

SYNTHESIS AND SPECTROSCOPIC STUDIES ON SOME RUTHENIUM(II) COMPLEXES

By

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تحضير ودراسات طيفية على بعض

متراكبات الروثينيوم الثنائي

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إستخدم متراكب ثنائي الكلوريد ثنائي الكربونيل للروثينيوم الثنائي كمادة أولية لتحضير متراكبات الروثينيوم الثنائي مع مرتببات أحادية المخلب المتعادلة وكذلك مع المرتببات ثنائية المخلب مثل اثلين ثنائي الأمين ومشتقات الفوسين ثيوسيمكربازون. ولقد تم التعرف على تلك المتراكبات باستخدام طيف الأشعة تحت الحمراء والرنين النووي المغناطيسي للبروتون وكذلك التحليل العنصري .

Key Words: Ruthenium(II) complexes, Ferrocenethiosemicarbazone

ABSTRACT

The salt $[\text{RuCl}_2(\text{CO})_2]_n$ has proved very useful precursor for the syntheses of a variety of organometallic complexes of transition metals. The compounds of dichlorodicarbonylruthenium(II) of the formula $[\text{RuCl}_2(\text{CO})_2\text{L}]$ or $[\text{RuCl}_2(\text{CO})_2\text{L}']$ where L= monodentate ligands such as tetramethylthiourea or substituted ureas, naphthioxazole, 2-aminobenzthiazole or thioacetamide and L' = bidentate ligands such as 1,2-diaminoethane, 2,2'-dipyridylamine, 1-acetylferrocenethiosemicarbazone (1-AFTSC) or 1-acetylferrocenesemicarbazone (1-AFSC) have been prepared. The versatile nature of these ligands (L or L') has shown that they react readily with $[\text{RuCl}_2(\text{CO})_2]_n$ giving very stable Ru(II) complexes. For example, the complex 1-acetylferrocenethiosemicarbazone, $\pi\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_3\text{C}=\text{N.NH.CS.NH}_2$. (1-AFTSC) or 1-acetylferrocenesemicarbazone, $\pi\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_3\text{C}=\text{N.NH.CO.NH}_2$. (1-AFSC) acts as bidentate ligand in which thiosemicarbazone or semicarbazone moiety acts as bridge between two metal systems giving bimetallic complexes. Thus, the reaction of $[\text{RuCl}_2(\text{CO})_2]_n$ with 1-AFTSC or 1-AFSC yields 1-acetylferrocenethiosemicarbazone dichlorodicarbonylruthenium (II) $[\pi\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_3\text{C}=\text{N.NH.CS.NH}_2\text{RuCl}_2(\text{CO})_2]$ or 1-acetylferrocenesemicarbazone dichlorodicarbonylruthenium(II) $[\pi\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_3\text{C}=\text{N.NH.CO.NH}_2.\text{RuCl}_2(\text{CO})_2]$ complexes respectively as shown in the scheme of reactions (Fig. 1). Similarly reactions of CuX_2 (X = Cl or Br) and $\text{NiCl}_2 \cdot \text{XH}_2\text{O}$ with 1-AFTSC yield respective organometallic complexes. All the complexes were identified by elemental analysis and were characterized by IR and $^1\text{H-NMR}$ spectroscopy and elemental analyses.

INTRODUCTION

The usefulness of the compound $[\text{RuCl}_2(\text{CO})_2]_n$ [1-2] has been proved by its versatile nature of bonding with a variety of ligands. Earlier workers have shown its reaction with phosphines, arsine or substituted amines. The ligands used were mostly neutral or negatively charged[3,4]. We have also shown the use of variety of ligands which react readily with $[\text{RuCl}_2(\text{CO})_2]_n$ to give complexes of the types $[\text{RuCl}_2(\text{CO})_2.2\text{L}]$ [5-7]. Recently we have reported the use of thiosemicarbazide which acts as bidentate ligand when

