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Synthesis, structural characterization, and DFT investigation of azoimine-ruthenium complexes containing aromatic-nitrogen ligands

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ABSTRACT

Seven ruthenium(II) complexes continuing substituted diimine ligands and the azoimine ligand (Az: $C_6H_5N=NC(COCH_3)=NC_6H_5$) are synthesized and characterized. *trans*-[Ru(II)(Az)(L)Cl₂] [L = 2,2'-bipyridine (bpy) **1**, 4,4'-dimethyl-2,2'-bipyridine (dmb) **2**, 4,4'-dimethoxy-2,2'-bipyridine (dmeb) **3**, 4,4'-di-tertbutyl-2,2'-bipyridine (dtb) **4**, 1,10-phenanthroline (phen) **5**, 5-amino-1,10-phenanthroline (NH₂phen) **6**, 5-chlorophenanthroline (Clphen) **7**, 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) **8**] are made by the reaction of RuCl₃ hydrate and the ligands in the presence of LiCl. These complexes have been characterized by cyclic voltammetry, UV–Vis spectroscopy, electrochemical measurements and X-ray diffraction analysis for **2** and **5**. The electrochemical parameters ($E_L(L)$) of the substituted diimine ligands (L) are reported. The absorption spectrum of **5** in acetonitrile has been modeled by time-dependent density functional theory (TD-DFT) using a hybrid functional, B3LYP, as well as the LanL2DZ basis set.

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1. Introduction

Complexes of Ru(II) with polypyridine ligands have been extensively studied because of their potential industrial applications [1]. Reversible half-wave potentials, obtained from electrochemical data, have been used to estimate the valence electronic energy levels for a number of metal complexes [2]. For instance, the correlation between optical and electrochemical properties of 2,2'bipyridine (bpy) complexes of ruthenium(II) has been examined in order to estimate the energy of metal-to-ligand charge transfer (MLCT) absorption processes from the electrochemical potential [3]. This relation provides a convenient method for determining the absolute position of the energy levels of ruthenium(II) complexes.

We have previously reported the syntheses and electrochemistry of *trans*-[Ru(bpy)XCl₂] (X = arylamidrazones). The arylamidrazone ligands, which contain the azoimine (-N=N-C=N-)chromophore, are analogous to 2-(arylazo)pyridine (aap) whose ruthenium chemistry has been of considerable interest for several years [4]. The electrochemical parameters E_L for the ligand X were calculated by Lever's method [5] and the magnitude of $E_L(X)$ was found to increased as the number of electron withdrawing substituents (Z) attached to the azoimine moiety increased [6].



The work reported herein presents the synthesis, characterization and photophysical properties of a series of mixed-ligand ruthenium complexes, *trans*-[Ru(Az)LCl₂], (L = substituted diimine). The effect of substituents of these ligands is expected to vary the π -acceptor properties of these ligands and thus "tune" the electronic properties of the ruthenium center and consecutively the energy of MLCT bands.



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The spectral studies, redox properties and single crystal X-ray structures (for two representative examples) of this family are described in this work. The electrochemical parameters ($E_L(L)$) of the substituted diimine ligands (L) are reported. These values have broad utilization across both organometallic and coordination chemistry and can be used to predict M^n/M^{n-1} redox potentials by assuming that all ligand contributions are additive.

2. Experimental

2.1. Materials

The reagents: aniline-, bipyridine- and phenanthroline-derivatives, lithium chloride and ruthenium trichloride hydrate, and solvents (reagent grade) 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. The synthesis and the physical characterization of the ligand, 1-(4-phenylimino)-1-(phenylhydrazono)propan-2-one (Az) and the complex *trans*-[Ru(bpy)(L)Cl₂] have been prepared as described in the literature [6].

2.2. General procedure for the preparation of trans- $[Ru(Az)(L)Cl_2]$ 2-8

A suspension of ruthenium trichloride trihydrate (0.26 g, 1.00 mmol) and the 1-(4-phenylimino)-1-(phenylhydrazono)-propan-2-one (Az) (0.023 mmol) in 100 mL absolute ethanol were reacted under reflux conditions. After 1 h, 1.0 mmol of the corresponding ligand and excess amount of LiCl (0.50 g, 11.8 mmol) were added. The reaction was heated for an additional 3 h, after which the solvent was removed by using a rotary evaporator. The crude product was dissolved in dichloromethane, filtered and washed with water to remove the unreacted ruthenium trichloride and lithium chloride. The filtrate was reduced to 20 mL and purified by chromatography (50 \times 3 cm) on alumina grade (III). Elution with acetone gave a yellow band which was discarded followed by a darkred band of the product. The products were recrystallized from slowly evaporating solution of dichloromethane.

