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Graphical Abstract

Synthesis, Structure, Redox Behavior, Catalytic Activity and DFT Study of a New Family of Ruthenium(III)-1-(arylazo)Naphtholate Complexes

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Synthesis, Structure, Redox Behavior, Catalytic Activity and DFT Study of a New Family of Ruthenium(III)-1-(arylazo)Naphtholate Complexes

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ABSTRACT

Treatment of $[RuCl_2(DMSO)_4]$ with 1-(arylazo)naphthol ligands in benzene under reflux afford the air-stable new ruthenium(III) complexes with general composition $[Ru(L-R)_3]$ (L= bidentate O, N donor; R = H, CH₃, OCH₃, Br, NO₂) in good yield. The 1-(arylazo)naphthol ligands behave as tris-bidentate O, N donors via naphtholic proton and azo nitrogen. The molecular and electronic structure of the complexes have been established by elemental analysis and spectral (FT-IR, UV-vis & EPR) methods. DFT calculations were also carried out on the complexes 1 and 3 along with X-ray crystallized geometry of complex 5. These complexes in dichloromethane solution show intense ligand-to-metal charge transfer (LMCT) transitions in the visible region. The absorption and g-tensor value of these complexes (1, 3 & 5) were also computed and compared along with the available experimental results. The redox behavior of the complexes has been investigated by cyclic voltammetry and the potentials are observed with respect to the electronic nature of substituents (R) in the 1-(arylazo)naphthol ligands. These complexes have shown great promise as catalysts for the conversion of aldehydes to primary amides in good yield.

Key words: Ruthenium(III); Arylazo ligands; Crystal structure; Redox properties; Catalytic activity; DFT study

1. INTRODUCTION

The coordination chemistry of the arylazo ligands containing oxygen and nitrogen donors with transition metal atom is of particular interest with reference to their role in biological [1, 2] and catalaytic processes [3-6]. The interest for these ligands is mainly based on the following reasons, i.e., the azo group can stabilize the metal atom in lower oxidation states due to its π acidic character and because of this property, the ligands are able to form metal-carbon bonds [7] and being a hard base, the oxygen donors stabilizes the higher oxidation states of the metal atom. The arylazo ligands prepared from β -naphthol provide more steric crowd compared to the phenyl group and these have not been used very often as ligands, only a few reports are available as co-ligands [4, 6, 8, 9]. The selected ligands (HL₁₋₅) are known bind to metal atom either as mono anionic O, N donors Fig. 1 (**I**, **II**) or O, N, C donors Fig. 1 (**III**) by cyclometalation.

Fig.1.

Further the complexation of ruthenium by these type ligands is of significant interest, largely because of their fascinating redox, photophysical, photochemical properties [10] and catalytic applications [11]. It has been found in the literature that the arylazo phenol/naphthol ligands are known to coordinate metal ion usually in a bidentate fashion with O, N donor or tridentate mode with C, N, O donor forming either five or six-membered chelate rings [6, 12]. Furthermore, transition metal complexes of ruthenium have proved to be useful catalysts in many reactions, such as oxidation, hydrogenation, carbonylation, hydroformylation and isomerization, by virtue of the accessibility of ruthenium in different oxidation states and ease of coordination with different ligands.

Amides are an important class of chemicals that have widely been used as chemical intermediates in organic synthesis. The conversion of carbonyl compounds such as aldehydes, ketones, and oximes is a good candidate for the synthesis of amides. The rearrangement of aldoximes into amides has been reported using transition metal catalysts containing Ni, Cu, Pd, Ir and Rh [13]. Crabtree *et al* reported the ruthenium precursor complex [RuCl₂(DMSO)₄] was used as catalyst for the conversion aldehydes to primary amides [14]. As reported in the earlier literature, ruthenium azo complexes have been extensively used as catalysts for transfer hydrogenation reactions [2]. To the best of our knowledge, only one report is available on ruthenium(II) complexes containing thiazolylazo ligands catalyzing aldehyde to amide conversions. As the source of ruthenium, we have selected the [RuCl₂(DMSO)₄] precursor complex, because of its demonstrated ability to accommodate more than one or two bidentate ligands through the displacement of dimethylsulfoxide and chlorides.

In view of rich interest to understand the coordination mode of arylazo ligands towards ruthenium, we have synthesized a number of ruthenium(III) complexes containing 1-(arylazo) naphtholate ligands. The molecular and electronic structure of the ruthenium(III) complexes is established with help of spectral methods, X-ray diffraction analysis and DFT calculations. Further, the catalytic efficiency of these ruthenium(III) complexes have been examined for the conversion of aldehydes to primary amides.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

Commercial RuCl₃.3H₂O was purchased from Himedia. All the used reagents were chemically pure or analytical reagent grade. Solvents were purified and dried according to

standard procedures. β -naphthol and primary amines were purchased from S.D. Fine-Chem Limited, India. The supporting electrolyte tetrabutyl ammonium perchlorate (*n*-Bu₄NClO₄) was dried in vacuum prior to use. [RuCl₂(DMSO)₄] was synthesized by a reported procedure [15]. The azo naphthol ligands were prepared by coupling diazotized aniline and *p*-substituted aniline with β -naphthol [16].

