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Synthesis & Characterization of Some Mixed Ligand Complexes of Pd(II), Rh(III) and Pt(IV) with Carboxylic Hydrazones as Primary and Dithiooxamide as Co-ligand

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Mixed ligand complexes of Pd(II), Rh(III) and Pt(IV) with 2-acetyl pyridyl-pyrazine-carboxylic hydrozone (apph)/2-carboxaldehyde pyridyl-pyrazinecarboxylic hydroazone (cpph) as primary and dithiooxamide (dto) as co-ligand have been synthesised and characterised on the basis of analytical, conductance, spectral and thermal data. Analytical data suggested 1:1:1 (M-L/L′-L″ Clx) Cly stoichiometric composition for the present complexes [where M = Pd(II), Rh(III) and Pt(IV), L = apph, L′ = cpph and L″ = dto, x = 0 for Pd(II) complexes and x = 2 for Rh (III) and Pt(IV) complexes, y = 1 for Rh(III) complexes and y = 2 for Pd(II) and Pt(IV) complexes]. Electrolytic conductance data (ΔM = 180-184.4 ohm^{-1}cm^{2} mol^{-1} for Pd(II) and Pt(IV) complexes and 120.2-124.4 ohm^{-1}cm^{2} mol^{-1} for Rh(III) complexes revealed 1 : 2 electrolytic nature of Pd(II) and Pt(IV) complexes and 1:1 electrolytic nature of Rh(III) complexes. IR spectra confirm the bidentate nature of all the three ligands. Reflectance spectra correspond to square planar geometry of Pd(II) and octahedral geometry of Rh(III) and Pt(IV) mixed ligand complexes. The thermal decomposition study of the complexes reveals that the hydrazone moiety is lost in 400-510ºC temperatuer range. At last metallic residue is left as the ultimate product in 670-710ºC temperature range. The mixed ligand complexes were screened for their antimicrobial activity against *E. coli* and *S. aureus*. The results of screening show that the complexes are more active against *E. coli* in comparison to *S. aureus*.

Key Words: Synthesis, Spectral and Biological studies, Mixed ligand complexes.

INTRODUCTION

The chemistry of Schiff base complexes continues to attract many researchers[1,2]. Schiff base complexes have gained additional importance due to their catalytic role in the expoxidation of olefins[3]. The complexes of aroyl hyrazones have been reported to act as inhibitors for enzymes[4]. Studies on synthesis, characterisation and electrical conductivities of some transition metal complexes of N-benzoyl-N′-*p*-hydroxy thiobenzhydazine have been carried out[5]. The coordination chemistry of aroyl hydrazones with transition metals has ben widely investigated due to their biological activities such as anticancer, antitumour, tuberculosis, leprosy & mental disorder[6-8]. The present paper reports the synthesis and characterization of some mixed ligand complexes of Pd(II), Rh(III) and Pt(IV) with 2-acetyl pyridyl-pyrazinecarboxylic hydrazone/2-carboxaldehyde pyridyl-pyrazinecarboxylic hydrazone as primary and dithiooxamide as co-ligand.

EXPERIMENTAL

Pyrazinamide, 2-acetylpyridine, 2-pyridine carboxaldehyde, dithiooxamide, Pd, Rh and Pt chloride salts were procured from Aldrich chemical company Inc. USA. I.R. spectra were recorded on Perkin-Elmer 621 spectrophotometer. Conductivity measurements were carried out on systronics conductivity bridge. Pyrazinecarboxylic hydrazide was prepared according to the literature procedure[9,10].

The ligands apph and cpph were prepared by mixing ethanolic solution (10 mmol) of 2-acetyl pyridine/2-pyridine carboxaldehyde with ethanolic solution (10 mmol) of pyrazinecarboxylic hydrazide. The mixture was refluxed for 4 to 5 h over water bath at 90ºC. The yellowish crystalline product was obtained in each case. It was filtered, washed properly and dried. Both the products were recrystallized from hot ethanol.

Preparation and isolation of the complexes

The respective hydrazone (apph/cpph) dissolved in ethanol (25 mL, 10 mmol) was mixed with ethanolic solution of dithiooxamide (10 mmol). To this mixture, ethanolic solution of the respective metal salt (10 mmol) was added with magnetically stirring. The resultant mixture was refluxed for 2-3 h. The coloured complexs seperated out on cooling. They were filtered off, washed properly and dried in vacuum over anhydrous $CaCl_2$ (yield 54-55 %).

RESULTS AND DISCUSSION

Analytical data reported in Table-1 suggested 1:1:1 (M-L/L′-L″) stoichiometric composition for the mixed ligand complexes [where L = apph, L´ = cpph, L´´ = dto, M = Pd(II), Rh(III) & Pt(IV)]. The complexes are insoluble in common organic solvents but dissolve in DMF and DMSO appreciably. The molar conductance data (Table-1) in DMF at the concentration 10^{-3}M revealed 1:2 electrolytic nature of Pd(II) and Pt(IV) complexes and 1:1 electrolytic nature of Rh(III) complexes.

Magnetic and reflectance spectral studies

Pd(II) complexes are diamagnetic. Reflectance spectra of Pd(II) complexes exhibit bands in the range 18,600-18,750, 22,800-23,100 and 25,400-25,700 cm^{-1} which are assigned to the transitions $^1A_{1g}\rightarrow{}^1A_{2g}$, $^1A_{1g}\rightarrow{}^1B_{1g}$ and $^1A_{1g}\rightarrow{}^1E_g$, respectively. The band positions are in close resemblance with those generally observed for square-planar Pd(II) complexes[11-13].