2.2.1. trans-[$Ru(Az)(dmb)Cl_2$] (2)

Yield (0.28 g, 46%). *Anal.* Calc. for $C_{27}H_{25}N_5ORuCl_2$: C, 53.38; H, 4.15; N, 11.53. Found: C, 53.70; H, 4.27; N, 11.47%. UV–Vis in acetonitrile: λ_{max} (ε_{max}/M^{-1} cm⁻¹): 370 (6.688 × 10³), 504 (5.146 × 10³). IR: v(N=N) 1486, v(C=N) 1616, v(C=O) 1717 cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 2.44 (6H, s, dmb), 2.73 (3H, s, COCH₃), 6.71 (1H, d, dmb), 7.05 (2H, d, H4), 7.31 (1H, d, dmb), 7.48 (1H, t, H6), 7.52 (2H, t, H5), 7.57 (1H, t, dmb), 7.62 (2H, t, H2), 7.80 (1H, t, H3), 7.95 (2H, d, H1), 8.30 (1H, s, dmb), 8.40 (1H, s, dmb).

2.2.2. trans- $[Ru(Az)(dmeb)Cl_2]$ (3)

Yield (0.31 g, 47%). Anal. Calc. for $C_{27}H_{25}N_5O_3RuCl_2\cdot H_2O$: C, 49.32; H, 4.14; N, 10.65. Found: C, 49.41; H, 4.18; N, 10.51%. UV–Vis in acetonitrile: $\lambda_{max}~(\epsilon_{max}/M^{-1}~cm^{-1})$: 378 (7.449 \times 10³), 500

 (6.55×10^3) . IR: v(N=N) 1490, v(C=N) 1612, v(C=O) 1705 cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 2.66 (3H, s, COCH₃), 3.97 (6H, s, dmeb), 6.67 (1H, d, dmeb), 6.75 (1H, d, dmeb), 6.83 (1H, d, dmeb), 7.30 (1H, t, H6), 7.34 (2H, d, H4), 7.45 (2H, t, H5), 7.49 (1H, d, dmeb), 7.59 (2H, t, H2), 7.80 (1H, t, H3), 8.96 (2H, d, H1), 8.09 (1H, s, dmeb), 8.16 (1H, s, dmeb).

2.2.3. trans-[Ru(Az)(dtb)Cl₂] (4)

Yield (0.36 g, 55%). Anal. Calc. for $C_{33}H_{37}Cl_2N_3ORu \cdot CH_2Cl_2$: C, 63.07; H, 6.07; N, 6.49. Found: C, 63.29; H, 6.39; N, 6.56%. UV–Vis in acetonitrile: λ_{max} (ϵ_{max}/M^{-1} cm⁻¹): 368 (6.40 × 10³), 506 (5.684 × 10³). IR: ν (N=N) 1480, ν (C=N) 1611, ν (C=O) 1701 cm⁻¹. ¹H NMR (DMSO-d₆): δ 1.34 (18H, s, dtb), 2.73 (3H, s, COCH₃), 6.84 (1H, d, dtb), 7.12 (1H, d, dtb), 7.17 (1H, d, dtb), 7.32 (2H, d, H4), 7.49 (1H, d, dtb), 7.50 (2H, t, H5), 7.54 (1H, t, H3), 7.61 (2H, t, H2), 7.83 (1H, t, H6), 7.96 (2H, d, H1), 8.47 (1H, s, dtb), 8.40 (1H, s, dtb).

