

# Synthesis, characterization and reactivity studies of dichloroacetylacetonato acetylacetonate ruthenium(III)

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## Summary

The Ru<sup>III</sup> complex [RuCl<sub>2</sub>(acac)(acacH)] (acacH = acetylacetonate) was isolated in high yield by reacting RuCl<sub>3</sub> with acacH. The compound was used as a convenient starting material for the synthesis of a variety of Ru<sup>III</sup> complexes, viz. [RuCl<sub>2</sub>(acac)L<sub>2</sub>] (L = PPh<sub>3</sub>, AsPh<sub>3</sub>, py, MeCN, Me<sub>2</sub>SO, *o*-phenylenediamine; L<sub>2</sub> = phen or bipy) and M<sub>2</sub>[RuCl<sub>4</sub>(acac)] (M = Me<sub>4</sub>N, Rb or Cs). The compounds were characterized by physicochemical and spectroscopic methods.

## Introduction

Known complexes of ruthenium(III) containing acetylacetonato, halogeno and triphenylphosphine or triphenylarsine groups include [RuX<sub>2</sub>(acac)(MPh<sub>3</sub>)<sub>2</sub>] (X = Cl or Br; M = P or As)<sup>(1–4)</sup>, which are generally prepared by reacting [RuX<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>], [RuX<sub>3</sub>(MPh<sub>3</sub>)<sub>3</sub>] or [RuX<sub>3</sub>(MPh<sub>3</sub>)<sub>2</sub>(MeOH)] (X = Cl or Br; M = P or As) with acetylacetonate in a neutral solvent. The only mixed halogeno-acetylacetonato complex of ruthenium reported to date is [RuCl<sub>2</sub>(acac)], which was obtained by the reaction of ruthenium(III) chloride with acetylacetonate at pH 1.2<sup>(5)</sup>. Complexes containing halides and neutral acetylacetonate molecules, or halides, acetylacetonate and acetylacetonate, have been described for some of the transition metal ions<sup>(6–9)</sup>, but no reports on syntheses of ruthenium(II) or ruthenium(III) complexes containing neutral acetylacetonate and other ligands are available. In the present work, the preparation and characterization of [RuCl<sub>2</sub>(acac)(acacH)] is reported. [RuCl<sub>2</sub>(acac)(acacH)] was used to synthesize compounds of the type [RuCl<sub>2</sub>(acac)L<sub>2</sub>] (L = PPh<sub>3</sub>, AsPh<sub>3</sub>, py, MeCN, Me<sub>2</sub>SO or *o*-phenylenediamine; L<sub>2</sub> = phen or bipy) and M<sub>2</sub>[RuCl<sub>4</sub>(acac)] (M = Me<sub>4</sub>N, Cs or Rb) are also described.

## Experimental

All the solvents were freshly distilled before use. RuCl<sub>3</sub>·3H<sub>2</sub>O was used as supplied by Arora-Matthey Ltd, Calcutta. The analyses for Cl were carried out by a standard method<sup>(10)</sup> after decomposition with a KOH/KNO<sub>3</sub> 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<sup>-1</sup> 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. <sup>1</sup>H-n.m.r. spectra were recorded on a Varian EM-390, 90 MHz spectrometer, in acetone-d<sub>6</sub>. 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 Voltmeter. The experiments were carried out in a three electrode configuration using a Pt disc as the working electrode. Reported potentials are uncorrected for the junction contribution.

## Preparation of [RuCl<sub>2</sub>(acac)(acacH)]

A solution of RuCl<sub>3</sub>·3H<sub>2</sub>O (0.25 g) in acetylacetonate (2 cm<sup>3</sup>) was heated in a water bath at ca. 85°C for 5 h, until a purple-red solution was obtained. The solution was concentrated to ca. 1 cm<sup>3</sup> in a water bath and cooled to room temperature. Et<sub>2</sub>O was added with stirring to give a red-violet coloured precipitate. This was centrifuged and washed 2–3 times with Et<sub>2</sub>O and dried *in vacuo*. The compound was recrystallized from a CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture. It analysed correctly for [RuCl<sub>2</sub>(acac)(acacH)]; yield: 0.22 g (62%).

