Synthesis, structure and redox properties of isomeric $[\text{RuCl}_2(\text{L})_2]$ ($\text{L} = N$ -aryl-1,2-arylenediimine) complexes formed by the oxidative dimerization of coordinated aromatic amines

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Received 11 July 2001; accepted 4 October 2001

Abstract

The di-arylamino complex $[\text{RuCl}_2(\text{ArNH}_2)_2\text{L}]$ (ArNH_2 = aromatic monoamine and $\text{L} = N$ -aryl-1,2-diimino arene) reacts spontaneously with aqueous H_2O_2 to produce two isomers of $[\text{RuCl}_2(\text{L})_2]$ via oxidative dimerization of the two coordinated aromatic amines. The geometries of two isomers are *cis* with respect to two chlorides and are *trans*, *cis*(tc) and *cis*, *cis*(cc) in the following sequence: NH(imine), HN(imine) and ArN(imine), ArN(imine). Of the above two, the tc- $[\text{RuCl}_2(\text{L})_2]$ forms good X-ray quality crystals. The structure of a representative has been solved by X-ray diffraction. The geometry of the cc- $[\text{RuCl}_2(\text{L})_2]$ is, however, revealed by the spectral data. The tc-isomer possesses a C_2 -symmetry axis and the two-coordinated diimine ligands are magnetically equivalent. As a result, a single NH resonance in tc- $[\text{RuCl}_2(\text{L})_2]$ appeared at approximately δ 12.40. By contrast, the cc-isomer is unsymmetrical and a complex pattern of ^1H NMR was observed in this case. Thus, there were two NH resonances observed in the range approximately δ 14.11–11.88. A semi-empirical extended Hückel MO calculations on a representative example showed strong metal–ligand overlap. A highly intense electronic transition that appeared in the visible range spectra of the complexes was assigned to a transition involving two molecular orbitals with considerable metal and ligand contributions. Both the isomers of the complex showed a high potential anodic response (0.8 V) due to the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ couple. The trivalent congeners $[\text{RuCl}_2(\text{L})_2]^+$ were generated in solution which showed characteristic rhombic EPR for the low spin d^5 ions. The distortion parameters have been computed using the observed g values. The axial distortion (Δ) in each case is found to be stronger than the rhombic (V) distortion. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ruthenium promoted reactions; Dimerization of aromatic amines; 1,2-Diimine; Structures; Redox

1. Introduction

Metal complexes of redox non-innocent dioxolene ligand series together with their nitrogen analogues are of considerable interest [1–3] because of their exceptionally rich redox and spectroscopic behavior, which originate from a strong degree of orbital mixing between metal ($d\pi$) and ligand ($p\pi$) frontier orbitals. Since the first report [4] of the ruthenium complex of bqdi, $[\text{Ru}(\text{bqdi})_3](\text{PF}_6)_3$ (benzoquinonediimine) by Warren, the

ruthenium complexes of bqdi and its redox partners have been the focus of many recent studies [5,6].

As a part of our ongoing work [7,8] in the area of metal promoted assembly of diimine complexes based on oxidation of aromatic amines we report herein the synthesis [7c], characterization, crystal structure and redox properties of isomeric $\text{RuCl}_2(\text{L})_2$ ($\text{L} = N$ -aryl-1,2-arylenediimine). The diimine ligand L is generated in situ by the oxidative dimerization of two coordinated aromatic amines (Scheme 1). It is proposed that the metal ion mediates these transformations by holding the amine residues in close proximity and also by taking part in the redox processes. In the present study two di-arylamino complexes [7b] of ruthenium of gen-

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Scheme 1.

eral formula $[\text{RuCl}_2(\text{ArNH}_2)_2(\text{L})]$ were chosen for the study of oxidation reaction. Oxidative deprotonation [9] of coordinated aromatic amines leading to the formation of metal–imido complexes was known in the literature. However, oxidative dimerization of coordinated amines of above type has been noted by us only in the recent past [7]. Furthermore, the transformation described in this work represents an example of an oxidation reaction, which led to the oxidation of internal substrate. Such reactions are important but are scanty [10].

2. Experimental

The solvents and chemicals used for synthesis were of analytical grade. The supporting electrolyte tetraethylammonium perchlorate (TEAP) and solvents for electrochemical work were obtained as before [11].

