

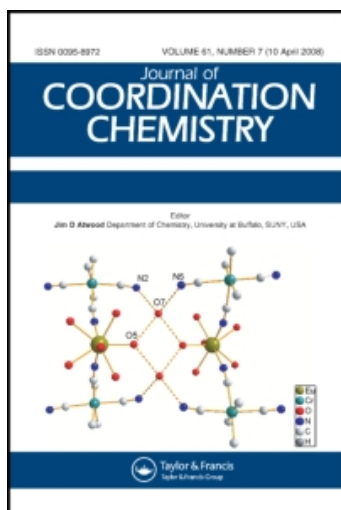
This article was downloaded by:

On: 23 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

### Ruthenium carbonyl derivatives of N-salicylidene-2-hydroxyaniline

Omyma A. M. Ali<sup>a</sup>; Laila H. Abdel-Rahman<sup>b</sup>; Ramadan M. Ramadan<sup>c</sup>

<sup>a</sup> Chemistry Department, University College for Girls, Ain Shams University, Cairo, Egypt <sup>b</sup> Faculty of Science, Department of Chemistry, Sohag South Valley University, Sohag, Egypt <sup>c</sup> Faculty of Science, Chemistry Department, Ain Shams University, Cairo, Egypt

First published on: 18 June 2007

**To cite this Article** Ali, Omyma A. M. , Abdel-Rahman, Laila H. and Ramadan, Ramadan M.(2007) 'Ruthenium carbonyl derivatives of N-salicylidene-2-hydroxyaniline', Journal of Coordination Chemistry, 60: 21, 2335 – 2342, First published on: 18 June 2007 (iFirst)

**To link to this Article:** DOI: 10.1080/00958970701263952

**URL:** <http://dx.doi.org/10.1080/00958970701263952>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Ruthenium carbonyl derivatives of N-salicylidene-2-hydroxyaniline

OMYMA A. M. ALI<sup>†</sup>, LAILA H. ABDEL-RAHMAN<sup>‡</sup>  
and RAMADAN M. RAMADAN<sup>\*§</sup>

<sup>†</sup>Chemistry Department, University College for Girls,  
Ain Shams University, Cairo, Egypt

<sup>‡</sup>Faculty of Science, Department of Chemistry,  
Sohag South Valley University, Sohag, Egypt

<sup>§</sup>Faculty of Science, Chemistry Department,  
Ain Shams University, Cairo, Egypt

(Received 31 October 2006; in final form 5 December 2006)

The ruthenium tricarbonyl derivative  $[\text{Ru}(\text{CO})_3(\text{sha})]$  (**1**), was synthesized from reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with N-salicylidene-2-hydroxyaniline ( $\text{shaH}_2$ ) Schiff base. The corresponding reactions of the ruthenium cluster with  $\text{shaH}_2$  in presence of a secondary ligand L, L = pyridine and triphenyl phosphine resulted in the formation of the dicarbonyl derivatives  $[\text{Ru}(\text{CO})_2(\text{shaH}_2)(\text{L})]$  (**2**, **3**). In the presence of L = 2-aminobenzimidazole or thiourea, two complexes  $[\text{Ru}(\text{CO})_2(\text{sha})(\text{L})]$  (**4**, **5**) were formed and the  $\text{shaH}_2$  ligand bonded to ruthenium oxidatively. The bipyridine(bpy) derivative had the molecular formula  $[\text{Ru}(\text{CO})_2(\text{shaH})(\text{bpy})]$  (**6**), with  $\text{shaH}$  coordinated bidentate. All complexes were characterized by elemental analysis and mass, IR,  $^1\text{H}$  NMR and UV–Vis spectroscopy. The spectroscopic studies of these complexes revealed several structural arrangements and different tautomeric forms.

