Inorganica Chimica Acta 387 (2012) 45-51

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Ruthenium complexes incorporating azoimine and α -diamine based ligands: Synthesis, crystal structure, electrochemistry and DFT calculation

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ARTICLE INFO

Article history: Received 23 October 2011 Received in revised form 21 December 2011 Accepted 26 December 2011 Available online 10 January 2012

Keywords: Ruthenium Complexes Azomethine X-ray structure Electrochemistry DFT calculation

1. Introduction

The chemistry of complexes built from heterocyclic nitrogenous ligands has developed in different dimensions due to photophysical, photochemical, catalytic and redox activities [1,2]. The major work focused on ruthenium(II) complexes containing poly-pyridine bases. The later bases may have different number of hetero-atoms, ring size and substituents which resulted in modifying the π -acidity and regulating the physical and chemical properties of these complexes [3].

Ruthenium(II) complexes based on azoimine ligands (Ph–N=N– C(R)=N–Ph), which is isoelectronic with the α -diimines (–N=C– C=N–), are being currently examined in our laboratory [4–9]. These ligands are strong π -acceptor and capable of stabilizing metals in their low oxidation states [4]. The extent of this stabilization depends on the substituents on the phenyl rings (Ph) and the R group to which the azo and imine groups' linkage are attached [5].

We have previously reported the syntheses and electrochemistry of *trans*-[Ru(Az)LCl₂] (Az is $C_6H_5N=N-C(R)=NC_6H_5$) where R is an acetyl and acetate group and L are bipyridine- and phenanthroline-derivatives [4,5]. The effect of the substituents R on the electronic properties of the ruthenium complexes was studied [4]. In

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ABSTRACT

Ru(II) complexes, *trans*-[RuCl₂(Azo)L] [where Azo = $C_6H_5N=N-C(C_6H_5)=NC_6H_5$, L = 2,2'-bipyridine (bpy) (C1), 4,4'-dimethyl-2,2'-bipyridine (dmb) (C2), 1,10-phenanthroline (phen) (C3), 5-amino-1,10-phenanthroline (NH₂phen) (C4)] were synthesized and characterized by spectroscopy (IR, UV–Vis, and NMR), cyclic voltammetry and crystallography. The new Azo ligand was isolated as amidrazones, H₂Azo {where H₂Azo is $C_6H_5N=N=C(C_6H_5)=NC_6H_5$ }, but oxidized to azoimines (Azo) during the formation of the Ru(II) complexes. A crystallographic analysis of C1 showed that the Ru-center is in a distorted octahedral coordination sphere in which the donor atoms around the Ru(II) center occupy cis:cis:trans *N*,*N*(Azo):*N*,*N*(bpy):Cl,Cl positions. The Ru(II) oxidation state is greatly stabilized by the novel Azo bidentate ligand showing Ru(III/II) oxidation couples ranging from 1.10 to 1.15 V. The absorption spectrum of C1 in acetonitrile was modeled by time-dependent density functional theory.

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addition, the electrochemical parameters $E_{\rm L}$ for the ligands L were calculated by Lever's method and the magnitude of $E_1(L)$ was found to increase as the withdrawing substituent attached to the L moiety is replaced with electron donating groups [5]. As part of our continuing interest in ruthenium azoimine chemistry, we report herein the synthesis of a new family of *trans*-[RuCl₂(Azo)L] (C1-C4) [Azo is $C_6H_5N=N-C(C_6H_5)=NC_6H_5$, and L is 2,2'-bipyridine (bpy) (C1), 4,4'-dimethyl-2,2'-bipyridine (dmb) (C2), 1,10phenanthroline (phen) (C3) and 5-amino-1,10-phenanthroline (NH₂phen) (C4)]. The effect of the substituents on the ligands L is expected to change the π -acceptor properties of these ligands and thus "tune" the electronic properties of the ruthenium center and consecutively the energy of MLCT bands. In addition, this work also presents and discusses the spectroscopic (IR, UV-Vis and, ¹H NMR) and electrochemical (cyclic voltammetry) behavior of C1-C4, and reports the X-ray structure for C1. The absorption spectrum of C1 in acetonitrile has also been modeled by time-dependent density functional.

