

Synthesis and Characterization of Some Iridium(III) Complexes of Thiosemicarbazones of 4-Aminoantipyridine

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In the present work, the synthesis of iridium(III) chloride complexes of ten thiosemicarbazones derived from 4-aminoantipyridine and various aromatic aldehydes has been reported. All the complexes have been characterized by elemental analyses, magnetic moments, infrared and electronic spectral studies. These complexes were found to have the composition $[\text{Ir}(\text{L})\text{Cl}_3]$ and have octahedral stereochemistry (L = various thiosemicarbazones).

Key Words: Iridium(III), Complexes, Thiosemicarbazone.

INTRODUCTION

In the past a number of workers have reported platinum metal-coordination compounds of thiosemicarbazones¹⁻³. But comparatively less is known about the metal-coordination compounds of thiosemicarbazones derived from 4-aminoantipyridine.^{4,5} In the present work, the author presents the synthesis and characterization of iridium(III) complexes of various thiosemicarbazones of 4-aminoantipyridine viz., 4[N-(benzalidene)amino]antipyridine thiosemicarbazone (BAAPTS), 4[N-(2-hydroxy benzalidene) amino] antipyridine thiosemicarbazone (HBAAPTS), 4[N-(4-methoxy benzalidene)amino]antipyridine thiosemicarbazone (MBAAPTS), 4[N-(4-dimethylaminobenzalidene) amino] antipyridinethiosemicarbazone (DABAAPTS), 4[N - (2' - nitrobenzalidene)amino]antipyridine thiosemicarbazone (2'-NO₂BAAPTS), 4[N-(3'-nitrobenzalidene)amino]antipyridine thiosemicarbazone (3'-NO₂BAAPTS), 4[N-(4'-nitrobenzalidene)amino]antipyridine thiosemicarbazone (4'-NO₂BAAPTS), 4[N-(4'-hydroxy-3'-methoxy benzalidene) amino] antipyridine thiosemicarbazone (HMBAAPTS), 4[N-(2'-hydroxy-1-naphthalidene)amino]antipyridine thiosemicarbazone (HNAAPTS) and 4[N-(cinnamalidene)amino]antipyridine thiosemicarbazone (CAAPTS).

EXPERIMENTAL

All the thiosemicarbazones derived from 4-aminoantipyridine were prepared by the reported method.⁶

All the iridium(III) chloride complexes of thiosemicarbazones were synthesized by the following general method. Hot ethanolic solution of IrCl₃ (0.001 mol) was mixed with hot ethanolic solution of the respective thiosemicarbazone

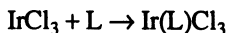
(0.001 mol). The reaction mixture was refluxed for *ca.* 3–4 h. The contents were cooled for a day after reducing the volume of the solution to half; it led to precipitation of the desired complexes. The complexes were filtered washed with hot ethanol and dried.

Physical measurements

The percentage of metal was determined by standard methods using EDTA as titrant employing Eriochrome Black-T as indicator, after decomposing the complexes with moderate conc. sulphuric acid and hydrogen peroxide, and dissolving the residue in water and by making necessary volume⁷. The chloro contents were estimated by Volhard method⁸. The percentage of nitrogen was determined by Kjeldahl method. Sulphur was estimated gravimetrically as BaSO₄. The conductivity measurements were carried out using a Toshniwal conductivity bridge type CL 01/01 and dip type cell operated at 220 volts A.C. mains. All the measurements were done at room temperature in PhNO₂. The magnetic measurements on powder form of the complexes were carried out at room temperature on Guoy's balance using anhydrous copper sulphate as calibrant. The infrared spectra of the complexes were recorded on Perkin-Elmer 621 automatic recording spectrophotometer. Electronic spectra were recorded in Nujol mull on Perkin-Elmer 524 and Beckmann DK-2 automatic recording spectrophotometers.

RESULTS AND DISCUSSION

The formation of the complexes may be represented by the following reaction:



(L = various thiosemicarbazones).

