Synthesis, characterization and reactivity studies of dichloroacetyl-
acetonato acetylacetone ruthenium(III)

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Summary

The Ru\textsuperscript{III} complex \([\text{RuCl}_2(\text{acac})(\text{acacH})]\) (acacH = acetyl-
acetone) was isolated in high yield by reacting \text{RuCl}_3 with \text{acacH}. The compound was used as a convenient starting
material for the synthesis of a variety of Ru\textsuperscript{III} complexes, viz. \([\text{RuCl}_2(\text{acac})(L)_2]\) (L = PPh\textsubscript{3}, AsPh\textsubscript{3}, py, MeCN, Me\textsubscript{2}SO, \text{o-phenylenediamine}; L\textsubscript{2} = phen or bipy) and M\textsubscript{2}[\text{RuCl}_4(\text{acac})] (M = Me\textsubscript{4}N, Rb or Cs). The compounds
were characterized by physicochemical and spectroscopic
methods.

Introduction

Known complexes of ruthenium(III) containing acetyl-
acetonato, halogeno and triphenylphosphine or triphenyl-
arsine groups include \([\text{RuX}_2(\text{acac})(\text{MPh}_3)_2]\) (X = Cl or Br; M = P or As)\textsuperscript{1-9}, which are generally prepared by reacting \([\text{RuX}_2(\text{PPh}_3)_3]\), \([\text{RuX}_2(\text{MPh}_3)_3]\) or \([\text{RuX}_2-
(\text{MPh}_3)_2(\text{MeOH})]\) (X = Cl or Br; M = P or As) with acetyl-
acetone in a neutral solvent. The only mixed halogeno-
acetylacetanato complex of ruthenium reported to date is
\([\text{RuCl}(\text{acac})]\), which was obtained by the reaction of
ruthenium(III) chloride with acetylacetone at pH 1.2\textsuperscript{[5]}. Complexes containing halides and neutral acetylacetone
molecules, or halides, acetylacetone and acetylacetone,
have been described for some of the transition metal
ions\textsuperscript{6-9}, but no reports on syntheses of ruthenium(II) or
ruthenium(III) complexes containing neutral acetylacetone
and other ligands are available. In the present work, the
preparation and characterization of \([\text{RuCl}_2(\text{acac})(\text{acacH})]\)
was reported. \([\text{RuCl}_2(\text{acac})(\text{acacH})]\) was used to synthesize compunds of the type \([\text{RuCl}_2(\text{acac})(L)_2]\) (L = PPh\textsubscript{3}, AsPh\textsubscript{3}, py, MeCN, Me\textsubscript{2}SO or \text{o-phenylenediamine}; L\textsubscript{2} = phen or bipy) and M\textsubscript{2}[\text{RuCl}_4(\text{acac})] (M = Me\textsubscript{4}N, Cs or
Rb) are also described.

Experimental

All the solvents were freshly distilled before use. \text{RuCl}_3-
\text{3H}_2\text{O} was used as supplied by Arora-Matthey Ltd, Calcutta. The analyses for Cl were carried out by a standard
method\textsuperscript{[10]} after decomposition with a KOH/KNO\textsubscript{3}
mixture. C, H, N analyses were obtained from the
Regional Sophisticated Instrumentation Centre, CDRI,
Lucknow (Table 1). I.r. spectra were recorded on a Perkin-
Elmer 983 IR spectrophotometer in the 4000–200 cm\textsuperscript{-1}
range and electronic absorption spectra were recorded in
solution on a Hitachi-330 spectrophotometer in the 800–
250 nm range. The results are given in Table 2. Magnetic
susceptibilities were measured on an EG & G PARC Vibrating
Sample Magnetometer at room temperature. \textsuperscript{1}H-
n.m.r. spectra were recorded on a Varian EM-390, 90 MHz
spectrometer, in acetone-\text{d}_6. Conductivity measurements
were made on Wayne Kerr, Automatic Precision Bridge
B905 conductivity meter with millimolar solutions in MeCN
and distilled water. Electrochemical measurements (c.v.)
were carried out on an EG & G PARC Voltameter. The
experiments were carried out in a three electrode con-
figuration using a Pt disc as the working electrode. Reported potentials are uncorrected for the junction con-
tribution.