The analysis of carbon, hydrogen, and nitrogen were performed in Carlo Erba 1106model 240 Perkin Elmer analyzer at Sophisticated Test and Instrumentation Centre (STIC), Cochin University, Kochi, India. FT-IR spectra were recorded in KBr Pellets with a JASCO 400 plus spectrophotometer. JASCO V- 630 UV–visible Varian spectrophotometer was used to record the electronic spectra. ESR spectra were recorded in the X-band frequency on a ESR-JEOL/82 ESR spectrometer with a microwave power of 1 mW and a modulation amplitude of 160.00. Electrochemical measurements were made using an instrument model CHI608E electrochemical analyzer. A three electrode cell was employed with glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode were used in the cyclic voltammetry experiments. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

2.2. Synthesis of ruthenium(III)1-(arylazo)naphtholate complexes

The complexes $[Ru(L_{1-5})_3]$ were synthesized from the reactions of $[RuCl_2(DMSO)_4]$ with the ligands L_1-L_5 by following a general procedure under anhydrous conditions.

1-(arylazo)naphthols (L_1 - L_5) (0.256-0.328g; 1.0 mmol) was dissolved in ethanol (40 mL), and to it was added triethylamine (100 mg, 1.00 mmol). Then, [RuCl₂(DMSO)₄] (0.1g, 0.20

mmol) was added to it. The mixture was then refluxed for 6h to yield a brown solution. The solvent was evaporated, and the solid mass thus obtained was subjected to purification by thinlayer chromatography on a silica plate. With benzene as eluant, a brown band separated, which was extracted with same eluant. On evaporation of an eluant, brown coloured complexes are obtained as solid form of >80% yield.

2.3. Typical procedure for the conversion of aldehyde to amides

Under an inert atmosphere a mixture containing aldehyde (1 mmol), NH₂OH.HCl (1 mmol), NaHCO₃ (1 mmol) and ruthenium catalyst (0.01 mmol) and the mixture was heated to reflux in toluene for appropriate period of time as mentioned. On completion of the reaction, 2–3 mL methanol was added to the mixture followed by filtration through Celite to remove the catalyst and NaHCO₃. The crude product was then purified by column chromatography (MeOH/CH₂Cl₂) and the formation of pure amide was obtained.

2.4. X-ray crystallography

Single crystal of the ruthenium complex **5** (R= NO₂) suitable for X–ray diffraction analysis were obtained by slow diffusion of hexane in to chloroform solution of the complex at room temperature. The X-ray diffraction data was collected on a Rigaku Saturn 724+ CCD diffractometer with a Mo-K α radiation source (1 = 0.71075 Å) at 120 K. The data integration and indexing were performed using Rigaku Crystalclear software [17] and numerical method was employed to correct for absorption. All the calculations were carried out using the programs in WinGX module [18] and the structure solution was solved by direct methods using SIR-92 [19]. The final refinement of the structure was carried out using full least-square methods on *F2* using SHELX-2014 [20]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically as rigid atoms in their idealized locations.

2.5. Computational modeling and TD-DFT calculations

Quantum chemical calculations were performed using Gaussian 09 program [21] Unrestricted B3LYP [22, 23] functional with a Los Alamos effective core potential double zeta valence basis set (LANL2DZ) [24, 25] on Ru was used and 6-31G(d) basis set was used for rest of the atoms. G-tensor values of all the complexes were obtained from the ORCA package [26] with B3LYP functional. Time dependent density functional theory (TDDFT) implemented in the Gaussian 09 program was used for the calculation of excitation energies for first 100 states.

3. RESULTS AND DISCUSSION

A series of ruthenium (III) complexes of the general formula $[Ru(L_n)_3]$ (n =1-5) incorporating 1-(arylazo)naphthol ligands have been synthesized conveniently (scheme 1). These ruthenium complexes were obtained as brown colored solids with up to 80% yield. The elemental analysis (CHN) data of the complexes have been found to be in good agreement with this general formula. All the ruthenium (III) complexes are found to be air-stable in both solid and liquid states at room temperature is non-hygroscopic. It follows that all ligands act as bidentate ligands via loss of naphtholic proton and azo nitrogen forming six membered chelate rings. To observe the influence of the different substituents (R) in phenyl ring on the redox potentials of the complexes, five 1-(arylazo)naphthols (L₁₋₅) have been used. It is interesting to note here that during the course of this synthesis, ruthenium undergoes a one-electron oxidation and aerial oxygen seems to have served as the oxidizing agent.

Scheme. 1.

