New Complexes of Ruthenium (II) with Thiosemicarbazide and β-diketone Ligands

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(Received 21st September, 1989, revised 25th March, 1990)

Summary: The reaction of thiosemicarbazide ($NH_2.NH.CS.NH_2$) with $[Rh(CO)_2Cl_2]_n$ in THF gives an air stable, off white solid $Ru(CO)_2Cl_2.NH_2.NH.CS.NH_2$. The ligand acts as bidendate and it has been suggested that it coordinates to the metal through N(1) and S atom. Also the salt $[Ru(CO)_2Cl_2]_n$ reacts with an excess of sodium acetylacetonate in THF and gives very stable red solid $Ru(CO)_2(acac)_2xH_2O$. Similar product is obtained when $[Ru(CO)_2Cl_2]_n$ is treated with acetylacetone in presence of a base such as triethylamine. The complexes were characterised by IR, NMR and elemental analyses.

Introduction

The application of transition metal complexes of thiosemicarbazide and its derivatives known as thiosemicarbazones have been well documented [1-3]. Such complexes have shown a remarkable biological activity against certain microbial, viral and tumour activity [4,5]. In some cases it is shown that the highest (in vitro) activity is due to the metal complex rather than thiosemicarbazone itself [4]. To our knowledge this is the first thiosemicarbazide complex with ruthenium (II) of the type $Ru(CO)_2Cl_2.NH_2.NH.CS.NH_2$. The versatile bonding nature of the ligand itself and its thiosemicarbazone derivatives opens a new avenue of research. We have reported recently on the complexes of Ru(II) with oxygen. sulphur and nitrogen donor ligands from these laboratories [6,7]. However, the

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spectroscopic properties of the complex shows that the ligand thiosemicarbazide acts as bidentate and it coordinates to the metal through N(I) and S atom. The complex was prepared on treatment of $[Ru(CO)_2Cl_2]_n$ [8] with thiosemicarbazide in THF giving, off white solid. The complex is soluble in polar solvents like alcohol and acetone but insoluble in diethylether or pet.ether. Similarly treatment of $[Ru(CO)_2Cl_2]_n$ with sodium acetylaceto nate or acetylacetone in the presence of a base such as triethylamine in THF yields a very stable red solid. The complex is insoluble in all the organic solvents but slightly soluble is hot water.

Experimental

The complex $[Ru(CO)_2Cl_2]_n$ was prepared as reported in the literature [8,9]. The ligand thiosemicarbazide was purchased from Fluka Inc. All reagents and solvents were commercial grade. THF was distilled over Li AlH_4. The IR spectra were measured as KBr pellets 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.

Preparation of Dichlorodicarbonyl Thiosemicarbazide Ruthenium (II).

In a small two neck round bottom flask fitted with water condenser and magnetic stirrer was added (1:1) mole ratio of $[Ru(CO)_2Cl_2]_n$ (200 mg, 0.87 mmole) and thiosemicarbazide (80 mg, 0.87 mmole) in 20 ml THF. The solution was refluxed for 1.5 h under constant stirring. The solvent was removed under reduced pressure. Addition of pet.ether (b.p. 40-60°C) to the flask separated a off white solid almost quantitatively [Analysis Found: C, 11.5; H, 1.66; N, 12.98 required for $C_3H_5O_2S$ Ru C, 11.21; H, 1.56; N, 13.16%] Fig. 1.

$NH_2.NH.CS.NH_2$
(1) (2) (3) (4)

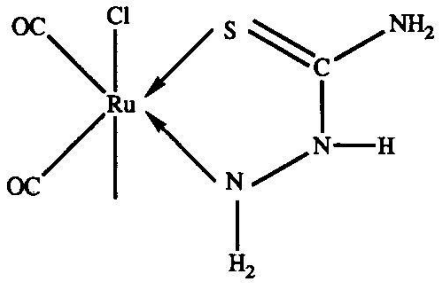

Fig. (1)

Preparation of Dicarbonyl-bis-Acetylacetonato-Ruthenium (II)

In a small two neck round bottom flask fitted with water condenser and magnetic stirrer was added $[Ru(CO)_2Cl_2]_n$ (0.2 g; 0.87 mmole) dissolved in THF 20 ml. To this was added an excess of sodium acetylacetonate (0.4g; 4 mmole). The mixture was refluxed for 2 h. The solvent was removed under reduced pressure. The mixture was washed with water and then with acetone and diethylether. A red solid of $Ru(CO)_2$ $(acac)_2.xH_2O$ (where x = 1,2,3) was obtained. This was dried in vacuo. [Analysis Found: C, 36.44; H, 3.61 required for $Ru(CO)_2$ $(acac)_2$. xH_2O C, 36.83; H, 4.6%]. Fig. 2.