2.1. Physical measurements

A Shimadzu UV 2100 UV–Vis spectrophotometer was used to record electronic spectra. The IR spectra recorded with a Perkin–Elmer 783 spectrophotometer. ^1H NMR spectra in CDCl_3 were recorded with a Bruker Advance DPX300 spectrophotometer. SiMe_4 was used as internal standard. A Perkin–Elmer 240C elemental analyzer was used to collect microanalytical data (C,H,N). Electrochemical measurements were performed under dry nitrogen with an EG&G PARC model 273A potentiostat/galvanostat based electrochemistry system. All potentials, reported in this work, are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contributions. EPR measurements were made with a Varian 109C E-line X-band spectrometer fitted with a flat cell. Spectra were calibrated with the help of DPPH ($g = 2.0037$). Electronic spectra were recorded on a JASCO V-570 spectrophotometer.

2.1.1. Synthesis of dianiline dichloro

N-phenyl-1,2-benzoquinone diimine ruthenium(II) $[\text{RuCl}_2(\text{L}^a)(\text{PhNH}_2)_2]$ (**1a**)

A sample of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.25 g, 0.95 mmol) was added to 0.5 ml of aniline, and the mixture was heated on an oil bath at 140°C for 30 min. The brown color changed gradually to violet and then an intense red

solution resulted. The crude mass was extracted with dichloromethane and was washed thoroughly with 1 M hydrochloric acid and finally washed with water. The acid free solution was dried over anhydrous sodium sulfate. Hexane was then layered over the red solution and after 2 days shiny brown crystals were obtained. Yield 60%. Calc. for $\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{N}_4\text{Ru}$ (540): C, 53.33; H, 4.44; N, 10.37. Anal. Found: C, 53.46; H, 4.50; N, 10.52%.

A similar reaction using *p*-toluidine instead of aniline afforded (**1b**) in 65% yield. Calc. for $\text{C}_{28}\text{H}_{32}\text{Cl}_2\text{N}_4\text{Ru}$ (596): C, 56.37; H, 5.37; N, 9.39. Anal. Found: C, 56.48; H, 5.27; N, 9.50%.

2.1.2. Synthesis of dichloro

bis(*N*-phenyl-1,2-benzoquinone diimine)ruthenium(II), *tc*- $[\text{RuCl}_2(\text{L}^a)_2]$ and *cc*- $[\text{RuCl}_2(\text{L}^a)_2]$ (**2a**)

To a dichloromethane solution of $[\text{RuCl}_2(\text{PhNH}_2)_2(\text{L}^a)] \cdot \text{CH}_2\text{Cl}_2$ (0.108 g, 0.2 mmol), 0.5 ml 30% weight/volume hydrogen peroxide solution was added and the mixture was stirred at room temperature for 30 min. An intense blue color resulted, which was evaporated at room temperature. The crude product, thus obtained, was purified on a TLC plate. Two intense blue bands moved with a 25% chloroform–acetonitrile mixture. The two geometrical isomers were collected by evaporation of the solvent at room temperature. The first blue isomer (*tc*-) was crystallized by slow diffusion of dichloromethane tetrahydrofuran solution of the complex into hexane. Analysis and yields of the two isomers are given below:

tc- $[\text{RuCl}_2(\text{L}^a)_2]$ (first blue), yield (35%). Calc. for $\text{C}_{24}\text{H}_{20}\text{N}_4\text{Cl}_2\text{Ru}$ (537): C, 53.63; H, 3.72; N, 10.43. Anal. Found: C, 53.65; H, 3.43; N, 10.52%.

cc- $[\text{RuCl}_2(\text{L}^a)_2]$ (second blue), yield (35%). Calc. for $\text{C}_{24}\text{H}_{20}\text{N}_4\text{Cl}_2\text{Ru}$ (537): C, 53.63; H, 3.72; N, 10.43. Anal. Found: C, 54.02; H, 3.33; N, 10.62%.

The *tc* and *cc* isomers of $[\text{RuCl}_2(\text{L}^b)_2]$ (**2b**) were similarly prepared following the above procedure.

tc- $[\text{RuCl}_2(\text{L}^b)_2]$, yield 32%. Calc. for $\text{C}_{28}\text{H}_{28}\text{N}_4\text{Cl}_2\text{Ru}$ (592): C, 56.76; H, 4.73; N, 9.46. Anal. Found: C, 56.85; H, 4.32; N, 9.45%.

cc- $[\text{RuCl}_2(\text{L}^b)_2]$, yield 32%. Calc. for $\text{C}_{28}\text{H}_{28}\text{N}_4\text{Cl}_2\text{Ru}$ (592): C, 56.76; H, 4.73; N, 9.46. Anal. Found: C, 56.76; H, 4.35; N, 9.36%.