**Keywords:** Metal carbonyls; Triruthenium dodecacarbonyl; Schiff bases; Complexes; Spectra; Isomerism

### 1. Introduction

The chemistry of ruthenium has promising photochemical and catalytic properties [1, 2]. Ru(II) carbonyl complexes containing O,N-donor ligands and heterocyclic bases showed redox properties as well as biological activity [3]. For example, ruthenium(II) carbonyl complexes containing bidentate Schiff bases and triphenyl phosphine or pyridine were found to be very efficient catalysts in oxidation of alcohols to aldehydes in the presence of N-methylmorpholine-N-oxide (NMO) as a co-oxidant [4–8]. Furthermore, ruthenium carbonyl carboxylate complexes containing bipyridine ligands have good catalytic activity in the homogeneous hydrogenation of  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$

\*Corresponding author. Email: r\_m\_ramadan@yahoo.com

bonds in hydroalcoholic solvents, which is an environmentally friendly process [9]. Also, the elucidation of the water gas shift reactions promoted by ruthenium carbonyls in acidic media started with the detection of the Ru(0), Ru(I), and Ru(II) intermediate complexes,  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Ru}_2[\mu-\eta^2\text{-OC}(\text{CF}_3)\text{O}]_2(\text{CO})_6$ , and  $\text{fac-}[\text{Ru}(\text{CF}_3\text{COO})_3(\text{CO})_3]^-$ , which accumulate when  $\text{CF}_3\text{COOH}$  is employed as an acid co-catalyst [10, 11]. The environment around the metal center such as coordination geometry, the number of coordinated ligands and their donor groups are controlling factors for metalloproteins to carry out specific physiological functions [12, 13]. On the other hand, ruthenium(0) carbonyl derivatives such as  $[\text{Ru}(\text{CO})(3'\text{-PyaiR})(\text{PPh}_3)_2]$  ( $3'\text{-PyaiR} = 2\text{-(3'-pyridylazo)imidazole}$ ) [14] and  $[\text{Ru}(\text{CO})_3(\text{LH}_2)]$  ( $\text{LH}_2 = \text{maleic hydrazide}$ ) [15] are expected to be important biological derivatives. Although Ru(I) complexes usually exist in dimeric forms such as  $[\text{Ru}(\text{OAc})(\text{CO})_2(\text{dpa})]_2$ ,  $\text{dpa} = \text{di(2-pyridyl)amine}$  [16] and  $[\text{Ru}_2(\text{C}_6\text{H}_5\text{CO}_2)_2(\text{CO})_4(\text{py})_2]$  [17], few Ru(I) complexes have been reported with mononuclear structure. For example, reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with salicylideneimine-2-thiophenol Schiff base ( $\text{satpH}_2$ ) in THF gave  $[\text{Ru}(\text{CO})_4(\text{satpH})]$ . Spectroscopic and magnetic studies of the complex revealed that it was paramagnetic with octahedral structure [18]. Recently, we reported that the reactions of  $[\text{Ru}_3(\text{CO})_{12}]$  with 2-(2'-pyridyl)benzimidazole (HPBI) alone or in the presence of pyridine or bipyridine, gave  $[\text{Ru}(\text{CO})_3(\text{HPBI})]$ ,  $[\text{Ru}(\text{CO})_3(\text{HPBI})] \cdot \text{py}$  and  $[\text{Ru}(\text{CO})_3(\text{HPBI})] \cdot \text{bpy}$ , respectively [19]. Also, reactions of  $[\text{Ru}_3(\text{CO})_{12}]$  with 2,3-bis(2'-pyridyl)quinoxaline (dpq) in the presence of either bipyridine or pyridine resulted in the formation of mononuclear complexes  $[\text{Ru}(\text{CO})_3(\text{dpq})]$  and  $[\text{Ru}(\text{CO})_2(\text{dpq})] \cdot \text{py}$  [20]. In a previous report, the reactions of  $[\text{M}(\text{CO})_6]$ ,  $\text{M} = \text{Cr, Mo and W}$  with N-salicylidene-2-hydroxyaniline ( $\text{shaH}_2$ ) were described [21]. In this manuscript, we report the reactions of  $[\text{Ru}_3(\text{CO})_{12}]$  with  $\text{shaH}_2$  alone or in the presence of pyridine, 2,2'-bipyridine, thiourea, 2-aminobenzimidazole or triphenyl phosphine as a secondary ligand.

