in an easily controlled manner to facilitate an individual application, thus providing easy access for understanding of details involved in DNA-binding and cleavage [28–31].

The paucity of ruthenium complexes containing dicarboxylic acid for use as catalyst precursors in organic synthesis has initiated the synthesis of such compounds. We previously reported the first crystal structure of a Ni(II) complex with pyridine-2,6-dicarboxylic acid as a ligand [32]. In this study, we describe the synthesis, electrochemical, and electronic spectroscopic properties of a mononuclear complex of Ru(II) with 1,10-phenanthroline (phen) and pyridine-2,6-dicarboxylate (dipic) (scheme 1).

2. Experimental

2.1. *Materials*

All reagents and solvents were of reagent grade. $(NH_4)_2$dipic was synthesized according to the literature [4]. *cis*-[Ru-(phen)$_2$Cl$_2$] $\cdot$ 2H$_2$O was synthesized according to published procedures [33]. Elemental analyses were performed by Heraeus CHNO-Rapid elemental analyzer. Infrared (IR) spectra were recorded as KBr pellets on a FTIR JASCO 460 spectrophotometer and electronic spectra on a JASCO 7850 spectrophotometer. Voltammetric experiments were performed with a Metrohm Computrace Voltammetric Analyzer model 757VA. A conventional three-electrode system was used with a carbon-paste working electrode (unmodified or modified), a saturated Ag/AgCl reference electrode, and a Pt wire as a counter electrode.

2.2. *Synthesis of cis-[Ru(phen)$_2$dipic]•9.5H$_2$O*

284 mg (0.5 mmol) of *cis*-[Ru-(phen)$_2$Cl$_2$] · 2H$_2$O and (NH$_4$)$_2$dipic 100.5 mg (0.5 mmol) were added to a nitrogen-deaerated ethanol/water mixture (*ca* 50 mL, 70% ethanol, 30% water). The mixture was heated at reflux for 12 h and then filtered. Deep red-brown crystals suitable for X-ray determination were obtained by letting part of the mixture evaporate slowly at room temperature for 1 week and then filtering the solution [Yield: (61%)]. Elemental Anal. Calcd for *cis*-[Ru(phen)$_2$dipic] · 9.5H$_2$O ($C_{31}H_{38}N_5O_{13.5}Ru$): C, 46.67; H, 4.80; N, 8.78. Found (%): C, 46.31; H, 4.52; N, 8.81.

2.3. *X-ray crystallographic study of cis-[Ru(phen)$_2$dipic]•9.5H$_2$O*

X-ray diffracted intensities were measured from a single crystal at 100 K on an Oxford Diffraction Gemini-R Ultra, Ruby CCD diffractometer using monochromated Mo-Kα ($\lambda = 0.71073$ Å). Data were corrected for Lorentz and polarization effects and absorption. The structure was solved by Patterson or direct methods and refined on F^2 using SHELX-97 crystallographic package [34–36]. Non-hydrogen atoms of non-disordered fragments were refined anisotropically using all reflections. The positions of hydrogen atoms were calculated and their atomic parameters were constrained to the bonded atoms during the refinement. No hydrogen atoms were located for crystalline water molecules.

3. Results and discussion

3.1. *Complex characterization*

New six-coordinate Ru(II) complex, *cis*-[Ru(phen)$_2$dipic], has been prepared by reacting dipicolinate with *cis*-[Ru-(phen)$_2$Cl$_2$] · 2H$_2$O in a 1 : 1 mole ratio. The dipicolinate replaces two Cl$^-$ from the starting complex to yield *cis*-[Ru(phen)$_2$dipic] and dipicolinate is a bidentate ligand in **1**. Deep red-brown crystals of *cis*-[Ru(phen)$_2$dipic] · 9.5H$_2$O were grown by slowly evaporating solution of the complex at room temperature. Elemental analysis of the complex was consistent with its formulation. The complex was further characterized by IR and UV-Vis spectroscopies and cyclic voltammetry (CV). Crystallographic data, bond lengths, and angles are reported in tables 1 and 2, respectively. As shown in figure 1 the central ruthenium is chelated by a dipicolinate and two phen ligands.