treated with $[\text{RuCl}_2(\text{CO})_2]_n$ [8]. However, 1-acetylferrocenethiosemicarbazone, ($\pi\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_3\text{C}=\text{N.NH.CS.NH}_2$) has proved very useful bidentate ligand. On treatment with $[\text{RuCl}_2(\text{CO})_2]_n$ in (1:1) molar ratio in boiling THF gave very stable orange yellow solid, 1-acetylferrocenethiosemicarbazone dichlorodicarbonyl ruthenium (II), $[\pi\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4.\text{CH}_3.\text{C}=\text{N.NH.CS.NH}_2\text{-Ru}(\text{CO})_2\text{Cl}_2]$ in which the metal ruthenium coordinates through the sulphur and hydrazinic nitrogen atoms as shown in Fig. 1.

Ru(II) complexes

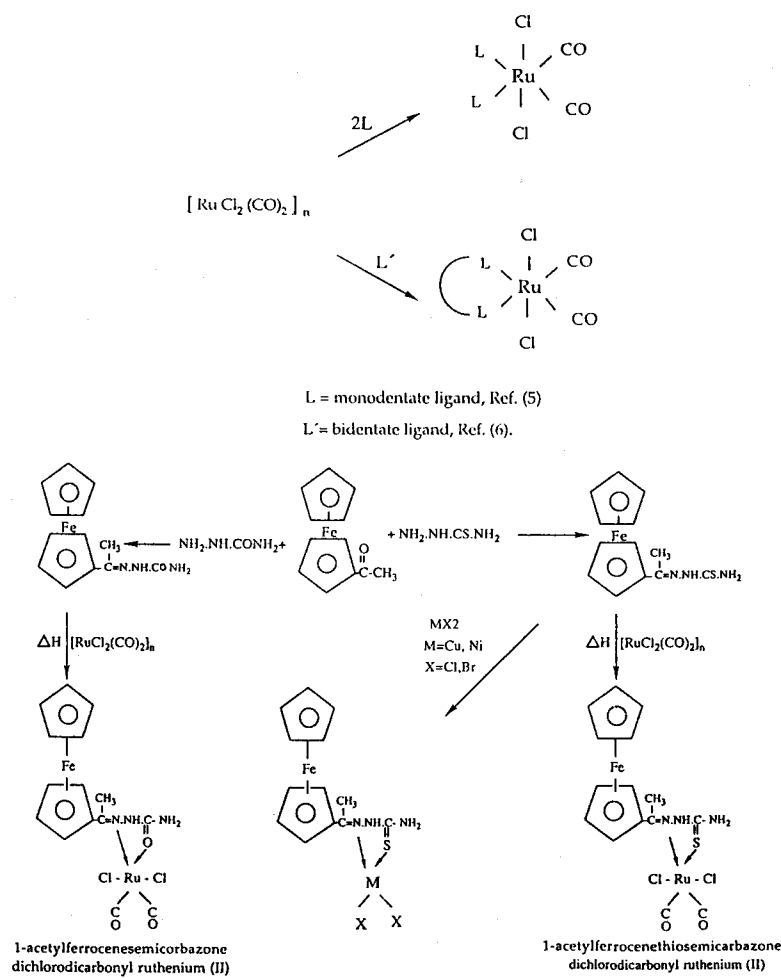


Figure 1. Scheme of Reaction

Similarly 1-acetylferrocenesemicarbazone, (π -C₅H₅FeC₅H₄.CH₃C=N.NHCONH₂) when treated with [RuCl₂(CO)₂]_n in methanol yields, pale yellow solid 1-acetylferrocenesemicarbazonedichlorodicyruthenium(II), [π -C₅H₅FeCH₄.CH₃ C = N.NH. CONH₂ Ru (CO)₂ Cl₂]. In these bimetallic complexes, the ligands, 1-acetylferrocenesethiosemi - carbazone (1-AFTSC) or 1-acetylferrocenesemi - carbazone(1-AFSC) acts as electron donor as well as a bridge between two metal systems. This behaviour was observed with other transition metal salts

such as CuX₂ (X = Br, Cl) or NiCl₂.xH₂O (Fig.1). Other bidentate ligand like 2-2'-dipyridylamine on treatment with [RuCl₂(CO)₂]_n gave very stable bright yellow crystalline solid[7]. All the complexes were characterized by IR (Table 1), ¹H NMR (Table 2) and elemental analyses (Table 3). The reaction of UO₂(NO₃)₂. 6H₂O with 1-acetylferrocenesemi - carbazone gave stable crystalline grey solid. The infrared spectrum and elemental analysis are all satisfactory. Further work is in progress and will be reported later.