2.2. Crystal structure determination

The crystallographic data for the compound *tc*- $[\text{RuCl}_2(\text{L}^a)_2]$ (**2a**) are collected in Table 1. Slow diffusion of a dichloromethane–THF solution of *tc*- $[\text{RuCl}_2(\text{L}^a)_2]$ in hexane yielded thin needle like crystals ($0.50 \times 0.05 \times 0.04 \text{ mm}^3$). Intensity data were collected on a SMART CCD diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.7107$

Table 1
Crystallographic data for [RuCl₂(L^a)₂].THF

Empirical formula	C ₂₈ H ₂₈ Cl ₂ N ₄ ORu
<i>M_r</i>	608.51
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	11.5638(7)
<i>b</i> (Å)	20.5507(11)
<i>c</i> (Å)	11.8331(7)
<i>β</i> (°)	96.062(2)
<i>U</i> (Å ³)	2796.3(3)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ^{−3})	1.445
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0698
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1520
Goodness-of-fit	1.033

Å). A total of 13 424 unique reflections were collected and 5719 with *I* ≥ 2σ(*I*) were used in the refinement [12]. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to *R* = 0.0698. The final Fourier difference maps showed residual extrema at 0.591, −0.570 e Å^{−3}.

3. Results and discussion

3.1. The starting compounds and synthesis

Hydrated ruthenium(III) chloride reacts [7b] with neat ArNH₂ at 130 °C to yield the brown complex, [RuCl₂(ArNH₂)₂L] [ArNH₂ = aniline, L = L^a and ArNH₂ = *p*-toluidine, L = L^b, Eq. (1)], which was used as the starting complex for carrying out the synthesis.

ArNH ₂	L	1
aniline	L ^a	1a
<i>p</i> -toluidine	L ^b	1b

Table 2
IR and NMR data

Compound	IR ^a (cm ^{−1})			¹ H NMR ^b (ppm)	
	ν(N–H)	ν(C=N)	ν(Ru–Cl)	δ Me	δ N–H(imine)
tc-[RuCl ₂ (L ^a) ₂]	3160	1540	360, 350		12.47
cc-[RuCl ₂ (L ^a) ₂]	3150	1545	360, 355		12.46, 12.00
tc-[RuCl ₂ (L ^b) ₂]	3160	1550	360, 345	2.33, 2.023	12.33
cc-[RuCl ₂ (L ^b) ₂]	3165	1560	360, 340	2.38, 2.32, 2.03, 1.94	14.11, 11.88
[RuCl ₂ (ArNH ₂) ₂ (L ^a)] ^c	3300, 3100	1580	360, 340		14.66
[RuCl ₂ (ArNH ₂) ₂ (L ^b)] ^c	3310, 3140	1580	350, 340	2.17, 2.08, 1.97, 1.96	14.51

^a In KBr.

^b In CDCl₃.

^c δN–H(–NH₂) appeared at 5.09, 4.84; 5.07, 4.80 ppm.

The complex **1** is poorly soluble in common organic solvents. A suspension of **1** in CH₂Cl₂, however, reacts instantaneously [7c] with 5% aqueous H₂O₂ at room temperature (300 K) to afford [RuCl₂L₂] (**2**) (Eq. (2)):

Preliminary work up followed by chromatographic purification yielded the two geometrical isomers of [RuCl₂L₂] (vide infra). In this reaction, the two coordinated amine residues have undergone oxidative coupling to give a 1,2-diamino ligand. This transformation, **1** → **2** is a combination of many operations: (i) isomerization of the starting complex **1** in order to bring two ArNH₂ in close proximity (*trans* → *cis*); (ii) oxidative coupling of two ArNH₂ residues to *ortho*-semidine (C–N bond making); and (iii) further oxidative dehydrogenation, *ortho*-semidine → 1,2-diimine (diamine → diimine).

