Synthesis and characterization of ruthenium(II) Schiff base carbonyl complexes

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Complexes of ruthenium(II) with tetradentate Schiff base ligands derived by the condensation of ethylenediamine and o-phenylenediamine with 3-, 4- and 5-methoxy, 5-chloro- and 3,5-dichloro-salicylaldehyde have been synthesized. The complexes have been characterized by elemental analysis, IR, UV-visible and $^1$H NMR studies.

The interaction of small molecules such as CO and $O_2$ with transition metal complexes particularly those containing a ruthenium metal center coordinated to nitrogen and oxygen donor ligands has attracted a great deal of interest in recent years.

In addition, the chemistry of chelating tetradentate Schiff base ligands with ruthenium has also been extensively studied. The complex bis(salicylaldehyde)-o-phenylenediaminodichloro-ruthenate(III) has been successfully utilized as a potential catalyst in carbylation, hydroformylation and oxidation reactions. Bis(salicylaldehyde)ethyleneimine-ruthenate(III) complex has also been employed as a catalyst in oxidation of various hydrocarbons.

Carbonyl complexes of ruthenium play an important role in homogeneous catalysis. Most of the investigations on metal carbonyls are restricted to lower oxidation states of metals which are stabilised by CO. Chlororuthenate(II) complexes readily react with carbon monoxide in acidic medium to form chlorocarbonyl species. In aqueous HCl, Ru(II) chloride reacts with formic acid to yield the aquochlorocarbonyl complex $[RuCl_4(CO)(H_2O)]^2-$. In our continuing efforts to synthesise and characterise ruthenium complexes by using simple and inexpensive Schiff base ligands we report in this paper the synthesis of a series of ruthenium(II) Schiff base carbonyl complexes of the type $[Ru^{II}L(CO)]$ where $L=$ Schiff base derived by the condensation of salicylaldehyde, 3-, 4- and 5-methoxy-, 5-chloro- and 3,5-dichloro substituted salicylaldehydes with ethylenediamine and o-phenylenediamine.

Experimental

RuCl$_3$.H$_2$O (Johnson-Mathey), salicylaldehyde, 3-methoxysalicylaldehyde, 4-methoxysalicylaldehyde, 5-methoxysalicylaldehyde, 5-chlorosalicylaldehyde, 3,5-dichlorosalicylaldehyde (Aldrich), ethylenediamine (Fluka) were used as such. o-Phenylenediamine (Alpha) was recrystallised twice from benzene prior to use. The Schiff bases derived from salicylaldehyde, 3-methoxysalicylaldehyde, 4-methoxysalicylaldehyde, 5-methoxysalicylaldehyde, 5-chlorosalicylaldehyde, 3,5-dichlorosalicylaldehyde and ethylenediamine or o-phenylenediamine were prepared by known procedure. The complex $Cs_2[RuCl_4(CO)(H_2O)]$ was prepared according to the reported method. All the complexes were prepared under an inert atmosphere by Schlenk tube technique.

Elemental analyses of the complexes were done on a Carlo Erba analyser model 1106. Molar conductances were measured at room temperature on a Digisun electronic conductivity bridge. The electronic spectra were recorded on a Shimadzu UV-visible spectrophotometer model 160. IR spectra were recorded on a Specord M-80 Carl Zeiss Jena spectrophotometer in KBr. The $^1$H NMR spectra were recorded at 99.55 MHz on a Jeol FX-100 FT NMR instrument, in the indicated solvent. Proton chemical shifts are positive down field relative to standard tetramethylsilane.

Preparation of complexes

(1) Bis(salicylaldehyde)ethyleneiminocarboxylruthenium(II), (2) bis(3-methoxysalicylaldehyde)ethyleneiminocarbonylruthenium(II), (3) bis(4-methoxysalicylaldehyde)ethyleneiminocarbonylruthenium(II), (4) bis(5-methoxysalicylaldehyde)ethyleneiminocarbonylruthenium(II), (5) bis(5-chlorosalicylaldehyde)ethyleneiminocarbonylruthenium(II), (6) bis(3,5-dichlorosalicylaldehyde)ethyleneiminocarbonylruthenium(II), (7) bis(salicylaldehyde)-o-phenylenedimino-carbonylruthenium(II), (8) bis(3-methoxysalicylaldehyde)-o-phenylenedimino-carbonylruthenium(II), (9) bis(4-methoxysalicylaldehyde)-o-phenylenedimino-carbonylruthenium(II), (10) bis(5-methoxysalicylaldehyde)-o-phenylenedimino-carbonylruthenium(II), (11) bis(5-chlorosalicylaldehyde)-o-phenylenedimino-carbonylruthenium(II) and (12)
The following general procedure was used for preparing complexes 1-12.

