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Synthesis, structure, catalytic and calculated non-linear optical properties of *cis*- and *trans*-, mer-chlorobis(triphenyl phosphine/triphenyl arsine)-dipicolinato ruthenium^{III} complexes

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ABSTRACT

The new mononuclear Ru^{III} complexes *cis*-, mer-[Ru(k^3 -dipic)(EPh₃)₂Cl]·2H₂O (E = P (1), As (2)), (L = 2,6pyridyldicarboxylate; dipic) have been synthesized and characterized. The X-ray crystal structure of 1 reveals that the coordination geometry around the Ru^{III} center is distorted octahedral in which three sites are occupied by tridentate dipic ligand and remaining three sites are occupied by two mutually *cis* triphenyl phosphine ligands and one chloride ions. In chloroform solvent, cis-, mer-[Ru(k^3 -dipic)- $(EPh_3)_2Cl_2H_2O$ (E = P (1), As (2)) complexes undergoes thermal rearrangement to more stable *trans*-, mer-[Ru(k^3 -dipic)(EPh₃)₂Cl] (E = P(**3**), As(**4**)) complexes. Complexes **1** and **2** show rhombic EPR spectral features, while complex 3 and 4 show tetragonal distortion. The new Ru^{III} complexes 1 and 2 display both Ru^{III}-Ru^{II} reduction and Ru^{III}-Ru^{IV} oxidation processes. These geometric isomers exhibit textbook differences both in spectroscopic as well as structural properties in the solid state. The new complexes 1 and 2 were found to catalyze the oxidation of alcohols to carbonyl derivatives using N-methyl morpholine-Noxide as co-oxidant. The first static hyperpolarizability (β) for all of the complexes have been investigated by density functional theory (DFT) which suggests β value increases from *trans* to *cis* form. Also, the solvent-induced effects on the non-linear optical properties (NLO) were studied by using self-consistent reaction field (SCRF) method. As the solvent polarity increases, the β value increases monotonically. The electronic absorption bands of 1 have been assigned by time dependent density functional theory (TD-DFT).

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1. Introduction

Over the decades, coordination complexes containing ruthenium as the metal center continued to attract attention due to their multifarious applications [1–5]. In particular, they are being used extensively as catalysts for a myriad of processes including oxidative and reductive reactions [6–8]. In the field of catalysis by transition-metal complexes, the ligands attached to the metal center play a pivotal role. The appropriate ligands allow for control of the steric and electronic properties and thus governance of the catalyst performance in terms of selectivity and efficiency.

Ruthenium^{III} complexes possessing tertiary phosphines have been extensively studied from synthetic perspective, and their role as potential catalysts is recognized recently for various organic transformations [6,7,9,10]. Amongst organic transformations, catalytic oxidation of alcohol to carbonyl compounds is an important reaction due to their utility in fine chemicals and pharmaceutical industries. Ruthenium complexes are known to mediate alcohol oxidation using variety of oxidants such as PhIO [11], NMO [12], BrO₃⁻ [13], S₂O₈⁻ [14], *t*-BuOOH [15], and O₂ or air [16].

More recently, there has been an increased interest in mixedligand complexes containing both phosphine types of donors and N types of donors as a result of the unique electronic properties that this combination of ligands is able to transmit to the metal center [17–22]. Due to this electronic transmission, these complexes could be the potential candidates for the study non-linear optical (NLO) properties. Also, the change in bulkiness of the donor atom in these complexes can lead to the change in the electronic transmission thereby influencing the optoelectronic properties.

Although, a number of first row transition-metal complexes containing dipicolinic acid (H_2 dipic) are reported in the literature, complexes of ruthenium containing dipicolinic acid have scarcely been studied [23–26]. Dipicolinic acid is known for its various coordination modes [27–29] and its potential use in analytical

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chemistry [30], corrosion inhibition [31], decontamination of nuclear reactors [32] and biological activity [33,34].

In the quest of some efficient catalysts and new NLO active materials, herein, we report the syntheses, spectroscopic, crystal structure, calculated NLO and catalytic studies of *cis*-, mer-[Ru(k^3 -dipic)(EPh₃)₂Cl]·2H₂O (E = P (**1**), As (**2**) and their thermal rearrangement to *trans*-, mer-[Ru(k^3 -dipic)(EPh₃)₂Cl] (E = P(**3**), As(**4**)) complexes.

