X-ray structure, electronic properties and density functional calculations: *trans*-Dihalo (1-(4-phenylimino)-1-(phenylhydrazono)-propan-2-one) (4,4'-di-tert-butyl-2,2-bipyridine) ruthenium(II) complexes

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The reaction of RuX₃ (X = F, Cl, Br) with arylazoimine (PhN=N(COCH₃)=NPh, Az) and (4,4'-di-tert-butyl-2,2-bipyridine, dtb) in refluxing ethanol affords a *trans*-Ru[Az](dtb)X₂. These complexes have been characterized through spectroscopic (IR, UV/Vis, and NMR) and electrochemical (CV) techniques. The complex *trans*-Ru[Az](dtb)Cl₂ has been X-ray crystallographically characterized. The crystals belong to the rhombohedral space group R₃. The two chlorine atoms are *trans* to each other. The 4,4'-di-tert-butyl-2,2-bipyridine ligand is bent and the Az ligand rings are rotated, due to inter-ligands steric interactions between H atoms of opposite pyridyl units across the Ru center. These complexes display a cyclic voltammetric one-electron metal oxidation peak in acetonitrile near 1.2 V versus NHE. The electronic absorption spectra of these complexes show a strong band in the visible region which is assigned to a (Ru(II)-to-azomethine) MLCT transition based on TD-DFT calculations.

1. Introduction

Transition-metal chelates incorporating azo ligands have drawn much attention in recent years. Among these, complexes of aryldiazo oximes [1], aryldiazophenols [2] and aryldiazoimines [3] are some notable examples. Ruthenium(II) complexes build from aryldiazoimine Y ligands are being currently examined in our laboratory. These ligands are strong π-acceptor and capable to stabilize metals in their lower oxidation states [4]. The extent of this stabilization depends on the substituent on the phenyl rings (Ph) and the R group to which the arylazo and imine groups’ linkage are attached [5].

Recently, a series of mixed-ligand Ru(II) complexes of a *trans*-Ru[Az]LCl₂ (L = substituted α-dimine and Az=PhN=N(COCH₃)=NPh) have been reported to study the effect of L on the ruthenium center [6]. Since, the dihalo complexes are precursors for the synthesis of many other complexes by direct reaction or through the intermediacy of the diaquo derivative [7–9], we herein report the a series of a dihalo complexes, *trans*-Ru[Az](dtb)X₂ (X = F, Cl, Br) to study the effect of halo ligands on the electronic properties of ruthenium center. The spectral studies (IR, UV/Vis, and NMR), redox properties, single crystal X-ray structure and DFT calculations for a representative complex will be described in this work.

2. Experimental

2.1. Starting materials

The reagents: lithium chloride, lithium bromide, lithium fluoride, ruthenium trichloride hydrate and 4,4’-di-tert-butyl-2,2’-bipyridine (dtb) were purchased from Aldrich and were used as received. Tetrabutylammonium hexafluorophosphate (TBAH) was recrystallized twice from 1:1 ethanol/water solution and then vacuum dried at 110 °C. 1-(4-Phenylimino)-1-(phenylhydrazono)-propan-2-one, Az ligand was prepared following literature methods [10].

2.1.1. *trans*-Ru[Az](dtb)Cl₂ (1)

Complex (1) was prepared according to the literature method [6]. A suitable single crystal for diffraction measurements was obtained from slowly evaporating solution of dichloromethane.
2.1.2. trans-[Ru(Az)(dtb)Br2] (2)

A 65-mg (0.25 mmol) quantity of RuCl3·3H2O was dissolved in 10 mL of absolute ethanol and 500 mg of LiBr in a 50-mL threenecked flask fitted with a dinitroin inlet tube. The solution was flushed with dinitroin and refluxed for 15 min. To this solution a 125 mg (0.50 mmol) of (Az) was added. After refluxing for 1 h, 134 mg (0.50 mmol) of dtb was added and the reaction was heated for additional 3 h. The solvent was then removed by rotary evaporator. The crude product was dissolved in 20 mL dichloromethane and purified by column chromatography (50 × 3 cm) containing 150 g of grade (III) alumina. The first pale yellow band of azomethine ligand (L) was eluted with hexane. Acetone was used to elute the second dark-red band of the product. Yield (0.35 g, 45%).