Preparation of \([\text{RuCl}_2(acac)/acacH)\]

A solution of \text{RuCl}_3, 3\text{H}_2\text{O} (0.25 g) in acetylacetone (2 cm\textsuperscript{3})
was heated in a water bath at ca. 85\textdegree{}C for 5 h, until a
purple-red solution was obtained. The solution was concen-
trated to ca. 1 cm\textsuperscript{3} in a water bath and cooled to room
temperature. Et\textsubscript{2}O was added with stirring to give a red-
violet coloured precipitate. This was centrifuged and washed
2–3 times with Et\textsubscript{2}O and dried \textit{in vacuo}. The compound
was recrystallized from a CH\textsubscript{2}Cl\textsubscript{2}/hexane mixture. It anal-
ished correctly for \([\text{RuCl}_2(acac/\text{acacH})]\); yield: 0.22 g
(62\%).

General method for reacting \([\text{RuCl}(acac)/acacH)\]
with various ligands

\([\text{RuCl}(acac/\text{acacH})]\) (0.2 g) was dissolved in MeOH
(10 cm\textsuperscript{3}), and a solution of the ligand in MeOH (5 cm\textsuperscript{3})
was added. The reaction mixture was boiled under reflux in
a water bath (ca. 85\textdegree{}C) for a few hours. The product,
which separated or was precipitated with Et\textsubscript{2}O after con-
centrating the mother liquor, was isolated by centrifuga-
tion and washed successively with MeOH and Et\textsubscript{2}O and
dried \textit{in vacuo}. Specific reaction conditions for each ligand
are given in Table 3.

Preparation of M\textsubscript{2}[\text{RuCl}_4(acac)] (M = Rb, Cs
or Me\textsubscript{4}N)

To a solution of \([\text{RuCl}_2(acac/\text{acacH})]\) (0.2 g) in MeOH
(10 cm\textsuperscript{3}), a solution of \text{MCl} (M = Cs, Rb or
Me\textsubscript{4}N) in MeOH (10 cm\textsuperscript{3}) (molar ratio 1:2) was added. The reaction
mixture was boiled under reflux for 1 h, and the precipitate
isolated by centrifugation, washed with MeOH and then
with Me\textsubscript{2}CO and dried \textit{in vacuo}.