Table-1: IR Spectra[a]

Compound	νO-H	νN-H	δN-H	νC...O Keto + νC....C	νM-CO	νC=S	Other bands
					2045	1098 (1155)[f]	1455, 1420,
[M][b]$NH_2.NH.CS.NH_2$	-	3355(3360)[f]	1585 (1625)	-			1355,1289
		3256 (3260)[f]	1500 [1612+1522]	-	1982		1259, 1240
		3138 (3175)[f]					855, 755
[M][c](acac)$_2$xH_2O	3500-3400	-	-	1575)1655)[f]	1980		1450, 1408
				1500(1610)[f]	1920		1350, 1235
							1185, 1005
							922, 805

a = IR spectra measured as KBr pellet b = $[Ru(CO)_2Cl_2]$ c = $[Ru(CO)_2$ f = free ligand

Table-2: Proton Magnetic Resonance Spectrum[a]

Complex	Band position in ppm (δ)	Multiplicity	Assignment
$Ru(CO)_2Cl_2.NH_2NH.CS.NH_2$	2.85 (2.85)[f]	singlet	NH_2 (uncoordinate N(4)
	7.9 (9.1)[f]	Broad NH	
	0.85	singlet	NH_2 (coordinated) N(I)

(a) = NMR spectrum measured in CD_3 CO CD_3 using TMS as internal reference f = free ligand.

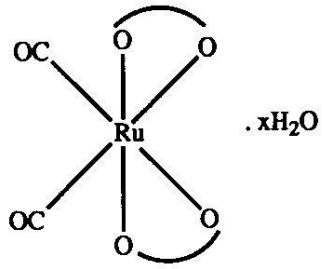

Fig. (2)

Results and Discussion

The IR spectra of the complex $Ru(CO)_2Cl_2.NH_2.NH.CS.NH_2$ in KBr pellets show two distinct bands at 2060 and 1990 cm^{-1} showing that the metal terminal carbonyls are cis [9]. The bands around 3355 and 3220 cm^{-1} are assigned to νNH_2 and the one near 3138 cm^{-1} to νNH. The other band at 1585 cm^{-1} may be attributed to δNH. In the free ligand this band splits and appears as a doublet at 1635 and 1612 cm^{-1}. The complex shows a band at 1098 cm^{-1} that may be assigned as thione (C=S) group and it shows a lowering of 57 cm^{-1} compared to the free ligand 1155 cm^{-1}. It is therefore, suggested that the one (C=S) group of the ligand is coordinated to the metal. Also no band was observed in the region of 2500-2600 cm^{-1} showing that there is no thiol group present in the solid complex. Thus the complex shows sharp bands corresponding to the ligand but a lower frequency. This indicates that there is a flow of electron density from the ligand to the metal. The ligand acts as bidentate forming a five membered chelate ring as shown in Fig. 1. A similar behaviour of thiosemicarbazone with other transition metals have been shown [10]. The NMR spectrum of the free ligand shows a single sharp band of both NH_2 (1) and NH_2(4) protons at δ 2.85. While the complex shows two signals of equal intensity at δ 0.8 and δ 2.75. The former may be assigned to NH_2 (1) (shielding effect) due its coordination to the metal, while the later signal to NH_2(4) proton. The NH(2) proton was observed at δ 7.6. The elemental analysis of the complex is consistant with the proposed structure as shown in Fig. 1.

The IR spectra of β-diketone complex $Ru(CO)_2(acac)_2.2H_2O$ shows a strong band in the region 1600-1550 cm^{-1} due to (C=O) and (C=C) ring system. This also shows a low shift of (70 cm^{-1}) compared to the free ligand. This low shift and disappearance of the broad (O-H) band suggests that bonding is through both the terminal oxygen atoms of the carbonyl groups. The spectra shows that the β-diketone acts as monobasic bidentate as expected. The NMR spectrum of the complex was not measured because it was not soluble in common solvents.

Acknowledgements

F.A. Ali and A.A. Al-Nahdi thank King Abdulaziz University for the scholarship.

References

1. M.J.M. Campbell, *Coord.Chem.Rev.* **15**, 279 (1975)
2. S Padhye and G.B. Kauffman, *Coord.Chem.Rev.*, **63**, 127 (1985).
3. G. Domagk, R. Behnick, F. Mietzsch and H. Schmidt, *Naturwissenchaften* **33**, 315 (1946).
4. W.E. Levinson, *Antibiot.Chemother.* **27**, 288 (1980).
5. D.D. Perrin and H. Stunzl, Metal Ions in Biological System (Edited by Sigel) Vol. 14, p. 207, Marcel Dekker, New York. 1975
6. A.O. Baghlaf, M. Ishaq and A.K.A. Rashed, *Polyhedron*, **6**, 837 (1986).
7. A.O.Baghlaf, M. Ishaq, S.A. Rahman, A.B. Al-Tahir, A. Zaidan and R.A. Kabli, *Pollyhedron*, **7**, 219 (1988).
8. R. Colton and R.H. Farthing, *Aust. J.Chem.* **20**, 1283 (1967).
9. L.J. Bellamy, "The Infrared Spectra of Complex Molecules" Metheun, London 1958.
10. P. Umpathy, A.P. Budhkar and C.S. Darai, *J.Ind.Chem.Soc.* **63**, 714 (1986).