Synthesis and properties of mixed chelates of ruthenium containing 1,2-diimine, 1,2-iminoquinone and dioxolene ligands

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Received 16 May 2001; revised 1 August 2001

The reaction of RuCl₂(PhNH₂)₂(L'₁) with 3,5-ditertiarybutylcatechol affords a blue RuCl₂(PhNH₂)₂(L'₁), 1 (L'₁=N-aryl-1,2-arenoquinomediimine) with 3,5-ditertiarybutylcatechol and a violet RuCl₂(PhNH₂)₂(L'₁), 2 (L'₁=N-phenyl-3,5-ditertiarybutyl) 1,2-benzoquinonediimine and a violet RuCl₂(PhNH₂)₂(L'₁), 3 (L'₁=3,5-ditertiarybutyl-1,2-semiquinone) compounds. These have been isolated in their pure states by column chromatography. The complexes have been fully characterized and their physicochemical data are reported. While the complex 2 displays two methyl resonances, the complex 3 shows four such signals as expected. Solution spectra of the complexes consist of multiple transitions. The most intense visible range transition for 2 appears at 625 nm, which is blue shifted to 520 nm in 3. These transitions involve the orbitals that have both metal and ligand characters. Cyclic voltammetry of these complexes has been studied. Metal redox associated with multiple ligand based responses are observed.

Metal complexes of the reoxy non-innocent quinone related ligands have been the subject of considerable interest because of their exceptionally rich redox and spectroscopic behaviour: intramolecular electron transfer and the oxidation state formalism for highly delocalised systems. These phenomena are related to a strong degree of orbital mixing between metal (dχr) and ligand (pχt) frontier orbitals which can render conventional oxidation state assignments difficult. The ruthenium complexes of 1,2-benzoquinone diimine (bqdi; N,N donor) and its reoxy partners have been the focus of many recent studies. However, the complexes of 1,2-benzoquinonediimine (bqi, N, O donor) have been scarce in the literature. Herein we wish to introduce an example of a mixed ligand bis-chelated complex of ruthenium containing N-aryl bqdi and N-aryl bqj ligands. To the best of our knowledge such a mixed ligand complex is not reported in the literature. It was obtained from an unusual metal promoted reaction of a ruthenated aniline complex. Another mixed ligand complex of the diimine and dioxolene ligand was also isolated from the reaction as a byproduct. The present work describes synthesis and studies of physicochemical properties of two mixed ligand quinone related complexes. A preliminary communication on this reaction was reported by us.

Experimental

Hydrated ruthenium trichloride was obtained from Arora Matthey, Kolkata and 3,5-ditertiarybutylcatechol was an Aldrich reagent. Tetrakis(oxymercury(II) perchlorate (TEAP) was prepared and recrystallized as reported earlier. All other chemicals and solvents were of reagent grade and used as received.

A Shimadzu UV-2100 uv/vis spectrophotometer was used to record electronic spectra. The IR spectra were obtained using a Perkin-Elmer 783 spectrophotometer, 1H NMR spectra were recorded in CDCl₃ using a Bruker-Avance DPX300 spectrometer and SiMe₄ as an internal standard. A Perkin-Elmer 240C elemental analyser was used to collect microanalytical data (C, H, N). Electrochemical measurements were performed under a dry nitrogen atmosphere on a PAR model 273-A electrochemistry system as described earlier. All potentials reported in this work are referenced to Ag/AgCl and are uncorrected for junction contribution.

Syntheses of complexes

Dianilinedichloro[N-phenyl-1,2-benzoquinonediimine]ruthenium(II), [RuCl₂(PhNH₂)₂(L'₁)]. I

A sample of RuCl₃,3H₂O (0.25g, 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 initial brown
colour gradually changed to violet and then an intense red colour developed. The crude mass was extracted with dichloromethane and was washed thoroughly with 1 M hydrochloric acid. The solution was finally washed with water, and dried over anhydrous sodium sulphate and finally crystallized from a dichloromethane-hexane (1:2) mixture. Yield and the analytical data for 1 are as follows:

1: Yield (60%). [Found: C, 53.46; H, 4.50; N, 10.52. Calc. For C\textsubscript{24}H\textsubscript{24}Cl\textsubscript{2}N\textsubscript{4}Ru: C, 53.33; H, 4.44; N, 10.37%.] IR(KBr): \(v(\text{N-H})\) 3300, 3100, \(v(\text{C=N})\) 1580, \(v(\text{C=C})\) 1600, \(v(\text{Ru-Cl})\) 360, 340 cm\(^{-1}\).