Results and discussion

The only reported halogeno–acetylacetanato complex of ruthenium(III), \([\text{RuCl}(acac)\text{Cl}]\), was prepared\textsuperscript{[9]} by reac-
tion of ruthenium(III) chloride with acetylacetone at pH 1.2.
Our attempts to obtain the above compound according to
the reported method were unsuccessful. However, we obtained a red–violet compound of the composition
\([\text{RuCl}(acac/\text{acacH})]\) by reacting ruthenium(III) chloride
with acetylacetone under neutral conditions. The low
value of the molar conductance (35\textsuperscript{±} \text{cm}^2\text{ mol}^{-1}\text{ cm}^{-1})
in acetonitrile, and the magnetic moment of 1.9 B.M. at room
temperature suggested that the complex covalently bonded
chloride, and that the metal ion was a d\textsuperscript{2}, low-spin system.
Table 1. Physical and analytical data for the complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M.p. (°C)</th>
<th>Found (%)</th>
<th>Calcd (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl₂(acac)(acacH)]</td>
<td>Red-violet</td>
<td>160-5</td>
<td>32.5</td>
<td>32.3</td>
</tr>
<tr>
<td>trans-[RuCl₂(acac)(PPh₃)₂]</td>
<td>Green</td>
<td>235</td>
<td>61.6</td>
<td>61.9</td>
</tr>
<tr>
<td>[RuCl₂(acac)(AsPh₃)₂]</td>
<td>Green</td>
<td>285</td>
<td>58.5</td>
<td>55.7</td>
</tr>
<tr>
<td>[RuCl₂(acac)(Me₂SO)₂]</td>
<td>Brown</td>
<td>215-20</td>
<td>25.5</td>
<td>25.3</td>
</tr>
<tr>
<td>[RuCl₂(acac)(MeCN)₂]</td>
<td>Light violet</td>
<td>220-5</td>
<td>31.2</td>
<td>30.6</td>
</tr>
<tr>
<td>[RuCl₂(acac)(py)₂]</td>
<td>Reddish brown</td>
<td>295-300</td>
<td>41.9</td>
<td>42.0</td>
</tr>
<tr>
<td>[RuCl₂(acac)(PDA)₂]</td>
<td>Blue violet</td>
<td>&gt;360</td>
<td>41.4</td>
<td>41.9</td>
</tr>
<tr>
<td>[RuCl₂(acac)(phen)]</td>
<td>Dark brown</td>
<td>205</td>
<td>44.9</td>
<td>45.2</td>
</tr>
<tr>
<td>[RuCl₂(acac)(bpy)]</td>
<td>Dark brown</td>
<td>300⁺</td>
<td>41.8</td>
<td>42.2</td>
</tr>
<tr>
<td>(Me₄N)₂[RuCl₄(acac)]</td>
<td>Orange</td>
<td>290⁺</td>
<td>31.8</td>
<td>31.8</td>
</tr>
<tr>
<td>Rb₂[RuCl₄(acac)]</td>
<td>Light violet</td>
<td>340⁺</td>
<td>9.7</td>
<td>(9.9)</td>
</tr>
<tr>
<td>Cs₂[RuCl₄(acac)]</td>
<td>Pink</td>
<td>350⁺</td>
<td>11.3</td>
<td>(11.7)</td>
</tr>
</tbody>
</table>

*Decomposes.

Table 2. Important i.r. and electronic absorption bands for the complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>I.r. bands (cm⁻¹)</th>
<th>λₘₐₓ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl₂(acac)(acacH)]</td>
<td>1629, 1545, 1517, 467, 350</td>
<td>525 (3200)</td>
</tr>
<tr>
<td>trans-[RuCl₂(acac)(PPh₃)₂]</td>
<td>1550, 1520, 456, 324</td>
<td>610 (235)</td>
</tr>
<tr>
<td>[RuCl₂(acac)(AsPh₃)₂]</td>
<td>1550, 1516, 474, 320</td>
<td>588 (293)</td>
</tr>
<tr>
<td>[RuCl₂(acac)(MeCN)₂]</td>
<td>2286, 1536, 1517, 466, 353, 325</td>
<td>530 (2360)</td>
</tr>
<tr>
<td>[RuCl₂(acac)(py)₂]</td>
<td>1545, 1517, 476, 320</td>
<td>600 (268)</td>
</tr>
<tr>
<td>[RuCl₂(acac)(phen)]</td>
<td>1545, 1515, 464, 350, 325</td>
<td>505sh (2740)</td>
</tr>
<tr>
<td>[RuCl₂(acac)(bpy)]</td>
<td>1545, 1515, 467, 332</td>
<td>510sh (2050)</td>
</tr>
<tr>
<td>[RuCl₂(acac)(Me₂SO)₂]</td>
<td>1545, 1514, 1106, 1089, 429, 392</td>
<td>542sh (25640)</td>
</tr>
</tbody>
</table>

(Contd.)
The i.r. spectrum of the compound in KBr exhibited three bands in the carbonyl stretching region (Table 2). Bands at 1545 and 1517 cm\(^{-1}\) may be assigned to a chelated O-bonded acetylacetonato group \(^1\). \(v(\text{CO})\) for coordinated neutral acetylacetone in the keto form is observed ca. 1700 cm\(^{-1}\) \(^6\), whereas for coordinated neutral acetylacetone in the enol form it is observed at a lower frequency, as in the case of \([\text{MnBr}_2(\text{acacH})_2]\) at 1627 cm\(^{-1}\) \(^6\). Thus, the 1629 cm\(^{-1}\) absorption for \([\text{RuCl}_2(\text{acac})(\text{acacH})]\) may be assigned to \(v(\text{CO})\) of neutral acetylacetone coordinated in the enol form to the metal.