2. Experimental

2.1. Materials

Ruthenium trichloride hydrate, lithium chloride, 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 1,10-phenanthroline, 5-amino-1,10phenanthroline, tetrabutylammonium hexafluorophosphate (TBAHF) and solvents (reagent grade) were purchased from Aldrich





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^{0020-1693/\$ -} see front matter \odot 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2011.12.050

and were used as received. *N*-phenylbenzenecarbohydrazonoyl chloride was synthesized following reported procedures [10].

2.2. Preparation of the N,N-diphenylbenzenecarbohydrazonamide ligand (H_2Azo)

A solution of aniline (1.86 g, 20 mmol) and triethylamine (2.40 g, 24.0 mmol) in 5.0 mL ethanol was added to a 10 mL solution of *N*-phenylbenzenecarbohydrazonoyl chloride (4.60 g, 20.0 mmol). The resulted reaction mixture was refluxed for 2 h. Condensing the solution followed by cooling produced a yellow solid which was collected by filtration, then washed with water and recrystallized from 2-propanol. Yield = 2.0 g, 35%. M.p 133–134 °C. ¹H NMR (DMSO) δ 10.25 (s, NH), 9.18 (s, NH), 7.96 (d, 2H, H7), 7.78 (d, 2H, H1), 7.50 (m, 7H, H2, H3, H6, H8, H9), 6.74 (t, 2H, H5), 6.61 (d, 2H, H4). M.p, 173–175 °C. *Anal.* Calc. for C₁₉H₁₇N₃: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.55; H, 6.18; N, 14.71%.

2.3. General procedure for the preparation of trans-[RuCl₂(Azo)L] (**C1–C4**)

A suspension of ruthenium trichloride trihydrate (0.26 g, 1.0 mmol) and the (H₂Azo) (0.29 g, 1.0 mmol) in 100 mL absolute ethanol were reacted under reflux conditions. After 1 h, 1.0 mmol of the ligand (L) and excess amount of LiCl (0.25 g, 5.90 mmol) were added. The mixture 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 (50×3 cm) on alumina grade (III). Elution with acetone gave a yellow band which was discarded followed by a dark-red band of the product. The products were recrystallized from slowly evaporating solutions of acetonitrile.

2.3.1. Trans-[RuCl₂(Azo)(bpy)] (**C1**)

Yield = 0.25 g, 52%. I.r. (KBr, cm⁻¹): v_N = 1490, v_C = 1618, ¹H-NMR (DMSO) δ 8.57 (d, 1H, bpy), 8.48 (d, 1H, bpy), 8.12 (t, 1H, H9), 8.01 (d, 1H, bpy), 7.99 (d, 2H, H7), 7.77 (t, 1H, H3), 7.60 (t, 2H, H8), 7.53 (t, 2H, H2), 7.48 (t, 2H, H5), 7.44 (m, 2H, H1, H6), 7.38 (m, 3H, H4, bpy), 7.32 (m, 2H, bpy), 7.22 (t, 1H, bpy), 7.13 (t, 1H, bpy), 7.01 (d, 1H, bpy). UV–Vis in acetonitrile: λ_{max} (nm) (ε_{max} , M⁻¹ cm⁻¹): 291 (3.27 × 10⁴), 513 (1.09 × 10⁴). Anal. Calc. for RuC₂₉H₂₃N₅Cl₂: C, 56.77; H, 3.78; N, 11.42. Found: C, 56.75; H, 3.61; N, 11.71%.

2.3.2. .Trans-[RuCl₂(Azo)(dmb)] (**C2**)

Yield = 0.31 g, 48%. I.r. (KBr, cm⁻¹): $v_N =_N = 1480$, $v_C =_N = 1610$, ¹H-NMR (DMSO) δ 8.41 (s, 1H, dmb), 8.33 (s, 1H, dmb), 7.98 (d, 2H, H7), 7.75 (t, 1H, H9), 7.58 (t, 2H, H8), 7.42 (m, 8H, H1, H4, H5, H6, dmb), 7.31 (m, 3H, H2, H3), 7.04 (d, 1H, dmb), 6.97 (d, 1H, dmb), 6.82 (d, 1H, dmb), 2.49 (s, 3H, CH₃), 2.43 (s, 3H, CH₃). UV– Vis in acetonitrile: λ_{max} (nm) (ε_{max} , M⁻¹ cm⁻¹): 286 (3.14 × 10⁴), 506 (1.01 × 10⁴). Anal. Calc. for RuC₃₁H₂₇N₅Cl₂: C, 58.04; H, 4.24; N, 10.92. Found: C, 58.25; H, 3.98; N, 10.83%.