2.2.4. trans-[Ru(Az)(phen)Cl₂] (5)

Yield (0.23 g, 40%). *Anal.* Calc. for $C_{27}H_{21}Cl_2N_3ORu$: C, 56.35; H, 3.68; N, 7.30. Found: C, 56.51; H, 3.87; N, 7.48%. UV–Vis in acetonitrile: λ_{max} (ε_{max}/M^{-1} cm⁻¹): 372 (9.015 × 10³), 505 (6.321 × 10³). IR: ν (N=N) 1495, ν (C=N) 1606, ν (C=O) 1711 cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 2.83 (3H, s, COCH₃), 7.24 (1H, d, phen), 7.33 (1H, dd, phen), 7.38 (1H, dd, phen), 7.53 (1H, t, H6), 7.58 (2H, d, H2), 7.50 (2H, t, H5), 7.75 (1H, t, H3), 7.84 (2H, d, H4), 7.95 (1H, d, phen), 8.12 (2H, d, H1), 8.25 (1H, d, phen), 8.29 (1H, d, phen),

2.2.5. trans-[Ru(Az)(aphen)Cl₂] (6)

Yield (0.30 g, 48%). *Anal.* Calc. for $C_{27}H_{22}Cl_2N_6ORu \cdot 0.5H_2O$: C, 51.68; H, 3.69; N, 13.39. Found: C, 51.34; H, 3.63; N, 13.70%. UV–Vis in acetonitrile: λ_{max} (ε_{max}/M^{-1} cm⁻¹): 378 (7.343 × 10³), 507 (6.464 × 10³). IR: v(N=N) 1490, v(C=N) 1637, v(C=O) 1705 cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 2.70 (3H, s, COCH₃), 5.76 (2H, s, NH₂), 6.73 (1H, s, aphen), 6.94 (1H, d, aphen), 7.14 (1H, d, aphen), 7.29 (1H, t, H6), 7.42 (2H, t, H5), 7.58 (2H, d, H4), 7.63 (1H, d, aphen), 7.65 (1H, t, aphen), 7.77 (2H, t, H2), 7.86 (1H, t, H3), 8.06 (2H, d, H1), 8.21 (1H, d, aphen), 8.80 (1H, d, aphen).

2.2.6. trans-[Ru(Az)(chphen)Cl₂] (7)

Yield (0.36 g, 50%). Anal. Calc. for $C_{27}H_{20}Cl_3N_5ORu \cdot CH_2Cl_2$: C, 46.53; H, 3.07; N, 9.69. Found: C, 46.82; H, 3.19; N, 9.92%. UV–Vis in acetonitrile: λ_{max} (ϵ_{max}/M^{-1} cm⁻¹): 374 (9.277 × 10³), 500 (8.62 × 10³). IR: ν (N=N) 1487, ν (C=N) 1632, ν (C=O) 1704 cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 2.73 (3H, s, COCH₃), 7.13 (1H, d, chphen), 7.43 (2H, d, H4), 7.59 (2H, t, H5), 7.60 (1H, t, chphen), 7.68 (2H, d, H2), 7.73 (1H, t, chphen), 7.74 (1H, d, chphen), 7.68 (1H, t, H3), 7.99 (2H, d, H1), 8.50 (1H, s, chphen), 8.65 (1H, d, chphen), 8.90 (1H, d, chphen).

2.2.7. trans-[Ru(Az)(tmphen)Cl₂] (8)

Yield (0.30 g, 46%). *Anal.* Calc. for C₃₁H₂₉Cl₂N₅ORu: C, 56.45; H, 4.43; N, 10.62. Found: C, 56.61; H, 4.10; N,10.87%. UV–Vis in acetonitrile: λ_{max} (ε_{max}/M^{-1} cm⁻¹): 372 (8.343 × 10³), 509 (6.195 × 10³). IR: ν (N=N) 1443, ν (C=N) 1623, ν (C=O) 1702 cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 2.04 (3H, s, tmphen), 2.10 (3H, s, tmphen), 2.70(3H, s, COCH₃), 6.69 (2H, s, tmphen), 7.40 (1H, t, H6), 7.45 (2H, d, H4), 7.59 (2H, t, H5), 7.72 (2H, t, H2), 7.89 (1H, t, H3), 7.97 (2H, d, H1), 8.3 (1H, d, tmphen).