3.2. Formulation and spectral characterization of isomeric [RuCl₂(L)₂]

The crude product, obtained from the reaction (1), contained two major blue fractions, which were separated on a preparative TLC plate. These were obtained in almost identical yields (ca. 35% each). FAB mass spectra of these two compounds are nearly identical which indeed confirm that these two are isomers. Due to the unsymmetric nature of L, there exist [13] five geometrical possibilities for [RuCl₂L₂]. The present complexes are characterized by two sharp and medium Ru–Cl stretches in the region 310–350 cm^{−1} (Table 2). Thus, the RuCl₂ fragments in these complexes are *cis* and three geometries A–C are possible (Scheme 2). The relative orientations (*trans/cis*) of the coordinated imine nitrogen atoms [N(H), N(H)] and aryl substituted imine nitrogen atoms [N(Ar), N(Ar)] in the isomeric [RuCl₂(L)₂] are *trans*, *cis* and *cis*, *cis* respectively (vide infra). We shall refer these two isomers as tc- (first blue) and cc- (second blue) isomers. Of the above two com-

pounds, the $\text{tc-}[\text{RuCl}_2(\text{L}^a)_2]$ formed suitable crystals for X-ray structure determination. The geometry of the cc-isomer was however, revealed by the spectral data.

The complexes showed well resolved ^1H NMR spectra in CDCl_3 at 300 MHz, chemical shift data are listed in (Table 2) and the spectra of two representatives are shown in Fig. 1. The spectrum of the tc-isomer is simpler than that of the cc-isomer. Each kind of proton in the tc-isomer gave rise to only one signal (singlet or multiplet), which indicates that the two L ligands in this isomer are magnetically equivalent. By contrast, the corresponding cc-isomer showed two signals for each kind of protons. In this geometry the two ligands are magnetically inequivalent and their spectral pattern is as expected. For comparison, while the $\text{tc-}[\text{RuCl}_2\text{L}_2]$ showed only one NH resonance [7d] at δ 12.40, the

Fig. 2. Molecular structure and atom numbering scheme for $\text{tc-}[\text{RuCl}_2(\text{L}^a)_2]$.

corresponding $\text{cc-}[\text{RuCl}_2\text{L}_2]$ displayed two such resonances at approximately δ 14.11 and 11.88. The two isomers of the complex with methyl substituted ligand, $[\text{RuCl}_2(\text{L}^b)_2]$ showed two (tc-) and four (cc-) methyl resonances, respectively, in the range δ 2.38–1.94. The ^1H NMR together with the IR spectral data, thus confirms the geometries of the two isomers of $[\text{RuCl}_2\text{L}_2]$.

Fig. 1. NMR spectra of (a) $\text{tc-}[\text{RuCl}_2(\text{L}^b)_2]$ and (b) $\text{cc-}[\text{RuCl}_2(\text{L}^b)_2]$ in CDCl_3 . Inset: resonances due to methyl protons.

3.3. Crystal structure, *tc*-[RuCl₂(L^a)₂]

The first blue fraction of RuCl₂(L^a)₂ formed suitable X-ray quality crystals for structure determination. A view of the molecule is shown in Fig. 2, which shows that one of the *N*-phenyl rings is disorder. Selected bond parameters are collected in (Table 3). The coordination sphere involves RuCl₂N₄. Two chlorides are *cis* to each other and the aryl substituted imine nitrogens are also in relative *cis* positions. The imine C–N bond lengths, average 1.316 Å are within the range of values expected for the diimine oxidation state of L [5e,7]. These bonds are much shorter than the two C–N single bonds, viz. C(7)–N(2) and C(19)–N(4), average 1.434 Å. Moreover, the C–C lengths (average 1.348 Å) at positions that would have localized double bond for the diimine form of the ligands are significantly shorter than the other C–C lengths (average 1.432 Å) in the same ring. The Ru–Cl lengths in this complex compare well with the corresponding lengths in the related complexes. The overall gross structural features of this conforms well with those of a related osmium(II) complex [7a], *tc*-[OsBr₂(L^a)₂]. Moreover, the average of Ru–N lengths in the present complex (average 1.995 Å) significantly smaller than Ru^{II}–N single bonds. For comparison, the Ru–N bond distances [10,11] in Ru^{II}–NH₃ and Ru^{II}–bpy (bpy = 2,2′-bipyridine) lie in the range 2.14–2.06 Å; which are appreciably longer than [9,12] Ru(II)–N(azo) lengths (ca. 1.98 Å) in [RuCl₂(pap)₂] complex where very strong metal (dπ) and ligand (pπ) interactions were noted. Thus the short Ru–N distances in the *tc*-[RuCl₂(L^a)₂] complex confirms strong dπ–pπ interactions. This effect has also been reflected in the high metal based anodic potentials (vide infra).

