Spectral Studies of Some Coordination Complexes of Pt(II) and Rh(I) with Benzothiazolines

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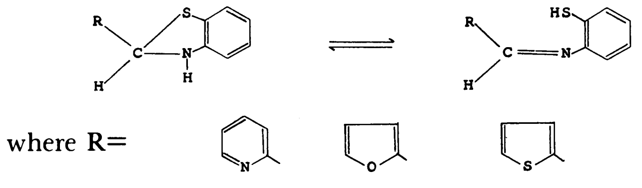
Synopsis. The present paper describes the synthesis and structural features of platinum(II) and rhodium(I) complexes of some benzothiazolines derived by the condensation of various heterocyclic aldehydes viz. 2-pyridinecarbaldehyde, 2-furancarbaldehyde, and 2-thiophenecarbaldehyde. The resulting complexes have been characterized by elemental analyses, conductance measurements and molecular weight determination. The mode of bonding and geometry of these complexes have been suggested on the basis of IR, ^{1}H NMR, electronic spectra, and magnetic studies.

Benzothiazolines derived from the condensation of 2-aminobenzenethiol with the carbonyl compounds constitute an important series of ligands with ONS and NS donor systems.[1] The condensation of 2-mercapto amine with an aldehyde does not normally lead to the isolation of the corresponding Schiff base, but rather to a thiazoline (with a 2-aminobenzenethiol) or a thiazolidine (with a 2-mercaptoalkylamine).[2–5] However, it has been shown that the metal ion acts as a template and favors the formation of the Schiff base rather than the 2,2′-bi(benzothiazoline) form.[6] Later Jadamus et al.[7] reported that even in the absence of metal ion the condensation product of aldehyde and ketone with 2-aminobenzenethiol forms a mixture of benzothiazoline and the Schiff base and an equilibrium may exist between the two as shown below:



The above equilibrium gets shifted to the right hand side in presence of the metal ion. Singh et al.[8] have studied the reactions of trimethylchlorosilane and dimethylchlorosilane with similar ligands and found that the complexes are five- and six-coordinated. Similarly Tandon et al.[9,10] have studied the reactions of these ligands with transition metals and the geometry of metal complexes have been deduced on the basis of various spectral studies.

Experimental

Preparation of Ligand. Benzothiazolines (HL) were prepared by the condensation of 2-aminobenzenethiol with 2-pyridine-, 2-furan-, and 2-thiophenecarbaldehyde.[11]

Preparation of Complexes. Cyclooctadienyl Complexes of Rhodium [C$_8$H$_{12}$RhL]: [C$_8$H$_{12}$RhOMe]$_2$ was prepared according to the literature method.[12,13] It was then dissolved in ethanol and an ethanolic solution of benzothiazoline in requisite amount was added to it. The solution was refluxed for three hours and cooled. The complex got separated, which was washed repeatedly with cyclohexane and dried in vacuo.

[Pt(HL)$_2$]Cl$_2$: K$_2$[PtCl$_4$] was dissolved in a 1 : 1 mixture of water and ethanol. To this solution, an ethanolic solution of ligand was added and it was then refluxed for about one hour. On cooling, the complex separated out, which was filtered and washed several times with a mixture of water and ethanol and dried in vacuo.

PtL$_2$: The 1 : 1 water-ethanol solution of K$_2$[PtCl$_4$] was mixed with an ethanolic solution of benzothiazoline. Aqueous ammonia was added to the above mixture dropwise until the solution was weakly alkaline. The mixture was refluxed for about two hours and the solid compound was filtered out. It was then washed with the mixture of water and ethanol and dried in vacuo.

Analytical Methods and Physical Measurements. Platinum was estimated gravimetrically[14] and nitrogen by the Kjeldahl's method. Carbon and hydrogen analyses were performed at the microanalytical laboratory of this department. Other measurements were carried out as reported earlier.[11]

Results and Discussion

The 1 : 1 and 1 : 2 molar ratio reactions of [C$_8$H$_{12}$RhOMe]$_2$ and K$_2$[PtCl$_4$] with benzothiazolines in ethanol medium take place as follows:

1. $$[\mathrm{C_8H_{12}RhOMe}]_2 + 2\,\overset{\frown}{\mathrm{N\,SH}} \longrightarrow \underset{\mathbf{I}}{2[\mathrm{C_8H_{12}Rh}(\overset{\frown}{\mathrm{N\,S}})_2]} + 2\mathrm{MeOH}$$