2.3. Instrumentation

Cyclic voltammetric studies were performed in acetonitrile (Aldrich, HPLC grade) using a voltalab 21 (PGP201). Three electrodes were utilized in this system, two platinum-disk working and counter (auxiliary) electrodes (platinum electrode, 2-mm diameter), and a silver wire pseudo-reference electrode with ferrocene (0.665 V versus NHE) as an internal reference [7]. To maintain the cell temperature at 25.0 ± 0.1 °C, a Haake D8-G refrigerated bath and circulator was used. Tetrabutylammonium hexafluorophosphate was twice recrystallized and vacuum dried at 120 °C, and used as the supporting electrolyte. Spectroscopic data were obtained using Cary 5 spectrophotometer. IR spectra were measured by FT-IR JASCO model 420. Nuclear magnetic resonances (¹H NMR) spectra were measured on a Bruker-Avance 400 MHz spectrometer. Elemental analyses were carried out on an Eurovector E.A.3000 instrument using copper sample-tubes.

Table 1

Crystallographic data and str	tructure refinement parameters f	or 2 and	5
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	Complex 2	Complex 5
Empirical formula	C ₂₇ H ₂₅ Cl ₂ N ₅ ORu	C27H21Cl2N5ORu
Formula weight	607.49	603.46
Temperature (K)	90(2)	90(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	ΡĪ	P2(1)/n
Unit cell dimensions		
a (Å)	9.2166(3)	9.7453(4)
b (Å)	12.3156(5)	13.6453(5)
c (Å)	12.6505(5)	18.4318(7)
α (°)	95.1135(6)	90
β(°)	99.5710(6)	90.079(1)
γ (°)	109.8525(5)	90
V (Å ³)	1315.28(9)	2451.01(16)
Ζ	2	4
D_{calc} (Mg/m ³)	1.534	1.635
Absorption coefficient (mm ⁻¹)	0.829	0.889
F(000)	616	1216
Crystal size (mm ³)	$0.28\times0.21\times0.12$	$0.19 \times 0.17 \times 0.04$
Crystal color and habit	red plate	red fragment
θ Range for data collection (°)	1.65-27.50	1.86-27.50
Index ranges	$-11 \le h \le 11$	$-12 \le h \le 12$
	$-15 \le k \le 15$	$-17 \le k \le 17$
	$-16 \le l \le 16$	$-23 \le l \le 23$
Reflections collected	19611	36655
Independent reflections (R_{int})	6020 (0.0268)	5625 (0.0429)
Completeness to θ = 27.50°	99.9%	100.0%
Absorption correction	semi-empirical from	semi-empirical from
Maximum and minimum	0.9071 and 0.8010	0.9653 and 0.8492
Goodness-of-fit on F^2	1 050	1 035
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0317$	$R_1 = 0.0302$
	$wR_{2} = 0.0714$	$wR_2 = 0.0703$
R indices (all data)	$R_1 = 0.0380$	$R_1 = 0.0403$
(un dutu)	$wR_2 = 0.0752$	$wR_2 = 0.0751$
Largest difference in peak and hole ($e Å^{-3}$)	1.305 and -0.889	0.732 and -0.289

2.4. Computational methods

The crystallographic geometries of **2** and **5** were used as examples for our calculations. All theoretical calculations were carried out using a Becke's three-parameter hybrid function [8] with LYP correlation function [9] (B3LYP), as implemented in the GAUSSIAN 03 program package [10]. LanL2DZ effective core potential basis set was employed for all atoms in acetonitrile solution [11]. The theoretical electronic spectra were simulated from the energy of the excited states and transition oscillator strengths calculated by the TD-DFT formalism as implemented in the GAUSSIAN 93 program [10]. A value equal to 3000 cm⁻¹ for the bandwidth at half height has been used in these simulations with Gaussian line shapes because this value often provides us with molar extinction coefficient values close to experimental data.

2.5. Crystallography

Crystals of compounds 2 and 5 were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo K α radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans 0.3° per frame for 5 s, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.77 Å. Cell parameters were retrieved using SMART [12] software and refined using SAINTPLUS on all observed reflections [13]. Data reduction and correction for Lp and decay were performed using the saintplus software. Absorption corrections were applied using sadabs [14]. The structure was solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package [15]. The structure was solved in the space group $P\bar{1}$ for complex **5** and P21/n for complex **2** by analysis of systematic absences. The ketone group was disordered in two positions with occupancies of 84:16% and all non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

3. Results and discussion

3.1. Synthesis

The new complexes *trans*-[Ru(Az)(L)Cl₂] **(2–8)** used in this study were prepared by stepwise equimolar addition of RuCl₃, 1-(phenylimino)-1-(phenylhydrazono)-propan-2-one (Az), substi-



Scheme 1.

tuted bipyridine or phenanthroline ligands (L_1-L_8) and then an excess of lithium chloride according to Scheme 1.