2. Experimental

2.1. Materials and physical measurements

All the synthetic manipulations were performed under ambient atmosphere. The solvents were dried and distilled before use following the standard procedures. 2,6-pyridinedicarboxlic acid (Aldrich), pyridine (Aldrich), and hydrated ruthenium^{III} chloride (Aldrich) were used as received. The precursor complexes [Ru- $Cl_2(EPh_3)_3$] (E = P, As) [35] were prepared and purified following the literature procedure.

Elemental analyses were performed on a Carlo Erba Model EA-1108 elemental analyzer and data of C, H and N is within $\pm 0.4\%$ of calculated values. IR(KBr) and electronic spectra were recorded using Perkin–Elmer FT-IR spectrophotometer and Shimadzu UV-1601 spectrometer, respectively. Mass spectral data were recorded using a waters micromass LCT Mass Spectrometer/Data system. Electron paramagnetic resonance (epr) spectra were recorded with a Varian 109 C (fitted with a quartz dewar for measurements at 300 K) and Bruker EMX 1444 spectrometer. The EPR spectra were calibrated with diphenylpicrylhydrazyl, DPPH (g = 2.0037).Electrochemical properties of the complexes were measured by cyclic voltammetry using platinum as working electrode and the supporting electrolyte was [NBu₄]ClO₄(0.1 M) in acetonitrile solution of 0.001 M of complex versus Ag/AgCl at a scan rate of 100 mV s⁻¹.

2.2. Synthesis of complexes

2.2.1. cis-, mer-[Ru(dipic)(PPh₃)₂Cl]·2H₂O (1)

[RuCl₂(PPh₃)₃] (0.982 g, 1 mmol) was added slowly to a solution of CH₃OH (15 mL), and water (15 mL) containing dipicolinic acid (0.167 g, 1 mmol) and pyridine (160 μ L, 2 mmol). The resulting solution was stirred at room temperature for 24 h. Slowly, color of the solution changed from light orange to dark red. The resulting solution was filtered and left at room temperature for slow crystallization. In a couple of days red color needle shaped diffraction quality crystals appeared. These were separated washed several times with diethyl ether, and vacuum-dried. Yield: (0.776 g, 90%). Anal. Calc. For C₄₃H₃₇ClNO₆P₂Ru: C, 59.86; H, 4.29; N, 1.62. Found: C, 59.76; H, 4.36; N, 1.64. IR (cm⁻¹, nujol): v = 3427, 3247, 3055, 1970, 1670, 1607, 1481, 1434, 1349, 1312, 1160, 1091, 998, 912, 747, 697, 593, 517, 436. UV/Vis(CHCl₃): λ_{max} (ε [dm³ mol⁻¹ cm⁻¹]) = 603(2767), 472(2187), 303(sh) 261(13,206). ESI-MS(m/z): 862.4(M⁺).

2.2.2. cis-, mer-[Ru(dipic)(AsPh₃)₂Cl]·2H₂O (2)

This complex was prepared by a similar method (1) except that $[RuCl_2(AsPh_3)_3]$ (1.090 g, 1 mmol) was used in place of $[RuCl_2(PPh_3)_3]$. A brownish red complex was obtained. Yield: (0.731 g, 80%). Anal. Calc. for $C_{43}H_{37}CINO_6As_2Ru$: C, 54.31; H, 3.89; N, 1.47. Found: C, 54.46; H, 4.12; N, 1.55. IR (cm⁻¹, nujol): v = 3428, 3246, 1970, 1680, 1610, 1480, 1436, 1348, 1310, 1161, 1090, 995, 910, 747, 696, 590, 516, 434. UV/Vis: λ_{max} (ε [dm³ mol⁻¹ cm⁻¹]) = 523(9471), 392(13,069), 323(3874), 265(15,124). ESI-MS(m/z): 950.2(M⁺).

2.2.3. trans-, mer-[Ru(dipic)(PPh₃)₂Cl] (3)

cis-[Ru(dipic)(PPh₃)₂Cl]·2H₂O(0.431 g, 0.5 mmol) was added slowly to a solution of CHCl₃ (15 mL). The resulting solution was refluxed under nitrogen atmosphere at room temperature for 7 h. Slowly, color of the solution changed from red to brown red color. The solution was filtered and rotary evaporated to afford a brownish red powder. Yield: (0.301 g, 70%). Anal. Calc. for C₄₃H₃₃ClNO₄-P₂Ru: C, 62.46; H, 3.99; N, 1.69. Found: C, 62.66; H, 4.26; N, 1.74. IR (cm⁻¹, nujol): v = 3300, 3247, 3055, 1970, 1659, 1607, 1481, 1433, 1352, 1312, 1160, 1091, 998, 912, 748, 690, 593, 510, 430. UV/Vis(CHCl₃): λ_{max} (ε [dm³ mol⁻¹ cm⁻¹]) = 409(6710), 266(9392). ESI-MS(*m*/*z*): 826.6(M⁺).