The 1-(arylazo)naphthols usually bind to a metal ion, via dissociation of the naphtholic proton, as bidentate O, N donors forming either five membered (I) or six-membered (II) chelate rings [6, 8]. These ligands are also known to coordinate ruthenium metal ion as dianionic tridentate C, N, O-donors (III) affording interesting cyclometallated complexes [6]. S. Halder *et al* reported that in 2-(arylazo)phenol ligands (IV) the carbon-carbon coupling was occurred between these two ligands linking the two *ortho* carbon atoms on the two phenyl rings in ruthenium complexes is very unusual and unprecedented [12].

We were expecting to have similar carbon-carbon coupling may occur between two *ortho* carbon atom of phenyl ring in the 1-(arylazo)naphtholate ligand in these ruthenium(III) complexes, and we end up with tris-bidentate mode of coordination with O, N donors in these ligands. It may be due to the bulky nature or steric congestion of naphthol group and prevents from the carbon- carbon coupling between *ortho*-carbon of phenyl ring in these ligands.

3.1. Characterization

Infrared spectra of all the complexes show multiple bands of varying intensities within the 4000-400 cm⁻¹. No attempt has been made to assign each individual band to a specific vibration. However, the infrared spectra of all the ligands exhibit bands around 1427-1438 cm⁻¹ and 1272-1280 cm⁻¹ corresponding to azo v (N=N–) and phenolic v(C–O) stretching frequencies respectively. On complexation v(N=N–) appears at lower frequency in the range 1386–1395 cm⁻¹ and this red shift supports the coordination of N(azo) to ruthenium ion [27]. This supports the assumption that the coordination of the nitrogen atom can reduce the electron density in the azo frequency due to the (d- π) Ru^(III)- π^* (L) back bonding effect [27b]. The band corresponding to phenolic v(C-O) stretching is shifted to higher frequency in the range 1279–1293 cm⁻¹ in all the complexes confirming that the other coordination site is the phenolic oxygen [4, 6]. This was further supported by disappearance of v(OH) band in the range 3430-3450 cm⁻¹ in all the complexes.

Electronic spectra of these complexes have been recorded in dichloromethane solution. Each complex shows intense absorptions in the ultraviolet and visible region. The absorptions in the ultraviolet region are believed to be due to transitions within the ligand orbitals. The selected electronic spectrum is shown in Figs. S1-S5 and spectral data are displaced in Table S6. The absorption observed in the region 450– 470 nm have been assigned to charge transfer LMCT transitions taking place from the highest occupied molecular orbital (HOMO) of the ligand to the singly lowest unoccupied molecular orbital (LOMO) of ruthenium. The bands in the regions at 370–385 nm are due to n– π * transition of non-bonding electrons present on the nitrogen of the arylazo group in the ruthenium(III) complexes. The band observed around 220–230 nm is assigned to π – π * transitions of the ligand. The pattern of the electronic spectra of all the complexes indicate the presence of an octahedral environment around ruthenium(III) ion similar to that of other ruthenium(III) octahedral complexes [28, 30].

The solid state EPR spectra of all the complexes were recorded in X-band frequencies at room temperature. All the complexes exhibit well-defined single isotropic feature near $g_{iso} = 2.0$ complexes 1-5; = 2.02-2.06). Such isotropic lines are usually the results of either intermolecular spin exchange, which can broaden the lines or occupancy of the unpaired electron in a degenerate orbital. However the EPR spectra of these complexes have been recorded in 1:1 dichloromethane / toluene solution at 77 K. Each complex shows a rhombic spectrum with three

distinct 'g' values ($g_x \neq g_y \neq g_z$). A selected spectrum is shown in Fig. 2 (Figs. S6-S11) and spectral data for all the complexes are given in Table 1. The rhombicity of the spectra reflects asymmetry of the electronic environment around ruthenium in these complexes [31]. These complexes are significantly distorted from the ideal octahedral geometry.

Fig. 2.

Table 1

3.2. X-ray structure

In order to determine the coordination mode and geometry of the complexes, the crystallization of the complex $[Ru(L_5)_3]$ (**5**) was performed by slow diffusion of hexane into chloroform. The summary of single crystal X-ray structures and refinement is shown in Table 2 and selected bond lengths and bond angles are given in Table 3. The Ball and Stick model of the complex(**5**) is shown in Fig. 3. The molecular structure shows that the 1-(arylazo)naphtholate ligands are coordinated to ruthenium ion *via* dissociation of the phenolic proton of the naphthyl ring in the arylazo fragment as a bidentate O, N donor ligand forming six membered chelating rings with bite angle of $87.73(3)^{\circ}$ O(7)-Ru(1)-N(1), 122.63(16)° Ru(1)-O(7)-C(8) and 124.54(19)° N(1)-Ru(1)-N(2) and bond lengths of 1.9934(2) Å Ru(1)-O(7), 2.0800(3) Å Ru(1)-N(1) and 1.3054(1) Å O(7)-C(8). The N–N distance is 1.2909(1) Å and is longer than the free azo bond length (1.25 Å) [32]. The increase in bond length is undoubtedly because of coordination of N(azo) that can lead to a decrease in the N–N bond order due to both σ - and π -acceptor character of the ligands, the latter character having a more pronounced effect and may be the reason for elongation [33]. This is an indication of metal–ligand π -interaction localized in the M-azo fragment. A six membered ring planar with the naphtholate ligand which is generated