These neutral complexes are air stable, diamagnetic and their structures were confirmed by ¹H NMR spectra and X-ray diffraction for complexes **2** and **5**. The ¹H NMR spectra of complexes **2**–**8** show featureless multiplets due to aromatic protons of the phenyl rings of the ligands. In their IR-spectra, all complexes show bands in the range of 1660–1712 cm⁻¹ assignable to C=O stretching frequency of the acetyl group and intense bands in the ranges of 1560–1590 and 1430–1500 cm⁻¹ which are assigned to the C=N and N=N stretching bands of azoimine ligands, respectively.

3.2. Crystal structures

The X-ray structures of (2) and (5) were determined and the perspective molecular views for the asymmetric units are shown in Figs. 1 and 2, respectively. The selected bond parameters are listed in Table 2. The ORTEP geometry of complex 5 as representative example for phenanthroline family is shown in Fig. 2. This complex crystallizes in the $P\bar{1}$ space group, which is different from P21/n of complex **2**. The coordination geometry of the complexes is distorted from regular octahedral as a consequence of the small bite angles of bidentate phen (77.31°) and bpy ligands (78.9°) , which deviate very much from the ideal octahedral angle of 90°. For both complexes (2 and 5) the chloride ligands are *trans* to each other and the azomethine and diimine nitrogen donor atoms are equatorially coordinated. Most bis bipyridine or phenanthroline complexes prefer a cis geometry because of steric hindrance between α protons in the *trans* geometry [16]. Steric hindrance is evidently not as great for the complexes of this study because the Az ligand phenyl rings can twist away from the α protons as shown in Figs. 1 and 2. The trans complexes of this study appear to be thermally stable in solution and we hope to explore their photochemical properties in the future. For complex **5**, the N(7)-Ru(1)-N(13)angle of the azomethine ligand has a value of 76.33. The azomethine ligand is known to participate strongly in $d\pi - \pi^{\uparrow}$ interactions with Ru(II). This has been reflected in the Ru–N(bpv). Ru–N(phen) and Ru-N(Az) bond distance data. The Ru-N(pv) bond distances for complex **5** and **2** fall within a narrow range of 2.121–2.146 Å. The Ru–N(bpy) and Ru–N(phen) distances are longer than those in the



Fig. 1. Thermal ellipsoid plot (30%) of 2. Hydrogen atoms omitted for clarity.



Fig. 2. Thermal ellipsoid plot (30%) of 5. Hydrogen atoms omitted for clarity.

Table 2Bond lengths [Å] and angles [°] for complex 2 and 5

Bond lengths [Å]		Bond angles [°]	
Complex 5			
N(7) - Ru(1)	1.9498(19)	N(20)-Ru(1)-N(31)	77.31(7)
C(9)-N(13)	1.361(4)	N(13)-Ru(1)-N(31)	104.23(8)
N(20)-Ru(1)	2.1200(19)	N(7)-Ru(1)-N(31)	176.80(7)
N(31)-Ru(1)	2.1610(19)	N(13)-Ru(1)-N(20)	174.25(7)
Cl(1)-Ru(1)	2.3714(6)	N(7)-Ru(1)-N(20)	102.44(8)
Cl(2)-Ru(1)	2.3564(6)	N(7)-Ru(1)-N(13)	76.33(8)
N(13) - Ru(1)	1.9919(19)	N(20)-Ru(1)-N(31)	77.31(7)
N(8) - C(9)	1.370(4)	N(13)-Ru(1)-N(31)	104.23(8)
N(7)-N(8)	1.301(4)	N(7)-Ru(1)-N(31)	176.80(7)
		Cl(2)-Ru(1)-Cl(1)	172.68(2)
Complex 2			
N(7)-N(8)	1.302(3)	N(13)-Ru(1)-N(20)	104.80(8)
N(7)-Ru(1)	1.9517(19)	N(13)-Ru(1)-N(33)	178.09(8)
N(13)–N(9B)	1.293(10)	Cl(1)-Ru(1)-Cl(2)	171.76(2)
N(13)-Ru(1)	1.9986(19)	N(8)-N(7)-Ru(1)	122.65(19)
N(20)-Ru(1)	1.362(3)	N(33)-Ru(1)-N(20)	76.27(7)
N(33)-Ru(1)	2.1119(18)	N(7)-Ru(1)-N(20)	179.30(8)
Cl(1)-Ru(1)	2.3443(6)	N(7)-Ru(1)-N(33)	103.13(8)
Cl(2)-Ru(1)	2.3780(6)	N(7)-Ru(1)-N(13)	75.81(8)