Table 1
Infrared Spectra (in KBr pellets), cm⁻¹

Compound	ν (M-CO)	ν (C=N)	ν CO/ ν CS	Other bands
[RuCl ₂ (CO) ₂] _n	2145, 2075, 2020(a)			
[RuCl ₂ (CO) ₂ -NISOX]	2060, 2000	1622		3050, 1575, 1527, 1428, 1245, 1173, 895, 805, 772, 750
[RuCl ₂ (CO) ₂ 2-ABTz]	2062, 1990	1608		3060, 1535, 1513, 1450, 1340, 1030, 750, 720
[RuCl ₂ (CO) ₂ ATU]	2040, 1980			1610, 1555, 1040, 985, 880, 717
[RuCl ₂ (CO) ₂ TAM]	2063, 1996			1640, 1470, 1370, 1160, 970, 700
[RuCl ₂ (CO) ₂ 2P(O ϕ) ₃]	2070, 1990			3060, 1210, 1185, 1155, 920, 760, 685, 765
[RuCl ₂ (CO) ₂ 2 DPA]	2040, 1974			3280, 3190, 1624, 1578, 1465, 1225, 1150, 1015
[RuCl ₂ (CO) ₂ TSC]	2045, 1982			3355, 3256, 3138, 1455, 1420, 1355, 1289, 1259, 1240, 1098, 855, 755
[RuCl ₂ (CO) ₂ 1-AFTSC]	2065, 1993	1545	-/1038	1433, 1295, 1106, 1096, 827
[RuCl ₂ (CO) ₂ 1-AFSC]	1065, 1996	1545	1659/-	1452, 1382, 1360, 1308, 1150, 1143, 1107, 998, 900, 827

(a) Ref. (2).

Table 2
Proton Magnetic Resonance Spectra (a)

Compound	Chemical Shift (δ)	Relative Intensity	Multiplicity	Assignment
RuCl ₂ (CO) ₂ 2-NISOX	9.9	1	1	HC=N
	8.1	2	(m)	Naphthalene ring
	7.7	4	(m)	
RuCl ₂ (CO) ₂ 2-ABTZ	8.1	3	broad	NH ₂ + benzthiazole ring
RuCl ₂ (CO) ₂ 2-ATU	8.1	3	broad	NH ₂ + NH
	5.8	1	(m)	-CH=
	5.3	2	(m)	CNH ₂
	4.1	2	(m)	=CH ₂
RuCl ₂ (CO) ₂ 2-TAM	9.5	2	broad	-NH ₂
	2.7	3	(s)	CH ₃
RuCl ₂ (CO) ₂ 2 P(O ϕ) ₃	7.3	-	(s)	P(OCHS) ₃
RuCl ₂ (CO) ₂ 2 DPA	9.1	(1)	(s)	NH
	8.6	2	(d)	3,6 (H)
	8.1	2	(m)	4,4'(H)
	7.2	2	(m)	5,5'(H)
RuCl ₂ (CO) ₂ 2 TSC	2.85	2	(s)	NH ₂ N(4)
	7.9	1	broad	NH
	0.85	1	(s)	NH ₂ N(1)
π C ₅ H ₅ FeC ₅ H ₄ CH ₃ C=N.NHCS.NH ₂ RuCl ₂ (CO) ₂	1.8	2	broad	NH ₂
	2.4	3	1	NH ₂
	4.35	5	1	π C ₅ H ₅
	4.6	2	t	π C ₅ H ₄ X
	4.75	2	t	π C ₅ H ₄ X
	7.3	1	1	NH
π C ₅ H ₅ FeC ₅ H ₄ CH ₃ C=N.NHCO.NH ₂ RuCl ₂ (CO) ₂	2.8	3	1	NH ₃
	4.4	5	1	π C ₅ H ₅
	4.6	2	t	C ₅ H ₅ X
	5.23	2	t	C ₅ H ₄ X
	6.7	2	broad	CH ₂
	9.8	1	broad	NH

(a) Using TMS as internal reference.