2.3.3. Trans-[RuCl₂(Azo)(phen)](C3)

Yield = 0.29 g, 46%. I.r. (KBr, cm⁻¹): $v_N = 1495$, $v_C = 1606$, ¹H-NMR (DMSO) δ 8.57 (d, 1H, Phen), 8.76 (t, 1H, Phen), 8.20 (t, 2H, H8), 8.04 (d, 2H, H7), 7.82 (d, 1H, Phen), 7.74 (t, 1H, Phen), 7.66 (m, 3H, H2, H9), 7.53 (m, 4H, H5, H4), 6.08 (m, 6H, H6, H1, H3, Phen), 7.28 (t, 1H, Phen), 7.19 (d, 1H, Phen). UV–Vis in acetonitrile: λ_{max} (nm) (ε_{max} , M⁻¹ cm⁻¹): 296 (3.04 × 10⁴), 513 (1.10 × 10⁴). *Anal.* Calc. for RuC₃₁H₂₃N₅Cl₂: C, 58.40; H, 3.64; N, 10.99. Found: C, 58.15; H, 3.72; N, 10.83%.

2.3.4. Trans-[RuCl₂(Azo)(NH₂phen)] (C4)

Yield = 0.27 g, 40%. I.r. (KBr, cm⁻¹): $ν_N = 1485$, $ν_C = 1630$, ¹H-NMR (DMSO) δ 8.57 (d, 2H, H7), 8.30 (d, 2H, H1), 7.86 (m, 3H, H8, H9), 7.58 (m, 7H, H2, H3, H4, (NH₂phen)), 7.45 (m, 6H, H5, H6, (NH₂phen)), 7.29 (t, 1H, (NH₂phen)), 7.24 (s, 1H, (NH₂phen)), 6.68 (s, 2H, NH2). UV-Vis in acetonitrile: $λ_{max}$ (nm) ($ε_{max}$, M⁻¹ cm⁻¹): 310 (2.95 × 10⁴), 484 (1.01 × 10⁴). *Anal.* Calc. for RuC₃₁H₂₄N₆Cl₂: C, 57.06; H, 3.71; N, 12.88. Found: C, 57.15; H, 3.80; N, 12.72%.

2.4. Instrumentation

The ¹H NMR spectra were measured on a Bruker-Avance 400 MHz spectrometer using TMS as an internal standard. Micro analyses (C, H, N) were performed using EURO VECTOR elemental analyzer model EA3000. IR spectra were obtained by FT-IR JASCO model 420. Electronic spectra were recorded on a Shimadzu 240-UV-Vis spectrophotometer. Electrochemical measurements were performed in 99.8% anhydrous acetonitrile (Aldrich, HPLC grade) using a computer controlled Volta Lab model PGP201 with a platinum working electrode, a platinum wire auxiliary electrode and silver wire pseudo-reference electrode. Ferrocene (0.665 V versus Normal Hydrogen Electrode (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 hexafluorophosphate (TBAHF) (0.1 M) was twice recrystallized and vacuum dried at 110 °C, and used as the supporting electrolyte. The experimental solutions were degased by bubbling with research grade dinitrogen.

2.5. X-ray crystallography

Single brown plate crystals of C1 were collected. Single crystal XRD data sets were collected at 100(1) K on a Bruker X8 Kappa APEXII equipped with graphite monochromator. Crystal data collection and refinement were performed using the package SMART [12], SAINT [13], SADABS [14] and SHELXL-97 [15]. Geometric calculations and molecular graphics were performed with CrystalMaker 6.0 [16]. The threshold expression of $F2 > 2\sigma(F2)$ was used only for calculating R-factors(gt) etc. and was not relevant to the choice of reflections for refinement. Details of the data collection and refinement are given in Table 1. The complex C1 was obtained by recrystallization/synthesis with many solvents such as H₂O, CH₂Cl₂, acetone, and acetonitrile. We were not able to decide the solvent multicomponent system that entered in the lattice, and for this reason we used squeeze. We deleted the correspondance diffraction pattern that belongs to this solvent. Molecule analysis by program PLATON [17] using the squeeze routine indicated void space of 264. Squeezing out this disordered region and continuing the refinement converged at R1 = 0.0372, S = 1.054 and largest electron density peak of 0.397 e Å⁻³ located off Ru1. All nonhydrogen atoms were refined anisotropically. No decomposition was observed during data collection. The crystal structure of the complex C1 is depicted in Fig. 1. Crystal data after void squeeze is given in Table 1.