corresponding $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ complexes, respectively [17]. For complex **2**, the Ru–N(bpy) distances (average, 2.121(3) Å) are shorter than Ru–N(phen) distances (average, 2.146(3) Å) revealing that bpy is more strongly coordinated than phen. For complex **5**, the average Ru–N(azo) and Ru–N(methine) distances of the azoimethine ligand is 1.971(3) Å which is shorter than Ru–N(phen) lengths (average, 2.146(3) Å). This shortening may be due to greater π -back donation from Ru-d orbital to the empty π^* orbital of the azoimine ligand, and this comes as an indication that the M–(Az) π interaction is localized in the M–azo fragment [18]. Reported Ru–Cl distances in chloro-Ru(II) complexes lie in the range 2.389–2.401 Å [19]. The average Ru–Cl bond lengths in **5** (2.364) is comparable to similar reported systems [19].

3.3. Electrochemistry

Formal oxidation and reduction potentials versus NHE were obtained from cyclic voltammograms recorded at a platinum elec-

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trode in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophospate. These data are listed in Table 3. Ru(III/II) values were obtained from an average of anodic and cathodic peak potentials. Complex 5, as a representative example (Fig. 3), displays a reversible oxidation peak at 1.18 V, being attributed to the metal-centered Ru(III/II) couple. The two reduction waves at -0.43 and -0.77V are assigned to azo(0/-) and azo(-/-2) ligand-centered processes. This reduction couples are shifted to more positive potentials by the electron withdrawing group attached to bipyridine and phenanthroline ligands. The electrochemical properties of Ru(II) complexes containing substituted phenanthroline ligand were guite similar to those of substituted bipyridine complexes. However, the half-wave potential of earlier complex was shifted anodically by 20 mV compared to those observed with later complexes. This relationship indicates that the donor ability of the phenanthroline ligand is slightly weaker than that of the bipyridine ligand [19]. The Ru(III/II) couple is slightly affected by changing the substituent on the phenanthroline ligand and is shifted to more positive potentials upon replacing the donating methyl group with the more withdrawing chloro group. Lever has developed an elec-

 Table 3

 Cyclic voltammetry and electronic spectroscopy data of trans-[Ru(II)(Az)(L)Cl₂]^a

Complex	Calculated $E_{L}(L)$ for ligand L^{b}	$(E_{1/2M}^{\circ})^{c}$	Azo $(0/-)^d$	$(\Delta E^\circ)^{\rm e}$	$\lambda_{\max} (nm) (E_{MLCT}))^{f}$
1	0.25	1.16	-0.48	1.64	(510) (2.43)
2	0.23	1.14	-0.50	1.64	(504) (2.46)
3	0.23	1.14	-0.52	1.66	(500) (2.48)
4	0.22	1.13	-0.45	1.58	(506) (2.45)
5	0.28	1.18	-0.43	1.61	(505) (2.45)
6	0.22	1.13	-0.44	1.57	(507) (2.44)
7	0.30	1.20	-0.45	1.65	(500) (2.48)
8	0.21	1.12	-0.44	1.56	(509) (2.44)

^a Solvent MeCN, supporting electrolyte Bu₄NPF₆ (0.1 M), scan rate 0.1 V s), Pt-disk working electrode, Pt-wire auxiliary electrode, reference electrode Ag at 25 °C.

^b Calculated using $E_{\text{Ru}(III/II)} = 0.97[\sum E_L] + 0.04$ in V vs. NHE, (E_L for Az = 0.42 and for chloride = -0.24) [29].

^c $E_{1/2M}^{\circ} = (E_{pa}^{\circ} - E_{pc}^{\circ})/2.$

^d The cathodic peak maximum.