The coordination geometry about ruthenium is a distorted octahedron. Ru(II) is bonded to two bidentate phen ligands and one pyridine and one carboxylate from dipicolinate. Another ionized carboxylate is uncoordinated. The Ru–N bond lengths are in the normal range for phen (2.045–2.064 Å) [37–40]. The Ru–N$_{\text{dipic}}$ (2.120(2) Å) bond distance in **1** is considerably larger than that of Ru–N in phen and Ru–O bond length found in **1** is shorter than the corresponding distances reported for similar

Table 1. Crystallographic data and structure refinement summary for *cis*-[Ru-(phen)$_2$dipic] · 9.5H$_2$O.

Empirical formula	$C_{31}H_{38}N_5O_{13.5}Ru$
Formula weight	797.73
Radiation (Å)	Mo-Kα radiation, $\lambda = 0.71073$
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	10.4633(2)
b	13.6332(4)
c	13.6637(4)
α	67.516(3)
β	69.757(2)
γ	77.201(2)
Volume (Å^3), Z	1680.74(8), 2
Calculated density (g cm^{-3})	1.576
Absorption coefficient (μ) (mm^{-1})	0.542
$F(000)$	822
Crystal size (mm^3)	$0.27 \times 0.23 \times 0.10$
Reflections collected	46,472
Independent reflections	11,502 [$R_{\text{int}} = 0.0311$]
Parameters	451
R_1 factor	0.0494
wR_2 factor	0.1394

Table 2. Selected bond lengths (Å) and angles (°) for *cis*-[Ru-(phen)$_2$dipic] · 9.5H$_2$O.

Ru(1)–N(11)	2.045(2)	O(1)–C(7)	1.273(3)
Ru(1)–N(21)	2.053(2)	O(2)–C(7)	1.245(3)
Ru(1)–N(11′)	2.056(2)	O(3)–C(8)	1.225(3)
Ru(1)–N(21′)	2.064(2)	O(4)–C(8)	1.283(3)
Ru(1)–O(1)	2.088(2)	N(1)–C(2)	1.349(3)
Ru(1)–N(1)	2.120(2)	N(1)–C(6)	1.367(3)
N(1)–Ru(1)–O(1)	78.74(7)	N(11)–Ru(1)–N(21′)	94.28(8)
N(21)–Ru(1)–N(21′)	79.89(9)	N(11′)–Ru(1)–O(1)	95.42(8)
N(11)–Ru(1)–N(11′)	80.11(8)	N(21′)–Ru(1)–N(1)	97.06(8)
N(11)–Ru(1)–N(21)	87.72(8)	N(11)–Ru(1)–N(1)	101.73(7)
N(21′)–Ru(1)–O(1)	90.11(8)	N(1)–Ru(1)–N(21)	170.30(8)
N(1)–Ru(1)–N(11′)	90.16(8)	N(11′)–Ru(1)–N(21′)	171.66(8)
N(21)–Ru(1)–O(1)	92.01(8)	N(11)–Ru(1)–O(1)	175.49(8)
N(11′)–Ru(1)–N(21)	93.65(9)	C(7)–O(1)–Ru(1)	116.44(16)

ruthenium complexes. Dipicolinate can be a tridentate ligand [41]. The coordinated carboxylate O1–C7–O2 in dipicolinate is a little deviated from the N1 pyridine ring with torsion angle of N1–C6–C7–O1: 2.5(4)° and uncoordinated carboxylate group is vertical to the pyridine ring of dipicolinate. The bond angles formed by two nitrogen atoms of phen and Ru(II) [N(11)–Ru–N(11′) 80.11(8)°, N(21)–Ru–N(21′) 79.89(9)°] are slightly larger than that formed by N and O of dipicolinate and Ru(II) [N(1)–Ru–O(1) 78.74(7)°]. Carboxyl oxygen atoms form multipoint hydrogen bonds with lattice water molecules. Due to the steric hindrance of lattice water molecules in the unit cell, the phen ligands in each complex cannot interact in a π–π fashion.