2.6. Molecular orbital calculations

The X-ray structure of complex **C1** was fully optimized using LanL2DZ/6-31+G(d,p) level of theory using the GAUSSIANO3 [18] and was used as starting coordinates to generate *trans*-[RuCl₂(Azo)L] (**C2–C4**) geometries. All theoretical calculations were carried out using Becke's three-parameter hybrid function with LYP correlation function [19,20] (B3LYP), as implemented in the GAUSSIANO3 program package [18]. The optimized geometric parameters for complex **C1** are gathered in Table 2. Generally, the calculated bond lengths and angles are in a good agreement with the values based

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Table	1
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Crystal data and structure refinement for **C1**.

Empirical formula	RuC29H23Cl2N5
Formula weight	613.49
T (K)	100(1)
Crystal color and shape	brown, plate
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	
a (Å)	23.767(5)
b (Å)	8.8496(18)
c (Å)	28.213(6)
α (°)	90
β (°)	90.50(3)
γ (°)	90
V (³ Å)	5934(2)
Ζ	8
$D_{\text{calc.}}$ (Mg/m ³)	1.376
Absorption coefficient (mm ⁻¹)	0.734
F(000)	2480
Crystal size (mm)	$0.65 \times 0.16 \times 0.09$
Theta range for data collection	1.44–25.68°
Index ranges	$-28\leqslant h\leqslant 28$, $0\leqslant k\leqslant 10$,
	$0 \leqslant l \leqslant 34$
Reflections collected	5629
Independent reflections	5629 $[R_{int} = 0.0000]$
Completeness to theta = 25.68°	99.9%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	1.0000 and 0.8161
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5629/0/335
Goodness-of-fit (GOF) on F ²	1.054
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0372, wR_2 = 0.0762$
R indices (all data)	$R_1 = 0.0527, wR_2 = 0.0816$
Largest difference in peak and hole	0.397 and -0.577
(e Å ⁻³)	

Calc. $w = 1/[\sigma^2 (F_o^2) + (0.0315P)2 + 3.5503P]$ where $P = (F_o^2 + c^2)/3$.

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) [21,22] 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



Fig. 1. Thermal ellipsoid drawing (30%) of C1 complex.

Table 2)
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Bond lengths [Å] and angles [°] for complex C1.

Bond lengths (Å) (experimental, optimized)	
Ru(1)–N(3)	1.940(3), 1.977
Ru(1)–N(5)	2.026(2), 2.080
Ru(1)–N(2)	2.092(3), 2.135
Ru(1)–N(1)	2.137(2), 2.186
Ru(1)-Cl(1)	2.359(9), 2.440
Ru(1)–Cl(2)	2.388(9), 2.468
N(3)-N(4)	1.329(3), 1.299
N(5)-C(17)	1.318(4), 1.316
Bond angles (°) (experimental, optimized)	
N(3)-Ru(1)-N(5)	76.23(10), 74.98
N(3)-Ru(1)-N(2)	103.41(10), 103.94
N(5)-Ru(1)-N(2)	173.04(10), 176.37
N(3)-Ru(1)-N(1)	177.66(10), 179.35
N(5)-Ru(1)-N(1)	103.78(10), 105.53
N(2)-Ru(1)-N(1)	76.87(9), 75.57
N(3)-Ru(1)-Cl(1)	89.74(8), 91.89
N(5)-Ru(1)-Cl(1)	87.51(8), 88.48
N(2)-Ru(1)-Cl(1)	85.53(7), 88.09
N(1)-Ru(1)-Cl(1)	92.60(7), 88.51
N(3)-Ru(1)-Cl(2)	95.49(8), 96.13
N(5)-Ru(1)-Cl(2)	94.80(8), 94.45
N(2)-Ru(1)-Cl(2)	92.16(7), 89.10
N(1)-Ru(1)-Cl(2)	82.17(7), 83.45
Cl(1)-Ru(1)-Cl(2)	174.65(3), 171.92

the electronic absorption spectrum for the complex **C1**. Orbital contribution was analyzed using GAUSSSUM software [23].