^e $\Delta E^{\circ} = \operatorname{Ru}(\operatorname{III}/\operatorname{II}) - \operatorname{Azo}(0/-).$

^f MLCT = $[1239.8/\lambda_{max} (nm)]$ eV.

trochemical parameterization method to calculate ruthenium(III/ II) couples of complexes with octahedral geometry as shown in Eq. (1) [4].

$$E_{\rm Ru(III/II)} = 0.97 \left[\sum E_{\rm L}\right] + 0.04 \text{ in V versus NHE}$$
(1)

where $\sum E_L$ is the sum of electrochemical parameters for each ligand in the complex. The parameter E_L is a measure of the stabilizing effect a ligand has on the Ru(II) state and so the greater the magnitude of positive E_L the more positive the Ru(III/II) couple. Based on the previously found ($E_L(Az) = 0.42$) [6], $E_L(CI) = -0.24$ [4]) and assuming ligand additivity, the Ru(III/II) couple for these octahedral complexes was used to find the ligand electrochemical parameters ($E_L(L)$) for unreported diimine ligands (L) using Eq. (1) and the data are listed in Table 3.

3.4. Electronic structure

Theoretical calculations were performed on **5**; relative percentages of atomic contributions to the lowest unoccupied and highest occupied molecular orbitals have been placed in Table 4. Moreover, the isodensity plots for the HOMOs and LUMOs orbitals are shown in Fig. 4. The lower unoccupied molecular orbitals (LUMOs) consists

Table 4

Relative percentages of atomic contributions to the lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO) of **5**

MO	Energy (ev)	Ru	phen	Azo-imine ring	Cl
HOMO – 6	-7.27	5	4	84	8
HOMO – 5	-7.15	2	14	80	3
HOMO – 4	-6.98	1	67	28	5
HOMO – 3	-6.78	16	8	74	2
HOMO – 2	-6.37	63	3	33	1
HOMO – 1	-6.16	30	1	29	40
номо	-5.53	61	2	7	29
LUMO	-3.41	26	9	60	5
LUMO + 1	-2.21	5	90	4	0
LUMO + 2	-2.11	0	95	5	0
LUMO + 3	-1.67	3	4	93	0
LUMO + 4	-0.92	1	86	12	0
LUMO + 5	-0.72	45	5	28	23
LUMO + 6	-0.57	20	8	70	2



mostly of a series of antibonding π^* orbital of azoimine together with a small contribution from π^* orbital of phenanthroline. Results indicate that the LUMO is constructed mainly from the π^{T} orbital of azoimine (60%) and has 26% metal d-orbital character which suggests significant back donation [20]. The other group of HOMOs, can be described as $t_{2}g$ Ru orbitals (HOMO to HOMO - 2) with small contributions from the azomethine ligands. Moreover, results indicate that π orbital of azoimine ligand contributes significantly to HOMO - 3.

The lowest 20 singlet-to-singlet spin-allowed excitation states were taken into account for the calculation of the electronic absorption spectrum of complex 5 using TD-DFT method. Excitation energies, oscillator strengths and corresponding transitions compositions for the simulated absorption bands in acetonitrile solution are listed in Table 5. Each excited state was interpolated by a Gaussian convolution with the full width at half-maximum (fwhm) of 3000 cm^{-1} . Both the experimental UV–Vis spectrum for complex 5 (as a representative example) and its simulated absorption spectrum reported in acetonitrile, shown in Fig. 5, were in good agreement. Experimentally, complex 5 has a maximum centered at 504 nm and a shoulder peak at 390 nm. Contrary to the experimental information, the simulated near-UV band is much higher than the visible one. Assuming that the appropriate fwhm values are chosen, the molar absorptivity of the band maximum in visible region is slightly underestimated, while the one in the near-UV region is significantly overestimated. Similar results in simulation of N3-type dye also exist [21]. The study of Tozer et al. also revealed that TD-DFT has difficulty in distributing intensity properly [22]. For the absorption band in visible region, TD-DFT calculations shows that the band centered at λ_{max} = 504 nm

Table 5

Computed excitation energies (eV), electronic transition configurations and oscillator strengths (f) for the optical transitions in the visible region of 5 (transitions with f > 0.01 are listed)