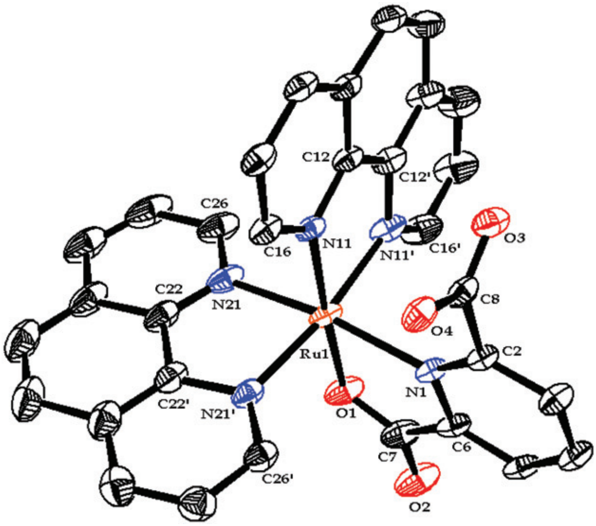


Figure 1. ORTEP structure of the *cis*-[Ru-(phen)$_2$dipic] · 9.5H_2O.

3.2. *IR spectra*

Strong bands at 1628 and 1721 cm^{-1} in IR spectra of **1** are assigned to $\nu(C=O)$ and another strong absorption at 1351 cm^{-1} is due to ν(C–O). The difference between $\nu(C=O)$ and ν(C–O) of dipicolinate is 300 cm^{-1} which indicates that the carboxyl groups are monodentate, consistent with the structure determination [42]. Two separate bands indicate two types of carboxylates, consistent with free and coordinated carboxylates. The medium intensity band at 1425 cm^{-1} corresponds to C–H deformation and the ring wagging vibrations of the pyridine groups are also observed at 731 and 783 cm^{-1}. A broad band at 3445 cm^{-1} is due to the presence of lattice water.

3.3. *Electronic absorption spectra*

Electronic spectrum of the complex was taken in water (figure 2). The intense absorption at 429 nm is assigned to metal-to-ligand charge transfer Ru(dπ) → phen(dπ*) by analogy to other Ru(II) phen complexes [41, 43]. The visible spectrum is similar to those of the corresponding phen or bpy complexes except that there is a blue shift in the maximum wavelength of absorption. This effect essentially reflects the enhanced π acidity of dipicolinate relative to that of phenanthroline [44–46]. The absorption bands in the UV region are assigned to spin-allowed ($\pi \rightarrow \pi^*$) transitions centered on the polypyridine part of the ligand [47, 48].

3.4. *Cyclic voltammetry*

Redox behavior of **1** was studied using CV at a Pt working electrode at a scan rate of 100 $mV\,s^{-1}$. KCl (0.1 $mol\,L^{-1}$) was used as a supporting electrolyte in H_2O of $2 \times 10^{-3}\,mol\,L^{-1}$ complex. The cyclic voltammogram of the complex is displayed

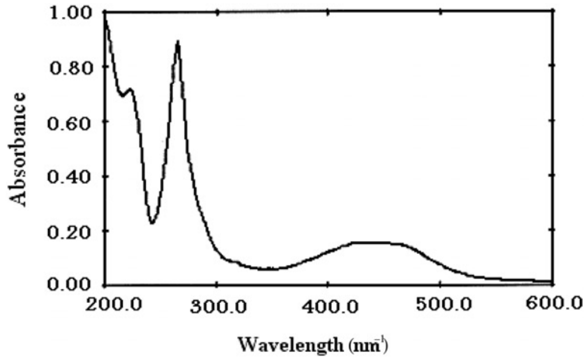


Figure 2. Absorption spectrum of *cis*-[Ru-(phen)$_2$dipic] in water.