3. Results and discussion

3.1. Synthesis

The *N*-phenylbenzenecarbohydrazonoyl chloride (**1**) was prepared by chlorination of *N*-phenylbenzohydrazide in carbon tetrachloride [10], then reacted with aniline to give the amidrazone ligand (H₂Azo) (Scheme 1). The ruthenium(II) complexes of this ligand *trans*-[RuCl₂(Azo)L] (**C1–C4**) were obtained by stepwise equimolar addition of RuCl₃, H₂Azo, substituted bipyridine or phenanthroline ligands (L) and then an excess of lithium chloride in refluxing ethanol (Scheme 1). Ethanol presumably acts both as a solvent and as a reducing agent for Ru(III) [4,5]. The ligand H₂Azo is oxidized to Azo by Ru(III) and/or atmospheric oxygen under the conditions of the synthesis. All the complexes are air stable as solids or in solution and are soluble in common organic solvents. Their structures were confirmed by ¹H NMR spectra, elemental analysis and X-ray diffraction for complex **C1**.

The ¹H NMR spectra of complexes **C1–C4** show multiplets due to aromatic protons of the phenyl rings of the the azoimine ligands and L. In their IR-spectra, all complexes show bands in the ranges of 1560–1630 and 1480–1495 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 structure of **C1** was determined and the perspective molecular view is shown in Fig. 1. The selected bond parameters are listed in Table 2. This complex crystallizes in the C2/*c* space group. The bond length for N(3)–N(4) and N(5)–C(17) are 1.329(3) and 1.318(4) Å, respectively,which is slightly longer than the bond length for the free azo (N=N) (1.266(3) Å and the free imine C=N (1.29 Å) bonds [24]. In addition, both the Ru–N(azo) and Ru–N(methine) distances of the azoimine ligand (1.940(3) and 2.026(2) Å) are shorter than Ru–N(bpy) lengths (average, 2.115 Å). This shortening may be due to the great π -back donation



Complex	CI	C2	C3	U 4	

Scheme 1. The chemical structures of ligand H₂Azo and complexes (C1-C4).

from Ru-d orbital to the empty π^* orbital of the azoimine ligand [25]. The Ru–N(bpy) distances are longer than those in the corresponding [Ru(bpy)₃]²⁺ complexes [26]. The average Ru–Cl bond lengths in C1 (2.374(9) Å) is comparable to those reported for similar systems [27]. The coordination geometry of the complex is distorted from regular octahedral as indicated from the bond angles [N(3)–Ru(1)–N(5), N(2)–Ru(1)–N(1) and Cl(1)–Ru(1)–Cl(2) are 76.23(10), 76.87(9) and 174.65(3), respectively].

3.3. Electrochemistry

Formal oxidation and reduction potentials of **C1–C4** versus NHE were obtained from cyclic voltammograms recorded at a platinum electrode in acetonitrile containing 0.1 M tetrabutylammonium hexaflurophospate (Table 3). Complex **C1**, as a representative example (Fig. 2), displays an irreversible reduction wave at -0.58 which is assigned to azo(0/-) ligand-centered processes. The reversible oxidation peak at 1.19 V, is attributed to the metal-centered Ru(III/II) couple. This couple is slightly affected by changing the bipyridine ligands by phenanthroline derivatives. However,

 Table 3

 Cyclic voltammetry and electronic spectroscopy data of trans-[RuCl₂(Azo)L] (C1-C4).^a

Complex	$(E^{o}_{1/2}, V)^{b}$	Azo(0/-) ^c	Electronic spectra λ_{max} (nm)
1	1.19	-0.58	513
2	1.13	-0.57	506
3	1.28	-0.50	513
4	1.23	-0.55	507

^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 $E^{o}_{1/2}{}^{M} = (E^{o}_{pa} + E^{o}_{pc})/2.$

^c The cathodic peak maximum.

the half-wave potential of earlier complex was shifted anodically by \sim 15 mV compared to those observed with later complexes. This relationship indicates that the donor ability of the phenanthroline ligands is slightly weaker than that of the bipyridine ligands [26]. The Ru(III/II) couple is slightly affected by changing the substituent on the phenanthroline and 2.2'-bipyrdine ligands.

