

Pharmaceutical Significance of Ruthenium (III) and Nickel(II) Complexes of Schiff Bases Derived from Thiosemicarbazide

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Abstract : Metal complexes formed by the interaction of bis (5-chloro salicylaldehyde) Thiosemicarbazone[CSALTSC], bis (terephthaldicarboxaldehyde) thiosemicarbazone [TALDICTSC], bis (2,4-pentanedione) thiosemicarbazone [PDITOTSC], bis (trifluoroacetyl-acetone) thiosemicarbazone [TFAATSC], bis (4-hydroxy benzaldehyde) thiosemicarbazone [HBLTSC], bis (p-methyl thiobenzaldehyde) thiosemicarbazone [MTBLTSC] and bis (trichloro acetyl acetone) thiosemicarbazone [TCAATSC] with ruthenium(III) chloride and nickel(II) chloride have been prepared. These complexes have been characterised by IR spectra, electronic spectra, TGA, molar conductance and their magnetic moment. These studies indicate octahedral geometry of ruthenium (III) metal complexes and square planar geometry of nickel (II) metal ion complexes. The complexes were also screened for antifungal and antibacterial activities.

Key words: Schiff base, thiosemicarbazone, nickel (II) complexes, ruthenium (III) complexes.

1. Introduction

Schiff bases are the condensation products of aldehydes and ketones with certain amines. Thiosemicarbazide and its schiff base possess important biological activities¹. Transition metal complexes of the schiff bases derived from thiosemicarbazide have been screened for medicinal properties². Synthesis and characterization of some transition metal complexes of schiff bases derived from condensation of 5-chloro

salicylaldehyde, terephthalaldehyde, 2, 4-pentanedione, trifluoroacetylacetone, 4-hydroxy benzaldehyde, p-methyl thiobenzaldehyde and trichloroacetylacetone with thiosemicarbazide have been reported.

Experimental

All the complexes used were A.R. Grade (B.D.H., Koch Light and Fluka).

Preparation of Schiff bases

The Schiff bases were prepared by the condensation of respective aldehyde with thiosemicarbazide. Thiosemicarbazide was dissolved in ethanol and refluxed for about half an hour. The requisite amount of the aldehyde was then added to the flask. The mixture was then refluxed for about six hours. The reaction mixture was kept for 24 hrs. obtaining crystals of the ligand and purified by recrystallisation.

Preparation of metal complexes

The complexes were synthesized by the addition of metal chlorides in methanol to the solution of ligand in DMSO. The precipitate thus obtained was washed with DMSO and dried over fused CaCl_2 .

Results and discussion

Complexes obtained are soluble in methanol. The molar conductance of all the complexes of Ru^{III} in CH_3OH , DMF and DMSO are found to be 72-185, 102-105 and 88-100 respectively, compatible with 1:3 electrolyte. The molar conductance of Ni^{II} recorded in MeOH are in the range of 165-185 $\text{cm}^2 \text{mol}^{-1}$ showing 1:2 electrolytic ratio. All the ruthenium (III) complexes show magnetic moment value in the range of 1.80 to 1.82 B.M. which correspond to the spin-only value, showing the absence of any metal-metal interaction. The similar observation is also seen with the nickel(II) complexes which have magnetic values in the range of 2.25 to 2.28 B.M. The spin-only value indicates the diamagnetic properties of ruthenium and nickel complexes³. The electronic spectral bands of ruthenium(III) complexes exhibited three bands lying in the range of 12900-13600 cm^{-1} , 16950-17680 cm^{-1} , and 21780-22650 cm^{-1} which may be assigned to $2\text{T}_{2\text{g}} \rightarrow 4\text{T}_{1\text{g}}$, $2\text{T}_{2\text{g}} \rightarrow 4\text{T}_{2\text{g}}$ and $2\text{T}_{2\text{g}} \rightarrow 2\text{A}_{2\text{g}}$, $2\text{T}_{1\text{g}}$ electronic transitions respectively. These spectral bands indicate octahedral geometry for the complexes. The nickel (II) complexes exhibited two bands at 13035 and 18500 cm^{-1} which have been assigned to $1\text{A}_{1\text{g}} \rightarrow 1\text{E}_{\text{g}}(\nu)$ and $1\text{A}_{1\text{g}} \rightarrow 1\text{B}_{2\text{g}}(\nu)$ transitions,

respectively. Since the Ni^{II} complex is diamagnetic in nature, hence a square planar geometry has been suggested.³ The IR spectra of ligands show two important peaks at 1625 and 1537 cm^{-1} which were shifted to 1655-1581 cm^{-1} in the spectra of all the complexes which indicates the coordination through N atoms of azomethine⁴ $\nu(\text{C}=\text{N})$ cm^{-1} and S atom of thio groups $\nu(\text{C}=\text{S})$ cm^{-1} . It was also observed that in the spectra of Ru (III) complexes a new medium intensity peak appeared at 725-910 cm^{-1} indicating the presence of coordinated water molecules⁵.

