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Synthesis and Characterization of Mixed Ligand Schiff Base Complexes of Aluminium with Isatin-3-Oxime

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The synthesis of some new mixed ligand complexes of aluminium containing Schiff bases and isatin-3-oxime (IO) derivatives have been reported. The complexes were prepared by the reaction of (Schiff base) aluminium isopropoxide with the isatin-3-oxime derivatives. The complexes were characterized by elemental analysis and spectral data. The studies reveal the formation of octahedral complexes.

Key Words: Mixed ligand complexes, Schiff base isatin-3-oxime, aluminium isopropoxide.

INTRODUCTION

Metal complexes especially containing nitrogen and oxygen donor atoms have continuously generated research interest[1, 2]. A large number of aluminium complexes with ligand incorporating nitrogen and oxygen donor atoms have been reported[3, 4]. This can perhaps be attributed to their potentiality for commercial applications[5] and scope for academic investigations. In view of this the preparation and characterization of some mixed ligand aluminium complexes with nitrogen and oxygen donor systems was undertaken.

EXPERIMENTAL

All the chemicals used were of AR grade. Adequate precautions were taken to exclude moisture during the preparation of the complexes. Melting points were determined in open capillary tubes and are uncorrected. The IR spectra were recorded on a Perkin-Elmer model 557 spectrometer and ^1H NMR spectra in $CDCl_3$/DMSO-D_6 on a FX 90Q JEOL type spectrophotometer using TMS as internal standard. Carbon, hydrogen, nitrogen were determined with a Coleman analyzer model-33. Aluminium was determined gravimetrically as oxinate.

1. Preparation of ligand

(a) Isatin-3-oximes: The oximes was prepared by the literature method[6]. A solution of the respective indole-2,3-dione (0.05 M) and hydroxylamine hydrochloride (0.05 M) in water (50 mL) was refluxed for 8 h. The precipitated oxime was filtered and crystallized from ethanol (50%) (yields: *ca.* 90%).

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(b) Schiff bases: The Schiff bases were prepared by the condensation of equimolar amount of salicylaldehyde with ethylenediamine and aniline in ethanol and benzene respectively. Bis-acetyl acetone ethylenediamine was prepared by reported method[7].

2. Preparation of [Schiff base] aluminium [Isatin-3-oximato] complexes

The general method employed for the preparation of the mixed complexes is outlined below:

[Schiff base] aluminium alkoxy derivatives were prepared by refluxing aluminium isopropoxide with the respective Schiff base, *i.e.*, N-phenylsalicylaldimine (1 : 2), N,N′-ethylene-4-amino-3-pentene-2-one (1 : 1) or bis(salicylaldehyde) ethylenediamine (1 : 1) in dry benzene. The mixed ligand complexes were obtained by the reaction of the corresponding [Schiff base] aluminium alkoxy derivatives with the respective isatin-3-oxime (*i.e.*, 5-H or Me or Br) in dry benzene. The completion of reaction was determined by estimating the liberated isopropanol collected azeotropically. The products were obtained as orange yellow solid after the removal of solvent under reduced pressure. They were purified by crystallization with benzene/pet ether (80 : 20). All the complexes gave satisfactory elemental analysis.

RESULTS AND DISCUSSION

The IR spectrum of isatin-3-oximes show broad absorption bands in the region 3400–3000 cm^{-1} for ν(N—H) and ν(O—H). The bands in the region 1680–1620 cm^{-1} have been assigned to ν(C═O) cyclic amido carbonyl and ν(C═N) respectively.

The IR spectra of the mixed complexes gives evidence for the bicoordinate nature of the oxime ligands. In the spectra the oximino ν(O—H) band is not observed. The band observed in the region 1650–1640 cm^{-1} has been assigned to the coordinated cyclic amido carbonyl, ν(C═O) on the basis of comparative IR data results of the precursors and mixed complexes. The lowering of this band (30–40 cm^{-1}) indicates the coordination of the group through oxygen. Besides other bands correspondence to ν(Al—N) and ν(N—H) was observed at 570–430 and 3200–3050 cm^{-1} respectively. Some important bands observed in the IR spectra of the complexes are given in Table-1.