Lever has developed an electrochemical parameterization method to calculate ruthenium(III/II) couples of complexes with octahedral geometry as shown in Eq. (1) [28]

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

where $\Sigma E_{\rm L}$ is the sum of electrochemical parameters for each ligand in the complex. The parameter $E_{\rm L}$ is a measure of the stabilizing effect a ligand has on the Ru(II) state and so the greater the magnitude of positive $E_{\rm L}$ the more positive the Ru(III/II) couple. Based on the previously found ($E_{\rm L}$ (bpy) = 0.259 [28], $E_{\rm L}$ (CI) = -0.24 [28]) and assuming ligand additivity, the Ru(III/II) couple for **C1** was used to find the ($E_{\rm L}$ (L)) for unreported (Azo) ligand and it was found to be 0.45 V. The large $E_{\rm L}$ value for Azo ($E_{\rm L}$ (Azo) = 0.45) suggests that this ligand is a stronger π -acid than bpy but it is almost the same as previously prepared Az ligand (Az = C₆H₅N=N-C(COCH₃)=NC₆H₅, $E_{\rm L}$ (Az) = 0.42 [4]).

3.4. Electronic structure

Theoretical calculations were performed on *trans*-[RuCl₂(Azo)L] (**C1–C4**); 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 for complex **C1** are shown in Fig. 3. Results indicate that the LUMOs are constructed mainly from the π^* orbital of azoimine (70%) and has 20% metal d-orbital character which



Fig. 2. Cyclic voltammogram for complex **C1** in acetonitrile 0.1 M TBAH at 25 $^{\circ}$ C, data reported in V vs. NHE with scan rate of 0.1 V/s.

suggests significant back donation [29]. The lower unoccupied molecular orbitals (LUMO+1 and LUMO+2) for these complexes consist mostly of a series of antibonding π^* orbital of bipyrdine and phenanthroline derivatives. The other group of HOMOs (HOMO to HOMO-2) can be described as t₂g Ru orbitals with small contributions from the azoimine and chloride ligands.

The lowest 20 singlet-to-singlet spin-allowed excitation states were taken into account for the calculation of the electronic

Table 4

absorption spectrum of **C1** (as representative example) 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. Both the experimental UV-Vis spectrum of C1 reported in acetonitrile and its simulated absorption spectrum shown in Fig. 4 are in good agreement for the band in the visible region whereas a blue shift for simulated absorption spectrum in the UV region is observed. The observed electronic absorption spectrum of C1 in acetonitrile is shown in Fig. 4. For the band in the visible region, TD-DFT calculations show that the band at λ_{max} = 513 nm which is detected experimentally (calculated at 510 nm) resulted from HOMO-1 (which has sizable contributions of $Ru(d\pi)$ orbitals mixed with chloride and azoimine orbitals) and HOMO-2 (which has sizable contributions of $Ru(d\pi)$ orbitals mixed with chloride orbitals) to LUMO which has a significant contribution from the π^* orbital of azomethine. Thus, this band is assigned to MLMLCT (metal-ligand to metal-ligand charge transfer). The near-UV region band centered at 439 nm (calculated) which appear as a shoulder in the experimental spectrum, arises mainly from the HOMO-3 which is mainly azoimine in character to LUMO, thus this band is assigned to LLCT or $\pi \rightarrow \pi^*$. The strong high energy band at 291 nm (calculated at 370 nm) resulted from HOMO-7, HOMO-8 and HOMO-9 which are mainly azoimine in character to LUMO. Thus, this band is assigned to LLCT or $\pi \to \pi^*$ too.

The MLCT band energy and Ru(III/II) couple for a Ru(II) mononuclear complex provide information about the relative energies of the complex's metal and ligand-based orbitals. The Ru(III/II) couple shifts to more positive potentials as the metal orbitals are

Relative percentages of atomic contributions to the lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO) of trans-[RuCl₂(Azo)L] (C1-C4).