150 g of grade (III) alumina. The first pale yellow band of azomethine ligand (L) was eluted with hexane. Acetone was used to elute the second dark-red band of the product. Yield (0.30 g, 40%).

2.1.3. trans-[Ru(Az)(dtb)F2] (3)

The difluoro complex was prepared by following the procedure used in the case of the bromo complex except that 500 mg of LiF instead of LiBr. Yield (0.30 g, 40%). Anal. Calc. for C33H37F2N5ORu: C, 54.91; H, 5.29; N, 9.44%. Found: C, 54.79; H, 5.39; N, 9.44%. UV–Vis in acetonitrile: λmax (εmax M⁻¹ cm⁻¹): 365 (4.78 × 10³), 506 (3.78 × 10³). IR: ν(C=O) 1705 cm⁻¹. 1H NMR (DMSO-d6): δ 1.36 (18H, dtb), 2.78 (3H, s, COCH3), 6.94 (1H, d, dtb), 7.15 (1H, d, dtb), 7.43 (2H, d, H4), 7.50 (1H, t, dtb), 7.55 (2H, t, H5), 7.62 (1H, t, H3), 7.65 (2H, t, H2), 7.83 (1H, t, H6), 7.98 (2H, d, H1), 8.48 (1H, s, dtb), 8.54 (1H, s, dtb).

2.2. Physical measurements

Micro analyses (C, H, N) were performed using elemental analyser EURO VECTOR model EA3000. IR-spectra were obtained by FT-IR Jasco model 420. Electronic spectra were recorded on a Shimadzu 240-UV–Vis spectrophotometer. The 1H spectra were measured on a Bruker Avance 400 MHz spectrometer at 400 MHz using TMS as an internal standard. Electrochemical measurements were performed in acetonitrile (Aldrich, HPLC grade) using Volta Lab model PGP201 with a platinum disk working electrode (1.6 mm diameter), a platinum wire counter electrode and a silver wire pseudo-reference electrode. Ferrocene (0.665 V versus NHE) is used as an internal reference [11]. To control the temperature, a Haake D8-G refrigerated bath and circulator was used to maintain the cell temperature at 25.0 ± 0.1 °C. Tetrabutylammonium was used as supporting electrolyte.

2.3. Crystal structure determination

Data were collected at 173(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, μ = 0.71073 Å). Cell parameters were retrieved using SMART [12] software and refined using SADABS [13] on all observed reflections [13]. Data reduction and correction for Lp and decay were performed using the SADABS software. Absorption corrections were applied using SADABS [13]. The structure was solved by direct methods and refined by least-squares method on F² using the SHELXL package program [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically, with N–H = 0.86 Å and C–H = 0.93 Å for dtb, and constrained to ride on their parent atoms, with Uiso(H) = 1.2Ueq (C, N).

No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1.

2.4. Computational methods

All DFT calculations were carried out using GAUSSIAN03 program package [15]. The X-ray crystallographic structure for trans-[Ru(Az)(dtb)Cl2] complex was used as a starting coordinates to

<table>
<thead>
<tr>
<th>Crystal data and structure refinement for 1.</th>
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</thead>
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<tr>
<td>CCDC No.</td>
</tr>
<tr>
<td>Formula</td>
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<tr>
<td>μ (mm⁻¹)</td>
</tr>
<tr>
<td>f(0 0 0)</td>
</tr>
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</table>

Crystal size (mm), color |
- Brown

Range for data collection |
- 35 < h < 35, 35 < k < 35, -27 < l < 27

Index ranges |
- 35 < h < 35, 35 < k < 35, -27 < l < 27

Largest difference in peak and hole (e Å⁻³) |
- 1.089 and -0.773

R₁ = Σ||Fobs| - |Fcalc||/Σ|Fobs|; wR₂ = Σ[w(Fobs² - Fcalc²)]/Σ[w(Fcalc²)]¹/².