## General method for reacting [RuCl<sub>2</sub>(acac)(acacH)] with various ligands

[RuCl<sub>2</sub>(acac)(acacH)] (0.2 g) was dissolved in MeOH (10 cm<sup>3</sup>), and a solution of the ligand in MeOH (5 cm<sup>3</sup>) was added. The reaction mixture was boiled under reflux in a water bath (ca. 85°C) for a few hours. The product, which separated or was precipitated with Et<sub>2</sub>O after concentrating the mother liquor, was isolated by centrifugation and washed successively with MeOH and Et<sub>2</sub>O and dried *in vacuo*. Specific reaction conditions for each ligand are given in Table 3.

## Preparation of M<sub>2</sub>[RuCl<sub>4</sub>(acac)] (M = Rb, Cs or Me<sub>4</sub>N)

To a solution of [RuCl<sub>2</sub>(acac)(acacH)] (0.2 g) in MeOH (10 cm<sup>3</sup>), a solution of MCl (M = Cs, Rb or Me<sub>4</sub>N) in MeOH (10 cm<sup>3</sup>) (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<sub>2</sub>CO and dried *in vacuo*.

## Results and discussion

The only reported halogeno-acetylacetonato complex of ruthenium(III), [RuCl<sub>2</sub>(acac)], was prepared<sup>(5)</sup> by reacting ruthenium(III) chloride with acetylacetonate 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 [RuCl<sub>2</sub>(acac)(acacH)] by reacting ruthenium(III) chloride with acetylacetonate under neutral conditions. The low value of the molar conductance (35 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) 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<sup>5</sup>, low-spin system.

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**Table 1.** Physical and analytical data for the complexes.

Compound	Colour	M.p. (°C)	Found (Calcd.)%		N	Cl
			C	H		
[RuCl <sub>2</sub> (acac)(acacH)]	Red-violet	160–5	32.5 (32.3)	4.1 (4.0)		19.8 (19.1)
<i>trans</i> -[RuCl <sub>2</sub> (acac)(PPh <sub>3</sub> ) <sub>2</sub> ]	Green	235	61.6 (61.9)	4.8 (4.7)		
[RuCl <sub>2</sub> (acac)(AsPh <sub>3</sub> ) <sub>2</sub> ]	Green	285	55.8 (55.7)	4.4 (4.2)		
[RuCl <sub>2</sub> (acac)(Me <sub>2</sub> SO) <sub>2</sub> ]	Brown	215–20	25.5 (25.3)	4.6 (4.4)		
[RuCl <sub>2</sub> (acac)(MeCN) <sub>2</sub> ]	Light violet	220–5 <sup>a</sup>	31.2 (30.6)	3.5 (3.7)	7.6 (7.9)	
[RuCl <sub>2</sub> (acac)(py) <sub>2</sub> ]	Reddish brown	295–300	41.9 (42.0)	3.8 (4.0)	6.7 (6.5)	
[RuCl <sub>2</sub> (acac)(PDA) <sub>2</sub> ]	Blue violet	>360	41.4 (41.9)	4.9 (4.7)	11.9 (11.5)	
[RuCl <sub>2</sub> (acac)(phen)]	Dark brown	205	44.9 (45.2)	3.4 (3.3)	6.5 (6.2)	
[RuCl <sub>2</sub> (acac)(bpy)]	Dark brown	300 <sup>a</sup>	41.8 (42.2)	3.5 (3.5)	6.7 (6.6)	
(Me <sub>4</sub> N) <sub>2</sub> [RuCl <sub>4</sub> (acac)]	Orange	290 <sup>a</sup>	31.8 (31.8)	6.6 (6.3)	5.6 (5.7)	29.5 (29.0)
Rb <sub>2</sub> [RuCl <sub>4</sub> (acac)]	Light violet	340 <sup>a</sup>	9.7 (9.9)	1.0 (1.2)		22.9 (23.4)
Cs <sub>2</sub> [RuCl <sub>4</sub> (acac)]	Pink	350 <sup>a</sup>	11.3 (11.7)	1.1 (1.4)		26.8 (27.7)

<sup>a</sup>Decomposes.**Table 2.** Important i.r. and electronic absorption bands for the complexes.

