Asian Journal of Chemistry Vol. 18, No. 4 (2006), 2809–2812

Studies and Characterization of Mixed Ligand Complexes of Aluminium with (N—O) and (N—S) Donor Ligands

Y.K. GOTHWAL*, JYOTI JOSHI† and BIDYA S. JOSHI
Department of Chemistry, University of Rajasthan, Jaipur-302 004, India
E-mail: jojo_jaipur@yahoo.com

The synthesis of some aluminium(III) mixed ligand complexes having $\overset{\frown}{NO}$ donor Schiffs bases, N-phenylsalicylaldimine (SLIMH) and 3-(phenylamino)-1-phenyl-2-butene-1-one (BZAMH), with 3-aryl-2-mercapto-4(3H)quinazolones (MAQH) has been reported. The mixed ligand complexes were obtained by the reaction of (Schiffs base)$_2$ aluminium isopropoxy precursors with the mercapto ligands. The complexes were characterized by elemental analysis and spectral studies. The studies reveal the formation of hexacoordinate complexes with $\overset{\frown}{NS}$ bonding of the mercapto ligands.

Key Words: Mixed aluminium(III) complexes, N-Phenylsalicylaldimine, 3-(Phenylamino)-1-phenyl-2-butene-1-one, 3-Aryl-2-mercapto-4(3H)quinazolones, hexacoordinate.

INTRODUCTION

A survey of literature reveals that research work on aluminium complexes with nitrogen and oxygen donor systems has been extensively pursued and continues to generate interest[1, 2]. The chemistry and potential applicability of several aluminium complexes with N- and/or O-donor systems have been observed and interesting observations reported[3, 4]. In the present paper, the preparation and characterization of some new mixed ligand complexes of aluminium(III) with Schiffs bases and mercapto quinazolones have been reported.

EXPERIMENTAL

All chemicals used were of AR grade. All solvents and reactants were dried by standard methods[5]. Adequate precautions were taken to exclude moisture during the preparation of precursors and products. Melting points were determined in open capillary tubes and are uncorrected. The IR spectra were recorded on a Perkin-Elmer model 557 spectrometer and ^{1}H NMR spectra in CDCl$_3$/DMSO-D$_6$ on a Jeol FX 90Q MHz spectrometer using TMS as internal standard, Carbon, hydrogen and nitrogen were determined with a Coleman analyzer model-33. Aluminum and sulphur was determined gravimetrically as oxinate and barium sulphate respectively. Isopropanol was estimated by chromate oxidimetric method[6].

---

†Department of Chemistry, Malviya National Institute of Technology, Jaipur-302 017, India.

Preparation of ligand

The Schiff bases were prepared by the condensation of salicylaldehyde[7] and benzoylacetone[8] with aniline.

3-Aryl-2-mercapto-4(3H)quinazolones (aryl = C_6H_5, p-$OCH_3C_6H_4$, p-BrC_6H_4 and p-ClC_6H_4) were prepared by the reaction of the arylisothiocynate with anthranilic acid and purified by precipitation[9] (Aryl (m.p.): C_6H_5 (304°C); p-$OCH_3C_6H_4$ (320°C); p-BrC_4H_4 (275°C); p-ClC_6H_{43} (20°C)).

Preparation of (Schiff base)$_2$Al[3-aryl-2-mercapto-4(3H)quinazolone] complexes

Aluminium isopropoxide and bis(Schiff base) aluminium isopropoxide[10] were prepared by reported methods[5]. The mixed complexes were obtained by reacting the bis(Schiff base) aluminium isopropoxy derivatives with the respective mercaptoquinazolones (1 : 1) in benzene. The reaction was monitored by estimating the liberated isopropanol collected azeotropically.

The products were obtained as light coloured or white solids. All complexes gave satisfactory elemental analysis. The melting points and analytical data of the complexes are given in Table-1.

RESULTS AND DISCUSSION

The IR spectra of the [SLIM]$_2$ aluminium [MAQ] complexes show absorption bands in the region 1305–1295 and 1620–1610 cm^{-1} for ν(C—O) phenolic and ν(C═N) azomethine respectively[7]. The mixed complexes with coordinated (BZAM) show bands corresponding to ν(C⋯O), νC⋯C) and νC⋯N) at 1595–1580, 1530–1520 and 1505–1495 cm^{-1} respectively[8].

The IR spectra of all the mixed derivatives show the absence of the ν(N—H) vibration (3400–3200 cm^{-1}) observed for the free (MAQH) ligand the characteristic bands for ν(C—O) vibration of bridging isopropoxy groups (1005–1000 cm^{-1}) and ν(Al—O—Al) vibration (750–740 cm^{-1})[10].

In the spectra coordinated MAQ anions show no significant shift in the position of the amido ν(C═O) vibration (1690–1680 cm^{-1})[9] and bands for ν(C═N) at 1620–1610 and ν(C—N) at 690–685 cm^{-1}. For the mixed complexes with (SLIM) and [MAQ] the azomethine vibrations overlap. The spectral data is inconsistent with the N—S coordination of the MAQ ligands[11]. Some important bands observed are given in Table-1.