Table (3)
Analytical Data (%)

Compound	Expected			Found			Colour
	C	H	N	C	H	N	
[RuCl ₂ (CO) ₂] _n	10.5			10.8			Yellow
RuCl ₂ (CO) ₂ 2-NISOX	50.8	2.4	4.9	50.3	2.5	4.7	Yellow
RuCl ₂ (CO) ₂ 2-ABTZ	39.9	3.0	10.6	41.0	3.2	10.0	Grey
RuCl ₂ (CO) ₂ 2 ATU	26.1	3.5	12.1	26.6	3.8	12.0	Yellow
RuCl ₂ (CO) ₂ 2 TA M	20.3	2.6	7.4	21.1	2.9	7.5	Yellow
RuCl ₂ (CO) ₂ 2 DPA	36.21	2.25	10.52	36.66	2.65	10.6	Pale Yellow
RuCl ₂ (CO) ₂ 2-TSC	11.5	1.66	12.98	11.21	1.56	13.16	V. Pale Yellow
RuCl ₂ (CO) ₂ 1-AFTSC	34.9	2.83	7.93	34.75	3.0	7.74	Yellow
RuCl ₂ (CO) ₂ 1-AFSC	35.01	3.11	8.17	34.99	3.20	7.8	Yellow
π C ₅ H ₅ FeC ₅ H ₄ CH ₃ C=N.NH.CS.NH ₂ CuBr ₂	29.8	2.9	8.0	30.2	3.0	7.8	Grey
π C ₅ H ₅ FeC ₅ H ₄ CH ₃ C=N.NH.CS.NH ₂ CuCl ₂	36.2	3.7	9.7	35.8	3.9	9.8	Grey

EXPERIMENTAL

The salt RuCl₃. xH₂O, 2,2'-dipyridylamine, thiosemicarbazide, substituted thioureas or urea and amines were purchased from Fluka Inc. or Aldrich Inc. 1-acetylferrocene was purchased from NEN TECH. LTD. UK and was used without further purifications. THF was distilled over Li[AlH₄]. The salt [RuCl₂(CO)₂]_n was

prepared as reported in the literature[2,3]. 1-acetylferrocenethiosemicarbazone was prepared by general method used for the preparation of Schiff's base condensation reactions. The IR spectra were measured as KBr discs using Pye-Unicam spectrophotometer model SP-1100. The proton magnetic resonance spectra were recorded on Varian EM 390-90 MHz spectrometer. Elemental analyses were

carried out by the microanalysis laboratory of King Abdulaziz University, Jeddah.

1-Acetylferrocene thiosemicarbazone

A typical reaction is described. In a 100 ml round bottom flask fitted with nitrogen gas inlet and water condenser containing 1-acetylferrocene (1.0g, 4.4 m mol) in 25 ml methanol was added thiosemicarbazide (0.4 g, 4.4 m mol) and a few drops of acetic acid. The mixture was refluxed with constant stirring for ~2 hrs. The solution was concentrated under reduced pressure and upon cooling it gave an orange yellow crystalline solid of $\pi\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_3\text{C}=\text{N.NH.CSNH}_2$. This was washed twice with petroleum ether (b.P. 30-40°C) and dried under vacuum to m.p. 143°C.

1-Acetylferrocene thiosemicarbazone dichlorodicarbonylruthenium (II)

In a 100 ml round bottom flask fitted with nitrogen gas inlet and water condenser was placed 1-acetylferrocenethiosemicarbazone (1.3 g; 4.4 m mol) dissolved in 25 ml THF. To this was added $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ (1.0g, 4.4 m mol). The mixture was refluxed for 0.5 to 1.0 hrs with continuous stirring. The yellow solution was reduced to minimum volume. Addition of petroleum ether (b.p.30-40°C) to the flask, separated yellow solid $\pi\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4.\text{CH}_3\text{C}=\text{N.NHCSNH}_2$, $\text{Ru}(\text{CO})_2\text{Cl}_2$. This was washed twice with petroleum ether and dried under vacuum.