3.4. Electronic spectra and redox properties

From the crystallographic data it is obvious that in the ruthenium complexes, under consideration, there exist strong metal–ligand dπ–pπ interactions. In order

Table 3
Selected bond lengths (Å) for *tc*-[RuCl₂(L^a)₂]

Ru–Cl(1)	2.402(2)	C(1)–C(2)	1.429(9)
Ru–Cl(2)	2.388(2)	C(2)–C(3)	1.360(10)
Ru–N(1)	1.996(5)	C(3)–C(4)	1.422(11)
Ru–N(2)	2.005(5)	C(4)–C(5)	1.337(11)
Ru–N(3)	1.982(6)	C(5)–C(6)	1.413(9)
Ru–N(4)	1.999(6)	C(6)–C(1)	1.453(9)
C(1)–N(1)	1.314(8)	C(13)–C(14)	1.429(12)
C(6)–N(2)	1.333(8)	C(14)–C(15)	1.332(14)
C(13)–N(3)	1.302(10)	C(15)–C(16)	1.420(2)
C(18)–N(4)	1.314(9)	C(16)–C(17)	1.362(14)
C(7)–N(2)	1.436(9)	C(17)–C(18)	1.445(11)
C(19)–N(4)	1.432(8)	C(18)–C(13)	1.447(10)

to have some insight into the nature of redox and spectroscopically relevant orbitals, a standard extended Hückel MO calculation using the crystallographic parameters was performed on *tc*-[RuCl₂(L^a)₂] using the CACAO programme [14] by Mealli and Proserpio. A partial energy level scheme is shown in Fig. 3. In this complex, the molecular orbitals, LUMO and HOMO-1 are heavily mixed orbitals where as HOMO is almost a pure ruthenium orbital. Pictorial representations of these three molecular orbitals are deposited as supplementary information.

The electronic spectral data are collected in (Table 4). Two representative spectra of isomeric (*tc*- and *cc*-) [RuCl₂(L^a)₂] are shown in Fig. 4. There are two major transitions in the range 1600–250 nm. The lowest energy transitions, occurring in the near IR region, is weak (λ, ca. 950 nm; ε, ca. 950 M^{–1} cm^{–1}) and broad compared to the next highly intense transition (λ, ca. 600 nm; ε, ca. 23 100 M^{–1} cm^{–1}) in the visible region. However, the intensity of NIR transition for the present complex is too intense for a d–d transition. This transition may be ascribed to HOMO Ru(dπ) → LUMO transition. The next highly intense transition at approximately 590 nm is due to a transition between two heavily mixed metal–ligand orbitals, LUMO and HOMO-1. This type of transitions are known to exist in other related complexes [7d,15] and their intensities are

Fig. 3. Partial energy level diagram of *tc*-[RuCl₂(L^a)₂].

Table 4
Electronic spectral data

Compound	Absorption ^a λ_{max} [nm (ϵ ($\text{M}^{-1}\text{cm}^{-1}$))]
tc-[RuCl ₂ (L ^a) ₂]	948 ^b (950), 590 (22682), 486 ^b (6993), 432 ^b (5748)
cc-[RuCl ₂ (L ^a) ₂]	970 ^b (942), 598 (23124), 482 ^b (6350), 432 ^b (5642)
tc-[RuCl ₂ (L ^b) ₂]	930 ^b (850), 592 (19500), 475 ^b (9580), 406 ^b (9933)
cc-[RuCl ₂ (L ^b) ₂]	930 ^b (840), 598 (20100), 476 ^b (9240), 419 ^b (9870)
[RuCl ₂ (ArNH ₂) ₂ (L ^a)]	585 ^b (2070), 492 (6840), 365 (2650)
[RuCl ₂ (ArNH ₂) ₂ (L ^b)]	590 ^b (6750), 495 (15350), 380 (5390)

^a Data obtained from absorption spectra.

^b Shoulder.

Fig. 4. Solution spectra of tc-[RuCl₂(L^a)₂] (—) and cc-[RuCl₂(L^a)₂] (---) in dichloromethane.

Table 5
Cyclic voltammetric data

Compound	Oxidation $E_{1/2}$ (V) ^a	Reduction $E_{1/2}$ (V) ^a
tc-[RuCl ₂ (L ^a) ₂]	0.81	−0.66 ^b , −1.41 ^b
cc-[RuCl ₂ (L ^a) ₂]	0.80	−0.65 ^b , −1.41 ^b
tc-[RuCl ₂ (L ^b) ₂]	0.70	−0.75 ^b , −1.48 ^b
cc-[RuCl ₂ (L ^b) ₂]	0.70	−0.78 ^b , −1.55 ^b
[RuCl ₂ (ArNH ₂) ₂ (L ^a)]	0.60	−0.73 ^b
[RuCl ₂ (ArNH ₂) ₂ (L ^b)]	0.52	−0.82 ^b

^a Experiments were carried out in CH₃CN at 298 K using TEAP as supporting electrolyte. The reported data correspond to a scan rate of 50 mV s^{−1}.