by the two carbon atom from the naphtholate group, the two nitrogen atoms from the coordinated diazo group, the oxygen atom from the phenolic group and ruthenium. Comparing the crystal data with the one reported by S. Halder *et al* [12] most of the bond angles of the crystal [Ru(L₅)₃] were larger due to the increased congestion around the ruthenium center. This is further supports why carbon-carbon coupling was not takes place between the phenyl rings of the two ligand fragment in these complexes. As all the complexes display similar spectral properties, the other four complexes are assumed to have similar structure to that of complex **5**.

Fig. 3. Table 2

Table 3

3.3. Redox behavior

To get an idea regarding the oxidation and reduction process, the complexes have been studied by cyclic voltammetry in acetonitrile solution. All the complexes $(1 \times 10^{-3} \text{ M})$ are electroactive with respect to the metal centers and exhibited two redox processes in the potential range +1.5 V to -1.5 V (0.05 M tetrabutyl ammonium perchlorate as supporting electrolyte at 298 K). Each complex shows an oxidative response on the positive side of SCE and a reductive response on the negative side. The complexes display a reversible oxidative (Ru^{IV}/ Ru^{III}) and reversible reductive (Ru^{III}/ Ru^{II}) responses on the positive and negative side of SCE, respectively at the scan rate of 100 mVs⁻¹. All the complexes showed well-defined waves $E_{1/2}$ lies at +0.39 to +0.67V (Ru^{IV}/ Ru^{III}) and -0.65 to -0.22V (Ru^{III}/ Ru^{II}). The potentials are summarized in Table 4 and a representative voltammogram is shown in Fig. 4 which remains unchanged upon changing the scan rate, and the i_{pa} is almost equal to the i_{pc} as is expected for a reversible electron-transfer

process. Potential of the Ru^{II/} Ru^{IV} oxidation and Ru^{II/} Ru^{II} reduction in all the complexes has been found to be sensitive to the nature of the substituent (R) in the phenyl ring of the arylazo fragment. The potential increases with increasing electron-withdrawing character of the substituent (R). The half-wave potentials ($E_{1/2}$) moves to negative value with electron donating substituent(s) in the aryl ring and reverse movement is observed for electron withdrawing group. The plot of formal potentials $E_{1/2}$ versus σ [34] (σ =Hammett *para* substituent constant of R; OCH₃ = -0.27, CH₃ = -0.17, H = 0.00, Br = 0.23, and NO₂ = 0.78) is found to be linear for both the couples Fig. 5. This linear correlation of the redox potentials with the electronic nature (σ) of the substituents (R) with reasonable slopes (ρ) clearly shows that a single substituent on the 1-(arylazo)naphtholate ligand, which is several bonds away from the electro active metal center, can still influence the metal-centered redox potentials in a predictable manner. Hence, it is inferred from the electrochemical data that the present 1-(arylazo)naphtholate ligand system is suitable for stabilizing higher oxidation state of ruthenium and the electron transfer reaction takes place without gross changes in the stereo-chemistry of the complexes.

Fig. 4.

Fig. 5.

Table 4

3.4. Electronic Structure of 1, 3 & 5

To probe the influence of different substituents on the phenyl arylazo fragment, detailed electronic structural calculations were carried out on the ruthenium (III) 1-(arylazo)naphtholate complex (1) with the substitution of OMe and NO₂ on the *para* position of phenyl ring of arylazo fragment (3 & 5). Preliminary geometrical information of complex 5 is obtained from X-ray crystallized coordinates Fig. 3. Ruthenium (III) 1-(arylazo)naphtholate complexes is found to

possess the doublet spin ground state with the fundamental $(d_{xy})^2 (d_{xz}d_{yz})^3 (d_z^2)^0 (d_{x2-y2})^0$ electronic configuration [35]. This is also consistent with the spin density plot of **1**, **3** & **5** Fig. 6 which shows that the presence of one unpaired electron is strongly delocalized on the ruthenium center especially on the d_{yz} orbital and slightly on the coordinated nitrogen and oxygen atoms. From the same values of Mulliken spin density of **1**, **3** & **5**, these complexes were found to have similar kind of electronic properties irrespective of the presence of different substituents on the *para* position of the phenyl group of arylazo fragments.

Fig. 6.