C1 LUM0+6 -0.47 21 9 0 UM0+5 -0.77 2 19 0	69 78 22
LUMO+6 -0.47 21 9 0	69 78 22
LUM0+5077 2 19 0	78 22
	22
LUMO+4 –1.03 4 74 0	
LUMO+3 –1.15 59 7 25	8
LUMO+2 –1.16 3 92 1	3
LUMO+1 –2.0 5 90 0	4
LUMO –3.04 19 9 3	70
HOMO –5.44 67 3 21	9
HOMO-1 –5.94 46 1 30	22
HOMO-2 –6.12 69 3 2	26
HOMO-3 –6.57 10 3 8	78
HOMO-4 –6.82 1 53 2	44
HOMO-5 –6.94 0 11 7	81
HOMO-6 –6.97 1 16 4	79
2	
LUMO+2 –1.14 5 90 1	4
LUMO+1 –1.91 4 92 0	3
LUMO –3.01 20 7 3	70
HOMO –5.41 68 3 20	9
HOMO-1 –5.92 47 2 29	23
HOMO-2 –6.09 70 3 2	25
ß	
LUMO+2 –2.01 6 89 0	5
LUMO+1 –2.34 0 99 0	1
LUMO –3.06 19 9 3	69
HOMO –5.45 67 4 21	9
HOMO-1 –5.94 42 8 28	23
HOMO-2 –6.09 58 24 1	18
(4	
LUMO+2 –1.93 6 90 0	4
LUMO+1 –2.22 0 99 0	1
LUMO –3.02 19 8 3	70
HOMO –5.43 67 4 20	9
HOMO-1 –5.9 36 20 23	21
HOMO-2 –6.02 43 43 4	10



Fig. 3. Isodensity plots of the HOMO and LUMO orbitals of complex C1.

Table 5

Computed excitation energies (nm), electronic transition configurations and oscillator strengths (*f*) for the optical transitions in the visible region of complex **C1** (transitions with $f \ge 0.02$ are listed, H stands for HOMO and L for LUMO).

λ	f	
510	0.1386	H-2 → L (28%), H-1 → L (63%)
439	0.0796	H-3 → L (89%)
391	0.0283	H-4 \rightarrow L (72%), H-1 \rightarrow L+1 (11%), H-2 \rightarrow L+1 (8%)
375	0.028	H-5 \rightarrow L(37%), H-8 \rightarrow L (27%), H-2 \rightarrow L+1 (12%)
373	0.0429	H-7 \rightarrow L (35%), H-2 \rightarrow L+1 (20%), H-5 \rightarrow L (13%)
370	0.0806	H-7 \rightarrow LUMO (42%), H-8 \rightarrow LUMO (16%), H-2 \rightarrow L+1 (16%)
358	0.0289	H-9 \rightarrow L (56%), H-10 \rightarrow L (22%), H-5 \rightarrow L (7%)
346	0.0226	$\rm H \rightarrow L{+}4$ (46%), H-12 \rightarrow L (12%), H \rightarrow L+6 (8%)

stabilized [29]. For the *trans*-[RuCl₂(Azo)L], the bipyrdine ligands shifts the Ru(III/II) couple approximately ~15 mV negative relative to phenanthroline analogs. This stabilization, however, does not result in 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) (Table 4). The difference in the energy $\Delta E = E_{HOMO} - E_{LUMO}$ for all complexes is ~2.4 eV.

4. Conclusions

The crystallography and electrochemistry of *trans*-[RuCl₂(Azo)L] (**C1–C4**) where Azo = C_6H_5N =NC(C_6H_5)=NC₆ H_5 , and L is a substituted bipyridine and phenanthroline ligands show that the new



Fig. 4. Uv-visible spectrum for complex C1 in acetonitrile (black line). Inset shows simulated absorption spectrum (red line) based on TD-DFT calculations, compared to excitation energies and oscillator strengths.

Azo ligand, is a strong π -acceptor that coordinates as a bidentate ligand via imine and Azo nitrogens. The π -acceptor properties of Azo, as qualitatively measured against Lever's electrochemical parameter E_L , is almost equal to that of the previously studied azo-imine ligands (Az = C_6H_5N =NC(COCH₃)=NC₆H₅) but significantly greater than that of 2,2'-bipyridine. The electronic absorption spectra of these complexes show two strong bands in the visible and near UV–Vis regions in acetonitrile solution. These two bands are assigned to a (Ru(II)-to-azomethine) MLMLCT and LLCT transition based on TD-DFT calculations.

Acknowledgements

This paper was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under Grant No. (2-662-D1432). The authors, therefore, acknowledge with the thanks DSR technical and financial support.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.12.050.

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