Wavelength nm (eV)	Oscillator strengths (f)	Contribution
550 (2.258) 453 (2.742)	0.0815 0.0221	81.1% HOMO – 1 → LUMO 97.38% HOMO → LUMO + 2
420 (2.9586)	0.0171	18.27% HOMO – 7 \rightarrow LUMO, 61.42% HOMO – 4 \rightarrow LUMO
405 (3.069) 395 (3.146)	0.0115 0.0374	91.04% HOMO – 5 → LUMO 26.44% HOMO – 1 → LUMO + 1, 61.72%
388 (3.204)	0.0624	$HOMO \rightarrow LOMO + 3$ 67.50% $HOMO - 6 \rightarrow LUMO, 10.06\%$ $HOMO - 2 \rightarrow LUMO + 1$
381 (3.257)	0.0292	20.08% HOMO – 6 → LUMO, 21.40% HOMO – 2 → LUMO + 1, 28.61% HOMO – 1 → LUMO + 1, 11.06% HOMO → LUMO + 3
375 (3.313)	0.0111	78.1% HOMO $-10 \rightarrow$ LUMO

(\approx 550 nm (calculated)) resulted from HOMO – 1 orbital, which have sizable contributions of $Ru(d\pi)$ orbitals mixed with azomethine to LUMO which has a significant contribution from the π orbital of azomethine. Thus this band is assigned to MLCT $(\operatorname{Ru}(d\pi) \to \pi^{T}$ azomethine). For the band in the near-UV region, the band centered at 390 nm (~388 nm (calculated)) arises from the overlap of several transitions, MLCT and $\pi \rightarrow \pi^{\uparrow}$. The MLCT band centered at 395 resulted from HOMO (mainly Ru) \rightarrow LU-MO + 3 (azomethine in character), while the $\pi \rightarrow \pi^{-}$ transition is at centered 388 nm and resulted from the HOMO – 6 (azomethine



Fig. 5. UV-Vis spectrum for 5 in acetonitrile. Inset shows simulated absorption spectrum. (black line) based on TD-DFT calculations, compared to excitation energies and oscillator strengths.

in character) \rightarrow LUMO. The observation of two MLCT transition may be explained by the low symmetry of this distorted octahedral Ru complexes [23–25].

The difference in the two successive redox responses at potentials positive and negative to NHE $[\Delta E^{\circ} = E^{\circ}_{1/2M} - E^{\circ}_{L_{e}}(0/-)]$ may be correlated with the low energy MLCT $[t(Ru) \rightarrow \pi \text{ (azomethine)}]$ transition [25]. Charge transfer transitions may be considered an intramolecular redox process [26–29] and the intense spin-allowed MLCT transition is expected to be linearly related to ΔE° with slope equal to unity. A least-squares plot of ΔE° versus lower energy MLCT (Fig. 6) gave a linear correlation ($E_{\text{MLCT}} = 0.39 \Delta E^{\circ} + 1.829$) however the slope of the line is only 0.39. This may result from solvent effects that become important for the small changes in energy that are seen in this group of complexes [26].

4. Conclusions

A series of complexes of general formula *trans*-[Ru(II)(Az)(L)Cl₂] where Az = C_6H_5N =NC(COCH₃)=NC₆H₅, and L is nitrogen substituted bipyridine and phenanthroline ligands have been prepared and their redox chemistry and UV–Vis spectroscopy examined. The structures for complex **2** and **5** have been further characterized by X-ray diffraction analysis. Crystallographic studies shows that bidentate azomethine ligands are strong π -acceptor that coordinate via imine and azo nitrogens. Electrochemical and photophysical data in acetonitrile showed that electron-donating groups in the bipyridine and phenanthroline ligands shifts the redox potentials to more negative values than those observed for the parent ligands. Assuming ligand additivity, the Ru(III/II) couple for these octahedral complexes was used to find the ligand electrochemical



Fig. 6. Linear correlation between MLCT band energies and ΔE° ($\Delta E^{\circ} = \text{Ru}(\text{III/II}) - \text{Azo}(0/-)$) in volts. The equation of the line is ($E_{\text{MLCT}} = 0.39\Delta E^{\circ} + 1.829$).

parameter $(E_{I}(L))$ for unreported diimine ligands (L). The electronic absorption spectra of these complexes show two strong MLCT band in the visible region and near UV-Vis region in acetonitrile solution. These two bands are assigned to a (Ru(II)-to-azomethine) MLCT transition based on TD-DFT calculations. Good agreement between computed and experimental absorption spectra was obtained.

5 Supplementary data

CCDC 690081 and 690082 contain the supplementary crystallographic data for **2** and **5**. 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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