All the complexes gave satisfactory elemental analyses results (Table-1). The complexes are quite stable and could be stored for months without any appreciable change. Most of the complexes have sharp melting points or decomposed on heating beyond 300°C. The complexes are generally insoluble in common organic solvents but soluble in DMF, DMSO and PhNO₂. The molar conductance values in PhNO₂ of these complexes are too low to account for any dissociation; therefore, we consider that all these complexes are non-electrolytes⁹. All the present Ir(III) complexes are diamagnetic as expected. This is inconsistent with an octahedral stereochemistry of the ligand around the central metal ion, forming sp^3d^2 hybridization.^{10, 11}

The electronic spectra of the complexes positively affirm an octahedral configuration around the central metal ion¹². In all the Ir³⁺ complexes the bands appear at 17800–17500, 23550–23250 and a few bands above 30000 cm⁻¹. The bands may be assigned to $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ transitions in increasing order of energy. The bands above 30000 cm⁻¹ may be assigned to charge transfer (Table-2).

TABLE-1
ANALYTICAL, CONDUCTIVITY AND MAGNETIC DATA OF Ir³⁺ COMPLEXES OF THIOSEMICARBAZONES

Complex	Colour, Yield (%)	m.p. (°C)	Analysis: Found (Calcd.), %				Ω_m (ohm ⁻¹ cm ² mole ⁻¹)
			Ir	N	S	Cl	
Ir(BAAPTSCl ₃)	Light yellow, 60	260	28.67 (28.98)	12.61 (12.67)	4.80 (4.83)	15.87 (16.07)	3.1
Ir(HBAAPTSCl ₃)	Yellow, 65	250	28.14 (28.29)	12.32 (12.38)	4.66 (4.71)	15.52 (15.69)	3.3
Ir(MBAAPTSCl ₃)	Yellowish brown, 65	300	27.60 (27.72)	12.07 (12.12)	4.58 (4.62)	15.21 (15.37)	3.7
Ir(DBAAPTSCl ₃)	Yellowish brown, 75	285	27.11 (27.21)	13.83 (13.89)	4.47 (4.53)	14.93 (15.09)	2.9
Ir(2'-NO ₂ BAAPTSCl ₃)	Yellowish brown, 75	220	27.07 (27.13)	13.80 (13.85)	4.46 (4.52)	14.92 (15.05)	3.3
Ir(3'-NO ₂ BAAPTSCl ₃)	Dark yellow, 60	285	27.05 (27.13)	13.79 (13.85)	4.45 (4.52)	14.90 (15.05)	2.9
Ir(4'-NO ₂ BAAPTSCl ₃)	Dark yellow, 65	195	27.06 (27.13)	13.80 (13.85)	4.46 (4.50)	14.90 (15.05)	3.1
Ir(HMBAAPTSCl ₃)	Mustard yellow, 60	230	27.00 (27.09)	11.79 (11.85)	4.45 (4.51)	14.87 (15.03)	3.5
Ir(HNAAPTSCl ₃)	Yellowish brown, 60	235	26.27 (26.35)	11.46 (11.53)	4.34 (4.39)	14.47 (14.61)	2.9
Ir(CAAPTSCl ₃)	Red brown, 65	240	27.76 (27.88)	12.13 (12.20)	4.59 (4.64)	15.33 (15.46)	2.7

TABLE-2
ELECTRONIC SPECTRAL BANDS (cm⁻¹) AND RELEVANT LIGAND FIELD PARAMETER OF Ir³⁺ COMPLEXES

Complex	Spectral bands (cm ⁻¹)	ν_2/ν_1	Δ	B (cm ⁻¹)	β
Ir(BAAPTSCl ₃)	17544, 23256, 38023	1.34	23810	272	0.41
Ir(MBAAPTSCl ₃)	17699, 23364, 30486, 37594	1.35	24020	274	0.42
Ir(CAAPTSCl ₃)	17793, 32529, 37594, 43860	1.33	24150	276	0.42