Notable structural parameters obtained from X-ray crystallographic coordinates of **5** along with DFT optimized geometries of **1**, **3** & **5** were collected in Table 5. It is clearly envisaged from the table, there is a progressive change in the specific structural parameters upon substituting the electron donating NO₂ group in **5** and the electron withdrawing OMe group in **3**. From the Table 5, the bond length of (Ru1-N8, Ru1-O2), and the bond angles (O2-Ru1-O4, N8-Ru1-O3) of complex **5** is largely deviated from the other two complexes **1** and **3**. This shows that influence of strong electron withdrawing NO₂ group on the phenyl group of arylazo fragment. Further, structural parameters of **5** obtained from the DFT calculations are in close agreement with the X-ray crystal geometrical parameters are summarized in Table S11. Upon comparison of both DFT structural parameters of **1**, **3** and **5** along with available X-ray structural parameters of **5**, the Ru-N(-O) bond lengths and the bond angles are deviated from the ideal octahedral geometrical parameters. This is clearly indicates that all the three complexes (**1**, **3** & **5**) possess a distorted octahedral coordination sphere.

Further, we would like to emphasis the bonding nature of three complexes with a view to understand the stabilization of their metal orbitals with respect to different substituents on the on the para position of phenyl ring of arylazo fragment. The ground state electronic configuration of these complexes is found to be $(d_{xy})^2 (dxz)^2 (dyz)^1 (d_z^2)^0 (d_x^2 d_{yz}^2)^0$ Key metal-ligand orbitals of 3 and 5 along with left and right side of the complex 1 are presented in Fig. 7. The relative eigenvalues are presented in eV with respect to lowest energy d_{xy} orbital. Complex 1 is found to have energy gap between singly occupied dyz molecular orbital (SOMO) and lowest unoccupied metal orbital $(d_z^2, LUMO)$ is about 4.72 eV whereas complexes 3 and 5 possess 4.69 eV and 4.86 eV respectively. The stabilization of all the metal orbitals with respect to complex is also provided in the Fig. 7. The stabilization of all the metal orbitals in 5 with respect to 1 is in the range of 0.17 to 0.31 eV whereas complex 3 possess 0.07 to 0.22 eV. From this one can understand the influence of electron donating nature of substituent OMe which reduces the energy gap between SOMO and LUMO thereby destabilizing all the metal centered orbitals. Whereas in the case of 5, strong electron withdrawing nature of nitro group stabilizes all the metal center orbitals eventually increases the energy gap between SOMO and LUMO orbitals. This will dramatically influence in the reactivity of the particular complexes. Hence complex 3 is found to have better catalytic ability whereas complex 5 is found to have a moderate reactivity upon conversion of aldehydes to amides.

Fig. 7.

3.5. Spectroscopic Properties of 1, 3 and 5

To facilitate the interpretation of the experimental spectroscopic data and gain further insight into the electronic structure of **1**, **3 & 5**, absorption spectra and the spin Hamiltonian parameters for these complexes were computed.

3.5.1. TD-DFT and g-tensor analysis

In order to rationalize the electronic structure of **5** and also to facilitate the interpretation of the experimental spectroscopic data, the TD-DFT absorption spectra for **1**, **3** and **5** were computed. TD-DFT computed absorption bands along with oscillator strength (f) and nature of electronic transitions of all the three complexes Table 5 were found to exhibits a set of absorption bands ranging from the 420 nm to 521 nm. These most intense computed absorption bands are largely derives from the ligands to metal charge transfer transition (LMCT). This is in good agreement with the experimental absorption spectrum of **5** where an intense LMCT band appears in the region of 450-470 nm. Analysis of Natural Transition Orbitals (NTO) of most intense transition bands of three complexes in Fig. 8 clearly shows that these transitions originated from the LMCT.

Fig. 8.

Table 5

The calculated g-tensor values of three complexes are collected in Table 5. Complexes 1, 3 and 5 found to possess a three distinct 'g' values. This shows that all the three complexes said to have a rhombic spectrum. Distorted octahedral geometry of these complexes clearly envisaged

from the rhombicity of the g-tensor values. The calculated g-tensor values are in good agreement with experimental values.

3.6. Catalytic conversion of aldehydes to amides

The scope of our catalytic system is applicable to aromatic, conjugated and heterocyclic aromatic aldehydes. These aldehydes were converted to their corresponding amides in good yield at one pot process and the results are summarized in Table 6. On screening different catalyst/substrate ratios (1:100, 1:500, 1:1000), 1:100 was found to be the optimum ratio of catalyst/substrate, with the maximum yield of 86%. Benzaldehyde was used as substrate and complex(1) was used as catalyst for the optimization in the presence of NH₂OH.HCl /NaHCO₃. The effect of solvents (toluene, benzene, dichloromethane and methanol etc.,) was studied for the optimization, and toluene is found to be the best solvent for the conversion of benzaldehyde to benzamide.