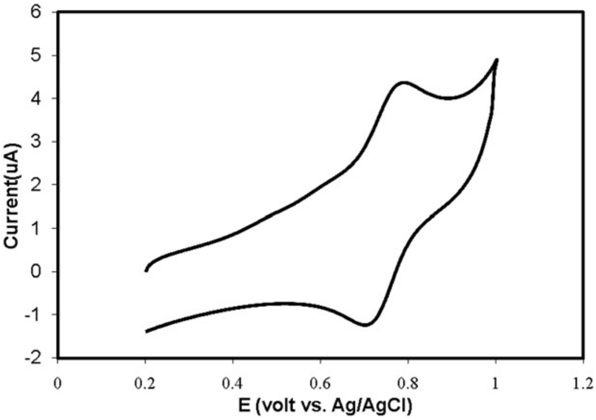


Figure 3. Cyclic voltammogram of *cis*-[Ru(phen)$_2$dipic] · 9.5H_2O in water, 0.1 mol L^{-1} KCl, at 100 mVs^{-1}.

in figure 3. The observed oxidation and reduction waves are due to metal-centered processes. The ruthenium(II) yields one quasi-reversible redox couple located at $E_{1/2} = 0.747$ V, which is assignable to Ru(II)/Ru(III) ($E_{1/2} = (E_{pa} + E_{pc})/2$) [41, 43]. The CV of H_2dipic shows two overlapping irreversible reduction peaks at -1.36 V and -1.56 V which do not display associated oxidation processes in the reverse scan, even at the highest scan rate [49]. The 1,10-phenanthroline is also electroactive, but at much more negative potentials. In **1**, the quasi-reversible reduction couple at -1.86 V is assigned to reduction of phen. The dipic shows irreversible behavior at -1.54 V.

3.5. *Catalytic reaction*

For catalytic investigation we chose alcohol oxidation with aim to obtain aldehyde as a target product, since aldehydes are important compounds in pharmaceutical chemistry.

With 4-methoxybenzyl alcohol as model compound, the effects of reaction conditions such as reaction time and the amount of the catalyst (*cis*-[Ru-(phen)$_2$dipic] · 9.5H_2O)

Table 3. Effect of various oxidants and solvents on the oxidation of 4-methoxybenzyl alcohol by *cis*-[Ru-(phen)$_2$dipic] · 9.5H_2O.

Solvent	Oxidant (1 mmol)	Yield[a] (%) after 30 min
CH_3OH/H_2O	$NaIO_4$	100
CH_3CN/H_2O	$NaIO_4$	82
CH_3OH	$NaIO_4$	76
CH_3CH_2OH/H_2O	$NaIO_4$	88
CH_2Cl_2/H_2O	$NaIO_4$	41
$CHCl_3/H_2O$	$NaIO_4$	28
CCl_4/H_2O	$NaIO_4$	11
CH_3OH/H_2O	Oxone ($KHSO_5$)	81
CH_3OH/H_2O	H_2O_2	68
CH_3OH/H_2O	H_2O_2/urea	55
CH_3OH/H_2O	NaOCl	42
CH_3OH/H_2O	No oxidant	14

[a]The reactions were performed in (1 : 1) mixture of CH_3OH/H_2O (1 mL) under air at room temperature. The gas chromatography (GC) yields (%) are measured relative to the starting substrate after 15 min.