2.2.4. trans-, mer-[Ru(dipic)(AsPh₃)₂Cl] (4)

cis-[RuCl(dipic)(AsPh₃)₂]·2H₂O(0.457 g, 0.5 mmol) was added slowly to a solution of CHCl₃ (15 mL). The resulting solution was refluxed under nitrogen atmosphere at room temperature for 7 h. Slowly, color of the solution changed from brown red to dark red color. The solution was filtered and rotary evaporated to afford a dark red powder. Yield: (0.320 g, 70%). Anal. Calc. for C₄₃H₃₃ClNO₄As₂Ru: C, 56.45; H, 3.61; N, 1.53. Found: C, 56.66; H, 3.46; N, 1.45. IR (cm⁻¹, nujol): v = 3410, 3246, 1970, 1671, 1610, 1480, 1434, 1344, 1310, 1160, 1077, 995, 915, 747, 690, 590, 520, 436. UV/Vis: λ_{max} (ε [dm³ mol⁻¹ cm⁻¹]) = 507(11,820), 371(2150), 316(9219), 272(9660), 265(10,534). ESI-MS(*m*/*z*): 914.1(M⁺).

2.3. X-ray crystallographic study

A crystal of suitable size was selected after careful examination under an optical microscope. Intensity data for **1** was collected on Bruker AXS SMART APEX CCD area detector diffractometers using graphite monochromatized Mo K α radiation at 293(2). SAINT and SMART software packages [36] were used for data collection and data integration for **1**. Structure solution and refinement were carried out using the SHELXTL-PLUS software package [36]. The nonhydrogen atoms were refined with anisotropy thermal parameters. All the hydrogen atoms were treated using appropriate riding models. The computer programme PLATON was used for analyzing the inter and intra molecular interactions and stacking distances [37,38].

2.4. Computational details

Geometry optimization of all the four ruthenium complexes were performed at the level of density functional theory (DFT) using B3LYP functional [39,40]. For all the atoms except Ru 6-31G** basis set was used. For Ru LANL2DZdp basis set was employed. The first static hyperpolarizability (β) for all the four compounds was calculated using the finite field perturbation method. The first static hyperpolarizability for 1, 2, 3 and 4 were calculated in vacuum as well as in the solvents having differing polarity using polarized continuum model (PCM) [41]. The energies and intensities of the 60 lowest-energy spin allowed electronic excitations for the complexes were calculated using time dependent-DFT (TD-DFT) at the same level of theory using polarized continuum model (PCM) [41]. The solvent parameters used where of chloroform. The single point energies of both the *cis* and *trans*-complexes **1** and **3** were calculated by employing their single crystal X-ray geometry. All calculations were performed using the Gaussian 03 programme [42]. Molecular orbital diagrams were constructed using the MOLDEN programme [43].

2.5. Catalytic reactions

The oxidation of alcohol was carried out in dichloromethane as the solvent at room temperature under aerobic conditions. Catalytic amounts of the complex (0.01 mmol) were dissolved in 15 ml of CH_2Cl_2 and 1 mmol of alcohol, and the co-oxidant *N*-methylmorpholine-*N*-oxide (3 mmol) was then added to it. The solution was heated under reflux for 5 h. The mixture was evaporated to dryness and extracted with petroleum ether (60–80 °C). The combined petroleum ether mixture was filtered and evaporated to give the corresponding aldehyde, which was then quantified as its 2,4-dinitrophenyl hydrazone derivative [44,45].