Compound	I.r. bands <sup>a</sup> (cm <sup>-1</sup> )	$\lambda_{\max}$ (nm) <sup>b</sup>	
		CHCl <sub>3</sub>	H <sub>2</sub> O
[RuCl <sub>2</sub> (acac)(acacH)]	1629, 1545, 1517, 467, 350	525 (3200) 385 (4170) 330sh (4830) 288 (8720)	530 (2670) 370 (3710) 330sh (4300) 285 (7420)
<i>trans</i> -[RuCl <sub>2</sub> (acac)(PPh <sub>3</sub> ) <sub>2</sub> ]	1550, 1520, 456, 324	610 (235) 388sh (2650) 300sh (23100)	
[RuCl <sub>2</sub> (acac)(AsPh <sub>3</sub> ) <sub>2</sub> ]	1550, 1516, 474, 320	588 (293) 394 (2250) 350 (2600)	
[RuCl <sub>2</sub> (acac)(MeCN) <sub>2</sub> ]	2286, 1536, 1517, 466, 353, 325	530 (2360) 390 (3880) 290 (7930) 236 (15650)	
[RuCl <sub>2</sub> (acac)(py) <sub>2</sub> ]	1545, 1517, 476, 320	600 (268) 520sh (442) 360sh (7500) 300 (11530)	
[RuCl <sub>2</sub> (acac)(phen)]	1545, 1515, 464, 350, 325	505sh (2740) 450 (3550) 390sh (2890) 320sh (6620) 270 (53000)	
[RuCl <sub>2</sub> (acac)(bipy)]	1545, 1515, 467, 332	510sh (2050) 470 (2200) 350sh (4185) 290 (25640)	
[RuCl <sub>2</sub> (acac)(Me <sub>2</sub> SO) <sub>2</sub> ]	1545, 1514, 1106, 1089, 429, 392, 349		

(Contd.)

Table 2. (Continued).

Compound	I.r. bands <sup>a</sup> (cm <sup>-1</sup> )	$\lambda_{\max}$ (nm) <sup>b</sup>	
		CHCl <sub>3</sub>	H <sub>2</sub> O
[RuCl <sub>2</sub> (acac)(PDA) <sub>2</sub> ]	1564, 1517, 451, 344		
(Me <sub>4</sub> N) <sub>2</sub> [RuCl <sub>4</sub> (acac)]	1545, 1516, 949, 453, 307		510 (416) 330 (2990) 285 (4700)
Rb <sub>2</sub> [RuCl <sub>4</sub> (acac)]	1533, 1515, 456, 312		510 (445) 340 (2930) 285 (4050)
Cs <sub>2</sub> [RuCl <sub>4</sub> (acac)]	1533, 1515, 454, 308		510 (640) 340 (3800) 285 (5230)

<sup>a</sup>I.r. in KBr; <sup>b</sup> $\epsilon$  is parenthesis; sh = shoulder.

Table 3. Conditions for the reactions of [RuCl<sub>2</sub>(acac)(acacH)] with various ligands.

Ligand	Molar ratio (compound:ligand)	Refluxing time (h)	Isolation method	Product composition
PPh <sub>3</sub>	1:2	1	(a)	[RuCl <sub>2</sub> (acac)(PPh <sub>3</sub> ) <sub>2</sub> ]
AsPh <sub>3</sub>	1:2	1.5	(a)	[RuCl <sub>2</sub> (acac)(AsPh <sub>3</sub> ) <sub>2</sub> ]
py	1:2	1	(a)	[RuCl <sub>2</sub> (acac)(py) <sub>2</sub> ]
MeCN <sup>(c)</sup>	—	2	(b)	[RuCl <sub>2</sub> (acac)(MeCN) <sub>2</sub> ]
Me <sub>2</sub> SO	1:2	2	(b)	[RuCl <sub>2</sub> (acac)(Me <sub>2</sub> SO) <sub>2</sub> ]
phen	1:1	2	(a)	[RuCl <sub>2</sub> (acac)(phen)]
bipy	1:1	1.5	(a)	[RuCl <sub>2</sub> (acac)(bipy)]
PDA	1:2	1	(b)	[RuCl <sub>2</sub> (acac)(PDA) <sub>2</sub> ]

<sup>(a)</sup>Compound separated out after the reaction, and was washed successively with MeOH and Et<sub>2</sub>O; <sup>(b)</sup>vol. of solution reduced to ca. 3 cm<sup>3</sup>, Et<sub>2</sub>O was added to precipitate the compound; <sup>(c)</sup>MeCN was used as solvent.