## 2. Experimental

$[\text{Ru}_3(\text{CO})_{12}]$ , pyridine (py) triphenyl phosphine ( $\text{PPh}_3$ ), 2-aminobenzimidazole (abz) thiourea (tu) and 2,2'-bipyridine (bpy) were purchased from Aldrich. N-salicylidene-2-hydroxyaniline ( $\text{shaH}_2$ ) was prepared as described [22]. All solvents used were of analytical grade and were purified by distillation according to standard methods.

Infrared measurements (KBr pellets) were carried out on a Shimadzu 8000 FT-IR spectrometer. Electronic absorption spectra were measured on a Unicam UV2-300 UV-Vis spectrophotometer. The spectra of the complexes in different solvents (DMF, benzene, THF and  $\text{CH}_2\text{Cl}_2$ ) were of concentrations ca  $1 \times 10^{-5} \text{ M}$ .  $^1\text{H}$  NMR measurements were performed on a Varian-Mercury 300 MHz spectrometer. Samples were dissolved in  $(\text{CD}_3)_2\text{SO}$  with TMS as internal reference. Magnetic measurements in the solid state (Gouy method) were carried out on a Sherwood magnetic susceptibility balance. The complexes were also characterized by elemental analysis (Perkin-Elmer 2400 CHN elemental analyzer) and mass spectrometry (70 eV, EI, Finnigan MAT SSQ 7000 spectrometer). Table 1 gives the elemental analysis and mass spectrometry data for the complexes.

Table 1. Elemental analysis and mass spectrometry data for ruthenium complexes.

Complex	%C Found (Calcd)	%H Found (Calcd)	%N Found (Calcd)	Mass spectrometry	
				M. wt	<i>m/z</i>
<b>1</b>	48.6(48.9)	2.4(2.5)	3.6(3.8)	368.31	369 [P] <sup>+</sup>
<b>2</b>	53.2(53.5)	3.3(3.6)	5.9(6.2)	449.43	450 [P] <sup>+</sup>
<b>3</b>	62.4(62.6)	4.0(4.1)	2.0(2.2)	632.60	605 [P – CO] <sup>+</sup>
<b>4</b>	52.5(52.7)	3.2(3.2)	10.8(11.2)	501.45	502 [P] <sup>+</sup>
<b>5</b>	43.1(43.2)	2.8(2.9)	9.3(9.5)	444.42	443 [P – 2H] <sup>+</sup>
<b>6</b>	56.9(57.1)	3.4(3.4)	7.5(7.9)	525.50	524 [P – H] <sup>+</sup>

### 2.1. Synthesis of $[Ru(CO)_3(sha)]$ (**1**)

A mixture of  $[Ru_3(CO)_{12}]$  (0.1 g, 0.16 mmol),  $shaH_2$  (0.1 g, 0.47 mmol) and benzene (ca 30 cm<sup>3</sup>) were heated to reflux for 8 h. The color of the solution changed from orange to dark grey. The reaction mixture was cooled and the solvent was removed by evaporation. The solid residue was washed several times with boiling petroleum ether and then recrystallized from DMF to give fine grey crystals in a yield of 55%.

### 2.2. Syntheses of $[Ru(CO)_2(shaH_2)(py)]$ (**2**), $[Ru(CO)_2(shaH_2)(PPh_3)]$ (**3**), $[Ru(CO)_2(sha)(abz)]$ (**4**), $[Ru(CO)_2(sha)(tu)]$ (**5**) and $[Ru(CO)_2(shaH)(bpy)]$ (**6**) complexes

A mixture of  $[Ru_3(CO)_{12}]$  (0.1 g, 0.16 mmol),  $shaH_2$  (0.1 g, 0.47 mmol) and L, L = pyridine,  $PPh_3$ , 2-aminobenzimidazole or thiourea, in benzene (ca 30 cm<sup>3</sup>) was heated to reflux for 2–4 h. The reaction mixture was cooled and the solvent was removed by evaporation. The complex was washed several times with boiling petroleum ether and then recrystallized from DMF. The color and yield of the complexes are: **2**, light brown, 76%; **3**, dark red, 54%; **4**, dark grey, 90%; **5**, dark brown, 49%; **6**, dark grey, 79%.