Table 2

<table>
<thead>
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<th>Bond distances (Å) (experimental and optimized)</th>
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<tr>
<td>Ru1–N1</td>
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<tr>
<td>Ru1–N4</td>
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<td>Ru1–N5</td>
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<tr>
<td>C7–N1</td>
</tr>
<tr>
<td>C7–N3</td>
</tr>
<tr>
<td>C7–N5</td>
</tr>
</tbody>
</table>

Bond angles (°) (experimental and optimized) |
- N1–Ru1–N3: 75.71 (19), (75.74) |
- N1–Ru1–N4: 179.08 (18), (177.31) |
- N1–Ru1–N5: 179.19 (17), (172.95) |
- N3–Ru1–N4: 103.68 (17), (105.48) |
- N3–Ru1–N5: 75.66 (17), (75.52) |
- N4–Ru1–C12: 92.01 (13), (92.68) |
- N3–Ru1–C13: 93.35 (13), (88.44) |
- N1–Ru1–C12: 88.71 (13), (89.75) |
- N3–Ru1–C13: 85.36 (13), (82.03) |
- N5–Ru1–C12: 87.21 (11), (84.58) |
- C7–N3–C13: 112.9 (7), (112.8) |
- C7–N1–C13: 87.1 (11), (89.97) |

Symmetry codes: (i) -y+1, x-y, z; (ii) -x+y+1, -x+1, z.
generate \(\text{trans}\)-\[Ru(Az)(dtb)X2\] (\(X = \text{Br}, \text{F}\)) geometries. The structures were then optimized using the Becke three parameters hybrid exchange [16] and the Lee-Yang-Parr correlation hybrid functional [17] (B3LYP). The optimized geometric parameters are gathered in Table 2. Generally, the calculated bond lengths and angles are in agreement with the values based upon the X-ray crystal structure data. LanL2DZ effective core potential basis set was employed for ruthenium and 6-31G* for the rest of the atoms in acetonitrile solution. Time-dependent density functional theory (TD-DFT) [18,19] and NBO analysis were performed using B3LYP functional and a mixed basis set, LanL2DZ/6-31+g(d,p), in acetonitrile as a solvent via polarized continuum model (PCM). The lowest 20 singlet-to-singlet spin-allowed excitation states were taken into account for the calculations of the electronic absorption spectrum for the complex 1. Orbital contribution was analyzed using Gauss-Sum software [20].

3. Results and discussion

3.1. Synthesis

The synthesis of \(\text{trans}\)-\[Ru(Az)(dtb)X2\] was achieved by the stepwise equimolar addition of azoimine ligands, dtb to RuX3. In this synthesis ethanol presumably acts both as a solvent and as a reducing agent.

These neutral complexes are air stable, diamagnetic and their structures were confirmed by \(^1\)H NMR and X-ray diffraction for complex 1. The aromatic region in the \(^1\)H NMR spectra of complexes 1–3 consists of several coupled multiplets due to aromatic protons of the phenyl rings of the t-bpy and azoimine ligands. The aliphatic region of the \(^1\)H NMR consists of two singlet peak in the range (2.60–2.75 ppm) and (1.30–1.50 ppm) which was assigned to acetyl and t-butyl protons respectively. The stability of such solutions usually increases as \(\text{Br} < \text{C1} < \text{F}\). In their IR-spectra, the IR-spectra of complexes 1–3 show bands in the range of 1700–1712 cm\(^{-1}\) assigned to aromatic carbonyl groups, amide I C=O stretching bands probably due to the small differences in \(\pi\)-back donation from Ru–d orbital to the empty \(\pi^*\) orbital of the azoimine ligand. The IR-spectra of complexes 1–3 show bands at 1470–1485 and 1600–1615 cm\(^{-1}\) assigned to the N–H stretching bands of azoimine ligands, N–H stretching bands probably due to the small differences in \(\pi\)-back donation from Ru–d orbital to the empty \(\pi^*\) orbital of the azoimine ligand.