\([\text{RuCl}_2(\text{acac})(\text{acacH})]\) has a labile acetylacetone molecule which is readily replaced by a wide variety of donors \(^{vide infra}\) and is released from the complex in non-coordinating solvents. Thus, the i.r. spectrum of the compound in chloroform showed two new bands at 3640 and 1715 cm\(^{-1}\), assigned to \(v(\text{OH})\) and \(v(\text{CO})\) of free acetylacetone released from the complex \(^{60}\). Other i.r. bands in solution are similar to those in KBr. The far-i.r. spectrum showed absorptions at 467 and 350 cm\(^{-1}\), which were assigned to \(v(\text{Ru—O})\) and \(v(\text{Ru—Cl})\), respectively \(^{60}\). The \(^1\)H-n.m.r. spectrum of \([\text{RuCl}_2(\text{acac})(\text{acacH})]\) in acetone-\(d_6\) also confirmed the presence of a neutral acetylacetone molecule, and exhibited signals at 2.1 and 2.4 ppm, assigned to the methyl protons of uncoordinated acetylacetone in its enol and \(\beta\)- diketone forms respectively \(^{12}\). Further proton signals at 5.42 and 4.27 ppm may be assigned to \(-\text{CH}=\) and \(-\text{COCH}_2\text{CO}−\) of the enol and \(\beta\)- diketone forms of free acetylacetone respectively \(^{12}\).

The cyclic voltammogram (Figure 1) of the complex for a ca. \(10^{-3}\) M solution in acetonitrile using tetraethylammonium perchlorate as supporting electrolyte showed only one reversible (or quasi-reversible, \(\Delta E = 90\text{ mV}\))
Reduction wave at a negative potential \(E_{1/2} = -0.29\) V, which corresponds to ruthenium(III)/ruthenium(II) reduction versus s.c.e.\(^{(4)}\).

Reactions of \([\text{RuCl}_2(\text{acac})(\text{acacH})]\) with ligands

\([\text{RuCl}_2(\text{acac})(\text{acacH})]\) is soluble in many organic solvents, viz. ethanol, methanol, acetonitrile, acetone, chloroform, etc., permitting a wide study of the reactivity of this compound with donors. As discussed above, neutral acetylacetone is weakly coordinated to the metal ion. Thus, in a solution, \([\text{RuCl}_2(\text{acac})]\) or \([\text{RuCl}_2(\text{acac})(\text{S})_2]\) \((S = \text{solvent})\) is obtained. This species reacts with donor molecules to give \([\text{RuCl}_2(\text{acac})(L)_2]\) \((L = \text{PPh}_3, \text{AsPh}_3, \text{py}, \text{MeCN}, \text{Me}_2\text{SO} \text{or o-phenylenediamine}; L_2 = \text{phen or bipy})\). The molar conductances of these complexes in acetonitrile at room temperature were very low \((20-30 \Omega^{-1}\text{ cm}^2\text{ mol}^{-1})\), confirming that the chlorides are covalently bound in all cases. The magnetic moments for \([\text{RuCl}_2(\text{acac})(L)_2]\) \((L = \text{py or L}_2 = \text{phen})\) lie in the range 1.8-2.0 B.M., confirming a low spin d\(^2\) ruthenium(III) system.