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<sup>-1</sup> may be assigned to a chelated O-bonded acetylacetonato group<sup>(11)</sup>.  $\nu(\text{CO})$  for coordinated neutral acetylacetonone in the keto form is observed ca. 1700 cm<sup>-1</sup><sup>(6)</sup>, whereas for coordinated neutral acetylacetonone in the enol form it is observed at a lower frequency, as in the case of [MnBr<sub>2</sub>(acacH)<sub>2</sub>], at 1627 cm<sup>-1</sup><sup>(6)</sup>. Thus, the 1629 cm<sup>-1</sup> absorption for [RuCl<sub>2</sub>(acac)(acacH)] may be assigned to  $\nu(\text{CO})$  of neutral acetylacetonone coordinated in the enol form to the metal.

[RuCl<sub>2</sub>(acac)(acacH)] has a labile acetylacetonone 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<sup>-1</sup>, assigned to  $\nu(\text{OH})$  and  $\nu(\text{CO})$  of free acetylacetonone released from the complex<sup>(6)</sup>. Other i.r. bands in solution are similar to those in KBr. The far-i.r. spectrum showed absorptions at 467 and 350 cm<sup>-1</sup>, which were assigned to  $\nu(\text{Ru—O})$  and  $\nu(\text{Ru—Cl})$ , respectively<sup>(6)</sup>. The <sup>1</sup>H-n.m.r. spectrum of [RuCl<sub>2</sub>(acac)(acacH)] in acetone-d<sub>6</sub> also confirmed the presence of a neutral acetylacetonone molecule, and exhibited signals at  $\delta$  2.1 and 2.4 ppm, assigned to the methyl protons of uncoordinated acetylacetonone in its enol and  $\beta$ -diketonone forms respectively<sup>(12)</sup>. Further proton signals at  $\delta$  5.42 and 4.27 ppm may be assigned to —CH= and —COCH<sub>2</sub>CO— of the enol and  $\beta$ -diketonone forms of free acetylacetonone respectively<sup>(12)</sup>.

The cyclic voltammogram (Figure 1) of the complex for a ca. 10<sup>-3</sup> M solution in acetonitrile using tetraethylammonium perchlorate as supporting electrolyte showed only one reversible (or quasi-reversible,  $\Delta E = 90$  mV)

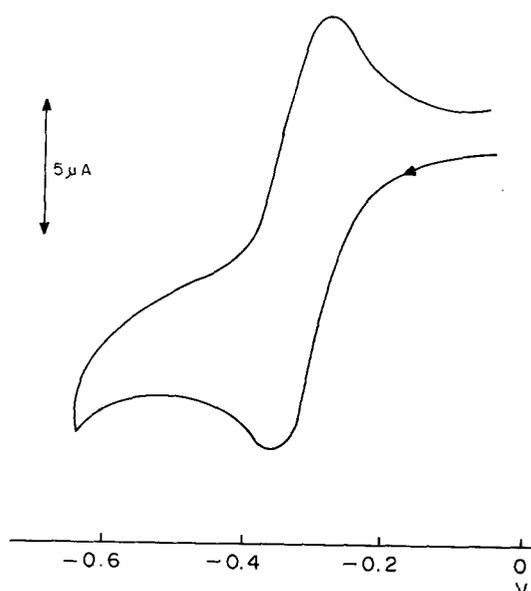


Figure 1. C.v. of [RuCl<sub>2</sub>(acac)(acacH)] (10<sup>-3</sup> M) in MeCN with 0.1 M TEAP as supporting electrolyte.

reduction wave at a negative potential ( $E_{1/2} = -0.29$  V), which corresponds to ruthenium(III)/ruthenium(II) reduction versus s.c.e.<sup>(4)</sup>.