TABLE-3
KEY IR BANDS (cm^{-1}) OF Ir(III) COMPLEXES OF THIOSEMICARBAZONES

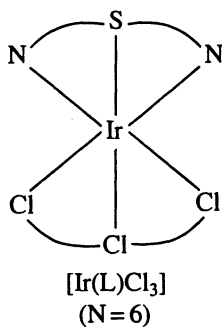
Complex	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \nu(\text{C}-\text{N})$	$\delta(\text{NCS}) + \delta(\text{CS})$	$\nu(\text{N}-\text{N})$	$\nu(\text{C}=\text{S})$	$\nu(\text{Ir}-\text{N}) / \nu(\text{Ir}-\text{S})$
BAAPTS	3440 s, 3270 s	1600 vs	1330 s, 1305 s	1120 m, 1095 m	1050 m	820 s, 760 vs	—
Ir(BAAPTS)Cl ₃	3445 m, 3270 m	1565 m	1380 s, 1330 m	1160 m, 1130 m	1062 m	765 m., 725 m	525 m, 425 w
HBAAPTS	3440 s, 3270 s	1610 vs	1290 s, 1260 vs	1125 m, 1080 m	1050 m	840 s, 760 vs	—
Ir(HBAAPTS)Cl ₃	3442 s, 3272 s	1562 s	1345 s, 1290 m	1170 m, 1120 m	1060 m	815 s, 725 m	525 m, 530 m
MBAAPTS	3420 s, 3310 s	1600 vs	1320 vs, 1195 m	1120 m, 1095 m	1060 m	840 s, 820 s	—
Ir(MBAAPTS)Cl ₃	3420 m, 3315 m	1562 s	1365 s, 1242 m	1172 m., 1130 m	1068 m	782 m, 755 m	520 m, 430 w
DABAAPTS	3360 s, 3330 s	1600 vs	1310 m, 1290 m	1115 m, 1195 w	1050 m	830 s, 730 m	—
Ir(DABAAPTS)Cl ₃	3358 m, 3325 s	1565 m	1365 m, 1342 m	1165 m, 1140 m	1065 m	760 m, 710 m	530 m, 435 m
2'-NO ₂ BAAPTS	3442 s, 3270 s	1600 vs	1330 s, 1305 s	1120 m, 1098 m	1050 m	822 s, 762 vs	—
Ir(2'-NO ₂ BAAPTS)Cl ₃	3440 s, 3272 m	1575 s	1370 s, 1338 m	1160 m, 1132 m	1065 m	780 s, 730 m	535 m, 425 w
3'-NO ₂ BAAPTS	3445 s, 3272 s	1605 vs	1332 s, 1305 s	1120 m, 1098 m	1052 m	820 s, 760 vs	—
Ir(3'-NO ₂ BAAPTS)Cl ₃	3445 s, 3270 s	1572 m	1372 m, 1345 m	1165 m, 1140 m	1065 m	785 s, 710 s	535 m, 425 w
4'-NO ₂ BAAPTS	3440 s, 3270 s	1610 vs	1315 m, 1292 m	1120 m, 1098 m	1055 m	825 s, 762 s	—
Ir(4'-NO ₂ BAAPTS)Cl ₃	3445 s, 3272 s	1572 m	1375 m, 1340 m	1162 m, 1140 m	1062 m	772 s, 748 m	545 m, 442 w
HMBAAPTS	3440 s, 3280 s	1600 vs	1315 s, 1185 m	1122 m, 1095 m	1040 m	840 s, 820 m, 780 s	—
Ir(HMBAAPTS)Cl ₃	3442 m, 3280 m	1558 s	1370 s, 1210 m	1162 m, 1130 m	1055 m	808 m, 782 m	530 m, 425 w
HNAAPTS	3300 s, 3200 s	1620 s	1295 s, 1265 s	1130 s, 1085 m	1045 m	840 m, 765 m	—
Ir(HNAAPTS)Cl ₃	3305 s, 3200 m	1565 s	1345 m, 1282 m	1160 m, 1110 m	1052 m	792 s, 720 m	515 m, 420 sh
CAAPTS	3315 s, 3200 s	1605 vs	1305 s, 1280 m	1125 s, 1085 m	1060 m	840 m, 770 s	—
Ir(CAAPTS)Cl ₃	3325 s, 3202 m	1570 s	1342 s, 1318 m	1145 m, 1122 m	1080 m	820 m, 750 m	535 m, 430 w