## 3. Results and discussion

A series of ruthenium carbonyl Schiff base complexes (**1–6**) have been synthesized from the reactions of  $[Ru_3(CO)_{12}]$  with *N*-salicylidene-2-hydroxyaniline ( $shaH_2$ ) alone or in the presence of a secondary ligand. The  $shaH_2$  Schiff base ligand acted either as a bidentate (ON) or a tridentate (ONO) donor depending on the oxidation state of the metal ion [21, 22]. The IR spectrum of the free Schiff base exhibited a strong band at 1631 cm<sup>−1</sup> due to the azomethine. This band shifted (1602–1611 cm<sup>−1</sup>) in the IR spectra of the complexes indicating coordination through the azomethine nitrogen (table 2) [21]. The bands at 1274 and 1243 cm<sup>−1</sup> in the spectrum of  $shaH_2$  are assigned to the phenolic C–O stretch. On complexation, these bands shifted to higher frequencies. Also, bands due to  $\nu(Ru-O)$  and  $\nu(Ru-N)$  stretches were observed in the region 533–574 and 426–500 cm<sup>−1</sup>, respectively. All other characteristic bands due to py, bpy,  $PPh_3$ , abz and tu were shifted to higher frequencies confirming coordination of these ligands to the ruthenium (table 2). The <sup>1</sup>H NMR spectra showed lower field shifts in the

Table 2. Important IR data for shaH<sub>2</sub> and its ruthenium complexes.

Compound	IR data (cm <sup>-1</sup> ) <sup>a</sup>					
	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{OH})$	$\nu(\text{CO})$	$\nu(\text{Ru}-\text{O})$	$\nu(\text{Ru}-\text{N})$
shaH <sub>2</sub>	1631(s)	1274(m) 1243(m)	3422(m)	—	—	—
<b>1</b>	1603(s)	1279(m) 1246(m)	—	2052(vs) 1981(vs) 1941(s)	533(m)	460(w)
<b>2<sup>b</sup></b>	1603(s)	1273(m) 1245(sh)	3424(b)	2045(m) 2117(s) 1972(s) 1931(vs)	533(m)	470(w)
<b>3<sup>c</sup></b>	1606(s)	1277(m) 1246(w)	3423(b)	2046(m) 1971(vs) 1946(vs)	557(m)	426(w)
<b>4<sup>d</sup></b>	1641(s) 1602(s)	1272(s)	—	2052s 2024s 1980s 1937vs	532m	500(w)
<b>5<sup>e</sup></b>	1611(s)	1276(b)	—	2020(vs,b) 1954(vs,b)	574(m)	493(w)
<b>6<sup>f</sup></b>	1603(s)	1282(m) 1251(m)	3420(b)	2042(m) 2025(m) 1970(sh) 1937(vs)	533(m)	493(w)

<sup>a</sup>s, strong; m, medium; w, weak; b, broad; sh, shoulder; <sup>b</sup> $\delta(\text{py}) = 696 \text{ cm}^{-1}$ ; <sup>c</sup> $\nu(\text{C}-\text{H})_{\text{phosphine}} = 1435, 745, 695 \text{ cm}^{-1}$ ; <sup>d</sup> $\nu(\text{N}-\text{H}) = 3379, 3061 \text{ cm}^{-1}$ ; <sup>e</sup> $\nu(\text{C}=\text{S}) = 1611, \nu(\text{N}-\text{H}) = 3322, 3189 \text{ cm}^{-1}$ ; <sup>f</sup> $\delta(\text{py}) = 697 \text{ cm}^{-1}$ .

Table 3. Important <sup>1</sup>H NMR data for shaH<sub>2</sub> and its ruthenium complexes.