#### Reactions of [RuCl<sub>2</sub>(acac)(acacH)] with ligands

[RuCl<sub>2</sub>(acac)(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 acetylacetonone is weakly coordinated to the metal ion. Thus, in a solution, [RuCl<sub>2</sub>(acac)] or [RuCl<sub>2</sub>(acac)(S)<sub>2</sub>] (S = solvent) is obtained. This species reacts with donor molecules to give [RuCl<sub>2</sub>(acac)L<sub>2</sub>] (L = PPh<sub>3</sub>, AsPh<sub>3</sub>, py, MeCN, Me<sub>2</sub>SO or *o*-phenylenediamine; L<sub>2</sub> = phen or bipy). The molar conductances of these complexes in acetonitrile at room temperature were very low (20–30 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>), confirming that the chlorides are covalently bound in all cases. The magnetic moments for [RuCl<sub>2</sub>(acac)L<sub>2</sub>] (L = py or L<sub>2</sub> = phen) lie in the range 1.8–2.0 B.M., confirming a low spin d<sup>5</sup> ruthenium(III) system.

The absence of the i.r. band at 1629 cm<sup>-1</sup> for [RuCl<sub>2</sub>(acac)L<sub>2</sub>] confirms that the neutral acetylacetonone molecule has been lost. However, two bands between 1550 and 1515 cm<sup>-1</sup> [assigned to ν(C=O) and ν(C=C)] and other characteristic bands of the O-bonded chelated acetylacetonato group are observed<sup>(13)</sup>. Bands between 476–455 cm<sup>-1</sup> and 350–320 cm<sup>-1</sup> may be assigned to ν(Ru—O) and ν(Ru—Cl), respectively. For the complexes of the nitrogen donor ligands, two medium intensity bands or one strong band in the 350–320 cm<sup>-1</sup> region may be assigned to ν(Ru—N) and ν(Ru—Cl), or a combination of the two. In the case of [RuCl<sub>2</sub>(acac)(Me<sub>2</sub>SO)<sub>2</sub>] two strong bands at 1106 and 1089 cm<sup>-1</sup> and a weak band at 392 cm<sup>-1</sup> are assigned to ν(S=O) and ν(Ru—S), respectively of S-bonded Me<sub>2</sub>SO groups<sup>(14)</sup>. For [RuCl<sub>2</sub>(acac)(MeCN)<sub>2</sub>] a weak intensity band at 2286 cm<sup>-1</sup> is assigned to ν(CN) of the two MeCN ligands bonded in a *trans* fashion<sup>(15)</sup>.

Reaction of [RuCl<sub>2</sub>(acac)(acacH)] with MCl (M = Me<sub>4</sub>N, Cs or Rb) resulted in complexes of the formula M<sub>2</sub>[RuCl<sub>4</sub>(acac)] (M = Me<sub>4</sub>N, Cs or Rb). These compounds are insoluble in most organic solvents, but are soluble in water. Molar conductance measurements in water at 25°C ( $\Lambda_M \approx 218$ – $250$  Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) indicate that the complexes are 2:1 electrolytes. The i.r. spectra in KBr showed two bands between 1515 and 1550 cm<sup>-1</sup> which may be assigned to a chelated O-bonded acetylacetonato group. A strong band between 312–307 cm<sup>-1</sup> and a medium intensity band around 455 cm<sup>-1</sup> are assigned to ν(Ru—Cl) and ν(Ru—O), respectively. The c.v.s of [RuCl<sub>2</sub>(acac)(PPh<sub>3</sub>)<sub>2</sub>] and [RuCl<sub>2</sub>(acac)(phen)] for 10<sup>-3</sup> M solution in acetonitrile using tetraethylammonium perchlorate as a supporting electrolyte showed one quasi-reversible ( $\Delta E = 90$ – $100$  mV) reduction wave at negative potentials,  $E_{1/2} = -0.30$  V and  $-0.28$  V, respectively, corresponding to ruthenium(III)/ruthenium(II) reduction versus s.c.e.<sup>(4)</sup>.