3. Results and discussion

3.1. Synthesis

The reaction of $[RuCl_2(EPh_3)_3]$ (E = P, As) with dipicolinic acid containing pyridine in 1:1 stoichiometric ratio in a mixture of water and methanol (1:1 v/v) under stirring at RT afforded kinetically favoured neutral mononuclear complexes with the general formulae *cis*-, mer-[Ru(k^3 -dipic)(EPh_3)_2Cl]·2H_2O (E = P (1), As (2)) in \approx 90% yield (Scheme 1). The thermodynamically favoured neutral *trans*-, mer- complexes [Ru(k^3 -dipic)(EPh_3)_2Cl] (E = P (3), As (4)) were synthesized in 70% yield by heating the isomeric *cis*-,



mer-[Ru(dipic)(EPh₃)₂Cl]·2H₂O (E = P (**1**), As (**2**)) to reflux in chloroform under nitrogen atmosphere for 4 h at 60 °C (Scheme 1). Synthesis of **3** and **4** has previously been described by Natarajan et al. following a different method employing ruthenium^{III} complexes [RuX₃(EPh₃)₃] (E = P, As; X = Cl, Br) [26]. In order to assess the relative energy difference between the *cis*-, mer-[Ru(dipic)(PPh₃)₂Cl] (**1**) and *trans*-, mer-[Ru(dipic)(PPh₃)₂Cl] (**3**) complexes, density functional theoretical (DFT) calculations were performed on both the isomers using the hybrid Lee–Yang–Parr (B3LYP) functional. The xyz coordinates were obtained from the single crystal X-ray difference between the less stable *cis* **1** and the more stable *trans* **3** is 163.69 kJ mol⁻¹. Hence, refluxing **1** in the chloroform under nitrogen atmosphere yielded **3**.

3.2. Characterization

All the complexes were isolated as air-stable, non-hygroscopic solids which were soluble in dimethylformamide, dimethylsulfoxide, methanol, acetonitrile and halogenated solvents but insoluble in petroleum ether and diethyl ether.

Information regarding the immediate environment about the metal center in all the complexes was obtained from EPR spectral studies. The X-band EPR spectra of all the complexes were recorded in CH₃CN at room temperatures. The EPR spectrum of **1** is shown in Fig. 1. The nature of the spectra revealed the absence of any hyperfine splitting due to interaction with any other nuclei present in the complexes. Complexes **1**, and **2** showed three lines with three different 'g' values ($g_x \neq g_y \neq g_z$) indicating rhombic distortion [26,46,47], while complexes **3** and **4** showed two lines with two different 'g' values ($g_x = g_y \neq g_z$) similar to previously reported by Natarajan et al. [26]. The 'g' values are in the range 2.32–1.87. The nature of spectra obtained is in good agreement with that of the previously reported Ru^{III} complexes [48,49].

The electronic absorption spectra of all the complexes were recorded at room temperature in CHCl₃ as the solvent. The spectra of the *cis*-complexes **1** and **2** exhibit transitions at lower than 400 nm corresponding to intramolecular $\pi \to \pi^*$ and $n \to \pi^*$ transitions [50]. The strong absorption band around 603-523 nm, which is responsible for the color of *cis*-complexes, can be assigned metal to ligand charge transfer transition $(M_{d\pi} \rightarrow L_{\pi*})$ and less intense one around 472–392 nm probably originate from $(L_{\pi*} \rightarrow M_{d\pi})$ ligand to metal charge transfer transitions [51]. The shoulder around 303–323 nm may originate from the $p_{\pi}(Cl^{-}) \rightarrow t_{2g}(Ru)$ LMCT transition [52]. However, trans-complexes 3 and 4 show MLCT transition at 409 and 507 nm, respectively. Comparing cis and trans isomers, it is found that the MLCT maxima of the *trans* complexes are shifted towards higher energy side compared to cis complexes. The electronic absorption spectrum for the complex 1 has been assigned with the help of TD-DFT calculations which confirms that the first lower energy band calculated at 566 nm with an oscillator strength (f) of 0.0036 is because of the metal to ligand charge transfer (Fig. 2). Also, the higher energy bands calculated at 397 nm (f = 0.009) and 304 nm (f = 0.0058) are because of the intraligand charge transfer (Fig. 2). The cis-, mer-[Ru(dipi $c)(EPh_3)_2Cl] \cdot 2H_2O$ (E = P (1), As (2)) is thermodynamically unstable with respect to *trans*-, mer-[Ru(dipic)(EPh₃)₂Cl](E = P ($\mathbf{3}$), As ($\mathbf{4}$)). It isomerizes into *trans*-, mer-[Ru(dipic)(EPh₃)₂Cl](E = P($\mathbf{3}$), As ($\mathbf{4}$)) in chloroform solution. This thermal rearrangement could be followed by using UV/Vis absorption spectroscopy. As can be seen in Fig. 3, heating of cis-, mer-[Ru(dipic)(PPh₃)₂Cl]·2H₂O(1) in chloroform resulted in a gradual decrease in intensity of the band at 603 nm and 472 nm and a concomitant appearance of bands at 409 nm, which are associated with the trans-, mer-[Ru(dipic)(PPh₃)₂Cl] (**3**) complex. The UV/Vis spectra show isosbestic points at 391 nm, indicating that thermoproduct is formed directly



Fig. 1. EPR spectrum of *cis*-, mer-[RuCl(dipic)(PPh₃)₂]·2H₂O (1) in CH₃CN at RT.