To a hot methanolic solution of ligand (1 mmol), the complex \( \text{Cs}_2[\text{RuCl}_4(\text{CO})(\text{H}_2\text{O})] \) (1 mmol) was added in small portions. The reaction mixture was refluxed for 12-14 hr in an argon atmosphere. The completion of the reaction was checked by TLC and the reaction mixture filtered in argon atmosphere in order to remove liberated CsCl. The filtrate was concentrated to about 10 ml and the complexes were precipitated by diethyl ether. The complexes were recrystallised from the same solvent and dried in vacuo; yield 60-65%.

Results and discussion

The analytical data of all ruthenium(II) Schiff base carbonyl complexes (Table 1) are in agreement with the general formula \([\text{Ru}^{II}L(\text{CO})]\) where \( L = \text{Schiff base} \). Milli-molar solutions of the complexes in DMF indicate that all these complexes are non-electrolytes (4-8 ohm\(^{-1}\)cm\(^2\)mol\(^{-1}\)).

The spectra of the complexes show a strong band in the region 1600-1590 cm\(^{-1}\) assignable to \( \nu(C=N) \) of the azomethine group coordinated to the complexes.

### Table 1—Elemental analysis, IR \(^1\text{H} \)NMR and UV-Vis data of ruthenium(II) Schiff base complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found(Calc.), %</th>
<th>( \nu(C=O) ) (cm(^{-1}))</th>
<th>( \delta() \text{HC} = \text{N} )</th>
<th>( \delta() \text{N} - \text{CH}_2 )</th>
<th>( \lambda_{\text{max}}[\text{M}^{-1} \text{cm}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ([\text{Ru}(\text{Salen})(\text{CO})])</td>
<td>51.02 (51.64)</td>
<td>1940</td>
<td>8.38</td>
<td>3.75</td>
<td>420(1555), 450(1559), 332(1710), 689Sh(185), 280(3150)*</td>
</tr>
<tr>
<td>2. ([\text{Ru}(3,3',-\text{dimethoxysalen})(\text{CO})])</td>
<td>49.44 (50.10)</td>
<td>1970</td>
<td>8.58</td>
<td>3.77</td>
<td>420(1511), 333(1723), 358(1560), 683Sh(166), 272(3274)*</td>
</tr>
<tr>
<td>3. ([\text{Ru}(4,4',-\text{dimethoxysalen})(\text{CO})])</td>
<td>49.78 (50.10)</td>
<td>1970</td>
<td>9.9</td>
<td>3.70</td>
<td>410(1630), 390(997), 626Sh(163), 275(3148)*, 330(1750)</td>
</tr>
<tr>
<td>4. ([\text{Ru}(5,5',-\text{dimethoxysalen})(\text{CO})])</td>
<td>49.53 (50.10)</td>
<td>1920</td>
<td>8.57</td>
<td>3.70</td>
<td>419(1646), 450(1626), 332(1788), 540Sh(895), 726Sh(83), 276(3260)*</td>
</tr>
<tr>
<td>5. ([\text{Ru}(5,5',-\text{dichlorosalen})(\text{CO})])</td>
<td>43.11 (43.96)</td>
<td>1975</td>
<td>8.40</td>
<td>3.70</td>
<td>419(1511), 450(1500), 332(1650), 676Sh(198), 277(3230)*</td>
</tr>
<tr>
<td>6. ([\text{Ru}(3,3',5,5',-\text{tetrachlorosalen})(\text{CO})])</td>
<td>37.37 (38.27)</td>
<td>1970</td>
<td>10.28</td>
<td>3.85</td>
<td>420(1425), 452(1438), 276(2437), 532(922), 690Sh(509), 350(1720)</td>
</tr>
<tr>
<td>7. ([\text{Ru}(\text{Saloph})(\text{CO})])</td>
<td>55.25 (56.88)</td>
<td>1940</td>
<td>9.35</td>
<td>—</td>
<td>419(1635), 450(1617), 332(1775), 546(1049), 698Sh(375), 274(3134)*</td>
</tr>
<tr>
<td>8. ([\text{Ru}(3,3',-\text{dimethoxysaloph})(\text{CO})])</td>
<td>54.02 (54.87)</td>
<td>1980</td>
<td>9.30</td>
<td>—</td>
<td>419(1559), 452(1548), 540(1383), 699Sh(91), 27(3200)*, 336(1720)</td>
</tr>
<tr>
<td>9. ([\text{Ru}(4,4',-\text{dimethoxysaloph})(\text{CO})])</td>
<td>54.18 (54.87)</td>
<td>1980</td>
<td>10.06</td>
<td>—</td>
<td>419(1609), 453(1596), 332(1758), 528Sh(1089), 696Sh(51), 280(3150)*</td>
</tr>
<tr>
<td>10. ([\text{Ru}(5,5',-\text{dimethoxysaloph})(\text{CO})])</td>
<td>53.98 (54.87)</td>
<td>1930</td>
<td>9.53</td>
<td>—</td>
<td>420(1554), 452(1569), 280(2499), 536Sh(1382), 700(92), 340(1760)</td>
</tr>
<tr>
<td>11. ([\text{Ru}(5,5',-\text{dichlorosaloph})(\text{CO})])</td>
<td>48.73 (49.21)</td>
<td>1930</td>
<td>9.32</td>
<td>—</td>
<td>419(1548), 453(1566), 279(2499), 554Sh(1335), 335(1720)</td>
</tr>
<tr>
<td>12. ([\text{Ru}(3,3',5,5',-\text{tetrachlorosaloph})(\text{CO})])</td>
<td>42.74 (43.37)</td>
<td>1950</td>
<td>10.13</td>
<td>—</td>
<td>419(1480), 452(1465), 277(2477), 554Sh(1082), 350(1750)</td>
</tr>
</tbody>
</table>