Comparison of the catalysts reveal that catalyst $[Ru(L_3)_3](3)$ has a better performance for both benzaldehyde and furan-2-aldehyde, implicating a good yield of 84% and 87%. The conversion obtained by using catalyst **4** and **5** was lower to the other catalysts indicating that the substituent (R) in the phenyl ring of arylazo fragment may play a significant role in these conversions. The catalytic activity of the catalysts **1-3** is similar (81-87%) for the conversion of furan-2-aldehyde to furan-2-amide. The conjugated aldehyde such as, cinnamaldehyde which was converted to the corresponding amide in good yield (81-83%).

Table 6

All the substrate aldehydes were smoothly converted to the corresponding amides in good yields. Our observation in this catalytic aldehyde to amide conversion is comparable with that of a recent observation using [RuCl₂(DMSO)₄] complex as catalyst [14]. It is interesting to note that this ruthenium(III) 1-(arylazo)naphtholate complexes efficient by catalyze the aldehyde to amide up to 87% yield. The obtained results revealed that the naphthol group plays a significant role in the aldehyde to amide conversion depends on the steric and electronic environment of the ruthenium. So, the prospective of these complexes as catalysts in the field of aldehydes to amide conversion can be further improved by fine-tuning of the ligand environment on ruthenium. As for as we know only few catalytic system on ruthenium [3, 36] have been reported to support the aldehyde to amide conversion, catalyst like ruthenium(III) 1-(arylazo)naphtholate complexes is new and novel for its tris-bidentate O, N-donor environment.

4. Conclusion

The present work describes the simple and convenient route to synthesize a new family of ruthenium(III) complexes incorporating O, N donors of 1-(arylazo)naphtholate ligands. The X-ray crystal structure of the complex (**5**) reveals on octahedral environment around ruthenium. The influence of substituents (**R**) present in the phenyl ring of 1-(arylazo)naphtholate ligand on metal center is studied by cyclic voltammetry. The electronic structure and bonding of **1**, **3** and crystallized geometry of complex **5** were investigated by DFT calculations. These ruthenium complexes have been tested as catalyst for the conversion of aldehyde to amides. The obtained results imply that the present catalyst system exploring a promising application of new family of ruthenium(III)1-(arylazo)naphtholate complexes. Based on the computed energy levels of

occupied and unoccupied metal orbitals of these three complexes, the effects of different substituents on the catalytic activity of these complexes were also illustrated.

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Appendix A. Supplementary material

UV-vis spectra of complexes (Figs. S1-S5), representative EPR spectra of the complexes (Figs. S7-S11) and optimized structure of complex **5** (Table. S6). CCDC reference number 1438173 for complex **5**.

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ACCEPTED MANUSCRIPT

Complexes	g _x	gy	gz	$-\epsilon$
1	2.20	2.08	1.91	
2	2.19	2.06	1.92	
3	2.23	2.09	1.96	
4	2.21	2.04	1.92	
5	2.19	2.09	1.93	

Table 1 EPR data of ruthenium(III) 1-(arylazo)naphtholate complexes.

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Empirical formula Formula weight	C ₄₈ H ₃₀ N ₉ O ₉ Ru 977.88
Temperature (K)	120
Wavelength (Å)	0.71075
Crystal system	Triclinic
Space group	P-1
a (Å)	11.8392(13)
b (Å)	14.199(2)
c (Å)	14.286(2)
α (°)	85.758(12)
β (°)	68.297(9)
γ (°)	66.961(8)
Volume (Å ³)	2046.3(5)
Z	2
Density Cacld. (g cm ⁻³)	1.587
μ (mm ⁻¹)	0.457
F(000)	994.0
Crystal size (mm ³)	0.12 X 0.16 X 0.28
θ range (°)	2.882 to 24.999
Reflections collected	7117
R indices (all data)	R1= 0.0315
	wR2 = 0.0355
Data/restraints/parameters	6568/0/604
Goodness-of-fit on F2	1.0201
Largest difference in peak and hole	0.306 and -0.536 (eA° - ³)

Table 2 Crystal data and structure refinement for complex 5.

Bond Length (A°) Bond angle (°)	Bond angle (°)			
Ru1-O7 1.9934 Ru1-O8 2.0136 Ru1-O9 1.9907 Ru1-N1 2.0800 Ru1-N4 2.0164 Ru1-N6 2.0403 O1-N7 1.2309 O2-N7 1.2243 O3-N8 1.2239 O4-N8 1.2249 O5-N9 1.2319 O6-N9 1.2257 O7-C8 1.3054 O8-C48 1.2919 O9-C32 1.3076 N1-N2 1.2909	O7- Ru1- O8 4(2) O7- Ru1- O9 5(3) O7- Ru1- N1 1(2) O7- Ru1- N1 1(2) O7- Ru1- N4 0(3) O7- Ru1- N6 4(3) O8- Ru1- O9 3(3) O8- Ru1- N1 9(1) O8- Ru1- N4 9(2) O9- Ru1- N1 9(2) O9- Ru1- N4 9(1) O9- Ru1- N4 9(2) O9- Ru1- N4 9(1) O9- Ru1- N6 9(2) O9- Ru1- N6 9(1) O9- Ru1- N6 9(2) O9- Ru1- N6 9(1) O9- Ru1- N6 9(1) O9- Ru1- N6 9(1) N1- Ru1- N6 9(2) O9- Ru1- N6 9(1) N1- Ru1- N6 9(2) N4- Ru1- N6 9(1) Ru1- O7- C8 9(1) Ru1- O8C-48 Ru1- O9C-32 Ru1- N1- N2 Ru1- N1- N2 Ru1- N1- C1	91.81 176.12 87.73 93.62 91.99 86.13 81.66 174.57 88.38 95.22 88.44 84.66 98.65 170.03 91.32 122.63 122.88 120.34 124.54 123.78			
	Ru1 N1 N2 Ru1- N1- C1 N2- N1- C1	123.78 110.52			