3.2. Molecular geometry

Single crystals of 1 were grown in dichloromethane solution. Selected bond lengths and angles are summarized in Table 2. ORTEP diagram is given in Fig. 1. The complex 1 exhibits a distorted octahedral arrangement about Ru atom; the dtb bite angle for N4–Ru1–N5 is 75.66 (16), while for the Az ligand the N1–Ru1–N3 is 75.71 (19). The Ru1–N1(azo) bond distance (1.958 (4) Å) and the Ru1–N3(methine) (1.988 (4) Å) is shorter than the average Ru–N(azo) (2.128 (4) Å). The shortening may be due to the greater \(\pi\)-back donation from Ru–d orbital to the empty \(\pi^*\) orbital of the azoimine ligand [21]. The extent of \(\pi\)-back donation for \([Ru(PhN(N)C=NPh)Cl]_2\) depends upon the substituent R group attached to azoimine ligand and the type of \(\pi\)-azo-imine ligands. For complex 1 and when R is acetyl group, the Ru–N(azo) bond distance is slightly longer than the Ru–N(azo) bond distance (1.946 (3) Å) [5] and (1.951 (3) Å) [22] when R is electron withdrawing acetyl group. However, it is interesting to note that the bond lengths Ru–N(azo) and Ru–N(methine) for complex 1 are slightly shorter than corresponding lengths in similar reported ruthenium azo–imine complex \(\text{trans}\)-\[Ru(Az)(bpy)Cl2\] (Ru–N(azo) = 1.956 (3) Å, Ru–N(methine) = 2.002 (3) Å [23]). The greater \(\pi\)-back donation for \(\text{trans}\)-\[Ru(Az)(bpy)Cl2\] suggests that the electron-donating groups in the bipyridine ligand make this ligand (dtb) a good donor ligand. The two axial chlorido ligands are slightly bent away from a linear trans geometry (Cl1–Ru1–Cl2 = 172.78(5)°): the two Ru–Cl bonds are bent toward the empty available space of dtb ligand due to the steric bulk of the approximately perpendicular diphenyl rings of the azo ligand. The average Cl–Ru–N (dtb) angle (87.15 (12)°) being smaller than the average Cl–Ru–N (Az) angle (92.85 (13)°). The average Ru–Cl bonds length of 2.366 (13) Å is in agreement with those related ruthenium(II) complexes [24, 25]. The amide group in Az ligand was disordered as shown in Fig. 1, with two orientations of approximately large different occupancy (27% and 73%), and both orientations of this group are

![Molecular structure of complex 1](image-url)
shown in Fig. 1. The occurrence of alternative conformations of this amide group, the crystallographic “disorder”, in this crystal structure seems not a sign of tight alternatives in the crystal packing but, rather, of looseness.

3.3. Electrochemistry

The electron-transfer behavior of the complexes in acetonitrile solution was examined by cyclic voltammetry and the corresponding results are summarized in Table 3. All these complexes show one metal centered oxidative response on the positive side of NHE reference electrode. A voltammogram is shown in Fig. 2. The oxidative response observed around 1.2 V is assigned to Ru(III/II) couples. This oxidation is quasi reversible with a peak-to-peak separation of 59–160 mV, and the anodic peak current (ipa) is almost equal to cathodic peak current (ipc). This couple is slightly affected by changing the substituent X and is shifted anodically upon replacing the strong electron-donating F ligand with the less donating Cl and Br ligands [26].

3.4. Electronic structure

All calculations were performed using GAUSSIAN03 program package [15], using default parameters of the program. The structure of the ligands as well as those of the complexes was optimized first. Single point calculations on trans-[Ru(Az)(dtb)X2] were performed using mixed basis set, LanL2DZ/6-31+g(d,p), in acetonitrile. Relative percentages of atomic contributions to the lowest unoccupied and highest occupied molecular orbitals for trans-[Ru(Az)(dtb)X2] (1–3) have been placed in Table 4. Moreover, the isodensity plots for the HOMO and LUMOs orbitals for 1 are shown in Fig. 3. Results indicate that the LUMO is constructed mainly from the π* orbital of azomine (58%) and (24%) Ru d-orbital which suggests significant back donation from Ru(dπ) to π*(Az) orbital [27]. The LUMO+1 is mostly dtb in character. For the HOMOs, the three highest energy orbitals (HOMO to HOMO-3) have a significant contributions of Ru(dπ) orbitals.

The lowest 20 singlet-to-singlet spin-allowed excitation states using TD-DFT method were taken into account to calculate the electronic absorption spectrum for complex 1 (as representative example). The calculated energy of excitation states and transition oscillator strength (f) (only f > 0.01 is listed) are shown in Table 5. The absorption spectrum of complex 1 was simulated using GaussSum software based on the obtained TD-DFT results [20]. Fig. 4 shows that the simulated and experimental spectra of complex 1 are in good agreement. TD-DFT calculations shows that the band centered at λ_{max} ≈ 504 nm (≈516 nm (calculated)) resulted from HOMO−1 and HOMO−3 orbitals (have sizable contributions of Ru(dπ) orbitals) to LUMO and LUMO+3 (have a significant contribution of π* orbital of azomethine); Thus this band is assigned to MLCT (Ru(dπ) → π* azomethine). The band centered at 390 nm (≈405 nm (calculated)) arises from the overlap of several transitions from the HOMO−6 and HOMO−7 which is mainly t-bpy in character to the azomethine π* orbital (LUMO).