Table 1. Analytical and physical data of the complexes

Compound	Metal% (Found/Calcd.)	% of Hydrogen (Found/Calcd.)	% of carbon (Found/Calcd.)	% of Nitrogen (Found/Calcd.)	% of Sulphur (Found/Calcd.)
Ru(TCAATSC)₂.H₂O]Cl₃	8.53 (9.00)	1.65 (2.00)	38.10 (37.70)	19.50 (20.00)	5.00 (5.44)
Ru(CSALTSC)₂.H₂O]Cl₃	6.40 (5.20)	-	-	9.29 (9.40)	11.00 (11.23)
Ru(TALDICTSC)₂.H₂O]Cl₃	13.00 (12.50)	2.99 (3.21)	49.50 (50.49)	9.82 (10.39)	8.00 (7.92)
Ru(PDIOTSC)₂.H₂O]Cl₃	14.00 (13.98)	5.03 (4.70)	37.01 (36.56)	12.01 (11.63)	9.02 (8.86)
Ru(TFAATSC)₂.H₂O]Cl₃	8.59 (9.33)	1.65 (2.03)	38.01 (37.70)	19.53 (21.07)	6.00 (5.91)
Ru(HBLTSC)₂.H₂O]Cl₃	11.66 (12.46)	2.90 (3.20)	43.65 (44.44)	9.99 (10.37)	8.02 (7.90)
Ru(MTBLTSC)₂.H₂O]Cl₃	11.22 (10.86)	4.00 (3.65)	44.00 (43.87)	8.82 (9.03)	21.00 (20.64)
[Ni(TCAATSC)]Cl₃	6.00 (5.05)	1.09 (2.00)	41.00 (40.80)	7.52 (8.20)	5.56 (6.00)
[Ni(CSALTSC)]Cl₃	6.67 (5.90)	-	-	8.89 (7.99)	10.90 (10.00)
[Ni(TALDICTSC)]Cl₃	7.57 (8.29)	4.01 (3.65)	56.59 (57.38)	12.00 (11.81)	8.82 (9.00)
[Ni(PDIOTSC)]Cl₃	8.55 (9.23)	4.99 (5.32)	40.00 (41.31)	12.99 (13.14)	9.86 (10.01)

[Ni(TFAATSC)]Cl ₃	6.04 (5.90)	1.96 (2.20)	41.00 (40.84)	7.52 (8.40)	5.58 (6.40)
[Ni(HBLTSC)]Cl ₃	7.92 (8.11)	4.01 (3.57)	50.01 (49.51)	12.04 (11.55)	9.00 (8.80)
[Ni(MTBLTSC)]Cl ₃	7.03 (6.96)	3.59 (4.01)	47.56 (48.17)	10.00 (9.91)	23.00 (22.66)

Table-2 (Analytical and Physical data of the complexes)

Compound	Molar Conductance in (cm ² mol ⁻²)			ν C=N (cm ⁻¹)	Water (cm ⁻¹)	ν C=S (cm ⁻¹)	Magnatic moment B.M.	M.P. °C	Colour
	MeOH	DMF	DMSO						
[Ru(TCAATSC) ₂ .H ₂ O]Cl ₃	73	103	88	1650	789	1665	1.79	250	Brownish Yellow
[Ru(CSALTSC) ₂ .H ₂ O]Cl ₃	72	105	90	1655	790	1570	1.82	240	Yellowish Brown
[Ru(TALDICTSC) ₂ .H ₂ O]Cl ₃	170	102	100	1610	880	1575	1.90	256	Greyish Brown
[Ru(PDIOTSC) ₂ .H ₂ O]Cl ₃	185	103	99	1622	890	1581	1.89	260	Greenish
[Ru(TFAATSC) ₂ .H ₂ O]Cl ₃	73	103	91	1580	790	1579	1.79	248	Chocolate Brown
[Ru(HBLTSC) ₂ .H ₂ O]Cl ₃	72	105	89	1605	788	1590	1.89	250	Dark Brown
[Ru(MTBLTSC) ₂ .H ₂ O]Cl ₃	785	103	90	1615	799	1578	1.91	256	Brown
[Ni(TCAATSC)]Cl ₃	170	-	-	1617	-	1582	2.25	235	Greenish Brown
[Ni(CSALTSC)]Cl ₃	178	-	-	-	-	-	2.26	245	Brown
[Ni(TALDICTSC)]Cl ₃	170	-	-	1566	-	1569	2.25	230	Green
[Ni(PDIOTSC)]Cl ₃	185	-	-	1630	-	1620	2.26	248	Brown
[Ni(TFAATSC)]Cl ₃	165	-	-	1582	-	1617	2.28	235	Reddish Brown
[Ni(HBLTSC)]Cl ₃	173	-	-	1601	-	1525	2.26	25	Green
[Ni(MTBLTSC)]Cl ₃	180	-	-	1510	-	1635	2.27	265	Brown