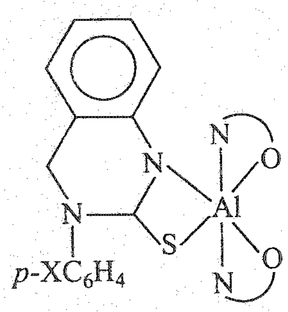
The ^{1}H NMR spectra of the mixed complexes show the absence of isopropoxy methyl (δ 1.1–1.2 ppm) and methine (δ 4.3–4.5 ppm) signals. The phenyl multiple is observed at δ 7.0–8.2 ppm and no peak corresponding to the N—H proton of the free ligand is present. The ═CH— proton signal for the mixed complexes with (SLIM) anions is at δ 8.2–8.4 ppm and for the complexes with (BZAM) at δ 5.4–5.6 ppm. Additional proton signals of substituted —CH_3 and —OCH_3 groups are observed at δ 2.0–2.4 ppm and δ 3.7–4.2 ppm, respectively[12]. The important ^{1}H NMR signals of the mixed complexes are given in Table-1.

The results of the analytical and spectral studies give evidence for the formation of hexacoordinated mixed complexes. On the basis of the data the structure shown in Fig. 1 can be proposed for the complexes.

TABLE-1
CHARACTERIZATION DATA OF SOME (SCHIFF BASE)$_2$*
[3-(-*p*-X-PHENYl)-2-MERCAPTO-4-QUINAZOLONATO] COMPLEX

Schiff base	X	m.p. (°C)	Elemental analysis %: Found (Calcd.)					IR spectral bands (cm^{-1})					^{1}H NMR (δ ppm)		
			C	H	N	S	Al	ν(C═N) ν(C┄N)	ν(C═O) ν(C┄O)	ν(C—O) ν(C┄C)	ν(C—S)	ν(Al—O)	Ar—H	═CH—	—CH$_3$ (—OCH$_3$)
SLIM	H	215	70.48	4.29	8.41	4.66	4.00	1610	1680	1305	686	677	7.2	8.4	—
			(71.43)	(4.31)	(8.33)	(4.76)	(4.01)	—	—	—					—
SLIM	*p*-Br	220	62.98	3.70	7.30	4.02	3.51	1615	1684	1300	688	675	7.8	8.2	—
			(63.93)	(3.72)	(7.45)	(4.26)	(3.59)	—	—	—					—
SLIM	*p*-OCH$_3$	205	72.00	4.43	7.94	4.58	3.89	1612	1682	1298	684	678	7.6	8.3	—
			(70.09)	(4.41)	(7.97)	(4.56)	(3.84)	—	—	—					4.0
SLIM	*p*-Cl	225	67.89	3.87	7.98	4.50	3.79	1620	1690	1302	690	680	8.0	8.4	—
			(67.95)	(3.96)	(7.92)	(4.53)	(3.81)	—	—	—					—
BZAM	H	212	73.20	4.89	7.39	4.29)	3.52	1611	1682	1305	684	674	7.4	5.5	2.0
			(73.41)	(4.91)	(7.44)	(4.33)	(3.58)	1495	1580	1520					—
BZAM	*p*-Br	200	66.20	4.30	6.70	3.82	3.20	1614	1684	1300	684	676	6.8	5.6	2.2
			(66.44)	(4.32)	(6.73)	(3.85)	(3.24)	1500	1590	1514					—
BZAM	*p*-OCH$_3$	195	72.12	4.90	7.01	4.00	3.38	1616	1685	1298	692	678	7.0	5.3	2.1
			(72.13)	(4.98)	(7.15)	(4.08)	(3.44)	1502	1592	1518					3.8
BZAM	*p*-Cl	215	70.00	4.52	7.10	4.01	3.39	1618	1690	1304	682	680	6.9	5.5	2.0
			(70.20)	(4.57)	(7.11)	(4.07)	(3.42)	1504	1595	1520					—

*SLIM = OC_6H_4CH: NPh and BZAM = $PhC(O)CHC(CH_3)NPh$.



(where X = H, OCH_3, Br and Cl; $\overset{\frown}{NO}$ = o-OC_6H_4 : NPh or PhC(O)CH : $C(CH_3)NPh$)

Fig. 1

REFERENCES

1. C. Baleizao, B. Gigante, F.R. Ribeiro, B. Ferrer, E. Palomares and G.H. Erhilio, *Photochem. Photobiol.*, **2,** 386 (2003).
2. N. Putkonen and L. Niinistoe, *J. Mater. Chem.*, **11,** 2340 (2001).
3. R.C. Yu, C.H. Hung, J.H. Huang, H.Y. Lee and J.T. Chen, *Inorg. Chem.*, **41,** 6450 (2002).
4. P. Hormnirum, E.L. Marshall, V.C. Gibson and A.J.P. White, *J. Am. Chem. Soc.*, **126,** 2688 (2004).
5. A.I. Vogel, A Text Book of Quantitative Organic Analysis, 3rd Edn., ELBS-Longmans, London (1973).
6. D.C. Bradley, P.M.A. Halim and W. Wardlaw, *J. Chem. Soc.*, 3450 (1950).
7. T.J. Line, C.S.C. Lane and A.J. Kandathil, *J. Am. Chem. Soc.*, **83,** 3782 (1961).
8. D.F. Martin, G.A. Janusonis and B.B. Martin, *J. Am. Chem. Soc.*, **83,** 73 (1961).
9. P.N. Bharagava and D. Ram, *Bull. Chem. Soc.* (*Japan*), **38,** 342 (1965).
10. A. Singh, A.K. Rai and R.C. Mehrotra, *Indian J. Chem.*, **11,** 978 (1973).
11. L.D. Dave and C. Mathew, *J. Indian Chem. Soc.*, **65,** 377 (1988).
12. R.M.S. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, 4th Edn, John Wiley & Sons, New York (1981).

(*Received*: 7 September 2005; *Accepted*: 25 April 2006) AJC-4803