1-Acetylferrocene thiosemicarbazone copper bromide

In a 50 ml Erlenmeyer flask was dissolved 1-acetylferrocene thiosemicarbazone (0.20 g, 0.66 m mol) in 10 ml methanol. To this was added copper bromide (0.15 g, 0.66 m mol). The solution was stirred for ~ 1 hour when brown grey solid was separated. This was filtered and washed twice with petroleum ether and finally with diethylether and dried. Similarly 1-acetylferrocenethiosemicarbazone was treated with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot x\text{H}_2\text{O}$ in 1:1 molar ratio.

RESULTS

All the ligands described in this work act as monodentate or bidentate. Treatment of these ligands with $[\text{Ru Cl}_2(\text{CO})_2]_n$ yields $[\text{Ru Cl}_2(\text{CO})_2.2\text{L}]$ or $[\text{Ru Cl}_2(\text{CO})_2. \text{L}']$ complexes.

The complexes are all yellow or dark yellow solids except $[\pi\text{-C}_5\text{H}_5 \text{Fe C}_5\text{H}_4. \text{CH}_3\text{C}=\text{N. NHCO.NH}_2.\text{UO}_2(\text{NO}_3)_2$ which is a violet grey solid and are all air stable in the solid state although they decompose slowly in solution.

The infrared spectra (Table 1) of all the organometallic complexes show only two strong bands in the region of 2000 cm^{-1} indicating that the terminal metal carbonyls (M-CO) are cis[9]. The decrease in the ν (M-CO) stretching frequency in all the complexes is due to $d\pi\text{-}p\pi$ back bonding of the metal d orbital and $p\pi^*$ of the carbonyl group.

All the bands corresponding to 1-acetylferrocenethiosemicarbazone (1-AFTSC) or 1-

acetylferrocenesemicarbazone (1-AFSC) are well defined near $3500\text{-}3000 \text{ cm}^{-1}$ region. Further the presence of a strong band around $1588\text{-}1616 \text{ cm}^{-1}$ is indicative of 1-AFTSC ligand coordinating to the metal ruthenium through the hydrazinic nitrogen $\nu(\text{C}=\text{N})$ atom. Also the presence of a medium band corresponding to $\nu(\text{C}=\text{S})$ around $1516\text{-}1546 \text{ cm}^{-1}$ and $700\text{-}750 \text{ cm}^{-1}$ suggests that 1-AFTSC ligand behaves as a bidentate and it coordinates through S atom to the ruthenium metal. Thus, the complex is essentially octahedral as shown in Fig. 1A. A similar trend was observed in 1-AFSC complex[8]. A strong band appears at 1659 cm^{-1} instead of 1700 cm^{-1} which corresponds to kets $\nu(\text{CO})$ group of the 1-AFSC ligand that occurs at a lower frequency because of its coordination to ruthenium metal. Thus there is a decrease in the stretching frequency on the coordination of these ligands with the metal. It is noteworthy that in complexes $[\text{RuCl}_2(\text{CO})_2\text{AFTSC}]$ and $\text{RuCl}_2(\text{CO})_2\text{AFSC}$ the ligand thiosemicarbazone or semicarbazone moiety acts as a bridge between the two different metal systems giving a bimetallic organometallic complexes with Cu(II), Ni(II), Ru(II) and uranium (VI) metal ions. The work of 1-AFSC with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is still in progress. All the spectra and elemental analysis are satisfactory and full details shall be reported soon.

¹H - NMR spectra (Table 2) show that all the organometallic complexes have very sharp signals corresponding to their respective hydrogen atoms, suggesting that the compounds are diamagnetic. The elemental analyses (Table 3) are also consistent with their proposed formulations and structures.

A wide range of reactions of these organometallic complexes, together with their investigations of any possible pharmacological activity and super conductivity behaviours are under considerations.

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