A study and comparison of infrared spectra of free ligands and their iridium(III) chloride complexes imply that these ligands behave as neutral tridentate and the metal ion is coordinated through N,N of two azomethine groups and of thio-keto-sulphur.

The strong bands observed at 3440–3270 cm^{-1} region in the free ligands have been observed due to $\nu(\text{NH})$ vibrations. Practically no effect on these frequencies after complexation precludes the possibility of complexation at this group. The absorption at *ca.* 1600 cm^{-1} in the free ligands can be attributed to $(\text{C}=\text{N})$ stretching vibrations of imine nitrogen which is in agreement with the observations of previous workers.^{13, 14} On complexation these frequencies were observed to be shifted to lower wavenumber (Table-3). These observations suggest involvement of unsaturated nitrogen atoms of the two azomethine groups in bonding with the metal ion. In the spectra of free ligands, the bands observed in 1300–1125, 1120–1095 and 840–730 cm^{-1} region are assigned to [$\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \nu(\text{C}-\text{N})$], $\delta(\text{N}-\text{C}-\text{S}) + \delta(\text{C}=\text{S})$ bending, and $\nu(\text{C}=\text{S})$ stretchings respectively.^{15, 16} Coordination of sulphur with the metal ion would result in the displacement of electrons toward the latter, thus resulting in the weakening of $(\text{C}=\text{S})$ bond. Hence on complexation $(\text{C}=\text{S})$ stretching vibrations should decrease and that of (CN) should increase.^{16, 17} In all the present complexes the frequencies in the range 1300–1125 cm^{-1} get an increase by nearly 50–60 cm^{-1} . Similarly bending modes of $(\text{N}-\text{C}-\text{S})$ and $(\text{C}=\text{S})$ also get increase but in lesser amount. On the other hand, on complexation the frequencies in 840–730 cm^{-1} are shifted to lower wavenumbers and intensities of the bands are also reduced. All these peculiar changes on complexation confidently preclude any unambiguous ascertain of metal-sulphur bond.

The possibility of thione-thiol tautomerism ($\text{H}-\text{N}-\text{C}=\text{S}$) \rightleftharpoons ($\text{C}=\text{N}-\text{SH}$) in these ligands has been ruled out for no bands around 2700–2500 cm^{-1} , characteristics of thiol group are displayed in the infrared absorption.^{18, 19} In all the complexes of HBAAPTS, HMBAAPTS and HNAAPTS, the stretching at *ca.* 3400 cm^{-1} region is attributed to $\nu(\text{OH})$. In all the complexes, the hydroxyl frequency appears at the same region as in the free ligands clearly indicating that the $-\text{OH}$ group is not taking part in coordination. In far infrared, $\nu(\text{Ir}-\text{N})$, $\nu(\text{Ir}-\text{S})$ and $\nu(\text{Ir}-\text{Cl})$ were tentatively assigned in 545–515, 442–420 and 330–310 cm^{-1} region respectively.^{2, 3, 20, 21}

On the basis of the above studies, the general structure of these complexes is:



ACKNOWLEDGEMENT

The author is thankful to Prof H.C. Rai, Department of Chemistry, L.S. College (BRA Bihar University), Muzaffarpur for his keen interest in the work.

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(Received: 17 October 2002; Accepted: 1 January 2003)

AJC-2949

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