Compound	<sup>1</sup> H NMR data (ppm) <sup>a</sup>
shaH <sub>2</sub>	7.55(m, Ph), 7.06(m, Ph), 9.03(s, N=CH), 13.75(s, OH), 9.7(s, OH)
<b>1</b>	6.6–7.4(m, Ph), 9.19(s, N=CH)
<b>2</b>	6.6–7.9(m, Ph), 8.96(m, py), 8.58(m, py), 9.19(s, N=CH), 9.04(s, N=CH), 13.74(s, OH), 9.69(s, OH)
<b>3</b>	6.6–7.8(m, Ph), 8.96(s, N=CH), 9.20(s, N=CH), 9.66(s, OH), 13.73(s, OH)
<b>4</b>	6.0–8.0(m, Ph), 8.97(s, N=CH), 9.03(s, N=CH), 11.26(s, NH), 11.46(s, NH), 5.39(s, NH <sub>2</sub> ), 5.08(s, NH <sub>2</sub> )
<b>5</b>	6.97(m, Ph), 5.35(s, NH <sub>2</sub> ), 8.97(s, N=CH)
<b>6</b>	6.5–8.5(m, Ph), 8.74(m, py), 9.29(s, N=CH), 9.27(s, N=CH), 9.50(s, OH)

<sup>a</sup>s, singlet; d, doublet; m, multiplet.

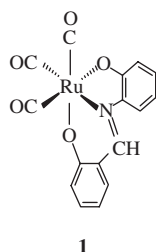
6.00–8.96 ppm region due to the aromatic protons of the coordinated pyridine, bipyridine, triphenyl phosphine, thiourea, 2-aminobenzimidazole and shaH<sub>2</sub> ligands (table 3) [23].

The IR spectrum of [Ru(CO)<sub>3</sub>(sha)] (**1**), exhibited three bands in the terminal metal carbonyl range at 2052, 1981 and 1941 cm<sup>-1</sup> due to three CO groups attached to the metal in a *facial* arrangement. From the number and pattern of the CO groups, it can be concluded that the ruthenium complex has an octahedral structure and the sha moiety coordinated to the metal from two *cis* and one *trans* sites [24]. The band due to the  $\nu(\text{OH})$  frequency of the ligand disappeared in the IR spectrum of the complex. The absence of the two OH groups was also confirmed by <sup>1</sup>H NMR spectroscopy.

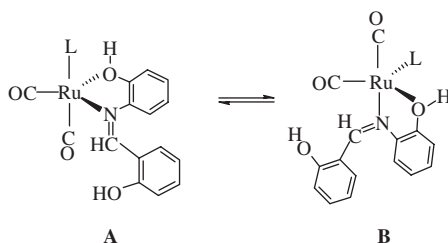
The elimination of the hydrogen from the OH groups indicated that the metal coordinated to the ligand oxidatively [25]. From the elemental analysis and the spectroscopic data, it can be concluded that the ruthenium species exists in  $a+2$  oxidation state with a proposed structure shown in scheme 1.

The IR spectra of  $[\text{Ru}(\text{CO})_2(\text{shaH}_2)(\text{py})]$  (**2**), and  $[\text{Ru}(\text{CO})_2(\text{shaH}_2)(\text{PPh}_3)]$  (**3**), showed a broad band at  $3423\text{--}3424\text{ cm}^{-1}$  and two bands in the range  $1383\text{--}1385$  and  $1346\text{--}1353\text{ cm}^{-1}$  due to one stretching and two bending OH frequencies. Also, the  $^1\text{H}$  NMR spectra of **2** and **3** displayed two signals around 9.6 ppm and 13.7 ppm indicating the presence of the two OH groups of the shaH<sub>2</sub>. In addition, the infrared spectra displayed four CO stretching vibrations in the terminal metal carbonyl region. According to the elemental analysis and the spectroscopic data, one can conclude that the two complexes exist in two isomeric forms (**A** and **B**) in equal proportions depending on the position of py or PPh<sub>3</sub> ligand. Each isomer contains two CO groups attached *cis* to each other. This postulation was confirmed from their NMR spectra which gave two signals at 9.19 and 9.04 ppm for **2**, and 8.96 and 9.20 ppm for **3** due to the presence of two azomethine groups (scheme 2). (Attempts to separate the two isomers did not succeed). The  $^1\text{H}$  NMR spectrum of the previously reported  $[\text{Mo}(\text{CO})_3(\text{pbiH})(\text{PPh}_3)]$  complex, pbiH = 2-(2'-pyridyl)benzimidazole showed two broad singlets for the NH proton indicating the presence of two equilibrated isomeric forms depending on the position of PPh<sub>3</sub> ligand [26]. In addition, the IR spectrum of **2** exhibited a medium band at  $696\text{ cm}^{-1}$  due to  $\delta\text{py}$ , while the spectrum of **3** displayed strong bands at 1474, 1433, 742 and  $693\text{ cm}^{-1}$  indicating the presence of PPh<sub>3</sub> ligand. Therefore, for **2** and **3**, a zerovalent ruthenium species exists in a trigonal bipyramidal structure with two *cis* CO groups (scheme 2).