#### Electronic absorption spectra

The spectra of [RuCl<sub>2</sub>(acac)(acacH)] in chloroform and water are similar (Table 2), showing four absorption bands having  $\epsilon$  in the 2600–8700 cm<sup>-1</sup> range. The high intensities of these bands indicate that none of them are due to d–d type transitions. The highest energy transition, around

285 nm, may be assigned to an intra-ligand ( $\pi \rightarrow \pi^*$ ) transition<sup>(16)</sup>, whilst the other absorptions around 575, 525 and 330 nm may be assigned to LMCT bands of the type  $\pi(\text{acac}) \rightarrow \text{Ru}(t_{2g})$  and  $\pi(\text{Cl}) \rightarrow \text{Ru}(t_{2g})$ <sup>(17,18)</sup>.

The spectrum of [RuCl<sub>2</sub>(acac)(MeCN)<sub>2</sub>] in chloroform is similar to that of [RuCl<sub>2</sub>(acac)(acacH)]. Aqueous solutions of [RuCl<sub>2</sub>(acac)(acacH)] are purple, but immediately turn bluish green on the addition of base (OH<sup>-</sup>). Addition of acid reversibly restores the original purple. The spectrum of the compound in basic solution contains a new band at 670 nm, whilst the band at 530 nm is absent. The colour of the solution in the presence of OH<sup>-</sup> may be due to the formation of the complex anion [RuCl<sub>2</sub>(acac)(OH)<sub>2</sub>]<sup>2-</sup>, the acidification of which may result in [RuCl<sub>2</sub>(acac)(H<sub>2</sub>O)<sub>2</sub>]. The visible spectrum of [RuCl<sub>2</sub>(acac)(H<sub>2</sub>O)<sub>2</sub>] is similar to that of [RuCl<sub>2</sub>(acac)(acacH)] in water, presumably due to formation of [RuCl<sub>2</sub>(acac)(H<sub>2</sub>O)<sub>2</sub>] in H<sub>2</sub>O.

The [RuCl<sub>2</sub>(acac)L<sub>2</sub>] complexes (L = PPh<sub>3</sub>, AsPh<sub>3</sub> or py) showed one band around 600 nm ( $\epsilon$  ca. 235 to 290) and two additional bands below 400 nm. The former can be assigned to a d–d transition ( ${}^2T_{2g} \rightarrow {}^2A_{2g}$  or  ${}^2A_{1g}$ ) in a low spin d<sup>5</sup> system<sup>(18)</sup>. Of the two bands in 400–300 nm region, one band having  $\epsilon = 10^4$  or above is assigned to the intra-ligand  $\pi \rightarrow \pi^*$  transition, whilst the other is assigned to an LMCT transition (*vide supra*). [RuCl<sub>2</sub>(acac)L], (L = bipy or phen) in chloroform exhibits similar features to that of [RuCl<sub>2</sub>(acac)(acacH)], except for the appearance of a new band around 450 nm assigned to the  $\pi(\text{bipy or phen}) \rightarrow \text{Ru}(t_{2g})$  transition.

The spectra of M<sub>2</sub>[RuCl<sub>4</sub>(acac)] (M = Me<sub>4</sub>N, Cs or Rb) in water showed one band at 510 nm ( $\epsilon$  ca. 415 to 645) and two more bands below 350 nm. The first of these can be assigned to a combination of a d–d transition ( ${}^2T_{2g} \rightarrow {}^2A_{2g}$  or  ${}^2A_{1g}$ ) and an LMCT  $\pi(\text{acac}) \rightarrow \text{Ru}(t_{2g})$  transition. The bands below 350 nm may be assigned to a  $\pi(\text{Cl}) \rightarrow \text{Ru}(t_{2g})$  transition.

#### Conclusion

The complex of ruthenium(II) containing neutral acetylacetonone, acetylacetonate and chloride is described, and its structural assignment is made on the basis of physico-chemical and spectroscopic methods. Its reactivity has been studied towards various donor ligands, when [RuCl<sub>2</sub>(acac)L<sub>2</sub>] (L = PPh<sub>3</sub>, AsPh<sub>3</sub>, py, MeCN, Me<sub>2</sub>SO, *o*-phenylenediamine; L<sub>2</sub> = phen or bipy) have been obtained with substitution of coordinated acacH.

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