2. $$\mathrm{K_2PtCl_4} + 2\,\overset{\frown}{\mathrm{N\,SH}} \longrightarrow \underset{\mathbf{II}}{[\mathrm{Pt}(\overset{\frown}{\mathrm{N\,SH}})_2]\mathrm{Cl_2}} + 2\mathrm{KCl}$$

3. $$\mathrm{K_2PtCl_4} + 2\,\overset{\frown}{\mathrm{N\,SH}} + 2\mathrm{NH_4OH} \longrightarrow \underset{\mathbf{III}}{[\mathrm{Pt}(\overset{\frown}{\mathrm{N\,S}})_2]} + 2\mathrm{KCl} + 2\mathrm{NH_4Cl} + 2\mathrm{H_2O}$$

All the newly synthesized complexes are colored and monomeric solids. The rhodium complexes are soluble in most of the common organic solvents, whereas complexes of platinum are soluble in *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The conductanec date of 10^{-3} M solutions (1 M=1 mol dm^{-3}) of complexes at the room temperature show that the complexes of the type **II** are 1 : 2 electrolytes (200—210 ohm^{-1} mol^{-1} cm^{-2}) and complexes **I** and **III** are nonelectrolytes (15—20 ohm^{-1} mol^{-1} cm^2). All the solids are diamagnetic as expected for the d^8 square planar complexes.

In the solid state IR spectra of benzothiazoline the absence of ν(SH) and appearance of ν(NH) at ca. 1670 cm^{-1} and 3400—3200 cm^{-1} is strong evidence for a ring structure.[15] Further in metal complexes ν(NH) disappears and in the complexes of type II band due to ν(SH) is observed at ca. 2520 cm^{-1} and which suggests the coordination of sulfur to the metal atom in these complexes.

However, the disappearance of ν(NH) band in the spectra of metal complexes shows its deprotonation and chelation of nitrogen of the ligand to the central metal atom. Further, in the spectra of metal complexes, a strong band around 1580±10 cm^{-1} may be ascribed to the coordinated $>$C=N group and this very well supports the fact that the resulting complexes are metal azomethine derivatives, as the benzothiazoline ring rearranges to give the azomethine form which in presence of metal ion finally acts as a monobasic bidentate ligand.

Further, in the spectra of rhodium complexes, a sharp band at ca. 1470 cm^{-1} may be due to ν(C=C) of cyclooctadiene moiety, lowered by coordinaton.[16]

To further confirm the bonding pattern in these complexes, proton magnetic resonance spectra of 2-(2-pyridyl)benzothiazoline and it's metal derivatives have been recorded in DMSO-d_6 using TMS as internal reference. The spectrum of 2-(2-pyridyl)benzothiazoline shows the N–H proton signal at δ 4.58 and it disappears in the corresponding metal complexes due to it's deprotonation. The signal due to azomethine proton is observed at δ 8.00 and shifts downfield (δ 8.40) in the spectra of metal complexes, suggesting coordination of azomethine nitrogen to the metal atom. In the spectra of complexes $[Pt(N\frown SH)_2]Cl_2$, the signal appearing at δ 4.85 is due to the SH group.[17] Further, two signals observed at δ 2.5 and 1.6 in the spectrum of rhodium complex may be assigned to the $-CH_2$ group of cyclooctadiene.

In the electronic spectra of platinum(II) complexes, three d–d spin allowed transitions are observed corresponding to the transitions from the three lower lying d levels to the empty $d_{x^2-y^2}$ orbital. The ground state $^1A_{1g}$ and the excited states corresponding to the above transitions are $^1A_{2g}$, $^1B_{1g}$, and ^1E_g, in order of increasing energy. Three different orbital parameters Δ_1, Δ_2, and Δ_3 have been calculated by first using the corelation, $F_2=10F_4=600$ cm^{-1} for the Slator–Condon interelectronic repulsion parameters (F_2 and F_4) and subseuqently the equations suggested by Gray and Ballhausen.[18] The parameters Δ_1, Δ_2, and Δ_3 lie in the