Dichloro[\text{N-phenyl-(3,5-ditertiarybutyl)-1,2-benzoquinoneimine}\text{][N-phenyl-1,2-benzoquinonedimine}\text{]ruthenium(II)}, \([\text{RuCl}_2(\text{L}^1)\text{]}\), 2 and bis[3,5-ditertiarybutyl semiquinone][\text{N-phenyl-1,2-benzoquinonedimine}\text{]ruthenium(II)}, \([\text{Ru}(\text{L}^1)(\text{L}^2)_2]\), 3

To a methanolic solution (10 ml) of 3,5-ditertiarybutylcatechol (0.67 g, 3 mmol), the compound, \([\text{RuCl}_2(\text{PhNH}_2)(\text{L}^1)\]), 1 (0.54 g, 1 mmol) was added and the mixture was stirred for 12 hr at room temperature. After evaporation of solvent, the crude mass was dissolved in chloroform and the compounds 2 and 3 were purified on a silica gel column. A minor violet band was first eluted with chloroform. Evaporation of the violet solution yielded the compound 3. This was finally crystallized from a chloroform-hexane (1:2) mixture. Subsequently, a blue band was eluted with 10:1 chloroform-acetonitrile mixture. Evaporation of solvent of the blue fraction followed by crystallization from a (1:2) dichloromethane-hexane mixture afforded crystalline 2 in a moderate yield. Yields and the analytical data for 2 and 3 are as follows:

2: Yield (60%). [Found: C, 59.53; H, 5.73; N, 6.23. Calc. for C\textsubscript{32}H\textsubscript{35}Cl\textsubscript{2}N\textsubscript{3}O\textsubscript{2}Ru: C, 59.16; H, 5.39; N, 6.47%] IR(KBr): \(v(\text{N-H})\) 2940, \(v(\text{C=O})\) 1525, \(v(\text{C=O})\) 1600, \(v(\text{C1})\) 320, 315 cm\(^{-1}\).

3: Yield (10%). [Found: C, 66.68; H, 6.67; N, 3.87. Calc. for C\textsubscript{40}H\textsubscript{38}O\textsubscript{2}N\textsubscript{2}Ru: C, 66.38; H, 6.50; N, 3.87%] IR(KBr): \(v(\text{N-H})\) 2950, \(v(\text{C=N})\) 1525, \(v(\text{C=O})\) 1580 cm\(^{-1}\).

**Results and discussion**

The synthesis and X-ray structural characterization of the starting diamine complex, \([\text{RuCl}_2(\text{PhNH}_2)_2(\text{L}^1)]\), 1 was reported recently by us\textsuperscript{7}. We were interested in studying the reactions of coordinated aniline in 1. Accordingly, this compound was reacted with 3,5-ditertiarybutylcatechol at room temperature (300K), which produced an intense blue solution. The crude mixture, upon chromatographic purification, produced a blue (2; major, 60%) and a violet (3; minor, 10%) compounds (Scheme 1). The compound 2 formed X-ray quality crystals for structure determination. However, identity of the product, 3 was based on elemental analysis and other physicochemical data. The formation of 3 is essentially the result of substitution of labile ligands in 1 by the two semiquinone (O, O) donors. The formation of the major blue product is of interest. It involves the coupling of a coordinated PhNH\textsubscript{2} with 3,5-ditertiarybutylcatechol with the formation of a new C-N bond. It is believed that oxidation of catechol to quinone followed by Schiff-base condensation with one of the two coordinated anilines are the key steps of the above mediated transformations.

![Scheme 1](image)

The compounds 2 and 3 are freely soluble in common organic solvents and are diamagnetic. The methyl and NH (imine) resonances have been used for the formulation of the above products. The aromatic proton resonances are complex due to serious overlap. However, the compound 3 displayed four methyl resonances, the compound 2 on the other hand showed two methyl resonances. Compounds 2 and 3
NOTES