^b Irreversible cathodic response, the potential corresponds to E_{pc} .

generally very high. For example, a similar transition at approximately 620 nm was noted [7a] for a related osmium complex, [OsBr₂(L^a)₂]. The spectral patterns of the two isomers of [RuCl₂(L)₂] are nearly identical

except the minor differences in band positions and intensities.

The redox properties of the ruthenium complexes have been studied by cyclic voltammetry with a platinum-working electrode in the range 1.8 to −1.5 V. Voltammetric data are collected in (Table 5) and representative voltammograms are displayed in Fig. 5. All the potentials are referenced to the saturated calomel electrode (SCE). Both the isomers of [RuCl₂(L)₂] show almost identical voltammograms. The difference in geometry seems to have negligible effects on the redox potentials. The complexes exhibited a reversible anodic response near 0.80 V and two irreversible cathodic responses in the potential range −0.60 to −1.60 V. The oxidation process in these complexes occurs at HOMO, which is primarily a metal orbital. One-electron coulometric oxidation of both the isomers of [RuCl₂(L^a)₂] afforded reddish-brown solutions. The voltammograms of the electrogenerated trivalent complexes are superposable (initial scan cathodic) on those of the corresponding isomers of [RuCl₂(L^a)₂] (initial scan anodic) showing that the metal redox processes are reversible. The EPR of the Ru(III) complexes were studied in acetonitrile-toluene glass at 77 K, which display rhombic EPR spectra with three distinct resonances (Table 6). The spectrum of a representative example cc-[RuCl₂(L^a)₂]⁺ is shown in Fig. 6. The trivalent ruthenium complexes may also be generated by the chemical oxidation of the bivalent complexes by Br₂. Unfortunately, the oxidized complexes are not stable

Fig. 5. Cyclic voltammograms (scan rate 50 mV s^{−1}, solvent CH₃CN, 0.1 M TEAP) of tc-[RuCl₂(L^a)₂] (—) and cc-[RuCl₂(L^a)₂] (---).

Table 6
EPR g -values ^a and derived parameters of the complex [RuCl₂(L^a)₂]⁺

Compound	Derived energy parameters ^b (cm ^{−1})				
	g_1	g_2	g_3	Δ	V
tc-[RuCl ₂ (L ^a) ₂] ⁺	2.404	2.256	1.882	5529	2014
cc-[RuCl ₂ (L ^a) ₂] ⁺	2.469	2.272	1.909	6676	3136

^a In 1:1 dichloromethane-toluene solution at 77 K.

^b Taking the value of the spin-orbit coupling constant (λ) for Ru(III) as equal to 1000 cm^{−1}.

Fig. 6. EPR spectrum of $cc\text{-}[\text{RuCl}_2(\text{L}^{\text{A}})_2]^+$ in frozen 1:1 dichloromethane–toluene solution at 77 K, showing computed splittings of t_2 orbitals. DPPH = diphenylpicrylhydrazyl.

enough for their isolation. They revert to the parent divalent complexes rapidly. The observed rhombicity of the EPR spectra in the present cases is understandable in terms of the gross molecular symmetry of these complexes, containing three non-equivalent axes. The distortion parameters have been computed [16] using the observed g values. The axial distortion (Δ , which splits t_2 into a and e) is indeed much stronger than the rhombic distortion (V , which splits e). Thus the EPR spectral data of the complexes indicate significant distortion from ideal octahedral arrangements which indeed in line with the observed structure of the parent bivalent complexes.

In conclusion it may be stated that the present work further demonstrates that aromatic primary amines are susceptible to metal mediated oxidative dimerization processes via the formation of a C–N bond. The isomeric complexes, RuCl_2L_2 , thus formed, represent an interesting family of ruthenium–diimines that show strong metal $d(\pi)$ –ligand $p(\pi)$ interactions. Chemical reactions including the chloride substitution at $[\text{RuCl}_2(\text{L})_2]$ are now under scrutiny.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 160040. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

Acknowledgements

Financial support received from the Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged.

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