Table 1. Physical Properties and Analysis of Metal Complexes

S.No.	Reactants		Molar ratio	Color and state of compound	Mp/°C	% Analysis (Found/Calcd)			
	Metal compound	Ligand				C	H	N	S
1	$(C_8H_{12}RhOMe)$	Pyridyl BT[a]	1:1	$C_8H_{12}Rh(C_{12}H_9N_2S)$	166d	56.4	4.8	6.5	7.2
		$(C_{12}H_{10}N_2S)$		Dark brown solid		(56.6)	(4.9)	(6.6)	(7.5)
2	$K_2[PtCl_4]$	Pyridyl BT[a]	1:2	$Pt(C_{12}H_{10}N_2S)_2Cl_2$	121d	41.0	3.0	8.0	9.1
		$(C_{12}H_{10}N_2S)$		Yellow solid		(41.5)	(2.9)	(8.1)	(9.2)
3	$K_2[PtCl_4]$	Pyridyl BT[a]	1:2	$Pt(C_{12}H_9N_2S)_2$	211d	46.2	2.8	8.9	10.1
		$(C_{12}H_{10}N_2S)$		Yellow solid		(46.4)	(2.9)	(9.0)	(10.3)
4	$(C_8H_{12}RhOMe)$	Furyl BT[b]	1:1	$C_8H_{12}Rh(C_{11}H_8ONS)$	*	54.9	5.0	3.3	7.6
		$(C_{11}H_9ONS)$		Brown solid		(55.1)	(5.1)	(3.4)	(7.7)
5	$K_2[PtCl_4]$	Furyl BT[b]	1:2	$Pt(C_{11}H_9ONS)_2Cl_2$	232d	39.0	2.6	4.0	9.2
		$(C_{11}H_9ONS)$		Dark green solid		(39.3)	(2.7)	(4.2)	(9.5)
6	$K_2[PtCl_4]$	Furyl BT[b]	1:2	$Pt(C_{11}H_8ONS)_2$	54d	43.9	2.8	4.6	10.4
		$(C_{11}H_9ONS)$		Grey solid		(44.1)	(2.7)	(4.7)	(10.7)
7	$(C_8H_{12}RhOMe)$	Thienyl BT[c]	1:1	$C_8H_{12}Rh(C_{11}H_8NS_2)$	154d	53.0	4.5	3.2	14.7
		$(C_{11}H_9NS_2)$		Black solid		(53.1)	(4.7)	(3.3)	(14.9)
8	$K_2[PtCl_4]$	Thienyl BT[c]	1:2	$Pt(C_{11}H_9NS_2)_2Cl_2$	140d	37.5	2.4	3.9	18.0
		$(C_{11}H_9NS_2)$		Brown solid		(37.5)	(2.5)	(4.0)	(18.1)
9	$K_2[PtCl_4]$	Thienyl BT[c]	1:2	$Pt(C_{11}H_8NS_2)_2$	78	41.6	2.5	4.1	19.9
		$(C_{11}H_9NS_2)$		Green solid		(41.8)	(2.5)	(4.4)	(20.3)

*; stable upto 320 °C. d; decompose. a) 2-(2-Pyridyl)benzothiazoline. b) 2-(2-Furyl)benzothiazoline. c) 2-(2-Thienyl)benzothiazoline.

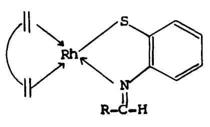
Table 2. Electronic Spectral Data of Pt(II) Complexes

S.No.	Complexes	Spectral bands/cm^{-1}	Transitions	Δ_1	Δ_2	Δ_3
					cm^{-1}	
1.	$[Pt(C_{12}H_{10}N_2S)_2]Cl_2$	20400	$^1A_{1g} \longrightarrow {}^1A_{2g}$			
		24700	$^1A_{1g} \longrightarrow {}^1B_{1g}$	22500	5500	3600
		28600	$^1A_{1g} \longrightarrow {}^1E_g$			
		30000 31050	C.T.			
2.	$[Pt(C_{11}H_8ONS)_2]$	20800	$^1A_{1g} \longrightarrow {}^1A_{2g}$			
		25600	$^1A_{1g} \longrightarrow {}^1B_{1g}$	22900	6000	1100
		27000	$^1A_{1g} \longrightarrow {}^1E_g$			

ranges, 22500—22900 cm^{-1}, 5500—6000 cm^{-1}, and 1100—3600 cm^{-1} respectively (Table 2) and which are in close agreement with the values reported earlier for the square planar geometry.[19,20)]

In the electronic spectra of rhodium(I) complexes, the d–d transitions generally appear between 20000—30000 cm^{-1}. However, in the present case intense bands appearing at 31000, 34500, and 37000 cm^{-1} may be due to metal to ligand charge transfer transitions.[21)]

Thus, on the basis of the above discussions the following structure can be proposed for the different type of complexes:



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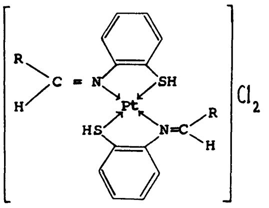

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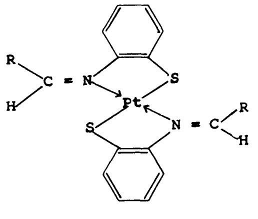

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