All the complexes were subjected to thermogravimetric analysis and TGA proved helpful in ascertaining the presence of coordinated water molecules in ruthenium (III) complexes. All above evidences suggest octahedral geometry for Ru(III) and square planar symmetry for Ni(II) complexes. Thiosemicarbazide and thiosemicarbazone posses N-C=S group which responds to the biocidal properties⁶. The complexes were screened for antifungal and antibacterial activities and zone inhibition diameter was observed.

Antibacterial activities of the complexes were determined by paper disc method against different bacteria as *B.subtilis*, *S.aureus*, *E.coli*, *B.bravis* and *P.aeruginosa*. and *B.cereus*. The antibacterial activity was carried out for 24hrs. as cultures of selected bacteria in cup plate technique⁷. Agar cups were made by preparing (12ml) melted agar at 50°C. and by boring 1 cm thick broth culture on a plate by 10 mm cork borer and two drops of the melted agar were then pipetted and incubation was carried for 24h. and zone of inhibition was observed⁸ and results obtained are presented in the table 3 & 5 Schiff base complexes were screened for antifungal activities against *aspergillus*, *rhizopus* and *saccharomyces* sp. The stock solution of 1000 ppm of each compound was prepared by dissolving each chemical (20 mg) in absolute alcohol (0.5ml) and the volume was made to 10 ml with sterilized distilled water. Small droplets (0.02ml) of spore suspension in equal quantity with solution of the test compound were seeded in the cavities of cavity slides. The slides were placed in petriplates lined with moist filter paper. The petriplates containing cavity slides were incubated at 25±1°C for 20 h. The germination of spores was recorded and percentage of spore germination inhibition was calculated.

Table3. Antibacterial activity at 3µg /disc (zone formation in mm)

Compound	<i>E. coli</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>B. bravis</i>	<i>P aeruginosa</i>	<i>B. cereus</i>
[Ru(TCAATSC)2. H2O]Cl3	12	7	12	8	7	10
[Ru(CSALTSC)2. H2O]Cl3	11	7	11	8	8	10
[Ru(TALDICTSC)2. H2O]Cl3	11	7	11	7	8	10
[Ru(PDIOTSC)2. H2O]Cl3	11	8	12	8	7	11
[Ru(TFAATSC)2. H2O]Cl3	11	8	11	7	8	11

[Ru(HBLTSC) ₂ .H ₂ O]Cl ₃	12	8	11	7	8	11
[Ru(MTBLTSC) ₂ .H ₂ O]Cl ₃	11	7	10	7	7	10
[Ni(TCAATSC)]Cl ₃	11	7	11	8	7	11
[Ni(CSALTSC)]Cl ₃	11	7	11	8	7	10
[Ni(TALDICTSC)]Cl ₃	11	7	12	8	7	11
[Ni(PDIOTSC)]Cl ₃	12	8	11	7	8	12
[Ni(TFAATSC)]Cl ₃	11	8	11	7	8	11
[Ni(HBLTSC)]Cl ₃	11	8	11	8	8	9
[Ni(MTBLTSC)]Cl ₃	12	7	12	8	7	10