Fig. 2. Selected orbital transitions for 1 (orbital contour value 0.05).

without the production of long-lived intermediates. Upon complete thermal rearrangement, no further changes in the absorption spectrum occur, which further indicates the thermostability of *trans*-, mer-[Ru(dipic)(PPh₃)₂Cl]. The cyclic voltammetric data are given in Table 1 and a representative cyclic voltammogram of complex *cis*-, mer-[Ru(dipic)(PPh₃)₂Cl]·2H₂O(1) is shown in Fig. 4. The $E_{1/2}$ of the oxidation process was in the range of 0.55–0.56 V and reduction process was



Fig. 3. UV/Vis absorption spectra of *cis*-, mer-[Ru(dipic)(PPh₃)₂Cl]-2H₂O in chloroform upon irradiation for (a) 1 min, (b) 10 min, (c) 25 min, (d) 40 min, (e) 50 min, (f) 1 h 20 min, (g) 1 h 40 min, (h) 2 h, (i) 2 h 20 min, (j) 2 h 40 min, (k) 3 h, (l) 4 h.

Table 1				
Cyclic voltammetric ^{a,b}	data of	new	Ru(III)	complexes

Complex RuIII–Ru ^{IV}			Ru ^{III} -Ru ^{II}					
	$E_{\rm pc}(V)$	$E_{\rm pa}(V)$	$E_{\rm f}({\sf V})$	$\Delta E_{\rm p}({\rm mV})$	$E_{\rm pc}(V)$	$E_{\rm pa}(V)$	$E_{\rm f}({\sf V})$	$\Delta E_{\rm p}({\rm mV})$
1	0.33	0.78	0.56	450	-0.34	-0.47	-0.41	130
2	0.33	0.76	0.55	430	-0.36	-0.47	-0.42	110

^a In acetonitrile solution (298 K) at a scan rate of 100 mV s⁻¹.

^b $E_{\rm f} = (E_{\rm pa} + E_{\rm pc})/2$, where $E_{\rm pa}$ and $E_{\rm pc}$ are anodic and cathodic peak potentials, respectively; $\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$.



Fig. 4. Cyclic voltammogram of complex cis-, mer-[RuCl(dipic)(PPh_3)2]·2H2O (1) (0.001 M) in CH₃CN at 25 °C at 100 mV s⁻¹ scan rate.

in the range of -0.41 to -0.42 V. The oxidation and reduction waves are due to the metal centered Ru^{III} \rightarrow Ru^{IV} and Ru^{III} \rightarrow Ru^{II} processes, respectively. Any redox behavior of the ligand in the

range 0.55 to -0.42 V is ruled out because dipicolinic acid showed quasi-reversible and irreversible processes only around -1.58 V in its complexes [53]. Moreover, potential difference between the two



Fig. 5. Molecular structure of 1 (30% thermal ellipsoids are shown; hydrogen atoms and solvent molecules omitted for clarity).

successive oxidation processes is $\approx 1.2 \text{ V}$ which agrees well with the average potential difference between the redox processes of the ruthenium center (Ru^{II}/^{III}–Ru^{III}/^{IV}) ($\sim 1.0-1.5 \text{ V}$) observed for other mononuclear complexes [54]. Complexes **1** and **2** exhibit quasi-reversible oxidative couples with peak to peak separations (ΔE_p) of 430–450 mV [55,56]. It has been observed from the electrochemical data that the present ligand system is ideally suitable for stabilizing the higher oxidation state of the ruthenium ion [57,58].

3.3. Molecular structure determination

Molecular structure of the *cis*-, mer-[Ru(dipic)(PPh₃)₂Cl] is presented in Fig. 5. Details about the data collection, solution and refinement are enlisted in Table 2 and selected bond lengths and bond angles are presented in Table 3, respectively. Complex **1** crystallizes in the monoclinic crystal system with space group P2(1). The structure of *trans*-, mer-[Ru(dipic)(PPh₃)₂Cl] has already been studied by Natarajan et al. [26]. The coordination geometry around

Table 2Crystallographic data for 1 at 293(2) K.