Table 1—Spectral and electrochemical data

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H NMR data (ppm)</th>
<th>$\lambda_{max}$, nm $^a$ (E/M cm$^{-1}$)</th>
<th>$E_{1/2}$, V($E_{Ea}$, mV$^a$)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$\delta$NH $\delta$CH$_3$ Aromatic Protons ($\delta$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>12.90 0.99, 1.27</td>
<td>6.0-7.8</td>
<td>1.03(80), -0.35$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1090(1100), 625(15195), 370(4725),</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>335(3350)</td>
<td>-0.68$^f$, -1.20$^f$</td>
</tr>
<tr>
<td>3</td>
<td>11.61 0.81, 1.13, 1.14, 1.26</td>
<td>5.0-7.6</td>
<td>0.96(120), 0.54(70), -0.34(80), -0.80(100)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1250(540), 1550(370), 675(4500), 520(7380), 425(3985)</td>
<td></td>
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</table>

$^a$ Solvent, CDCl$_3$, SiMe$_4$ as internal standard. Aromatic proton resonances for 2 occur between 6.0 and 7.8 $\delta$. For 3 aromatic proton resonances occur between 5.0 and 7.6 $\delta$. $^b$ Solvent CH$_3$CN. $^c$ Shoulder. $^d$ Conditions: solvent, acetonitrile, supporting electrolyte, NEt$_4$ClO$_4$ (0.1 M); Working electrode, platinum; reference electrode, Ag-AgCl; solution concentration, 10$^{-3}$ M. $^e$ $E_{1/2}$ is calculated as the average of anodic ($E_{Ea}$) and cathodic ($E_{Ep}$) peak potentials; $\Delta E_{Ep}=(E_{Ep}-E_{Ea})$. $^f$ Irreversible $E_{Ep}$.

also displayed one broad NH resonance$^g$ at 12.90 and 11.61 $\delta$ respectively. Thus, the $^1$H NMR spectral data are consistent with the above formulations. The question of the charge distributions in these compounds is important. In principle, there could be a number of possibilities. The bond lengths$^1$ in 2 clearly indicated the presence of the oxidized forms of the N, N and N, O ligands. Unfortunately, we have not been able to grow X-ray quality crystal of 3 for its structure determination. However, if it is assumed that the oxidation states of the N, N donor (L$^1$) and the central ruthenium metal have not changed during the course of the synthetic reaction, the plausible composition of the violet compound may be best described as shown in 3 (Scheme 1). In this compound it is proposed that the two O, O- donors are in their semiquinone oxidation states and the central ruthenium is bivalent. Notably, our proposition is analogous to the proposed charge distributions in the previously reported$^{13}$ similar compounds, [Ru(bpy)(dpsq)$_2$] and [Ru(PPPh$_3$)$_2$(dpsq)$_2$] [bpy=2,2'-bipyridine and dpsq=3,5-di-tert-butylsemiquinato].

The electronic spectrum of 3 is more complex than that of 2. The spectrum of 2 displayed a moderately intense band at 1090 nm and a strong visible range charge transfer transition at 625 nm. The visible range spectrum of 3 consisted of a strong absorption 520 nm which was associated with a shoulder at 675 nm. The strong visible range absorptions in related diimine complexes have been assigned to transitions involving$^k$ molecular orbitals that have considerable metal and ligand character. The low energy visible range transitions in 2 and 3 are presumably$^l$ due to metal to ligand transfer (HOMO $\rightarrow$ LUMO).

Fig. 1—Cyclic voltammogram of the compound 2 in CH$_3$CN using a platinum working electrode: (a) anodic scan. (b) cathodic scan.
The redox properties of the complexes 2 and 3 were studied by cyclic voltammetry (CV) with a platinum working electrode. Voltammetric data are collected in Table I and representative voltammograms are displayed in Fig. 1. The complex 2 showed four responses in the range +1.5 to -2.0 V. Three of these are cathodic, while the fourth occurring at 1.03 V is reversible and anodic. The anodic response is assigned to a Ru^{III}/Ru^{II} process and the cathodic waves are due to reductions of coordinated ligands. It is known that each of the coordinated organic ligands, under consideration, can undergo two-step reductions. The voltammetric behaviour of 3 is similar to that of the redox series of [Ru(bpy)(dpsq)2] and [Ru(PPh3)2(dpsq)2]. There are two anodic responses, which are associated with two cathodic responses in the aforesaid potential range. The least potential reversible anodic wave at 0.54 V is due to a Ru^{III}/Ru^{II} couple in 3.

In conclusion it may be stated that we have described herein a novel chemical reaction of a coordinated aniline to ruthenium center. Oxidative dehydrogenation of coordinated aniline in 1 forms an amido complex whose chemical reactivities are now under active search.

Acknowledgement

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

References