Table 3 Selected bond length (A°) and angle ($^{\circ}$) for complex **5**.

Complexes	Ru ^{IV} /Ru ^{III}			Ru ^{III} /Ru ^{II}				
	$E_{\rm pa}\left({ m V} ight)$	$E_{\rm pc}$ (V)	$E_{1/2}(V)$	$\Delta E_{\rm p}~({\rm mV})$	$E_{\rm pa}\left({ m V} ight)$	$E_{\rm pc}$ (V)	$E_{1/2}$ (V)	$\Delta E_{\rm p}({\rm mV})$
1	+0.532	+0.453	+0.492	79	-0.633	-0.556	-0.594	77
2	+0.456	+0.374	+0.415	82	-0.678	-0.585	-0.632	93
3	+0.431	+0.359	+0.395	72	-0.683	-0.625	-0.654	58
4	+0.585	+0.500	+0.542	85	-0.495	-0.429	-0.462	66
5	+0.703	+0.637	+0.670	66	-0.250	-0.192	-0.221	58
						-		

Table 4 Electrochemical data of the ruthenium(III)1-(arylazo)naphtholate complexes.

Supporting electrolyte: NBu₄ClO₄ (0.005 M); complex: 0.001 M; solvent: CH₃CN; Δ Ep = Epa-Epc where Epa and Epc are anodic and cathodic potentials respectively; $E_{1/2} = 0.5$ (Epa + Epc); scan rate: 100 mV s⁻¹.

Table 5 TD-DFT (B3LYP/SCRF-PCM/DCM) Calculated Electronic Transitions for 5.

λ/nm	f		Transitions				
Complex 1							
515.7	0.025	HOMO-2 ($\alpha \rightarrow LUMO+2$	(α) (69%)			
		HOMO-2 ($\beta \rightarrow LUMO+3$	(β) (54%)			
500.9	0.058	HOMO-3 (α) \rightarrow LUMO (α	t) (45%)			
		HOMO (α) \rightarrow LUMO+4 (α) (22%)					
487.8	0.095	HOMO-1 ($\alpha \rightarrow LUMO (\alpha)$	a) (23%)			
		HOMO-3 (0	HOMO-3 (α) \rightarrow LUMO+2 (α) (19%)				
		HOMO-1 (β) \rightarrow LUMO+2	(β) (17%)			
485.3	0.050	HOMO-1 ($(\alpha) \rightarrow LUMO (\alpha)$	a) (23%)			
		HOMO-2 (β) \rightarrow LUMO+2	(β) (26%)			
		HOMO-5 (β) \rightarrow LUMO+1	l (β) (17%)			
	-	Comple	ex 3				
506.7	0.086	HOMO-11	$(\beta) \rightarrow LUMO$ (β) (42%)			
		HOMO-3 ($(\beta) \rightarrow LUMO+1$	(β) (42%)			
486.9	0.097	HOMO-2 (0	α) \rightarrow LUMO (α	a) (34%)			
		HOMO-3 ($(\beta) \rightarrow LUMO+1$	(β) (37%)			
477.9	0.056	HOMO (α)	HOMO (α) \rightarrow LUMO+1 (α) (20%)				
		HOMO-11 (β) \rightarrow LUMO (β) (35%)					
445.8	0.184	HOMO-2 (0	$\alpha \rightarrow LUMO+2$	<i>L</i> (α) (79%)			
420.9	0.141	HOMO-2 (β) \rightarrow LUMO+3	(β) (95%)			
		Comple	ex 5				
520.6	0.198	HOMO-1 (α) \rightarrow LUMO+1	(α) (46%)			
		HOMO-1 ($\beta \rightarrow LUMO+2$	(β) (41%)			
462.1	0.094	HOMO-2 ($(a) \rightarrow LUMO+2$	<i>α</i> (α) (69%)			
<u> </u>		HOMO-2 (β) \rightarrow LUMO+3 (β) (54%)					
457.4	0.082	HOMO-3 (α) \rightarrow LUMO (α) (44%)					
		HOMO (α) \rightarrow LUMO+4 (α) (22%)					
447.5	0.075	HOMO-4 (β) \rightarrow LUMO+1	(β)			
		(58%)HOM	$IO-10 (\beta) \rightarrow LU$	J MO (β)			
)		(18%)	(18%)				
443.9	0.096	HOMO-3 (0	α) \rightarrow LUMO+1	(α) (17%)			
7		HOMO-4 ($(a) \rightarrow LUMO+2$	<i>α</i> (α) (37%)			
g-ten	sor	g _{xx}	g _{yy}	g _{zz}			
1							
3		2.17	2.07	1.99			
5		2.16	2.08	1.99			