	1
Empirical formula	C43H37CINO6P2Ru
Formula weight	862.20
Color and habit	Red, needle
Crystal size (mm)	$0.20\times0.24\times0.30~mm$
Crystal system, space group	Monoclinic, P2(1)
a (Å)	12.523(5)
b (Å)	10.682(4)
<i>c</i> (Å)	15.235(6)
β (°)	101.554(6)
γ (°)	90.00
$V(Å^3)$	1996.8(13)
$Z, D_c (\mathrm{mg}\mathrm{m}^{-3})$	2, 1.434
$\mu (\mathrm{mm}^{-1})$	0.588
Т (К)	293(2)
λ (Mo Kα) (Å)	0.71073
No. of reflections/unique	22,425/9373
No. of refined parameter	491
R factor $[I > 2(I)]$	0.0802
wR2 [I > 2(I)]	0.2048
R factor (all data)	0.0934
wR2 (all data)	0.2126
GoF	1.071

Table 3									
Selected bond	lengths	(Å)	and	bond	angles	(°)	for	1	at
293(2) K.									

	1
Ru(1)-Cl(1)	2.224(5)
Ru(1)—N(1)	1.997(6)
Ru(1)—O(4)	2.118(6)
Ru(1)—O(3)	2.135(6)
Ru(1) - P(1)	2.2752(18)
Ru(1)—P(2)	2.357(2)
N(1) - Ru(1) - O(4)	78.8(2)
N(1) - Ru(1) - O(3)	77.5(2)
O(4) - Ru(1) - O(3)	155.7(2)
N(1) - Ru(1) - P(1)	90.49(16)
Cl(1)-Ru(1)-P(1)	171.45(14)
P(1) - Ru(1) - P(2)	97.71(7)
Cl(1)-Ru(1)-P(2)	90.78(14)
N(1) - Ru(1) - P(2)	171.76(17)
N(1) - Ru(1) - Cl(1)	81.0(2)
O(4) - Ru(1) - P(1)	93.95(16)
O(3) - Ru(1) - P(1)	91.58(17)
O(4)— $Ru(1)$ — $P(2)$	99.66(15)
O(3) - Ru(1) - P(2)	103.00(17)
Cl(1)- $Ru(1)$ - $P(2)$	90.78(14)
O(4)-Ru(1)-Cl(1)	85.6(2)
O(3) - Ru(1) - Cl(1)	85.5(2)



Fig. 6. Single helical structure in **1** resulting from intra- and intermolecular C—H \cdots π and π - π interactions.



Fig. 7. Axial view of the complexes (1) and (3) exhibiting different stacking arrangements of the phenyl rings to dipic ligand.

Ru^{III} is distorted octahedral with the equatorial sites occupied by one nitrogen N1 and two oxygen O3, O4 atoms from dipic ligand, and one phosphorus atoms P2 of the triphenylphosphine ligand. The axial sites are occupied by the Cl1 and P1 atom from other triphenylphosphine ligand. Distorted stereochemistry is to be expected for Ru^{III} as a consequence of the nonspherical symmetry of the low-spin d^5 electronic configuration. The N(1)-Ru(1)-Cl(1) bond angle is 81.0(2)° showing that Cl atom lies *cis* to ring nitrogen. The bite angle around Ru(III) are N(1)—Ru(1)— $O(4) = 78.8(2)^{\circ}$; N(1)—Ru(1)— $O(3) = 77.5(2)^{\circ}$; O(4)-Ru(1)-P(2) = 99.66(15)°; O(3)-Ru(1)-P(2) = 103.00(17)°, summing up the in-plane angle to be exactly 358.96°. This shows high planarity of the one PPh₃ and O, N, O donor atoms of dipicolinic acid. The Ru(1)-P(1) and Ru(1)—P(2) bond distances are 2.2752(18) and 2.357(2) Å, respectively and are comparable with those reported for complexes of cis-{Ru(PPh₃)₂}^{2+ or 3+} [59–62]. The bond angle P(1)—Ru(1)— $P(2) = 97.71(7)^{\circ}$ shows that two PPh₃ groups are *cis* to each other, and larger than the ideal 90° for a regular octahedron, as a result of the repulsion between the two bulky triphenylphosphine ligands. The Ru(1)–Cl(1) bond distance is 2.224(5)Å which is shorter than other ruthenium complexes [63-65] but longer than [Ru(apahCH₃)(PPh₃)₂Cl] [66]. This may be due to steric effect of *cis* bulky triphenylphosphine ligands. The Ru—O and Ru—N bond distances agree well with that reported for similar ruthenium complexes [67].