TABLE-1
ANALYTICAL & CONDUCTANCE DATA OF MIXED LIGAND COMPLEXES OF Pd(II), Rh(III) AND Pt(IV)

Complexes	Elemental analysis % Calculated (Found)						ΩM (ohm^{-1} cm^{2} mol^{-1})
	C	H	N	S	Cl	Metal	
1. $[\mathrm{PdLL''}]\mathrm{Cl_2}$	31.19	2.78	18.19	11.88	13.16	19.81	180.0
	(31.02)	(2.80)	(18.04)	(11.78)	(13.05)	(19.66)	
2. $[\mathrm{PdL'L''}]\mathrm{Cl_2}$	29.73	2.48	18.68	12.20	13.52	20.33	182.8
	(29.88)	(2.46)	(18.57)	(12.28)	(13.41)	(20.21)	
3. $[\mathrm{RhLL''Cl_2}]\mathrm{Cl}$	29.46	2.63	17.18	11.22	18.64	18.04	124.4
	(29.62)	(2.64)	(17.10)	(11.14)	(18.76)	(18.15)	
4. $[\mathrm{RhL'L''Cl_2}]\mathrm{Cl}$	28.04	2.33	17.61	11.51	19.11	18.50	120.2
	(27.86)	(2.34)	(17.54)	(11.44)	(19.01)	(18.64)	
5. $[\mathrm{PtLL''Cl_2}]\mathrm{Cl_2}$	24.06	2.14	14.04	9.17	20.31	27.96	183.2
	(24.24)	(2.12)	(14.12)	(9.10)	(20.16)	(27.80)	
6. $[\mathrm{PtL'L''Cl_2}]\mathrm{Cl_2}$	22.81	1.90	14.33	9.35	20.73	28.53	184.4
	(22.94)	(1.89)	(14.26)	(9.59)	(2061)	(28.64)	

L = $C_{12}H_{11}N_5O$, L′ = $C_{11}H_9N_5O$ and L′′ = $C_2H_4N_2S_2$

The μ_{eff} values of Rh(III) complexes lie in 0.56-0.60 B.M. range. The complexes show bands at 11,450-11,550, 15,700-15,800, 17,700-18,850 and 20,300-20,450 cm^{-1} which are assigned to $^1A_{1g}\rightarrow{}^3T_{1g}$, $^3T_{2g}$, $^3T_{1g}$ and $^3T_{2g}$ transitions, respectively. These spectral bands are consistent with an octahedral geometry of these complexes.

Pt(IV) complexes exhibit bands at 17,200-17,300, 21,400-21,500 and 26,400-26,700 cm^{-1} with an intense CT band at *ca.* 33,00 cm^{-1} characteristic of an octahedral geometry around the metal ion[14,15].

IR spectra

IR spectra of the hydrazones (apph and cpph) show bands at 1615-1605, 1665-1660, 1520-1505 and 1335-1320 cm^{-1} which may respectively be assigned to ν(C=N), amide I, amide II and amide III bands[16]. Strong band observed at 1615-1605 cm^{-1} due to ν(C=N) shifts to lower frequency side (1585-1595 cm^{-1}) in the complexes which confirms the participation of azomethine nitrogen in coordination. Further, a weak band existing at 970-980 cm^{-1} in the hydrazone ligands characteristic of N-N stretching vibrations, undergoes a +ve shift of *ca.* 20-30 cm^{-1} in the spectra of complexes, thus confirming the monodentate coordination of N-N moiety. The amide I, amide II and amide III bands appear in the regions 1650-1640, 1530-1525 and 1310-1300 cm^{-1} in the spectra of complexes suggesting the coordination of carbonyl oxygen. The non-coordination of the pyridine and pyrazine ring nitrogen in the complexes was inferred by the unaltered position of the ring deformation modes.

Thioamide band-I and thioamide band-II existing at 1,530 and 1,295 cm^{-1}, respectively in the spectrum of dithiooxamide show positive shift in the complexes, which is indicative of the participation of sulphur of the thioamide group in bond formation with the metal ion. Further, ν(C=S) vibration, characteristic of thiocarbonyl group, observed as medium band at 825 cm^{-1} in dithiooxamide, gets shifted to a lower frequency band (800-785 cm^{-1}) in the spectra of complexes, is suggestive of coordination of thiocarbonyl sulphur in thione form.

Some non-ligand bands have been found in the far infra-red region (in complexes) at 430-440, 500-515 and 330-340 cm^{-1} which are assigned to ν(M-N), ν(M-O) and ν(M-S) vibrations. A band at *ca*. 220 cm^{-1} is also seen in the spectra of complexes which may be due to ν(M-Cl) vibration (exception Pd complexes).

Thermal behaviour

The complexes are thermally stable below 400ºC, the hydrazone ligand is lost in 400-510ºC temperature range. Chlorine gas also escape out in this temperature range. Further decomposition of these mixed ligand complexes takes place in 670-710ºC temperature range and the dithiooxamide moiety is also eliminated leaving metallic residue in each case.

Antimicrobial activity

The ligands and the mixed ligand complexes were screened for their antimicrobial activity againt *E. coli* and *S. aureus*. The compounds were dissolved separately in DMF maintaining 100, 200, 400 and 1000 ppm concentrations. The percentage inhibition showed that the compounds are more active against *E. coli*. Further, it was noted that the complexes are more active than the parent ligands.

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