Table 4. The effects of reaction conditions on the oxidation of 4-methoxybenzyl alcohol by the *cis*-[Ru-(phen)$_2$dipic] · 9.5$H_2O/NaIO_4$ catalytic system.[a]

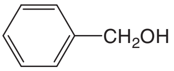
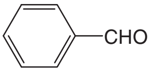
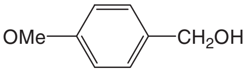
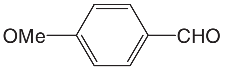
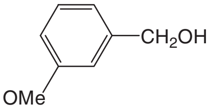
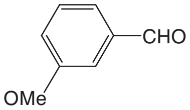
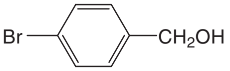
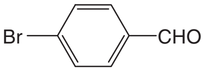
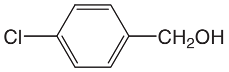
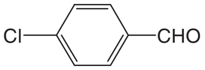
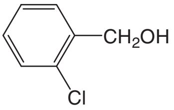
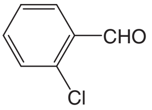
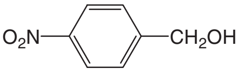
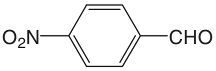
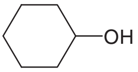
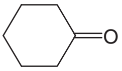
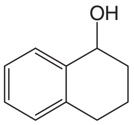
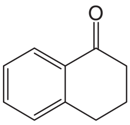
Amount of catalyst (mmol)	Amount of $NaIO_4$ (mmol)	Time (min)	Yield[a] (%)
0.0001	0.4	25	41
0.0002	0.4	25	55
0.0003	0.4	25	74
0.0004	0.4	25	89
0.0005	0.4	25	100
0.0006	0.4	25	100
0.0005	0.1	25	51
0.0005	0.2	25	65
0.0005	0.3	25	82
0.0005	0.5	25	100
0.0005	0.4	15	58
0.0005	0.4	20	81
0.0005	0.4	30	100

[a]The reactions were performed in (1 : 1) mixture of CH_3OH/H_2O (1 mL) under air at room temperature. The GC yields (%) are measured relative to the starting substrate after 15 min.

have been investigated. Mixture of CH_3OH/H_2O was chosen as solvent and $NaIO_4$ as oxidant for the reaction; the results are listed in tables 3 and 4. Varying amount of catalyst from 0.0001 to 0.0005 mmol results in an increase in the conversion of 4-methoxybenzyl alcohol from 41% to 100%. Similarly, with varying amount of $NaIO_4$ from 0.1 to 0.4 mmol the conversion of 4-methoxybenzyl alcohol increased drastically from 51% to 100%.

After optimization, the oxidations of various alcohols were investigated using the ruthenium complex as catalyst. As shown in table 4, alcohols are effectively oxidized to corresponding aldehydes as major products. Good chemical yields of products depending on the nature of the alcohol, in the range of 68–100%, were obtained for all cases. The results show benzyl alcohols are completely oxidized to the corresponding aldehydes (table 5).

Table 5. Oxidation of alcohols catalyzed by *cis*-[Ru-(phen)$_2$dipic] · 9.5H$_2$O/NaIO$_4$.[a]

Alcohol	Product	Yield (%)	Time (min)
		88	30
		100	30
		93	30
		81	30
		74	30
		82	35
		78	40
		68	45
		75	45

[a] The molar ratios for *cis*-[Ru-(phen)$_2$dipic] · 9.5H$_2$O : substrate : oxidant are 1 : 400 : 800. The reactions were performed in (1 : 1) mixture of CH$_3$OH/H$_2$O (1 mL) under air at room temperature.

4. Conclusion

cis-[Ru(phen)$_2$dipic] · 9.5H$_2$O (dipic = dipicolinate or pyridine-2,6-dicarboxylate) has been synthesized and characterized by single-crystal X-ray diffraction and physico-chemical methods. Dipicolinate coordinates to Ru(II) in a O,N-bidentate coordination mode. Distorted octahedral coordination at Ru(II) is formed by the two donors of dipicolinate in addition to two phen ligands. Also, there is another ionized carboxylate uncoordinated.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary material (CCDC No. 717488).

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