*Recorded at \( 5 \times 10^{-4} M \) conc in DMF
metal ion. For the free ligands, this band occurs at somewhat higher wavenumbers. A sharp band in the region 1920-1980 cm\(^{-1}\) is assigned to the \(\nu(\text{C} \equiv \text{O})\) mode of the coordinated carbonyl group. The band for free carbon monoxide is observed at 2155 cm\(^{-1}\).

Carbonyl complexes offer a good opportunity for a study of the variation of the bonding of CO to a metal ion as a function of the metal ion, its oxidation state and the nature of the other ligands in its coordination sphere. In most of the Ru(II) carbonyl complexes the \(\nu(\text{C} \equiv \text{O})\) lies between 1890 and 1988 cm\(^{-1}\) (refs 20-26) while in Ru(III) carbonyl complexes this band lies above 2000 cm\(^{-1}\) (ref. 10) indicating a stronger metal-carbon bond in Ru(II) carbonyls as compared to that in Ru(III) carbonyl complexes.

The electronic spectra of the complexes show an intense band near 280 nm (\(\epsilon = 2500\)) which is also present in the free ligands and has been assigned to \(\pi - \pi^*\) transition of the azomethine group. The band around 330 nm (\(\epsilon = 1700\)) is due to \(n - \pi^*\) transition of non-bonding electrons present on the nitrogen of azomethine group in the Schiff bases\(^{27}\). This band undergoes a hypsochromic shift on coordination to the metal ion. The bands in the range 450 to 700 nm\(^{28,29}\) show strong similarities to those reported for other five coordinated Ru(II) complexes, such as RuCl\(_2\)(PPh\(_3\))\(_3^{30}\) and [RuX(dcpe)]BPh\(_4\)(X=Cl, Br, I)\(^{31}\) where a square pyramidal geometry was suggested for the complexes. The square pyramidal geometry of RuCl\(_2\)(PPh\(_3\))\(_3\) was determined by single crystal X-ray studies\(^{32}\). Since a Schiff base itself is a rigid system and has a planar arrangement of the coordinated groups, a trigonal bipyramidal geometry for the complexes may be ruled out on the basis of severe distortion expected in the Schiff base framework.

The \(^1\)H NMR spectra of the complexes in DMSO-\(d_6\) show the resonance for aromatic protons at \(\delta 6.16-7.76\) ppm in all saloph complexes and at \(\delta 6.36-7.82\) in all salen complexes. The methylene proton in all salen complexes give a signal at \(\delta 3.75\). The resonance due to azomethine proton (H- C=N) in the salen complexes 1-6 is observed in the range \(\delta 8.38-10.28\) while in saloph complexes 7-12 it lies in the range \(\delta 9.39-10.13\). The greater downfield shift in saloph complexes as compared to salen complexes is due to the presence of an additional phenyl group in saloph complexes. Substituents at positions 3 and 5 do not have any significant effect (except in the disubstituted ones, i.e., 6 and 12) as these positions are \textit{meta} with respect to azomethine group while substituent at position 4 which is \textit{para} with respect to azomethine group has got a pronounced effect (Table 1).

On the basis of analytical data and spectroscopic studies all Ru(II) Schiff base carbonyl complexes have been assigned a square pyramidal geometry represented by Structure I.

\begin{center}
\begin{tabular}{|c|c|c|}
\hline
W = CH\(_2\)\(\text{CH}_2\), & = C\(_6\)H\(_5\), & \(\text{TiCl}_2\) \\
R\(^+\) = R\(^-\), & - H, - OCH\(_3\), & Cl \\
R\(^0\) = H, - OCH\(_3\). & \\
\hline
\end{tabular}
\end{center}

\textbf{References}