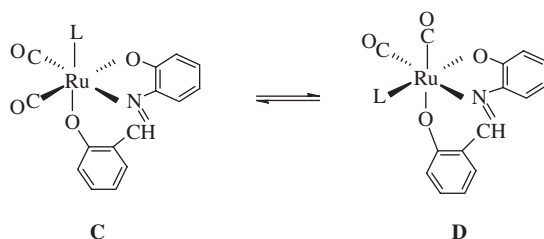
Similarly, the IR spectra of  $[\text{Ru}(\text{CO})_2(\text{sha})(\text{abz})]$  (**4**), and  $[\text{Ru}(\text{CO})_2(\text{sha})(\text{tu})]$  (**5**) showed the shaH<sub>2</sub> ligand bands and a set of four CO bands in the terminal carbonyl range (table 2). Additional bands correspond to either abz or tu shift to higher



Scheme 1. The proposed structure for  $[\text{Ru}(\text{CO})_3(\text{sha})]$  complex.



Scheme 2. The proposed structures for  $[\text{Ru}(\text{CO})_2(\text{shaH}_2)\text{L}]$  complexes, L = py (**2**) or PPh<sub>3</sub> (**3**).



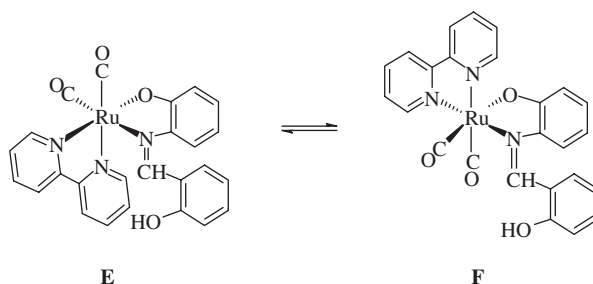
Scheme 3. The proposed structures for  $[\text{Ru}(\text{CO})_2(\text{sha})\text{L}]$  complexes,  $\text{L} = \text{abz}$  (**4**) or  $\text{tu}$  (**5**).

frequencies indicating coordination. Furthermore, the IR spectra of these complexes exhibited no bands due to OH of the  $\text{shaH}_2$ . The  $^1\text{H}$  NMR spectra confirm the absence of these two OH groups. Again, from the available elemental and spectroscopic data, it can be concluded that **4** and **5** exist in two isomeric forms (**C** and **D**) and the ruthenium atom has  $a + 2$  formal oxidation state (scheme 3). Each abz or tu group coordinates to ruthenium in a *trans* position to an oxygen of the  $\text{shaH}_2$ ; two COs in *cis* positions complete the six coordination.