С	Complexes	Aldehydes ^a	Amides	Yields ^b (%)	
		~			
	1	Benzaldehyde	Benzamide	11	
		Furan2-carbaldehyde	Furan2-amide	86	
		Cinnamaldehyde	Cinnamide	81	
	2	Benzaldehyde	Benzamide	66	
		Furan2-carbaldehyde	Furan2-amide	81	
		Cinnamaldehyde	Cinnamide	-80	
		-			
	3	Benzaldehyde	Benzamide	84	
		Furan2-carbaldehyde	Furan2-amide	87	
		Cinnamaldehyde	Cinnamide	83	
		, i i i i i i i i i i i i i i i i i i i			
	4	Benzaldehyde	Benzamide	76	
		Furan2-carbaldehyde	Furan2-amide	65	
		Cinnamaldehyde	Cinnamide	77	
		Ş			
	5	Benzaldehvde	Benzamide	69	
		Furan2-carbaldehvde	Furan2-amide	78	
		Cinnamaldehyde	Cinnamide	75	
		c conjuc			

Table 6 One pot conversion of aldehyde to amide using $[Ru(L_n)_3]$ (1-5).

^a Aldehyde 1 mmol, NH₂OH.HCl (1 mmol) and catalyst (1 mol%) were refluxed

for18 h in toluene.

^b Isolated yield after column chromatography.

Table and Figure Captions

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Table 6 One pot conversion of aldehyde to amide using $[Ru(L_n)_3]$ (1-5).

Fig. 1. Coordination modes of arylazo ligands.

Scheme 1. Preparation of new Ru(III) complexes.

Fig. 2. EPR spectrum of the ruthenium complex (5) in CH₂Cl₂/ Toluene.

Fig. 3. The ball and stick diagram of the complex $[Ru(L_5)_3]$ (5).

Fig. 4. Cyclic voltammogram of the complexes (1-5).

Fig. 5. Least-squares plot of (i) $E_{1/2}$ values of oxidation (Ru^{IV}/Ru^{III}) and (ii) $E_{1/2}$ values of

reduction (Ru^{III}/Ru^{II}) potentials of complexes.

Fig. 6. X-ray crystallized (Compound **5**) and DFT optimized geometry of **1**, **3** & **5** along with the computed spin densities.

Fig. 7. Computed high-lying occupied and low-lying unoccupied Metal orbitals of **1**, **3** and **5** and their relative energies in eV with respect to lowest energy MO.

Fig. 8. Natural Transition Orbitals (NTOs) of intense absorption bands for complexes **1**, **3** and **5** shown on occupied (holes) and unoccupied (electrons) NTO pairs.





Fig. 2. EPR spectrum of the ruthenium complex (5) in CH_2Cl_2 / Toluene.



Fig. 3. The ball and stick diagram of the complex $[Ru(L_5)_3]$ (5).



Fig. 5. Least-squares plot of (i) $E_{1/2}$ values of oxidation (Ru^{IV}/Ru^{III}) and (ii) $E_{1/2}$ values of reduction (Ru^{III}/Ru^{II}) potentials of complexes.



Fig. 6. X-ray crystallized (Compound **5**) and DFT optimized geometry of **1**, **3** & **5** along with the computed spin densities.



Fig. 7. Computed high-lying occupied and low-lying unoccupied Metal orbitals of **1**, **3** and **5** and their relative energies in eV with respect to lowest energy MO.



Fig. 8. Natural Transition Orbitals (NTOs) of intense absorption bands for complexes **1**, **3** and **5** shown on occupied (holes) and unoccupied (electrons) NTO pairs.

Research Highlights

Synthesis, Structure, Redox Behavior, Catalytic Activity and DFT Study of a New Family of Ruthenium(III)-1-(arylazo)Naphtholate Complexes

Madhan Ramesh^a, Mani Kalidass^a, Madhavan Jaccob^{*b}, Dhananjayan Kaleeswaran^c, Galmari Venkatachalam^{*a}

- New Family of ruthenium(III)1-(arylazo)naphtholate complexes containing tris-bidentate O,N donors of ligands have been synthesized and characterized.
- DFT calculations are also carried out.

- The effects of substituents on the phenyl ring present in the complexes are studied.
- Catalytic activities of the complexes are evaluated.