The absence of the i.r. band at 1629 cm\(^{-1}\) for \([\text{RuCl}_2(\text{acac})(L)_2]\) confirms that the neutral acetylacetone molecule has been lost. However, two bands between 1550 and 1515 cm\(^{-1}\) \((\text{assigned to } \nu(\text{C}=\text{O}) \text{ and } \nu(\text{C}==\text{C}))\) and other characteristic bands of the O-bounded chelated acetylacetronato group are observed\(^{(13)}\). Bands between 476-455 cm\(^{-1}\) and 350-320 cm\(^{-1}\) may be assigned to \(\nu(\text{Ru--O})\) and \(\nu(\text{Ru--Cl})\), respectively. For the complexes of the nitrogen donor ligands, two medium intensity bands or one strong band in the 350-320 cm\(^{-1}\) region may be assigned to \(\nu(\text{Ru--C})\) and \(\nu(\text{Ru--N})\), or a combination of the two. In the case of \([\text{RuCl}_2(\text{acac})(\text{Me}_2\text{SO})_2]\) two strong bands at 1106 and 1089 cm\(^{-1}\) and a weak band at 392 cm\(^{-1}\) are assigned to \(\nu(\text{S}==\text{O})\) and \(\nu(\text{Ru}==\text{O})\), respectively of S-bonded \(\text{MeESO}\) groups \(^{(14)}\). For \([\text{RuCl}_2(\text{acac})(\text{Me}_2\text{SO})(\text{OH})]\)_2 the acidification of which may result in \([\text{RuCl}_2(\text{acac})(\text{H}_2\text{O})_2]\). The visible spectrum of \([\text{RuCl}_2(\text{acac})(\text{H}_2\text{O})_2]\) is similar to that of \([\text{RuCl}_2(\text{acac})(\text{acacH})]\) in water, presumably due to formation of \([\text{RuCl}_2(\text{acac})(\text{H}_2\text{O})_2]\) in \(H_2O\).

The \([\text{RuCl}_2(\text{acac})(L)_2]\) complexes \((L = \text{PPh}_3, \text{AsPh}_3, \text{py}, \text{MeCN}, \text{Me}_2\text{SO} \text{or o-phenylenediamine}; L_2 = \text{phen or bipy})\) show one band around 600 nm \((\epsilon = 235 \text{ to } 290)\) and two additional bands below 400 nm. The former can be assigned to a d–d transition \(2T_g \rightarrow 2A_2g\) or \(2A_2g \rightarrow 2A_1g\) in a low spin d\(^6\) system\(^{(16)}\). Of the two bands in 400-300 nm region, one band having \(\epsilon = 10^3\) or above is assigned to the intraligand \(\pi \rightarrow \pi^*\) transition, whilst the other is assigned to an LMCT transition \((\text{vide supra})\). \([\text{RuCl}_2(\text{acac})(L)_2]\), \((L = \text{bipy or Phen})\) in chloroform exhibits similar features to that of \([\text{RuCl}_2(\text{acac})(\text{acacH})]\), except for the appearance of a new band around 450 nm assigned to the \(\pi(\text{bipy or Phen}) \rightarrow Ru(t_{2g})\) transition.

The spectra of \([\text{M}_2[\text{RuCl}_2(\text{acac})]\) \((M = \text{Me}_4\text{N}, \text{Cs} \text{ or Rb})\) in water showed one band at 510 nm \((\epsilon = 415 \text{ to } 645)\) and two more bands below 350 nm. The first of these can be assigned to a combination of a d–d transition \(2T_g \rightarrow 2A_2g\) and \(2A_2g \rightarrow 2A_1g\) and an LMCT transition \((\text{vide supra})\). The bands below 350 nm may be assigned to \(\pi(\text{phen}) \rightarrow Ru(t_{2g})\) transition.

Conclusion

The complex of ruthenium(II) containing neutral acetylacetone, acetylacetone and chloride is described, and its reactivity has been studied towards various donor ligands, when \([\text{RuCl}_2(\text{acac})(L)_2]\) \((L = \text{PPh}_3, \text{AsPh}_3, \text{py}, \text{MeCN}, \text{Me}_2\text{SO} \text{or o-phenylenediamine}; L_2 = \text{phen or bipy})\) have been obtained with substitution of coordinated \(\text{acacH}\).

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References


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