Table 4. Response of the test compound (at 1 mg /ml) against fungi

Compound	A.niger	Rhizopus sp.	A.fumigatus	Aspergillus sp.	Sacchar-omyces
[Ru(TCAATSC) ₂ . H ₂ O]Cl ₃	+	+	+	-	+
[Ru(CSALTSC) ₂ . H ₂ O]Cl ₃	+	+	+	-	+
[Ru(TALDICTSC) ₂ . H ₂ O]Cl ₃	+	+	+	-	+
[Ru(PDIOTSC) ₂ . H ₂ O]Cl ₃	+	+	+	-	+
[Ru(TFAATSC) ₂ . H ₂ O]Cl ₃	+	+	+	-	+
[Ru(HBLTSC) ₂ . H ₂ O]Cl ₃	+	+	+	-	+
[Ru(MTBLTSC) ₂ . H ₂ O]Cl ₃	+	+	+	-	+
[Ni(TCAATSC)]Cl ₃	+	+	+	-	+
[Ni(CSALTSC)]Cl ₃	+	+	+	-	+
[Ni(TALDICTSC)]Cl ₃	+	+	+	-	+

[Ni(PDIOTSC)]Cl ₃	+	+	+	-	+
[Ni(TFAATSC)]Cl ₃	+	+	+	-	+
[Ni(HBLTSC)]Cl ₃	+	+	+	-	+
[Ni(MTBLTSC)]Cl ₃	+	+	+	-	+

(+)Not active, (-)active

Table5. Antibacterial screening in DMF

Compound	Diameter of zone of inhibition(mm)			
	<i>E.coli</i>	<i>S.aureu</i>	<i>B.subtilis</i>	<i>P.aeruginosa</i>
[Ru(TCAATSC)2. H ₂ O]Cl ₃	11.4	8.0	11.0	7.5
[Ru(CSALTSC)2. H ₂ O]Cl ₃	11.3	7.0	11.1	7.3
[Ru(TALDICTSC)2. H ₂ O]Cl ₃	10.5	7.5	11.2	8.0
[Ru(PDIOTSC)2. H ₂ O]Cl ₃	11.0	8.2	10.7	8.4
[Ru(TFAATSC)2. H ₂ O]Cl ₃	10.6	7.9	11.4	8.2
[Ru(HBLTSC)2. H ₂ O]Cl ₃	11.0	7.2	10.3	7.8
[Ru(MTBLTSC)2. H ₂ O]Cl ₃	10.5	7.2	11.2	7.9
[Ni(TCAATSC)]Cl ₃	10.4	7.3	11.0	8.2
[Ni(CSALTSC)]Cl ₃	10.5	7.4	10.5	8.3
[Ni(TALDICTSC)]Cl ₃	11.9	7.4	11.1	8.2
[Ni(PDIOTSC)]Cl ₃	11.0	7.9	11.3	8.1
[Ni(TFAATSC)]Cl ₃	11.5	7.6	11.2	8.3
[Ni(HBLTSC)]Cl ₃	11.6	7.3	11.1	8.2
[Ni(MTBLTSC)]Cl ₃	11.2	7.1	11.0	8.4

Table6. Average % spore germination after 72 h.

Compound	A. niger (conc in ppm)			Rhizopus sp. (conc in ppm)			A.fumigatus (conc in ppm)		
	100	500	1000	100	500	1000	100	500	1000
[Ru(TCAATSC)2. H2O]Cl3	55	52	45	55	47	48	46	50	61
[Ru(CSALTSC)2. H2O]Cl3	52	52	54	57	48	51	49	56	60
[Ru(TALDICTSC)2. H2O]Cl3	51	56	63	48	50	63	45	47	62
[Ru(PDIOTSC)2. H2O]Cl3	47	49	61	52	55	65	57	52	60
[Ru(TFAATSC)2. H2O]Cl3	49	50	51	52	50	54	41	58	57
[Ru(HBLTSC)2. H2O]Cl3	48	51	57	53	56	57	48	55	60
[Ru(MTBLTSC)2. H2O]Cl3	62	50	51	52	54	61	49	53	60
[Ni(TCAATSC)]Cl3	51	52	59	50	56	62	47	51	59
[Ni(CSALTSC)]Cl3	49	58	61	45	51	61	45	49	60
[Ni(TALDICTSC)]Cl3	50	56	59	47	55	60	48	52	63
[Ni(PDIOTSC)]Cl3	54	57	62	50	54	61	50	51	61
[Ni(TFAATSC)]Cl3	42	53	61	49	54	60	49	54	59
[Ni(HBLTSC)]Cl3	51	53	58	50	53	62	50	52	56
[Ni(MTBLTSC)]Cl3	50	54	60	49	52	58	51	58	61

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