Interaction of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{shaH}_2$  in the presence of bipyridine results in formation of  $[\text{Ru}(\text{CO})_2(\text{shaH})(\text{bpy})]$  (**6**). The IR spectrum of the complex showed a  $\nu(\text{OH})$  stretch at  $3420\text{ cm}^{-1}$  and also displayed four strong bands in the metal carbonyl region at  $2042$ ,  $2025$ ,  $1970$  and  $1937\text{ cm}^{-1}$  due to the carbonyl ligands [18]. The  $^1\text{H}$  NMR spectrum of **6** has a resonance at  $9.50\text{ ppm}$  for the proton of the hydroxyl group ortho to the azomethine. The disappearance of the signal due to the other hydroxyl proton of the ligand ( $13.86\text{ ppm}$ ) indicates that coordination metal occurred through it with proton displacement [27]. The bpy ligand itself has three multiplets at  $7.0$ ,  $7.4$  and  $8.5\text{ ppm}$ . The observed downfield shifts were consistent with complex formation. As expected from a proposed formula with a Ru(I), the magnetic study of the complex showed paramagnetism. The magnetic measurements at  $298\text{ K}$  gave a value of  $1.32\text{ BM}$  for the effective magnetic moment, less than the spin only value of one unpaired electron ( $1.73\text{ BM}$ ). The previously reported  $[\text{Ru}(\text{CO})_4(\text{satpH})]$  complex with a Ru(I) electronic configuration gave a  $\mu_{\text{eff}}$  of  $1.49\text{ BM}$  [18]. Further confirmation of the formula of **6** was obtained from mass spectrometry. The mass spectrum showed a molecular ion peak at  $m/z = 524$  ( $5.7\%$ ) due to the parent ion  $[\text{P} - \text{H}]^+$ . Also, it exhibited fragments at  $m/z = 469$  ( $31.6\%$ ) due to  $[\text{P}(\text{CO})_2]^+$ ,  $313$  ( $14.6\%$ ) due to  $[\text{P}(\text{bpy} + (\text{CO})_2)]^+$ ,  $211$  ( $10.3\%$ ) due to sha moiety,  $156$  ( $100\%$ ) due to bpy. Therefore, it can be concluded that ruthenium is in  $a + 1$  ( $d^7$ ) formal oxidation state in an octahedral arrangement with two isomeric forms (**E** and **F**); as shown in scheme 4.

### 3.1. Electronic absorption spectra

The UV–Vis spectra of  $\text{shaH}_2$  and its complexes were measured in THF,  $\text{CH}_2\text{Cl}_2$ , DMF and  $\text{C}_6\text{H}_6$  (table 4). The electronic absorption spectrum of  $\text{shaH}_2$  itself consisted of two bands in the range of  $262\text{--}272$  and  $352\text{--}357\text{ nm}$  due to  $\pi\text{--}\pi$  and  $n\text{--}\pi$  transitions, respectively. A bathochromic shift in the  $\pi\text{--}\pi$  electronic transitions was observed in the spectra of the complexes, while the  $n\text{--}\pi$  bands exhibited hypsochromic shifts with a considerable change in absorbance. In addition, new bands in the visible region occurred around  $400\text{--}500\text{ nm}$ , assigned to metal-to-ligand (MLCT) charge transfer

Scheme 4. The proposed structure for  $[\text{Ru}(\text{CO})_2(\text{shaH})(\text{bpy})]$  (**6**) complex.Table 4. The UV–Vis data for shaH<sub>2</sub> and its ruthenium complexes.

Compound	DMF	THF	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>
shaH <sub>2</sub>	272	268	270	268
	356	352	357	356
<b>1</b>	275	274	275	277
	354	326	289	293
<b>2</b>	403(b)	402(b)	400(b)	400(b)
	280	281	260	274
	313	327	282	290
	410(b)	413(b)	411(b)	418(b)
	445(sh)		445(sh)	440(sh)
	490(sh)			490(sh)
<b>3</b>	285	281	285	285
	308	334(b)	324(b)	324(b)
<b>4</b>	500(b)	473(b)	492(b)	474(b)
	282	276	265	272
	293	290	290	290
<b>5</b>	419(b)	418(b)	412(b)	414(b)
	275	280	Insol.	Insol.
	290	324		
<b>6</b>	420(sh)	420(sh)		
	284	275	285	273
	304	327	300	304
	424(b)	427(b)	420(b)	428(b)
	453(sh)	455(sh)	450(sh)	460(sh)

transitions [28]. The UV–Vis spectrum of **1** showed a broad absorption band around 400 nm in all solvents, while complexes **2–6** exhibited a broad absorption band with a shoulder at lower energies than **1**. The presence of different acceptor levels in these complexes may be responsible for the observed multiple absorptions. Other previously reported ruthenium complexes exhibited visible bands due to metal to ligand charge transfer [8, 14, 18, 19, 26].