The MLCT band energy and Ru(III/II) couple for a Ru(II) mononuclear complex provide information about the relative energies

![Fig. 2. Cyclic voltammogram for trans-[Ru(dtp)(Az)X2] (1-3) in acetonitrile 0.1 M TBAH at 25 °C, data reported in V vs. NHE with scan rate of 0.1 V/s.](image-url)

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<th>Complex</th>
<th>MO</th>
<th>Energy (eV)</th>
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<th>dtb</th>
<th>Azo ring</th>
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of the complex’s metal and ligand-based orbitals. The Ru(III/II) couple shifts to more positive potentials as the metal orbitals are stabilized. This has been demonstrated, for example, by the replacement of \(\sigma\)-donating ammine ligands with pyridine-type ligands [26,27]. In this study, the energy of the HOMO and LUMO for three trans-[Ru(Az)(dtb)X2] complexes has been theoretically investigated using DFT/B3LYP protocol. For the trans-[Ru(Az)(dtb)F2], the electron-donating ability of the fluoride ligand shifts the Ru(III/II) couple approximately 100 mV negative relative to their less (Cl and Br) donating analogues. This stabilization, however, does not result a noticeable shift in the MLCT band energy due to the equivalent stabilization of the orbitals involved in MLCT events (HOMO’s and the LUMO azoimine ligand).

### 4. Conclusions

Three neutral Ru(II) complexes each containing two bidentate, azoimine and dtb, and two anionic halides ligands have been prepared and characterized by standard spectroscopic techniques. X-ray structural analysis and their electrochemical properties were also studied. Crystal structure of 1 shows that bidentate azomethine ligands coordinate via imine and azo nitrogens. Cyclic voltammetric studies of trans-[Ru(Az)(dtb)X2] complexes show quasi reversible ruthenium-based oxidation–reduction processes. The

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**Table 5**

Computed excitation energies (nm), electronic transition configurations and oscillator strengths (\(f\)) for the optical transitions in the visible region of complex 1 (transitions with \(f > 0.01\) are listed, \(H\) stands for HOMO and \(L\) for LUMO).

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>(f)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>540.96</td>
<td>0.0375</td>
<td>H-3 (\rightarrow) LUMO (27%), H-2 (\rightarrow) LUMO (42%), H-1 (\rightarrow) LUMO (16%)</td>
</tr>
<tr>
<td>524.99</td>
<td>0.0244</td>
<td>H-3 (\rightarrow) LUMO (10%), H-1 (\rightarrow) LUMO (10%), HOMO (\rightarrow) L+3 (66%)</td>
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<tr>
<td>516.27</td>
<td>0.0484</td>
<td>H-3 (\rightarrow) LUMO (41%), H-1 (\rightarrow) LUMO (21%), HOMO (\rightarrow) L+3 (21%)</td>
</tr>
<tr>
<td>419.18</td>
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<td>H-8 (\rightarrow) LUMO (27%), H-7 (\rightarrow) LUMO (39%), H-6 (\rightarrow) LUMO (22%)</td>
</tr>
<tr>
<td>405.45</td>
<td>0.1035</td>
<td>H-7 (\rightarrow) LUMO (24%), H-6 (\rightarrow) LUMO (56%)</td>
</tr>
<tr>
<td>361.86</td>
<td>0.0244</td>
<td>H-2 (\rightarrow) L+3 (38%), H (\rightarrow) L+2 (23%)</td>
</tr>
</tbody>
</table>

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**Fig. 3.** Isodensity plots (isodensity contour = 0.05) of the HOMO and LUMO orbitals of complex 1.

**Fig. 4.** UV–Vis spectrum for trans-[Ru(dtb)(Az)X2] (1–3) in acetonitrile. Inset shows simulated absorption spectrum for 1, based on TD-DFT calculations, compared to excitation energies and oscillator strengths.
electronic effect of the halides was shown in the ruthenium couple. This couple is slightly shifted to more negative values when stronger electron-donating halide (F–) was introduced. The electronic absorption spectra of these complexes show a strong band in the visible region which is assigned to a (Ru(II)-to-azomethine) MLCT transition based on TD-DFT calculations.

5. Supplementary data

CCDC 740722 contains the supplementary crystallographic data for 1–3. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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