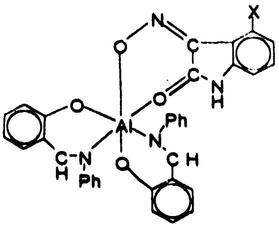
The ^1H NMR spectra of the oximes show peaks in the region δ 11.3 ppm and *ca.* δ 8.6 ppm for the oximo O—H and cyclic N—H protons. The methyl signal in the substituted 5-methyl oxime derivatives is observed at *ca.* δ 2.5 ppm and the phenyl multiplet at δ 6.7–7.5 ppm. The ^1H NMR spectra of the mixed complexes show no signal corresponding to the oximo O—H proton; the cyclic N—H proton is observed at *ca.* δ 11.1–11.3 ppm and phenyl multiplets at δ 7.2–8.2 ppm. The multiplet corresponding to the CH_3CH_2O— protons of the bridging isopropoxy group is not observed in the mixed complexes. The signal for ═CH— proton, of the coordinated N-arylsalicylaldiminato and N,N′-ethylenebis (salicylideneiminato) Schiff bases is observed *ca.* δ 8.4 ppm and for β-ketoaminato at *ca.* δ 5.4 ppm. The $—(CH_2)_2^-$ protons in the spectra of mixed

TABLE-1
CHARACTERIZATION DATA OF (SCHIFF BASE)$_n$ (5-X-ISATIN-3-OXIMATO) ALUMINIUM(III) COMPLEXES

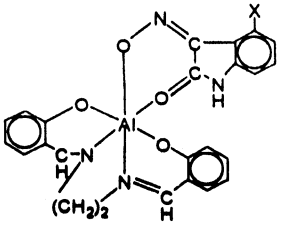
Schiff base	X	m.p. (°C)	Elemental analysis % Found (Calcd.)				IR bands (cm^{-1})				^{1}H NMR (δ ppm)			
			C	H	N	Al	ν(C=O)	ν(C=N)	ν(C—O)	ν(Al—O)	N—H	Ar—H	—CH$_3$	—(CH$_2$)$_2$ (m)
o-$OC_6H_4CH\cdot NPh$	H	140	60.20 (70.35)	4.36 (4.30)	9.62 (9.65)	4.65 (4.64)	1650	1612 1620	1298	680	11.2	8.1–7.0		
o-$OC_6H_4CH\cdot NPh$	CH_3	165	62.02 (61.93)	3.52 (3.64)	8.20 (8.50)	4.31 (4.09)	1645	1615 1620	1302	682	11.1	8.2–7.2	2.2–2.4	
o-$OC_6H_4CH\cdot NPh$	Br	180	70.68 (70.72)	4.56 (4.54)	9.32 (9.42)	4.32 (4.53)	1648	1610 1615	1300	684	11.3	8.1–7.1		
(*o*-$OC_6H_4CH\cdot NCH_2)_2$	H	148	63.20 (63.45)	4.28 (4.18)	13.10 (12.33)	6.02 (5.93)	1642	1615 1618	1304	680	11.2	8.0–7.0		3.5
(*o*-$OC_6H_4CH\cdot NCH_2)_2$	CH_3	170	53.98 (54.06)	3.32 (3.37)	10.20 (10.51)	5.40 (5.06)	1644	1612 1620	1298	685	11.1	8.2–7.2	2.2–2.4	3.4
(*o*-$OC_6H_4CH\cdot NCH_2)_2$	Br	190	63.96 (64.11)	4.50 (4.48)	12.01 (11.96)	5.26 (5.76)	1650	1610	1302	684	11.3	8.1–7.1		3.5
$[CH_3C(O)CHC(CH_3)NCH_2]_2$	H	158	59.02 (58.55)	5.56 (5.60)	12.72 (13.66)	6.53 (6.57)	1510 1640	1505 1610	1305	682	11.2	8.2–7.2	2.0	3.4
$[CH_3C(O)CHC(CH_3)NCH_2]_2$	CH_3	154	48.99 (49.10)	4.52 (4.49)	11.51 (11.45)	5.61 (5.51)	1512 1645	1510 1615	1301	680	11.1	8.1–7.1	1.9 2.2	3.3
$[CH_3C(O)CHC(CH_3)NCH_2]_2$	Br	152	59.02 (59.45)	5.86 (5.89)	13.30 (13.20)	6.36 (6.35)	1515 1640	1508 1620	1296	682	11.3	8.1–7.0	2.0	3.4

ligand complexes having tetradentate ligands are observed at δ 3.3–3.5 ppm and the CH_3 protons of the β-ketoamine at δ 1.9–2.2 ppm. The CH_3 signal of 5-methyl oxime derivatives is observed at *ca.* δ 2.2–2.4 ppm. The important ^1H NMR signals of the complexes are given in Table-1.

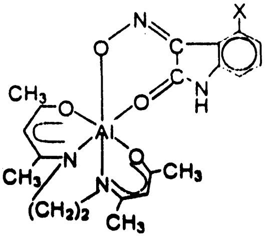
The spectral data of the mixed complexes reveal the monofunctional bidentate coordination of the isatin-3-oximes. The results of analytical and spectral studies give evidence for the formation of hexacoordinate complex with octahedral geometry as shown in Fig. 1.



(i)



(ii)



(iii)

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