## References

- [1] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi. *Solar Ener. Mater. Solar Cells*, **38**, 159 (1995).
- [2] V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni. *Chem. Rev.*, **96**, 759 (1996).
- [3] K.K. Naresh, R. Ramesh. *Spectrochim. Acta Part A*, **60**, 2913 (2004).

- [4] R.I. Kureshy, N.H. Khan, S.H.R. Abdi. *J. Mol. Catal.*, **96**, 117 (1995).
- [5] A.M. El-Hendawy, A.H. Alkubaisi, M. Abd EL-Ghany, A. El-Kourashy, M.M. Shanab. *Polyhedron*, **12**, 2343 (1993).
- [6] A.M. El-Hendawy, M. Abd EL-Ghany, A. El-Kourashy, M.M. Shanab. *Polyhedron*, **11**, 523 (1992).
- [7] G. Bhowon, K. Li, H. Wah, R. Narain. *Polyhedron*, **18**, 341 (1999).
- [8] P. Viswanathamurthi, R. Karvembu, V. Tharaneeswaran, K. Natarajan. *J. Chem. Sci.*, **117**, 235 (2005).
- [9] A. Salvini, P. Frediani, E. Rivalta. *Inorg. Chim. Acta*, **351**, 225 (2003).
- [10] G. Fachinetti, T. Funaioali, L. Lecci, F. Marchetti. *Inorg. Chem.*, **35**, 7217 (1996).
- [11] E. Rosenberg, D.M. Skinner, S. Aime, L. Milone, R. Gobetto, D. Osella. *Gaz. Chim. Italiana*, **121**, 313 (1991).
- [12] J. Chakraborty, R.N. Patel. *J. Ind. Chem. Soc.*, **73**, 191 (1996).
- [13] R. Klement, F. Stock, H. Ellias, H. Paulus, P. Pelikan, M. Valko, M. Mazur. *Polyhedron*, **18**, 3617 (1999).
- [14] T. Mathur, J. Dinda, P. Datta, G. Mostafa, T.H. Lu, C. Sinha. *Polyhedron*, **25**, 2503 (2006).
- [15] A.M. Hassan, S.A. Ali, R.M. Ramadan. *Spectrochim. Acta, Part A*, **64**, 913 (2006).
- [16] C.M. Kepert, G.B. Deacon, L. Spiccia. *Inorg. Chim. Acta*, **355**, 213 (2003).
- [17] L. Xu, Y.J. Sasaki. *Organometal. Chem.*, **585**, 246 (1999).
- [18] M.M.H. Khalil, M.M. Aboaly, R.M. Ramadan. *Spectrochim. Acta Part A*, **61**, 157 (2005).
- [19] M.M.H. Khalil, S.A. Ali, R.M. Ramadan. *Spectrochim. Acta Part A*, **57**, 1017 (2001).
- [20] A.A. Abdel-Shafi, M.M.H. Khalil, H.H. Abdalla, R.M. Ramadan. *Trans. Metal. Chem.*, **27**, 69 (2002).
- [21] S.M. El-Medani, O.A.M. Ali, R.M. Ramadan. *J. Mole. Struct.*, **738**, 171 (2005).
- [22] S.M. El-Medani. *J. Coord. Chem.*, **57**, 115 (2004).
- [23] J.R. Dyer. *Application of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall, New Jersey (1978).
- [24] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, Wiley, New York (1986).
- [25] J. Collman, L.S. Hegedus. *Principles and Application of Organotransition Metal Chemistry*, University Science Book, California (1980).
- [26] M.M.H. Khalil, H.A. Mohamed, S.M. El-Medani, R.M. Ramadan. *Spectrochim. Acta Part A*, **59**, 1341 (2003).
- [27] O.A.M. Ali, M.M.H. Khalil, G.M. Attia, R.M. Ramadan. *Spect. Lett.*, **36**, 71 (2003).
- [28] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, New York (1984).