A structural comparison between *cis-* and *trans-*, mer-[Ru(dipic)(PPh₃)₂Cl] illustrates many interesting differences. Crystal packing in **1** is stabilised by intra- and intermolecular C—H···X (X=O, Cl, π), and π - π hydrogen bond interactions (ESI† Tables S1 and S2). An interesting feature of the crystal packing in **1** is single helical motifs resulting from intra- and intermolecular C—H··· π and π - π interactions (Fig. 6). However, no single helical motifs are found in **3** when expands the crystal lattice through these interactions (ESI† Fig. S1).

The intermolecular interaction distances for C—H··· π and π – π interactions are 2.471–2.832 Å and 3.151–3.366 Å. These distances are within the range reported by other workers [68]. It is interesting to see that the two *trans* PPh₃ molecules are fully eclipsed in the complex **3** as compared to less eclipsed arrangement in complex **1** (Fig. 7). Complex **1** shows C—H···Cl intra- and intermolecular interactions, which involve Cl and an adjacent hydrogen atom attached to the phenyl(PPh₃) rings lead to single helical motifs,



(a)



Fig. 8. Solid-state packing diagrams of (a) cis-, mer-[RuCl(k³-dipic)(PPh₃)₂]·2H₂O (1) and (b) trans-, mer-[RuCl(k³-dipic)(PPh₃)₂] (3) (view along the b axis).

while in **3** this type of interactions results in the formation of parallel chains structure (ESI† Fig. S2). Weak C—H…O interactions connects parallel chains into two-dimensional network both the complexes **1** and **3**.

A comparison of space-filling representations for the packing of complexes **1** and **3** is shown in Fig. 8. This figure illustrates that the geometric isomerization leads to large differences in the molecular shape, which in turn results in completely different packing. In the **1** packing view shown in Fig. 8a, the lack of voids or channels is clearly evident, whereas in the **3** packing view in shown Fig. 8b, the presence of the channels is equally apparent.

3.4. Non-linear optical property

In order to gain some insight into the non-linear optical (NLO) property of the ruthenium complexes, the first static hyperpolarizability (β) were calculated with double numerical differentiation of energies, that is by the finite field perturbation method in vacuum as well as incorporating the solvent factors with increasing polarity. Hyperpolarizability is given by the coefficients in the Taylor's series expansion [69,70] of the energy in the external electric field. If the external electric field is weak and homogenous, the expansion becomes:

$$E = E^{\circ} - \mu_{\alpha}F_{\alpha} - 1/2\alpha_{\alpha\beta}F_{\alpha}F_{\beta} - 1/6\beta_{\alpha\beta\gamma}F_{\alpha}F_{\beta}F_{\gamma} + \dots$$

where E° is the energy of the unperturbed molecules, F_{α} is the field of origin, μ_{α} , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment,

polarizability and the first hyperpolarizability, respectively. The mean first hyperpolarizability β_{vec} is defined [69,70] as

$$\beta_{\rm vec} = (\beta_{\rm v}^2 + \beta_{\rm v}^2 + \beta_{\rm z}^2)^{1/2},$$

where β_x , β_y and β_z are defined as

$$\beta_{x} = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$
$$\beta_{y} = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}$$
$$\beta_{z} = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$$

For ruthenium complexes, the β value increases monotonically with polarity of the solvent (Table 4). Also, from the table it is apparent that the *trans* complex **3** have lower β as compared to the *cis* complex **1**. The hyperpolarizability data indicates that the β value increases on the changing the donor atom from phosphorus to arsenic. As indicated in the electronic absorption spectrum of **1**, the charge transfer transitions are of ligand to metal (LMCT) and intraligand type, which are primarily responsible for good NLO properties of these complexes.

3.5. Catalytic studies

The oxidation of benzyl alcohol, cyclohexanol and cinnamyl alcohol to their corresponding carbonyl derivatives were carried out with new ruthenium complexes **1** and **2** in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidant in refluxing

Table 4

Dielectric constant (ε) for solvent and calculated static second-order polarizability (β) (10⁻³⁰ esu) for the complexes in different medium.

Medium ε β_x	β_y β_z	β_{vec}
1		
Vaccum – -5.1	7 –2.48	0.52 5.76
Chloroform 4.9 –14.0	6 –12.93 –	-0.10 19.12
Methanol 32.63 –20.8	8 –23.43 –	-0.29 31.38
Acetonitrile 36.64 –20.8	9 –25.08	1.49 32.67
2		
Vaccum – 0.6	7 –0.69 1	0.18 12.33
Chloroform 4.9 0.7	6 –14.14 2	20.23 24.69
Methanol 32.63 0.8	2 –18.89 2	26.60 32.63
Acetonitrile 36.64 0.7	8 –18.86 2	27.44 33.30
3		
Vacuum – – –6.4	6 –4.50 –	-3.76 7.89
Chloroform 4.9 –13.5	4 –10.67 –	1.07 17.27
Methanol 32.63 –17.1	1 –26.23 –	-0.18 23.95
Acetonitrile 36.64 –17.2	1 -16.68 -1	5.85 27.80
4		
Vaccum – 0.2	3 12.74 –	1.48 12.82
Chloroform 4.9 0.6	8 –13.96 2	20.07 24.46
Methanol 32.63 0.7	8 –18.33 2	26.11 31.91
Acetonitrile 36.64 0.7	09 33.42	3.23 33.58

Table

Catalytic activity of new Ru^{III} complexes 1 and 2.

Complex	Substrate	Yield ^a	Turnover ^b	TOF $(h^{-1})^{c}$
1	Benzyl alcohol Cinnamyl alcohol	60 67	59 66	11.8 13.2
	Cyclohexanol	45	45	9
2	Benzyl alcohol	46	47	9.4
	Cinnamyl alcohol	60	61	12.2
	Cyclohexanol	39	40	8

^a Yield based on substrate.

^b Turn over number = moles of product per mole of catalyst.

^c Turnover frequency (TOF) = turnover number (TON)/h.

dichloromethane as solvent for 5 h. The data of catalytic oxidation are given in Table 5. Benzaldehyde, cinnamaldehyde, and cyclohexanone were formed from benzyl alcohol, cinnamyl alcohol, and cyclohexanol, respectively, after stirring for about 5 h, and then quantified as their 2,4-dinitrophenylhydrazone derivatives [71] and no side products such as decarbonylation of benzaldehyde to benzene and transfer hydrogenation of cinnamyl alcohol to the saturated 3-phenyl-1-propanol have been observed. In no case was there any detectable oxidation of alcohols in the presence of NMO alone and without the ruthenium complex. This indicates that new ruthenium complexes 1 and 2 gave high selectivities to carbonyl derivatives which is the primary product but the yield and the turnover vary with the different catalysts used. The relatively higher product yield obtained for oxidation of cinnamyl alcohol compared with benzyl alcohol and cyclohexanol is due to the fact that α -CH unit of cinnamyl alcohol are more acidic than benzyl alcohol and cyclohexanol [72,73]. The yields obtained from the reactions catalyzed by **1** are greater but not that great as compared with that of **2**. This observation is consistent with Nataraian et al. findings [74]. A high valency Ru^V-oxo complex is expected to be the active species in the catalytic processes as reported previously [72,73]. Comparison of this catalytic system with the previously reported systems shows lower activity [10,44,45] which is due to the stronger chelation of the ligand which may hinder the formation of catalytically active species but almost similar to trans-, mer-[Ru(dipic)(EPh₃)₂Cl]·2H₂O (E = P (**3**), As (**4**)) complexes which are known to be catalytically active [26]. This indicates that surely the *cis* complexes will simply transform to the *trans* in refluxing solvent.

4. Conclusion

In this work, we have presented the synthesis of the *cis* and *trans*-, mer-ruthenium^{III} complexes $[Ru(k^3-dipic)(EPh_3)_2CI]$ and compared their properties. Our study illustrates how the geometric isomerization leads to micro changes in ligand environment in solution but results in macro changes in the solid-state packing. The solid-state packing differences influence the solid-state electronic properties, which are dominated by intermolecular interaction. Also, it can be concluded that the optoelectronic performance of the ruthenium^{III} complexes can be enhanced replacing lighter donor atom with heavier ones. Additionally, the NLO properties can further be improved by increasing the polarity of the solvent. These complexes were found to be moderate catalysts for the oxidation of benzyl alcohol, cinnamyl alcohol and cyclohexanol to benzaldehyde, cinnamaldehyde and cyclohexanone respectively using *N*-methylmorpholine-*N*-oxide as a co-oxidant.

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Appendix A. Supplementary material

The crystallographic data in CIF format has been deposited with CCDC (CCDC deposition number is 736364). This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.02.044.

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