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MIXED ALDIMINE DERIVATIVES OF ALUMINIUM

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Abstract—1:1:1 Molar reactions of $Al(OPr^i)_3$ with monofunctional bidentate and bifunctional tridentate Schiff bases have yielded mixed Schiff base derivatives of the type (S'B')Al(SB) (where $S'B'^{2-}$ and SB^- are the anions of bifunctional tridentate and monofunctional bidentate Schiff bases respectively). If these complexes are monomeric, the central aluminium atom will be pentacoordinated, and this is suggested by the addition reaction with pyridine. Structures based on IR and NMR spectra have been suggested.

INTRODUCTION

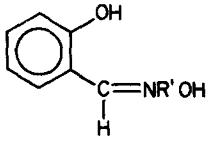
In recent years, the synthesis of complex compounds of diverse stereochemistries and of unusual coordination numbers has proliferated. Aluminium with the electronic configuration, $3s^2p^1$ exhibits tricovalency and coordination numbers 4 and 6 are quite common. However, 5-coordinate complexes of aluminium are also known[1–4].

To obtain mixed Schiff base derivatives with coordination number five for the central metal atom, the following types of reactions have been studied:

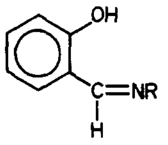
(i) $Al(OPr^i)_3$ and Schiff base (I) were reacted in 1:1 molar ratio.

(iia) After two moles of isopropanol were collected azeotropically from the above reaction, one mol of Schiff base (II) was added and the reaction mixture again refluxed.

(iib) Alternatively, the product $(S'B')Al(OPr^i)$ (where, $S'B'^{2-}$ is the anion of Schiff base (I) was isolated and then reacted with Schiff base (II) in unimolar ratio.



(I)



(II)

(where, R = $-C_2H_5$, n-C_3H_7, iso-C_3H_7, n-C_4H_9, t-C_4H_9, iso-C_4H_9, o-$C_6H_4CH_3$, p-$C_6H_4CH_3$, m-$C_6H_4CH_3$, o-$C_6H_4OCH_3$, m-$C_6H_4OCH_3$, p-$C_6H_4OCH_3$ and $-C_6H_5$, R' = $-CH_2CH_2-$).

The general reactions can be represented as follows:

(i) $Al(OPr^i)_3 + S'B'H_2 \longrightarrow (S'B')Al(OPr^i) + 2Pr^iOH$

(ii) $(S'B')Al(OPr^i) + SBH \longrightarrow (S'B')Al(SB) + Pr^iOH$

(where $S'B'H_2$ and SBH are the bifunctional tridentate(I) and monofunctional bidentate (II) Schiff bases and $S'B'^{2-}$ and SB^- are their corresponding anions).

EXPERIMENTAL

All these reactions were carried out under strictly anhydrous conditions. Schiff bases were prepared by condensing salicylaldehyde with corresponding primary amine or hydroxy alkylamine[5–7]. Their physical properties are given in Table 1.

Synthesis of aluminium derivatives

(i) One mol of aluminium isopropoxide was dissolved in dry benzene and then the calculated amount (1 mol) of the Schiff base (I) was added. The contents were refluxed over a fractionating column and progress of the reaction was checked by the estimation of isopropanol in the azeotrope.

(iia) After two mols of isopropanol were collected one mol of Schiff base (II) was added, and refluxing continued for 2–3 hr, when the remaining mol of isopropanol was collected azeotropically with benzene.

(iib) Alternatively, product $(S'B')Al(OPr^i)$ was first isolated, dried under reduced pressure and analyzed. Then to one mole of this compound in benzene, 1 mol of Schiff base (II) was added. The reaction mixture was refluxed and the isopropanol liberated was removed azeotropically with benzene.

The resulting solid products were dried at 50–60°C/0.5 mm. These compounds are stable upto 210°C but decompose on distillation under reduced pressure. Analyses are recorded in Table 2.

Analytical methods and physical measurements

Aluminium was estimated as oxinate and nitrogen by the Kjeldahl's method. Isopropanol was estimated by oxidation with normal $K_2Cr_2O_7$ solution in 12.5% H_2SO_4. Molecular weights of the complexes were determined ebulliosocopically in benzene with the help of a semi-micro ebulliometer (Gallenkamp) using thermistor sensing.

IR spectra were recorded as Nujol mulls or neat liquids (Perkin-Elmer-557 IR Spectrophotometer). PMR spectra were recorded in CCl_4 or $CDCl_3$ (Perkin-Elmer R-12B Spectrometer) using TMS as internal standard.

RESULTS AND DISCUSSION

Mixed Schiff base complexes of aluminium of type (III) are light coloured solids. Few of them are soluble in benzene, others are either partially soluble or insoluble in most common organic solvents. They are highly susceptible to moisture and this may be due to the tendency of aluminium to acquire coordination number six by combining with a water molecule. They decompose on distillation under reduced pressure. The pentacoordination state in aluminium is relatively uncommon, but it has been claimed to exist in the aluminium-isopropoxy-β-dicarbonyl[1], complexes of aluminium hydride with amines[2] and those of trialkyl aluminium with diamines[3] and tetramethyltetrazene[4].

If all of the compounds are monomeric (like 2 and 10

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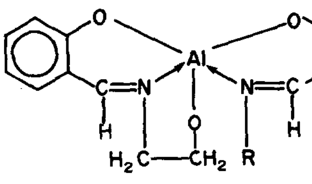
Table 1. Schiff bases and their physical properties

S.No.	Schiff base	Colour	M.p. (°C)	B.p. (°C/mm)
1	$R = -C_2H_5$	Deep yellow	—	74–75/0.4
2	$R = -n\text{-}C_3H_7$	Deep yellow	—	90–91/1.0
3	$R = \text{iso-}C_3H_7$	Deep yellow	—	52–55/1.0
4	$R = n\text{-}C_4H_9$	Deep yellow	—	84–85/0.1
5	$R = \text{iso-}C_4H_9$	Deep yellow	—	102/2.5
6	$R = t\text{-}C_4H_9$	Deep yellow	—	94–95/2.4
7	$R = -C_6H_5$	Yellow, crystalline	51–52	—
8	$R = o\text{-}CH_3C_6H_4$	Yellow, crystalline	44	—
9	$R = m\text{-}CH_3C_6H_4$	Deep yellow	—	162–64/3.0
10	$R = p\text{-}CH_3C_6H_4$	Yellow needles	94	—
11	$R = o\text{-}OCH_3C_6H_4$	Yellow	52	—
12	$R = m\text{-}OCH_3C_6H_4$	Yellow	57–58	142–43/0.1
13	$R = p\text{-}OCH_3C_6H_4$	Gray, crystalline	84	—
14	$R = -CH_2CH_2-$	Yellow, viscous	—	137–39/1.0

Table 2. Reactions of $Al(OPr^i)_3$ with $HOC_6H_4CH{:}NCH_2CH_2OH[X]$ and $HOC_6H_4CH{:}NR$ in 1 : 1 : 1 molar ratio

S. No.	Reactants (g) $Al(OPr^i)_3$	Reactants (g) [X]	Reactants (g) R	Refluxing time (*h*)	Yield (*g*)	Characteristics	Isopropanol in the azeotrope (g) Found (Calcd)	Analysis (%) N Found (Calcd)	Analysis (%) Al Found (Calcd)	Mol. wt. Found (Calcd)
1	1.20	0.97	$-C_2H_5$ (0.85)	6	1.97	Yellow solid	1.04 (1.05)	8.25 (8.35)	7.92 (8.05)	—
2	2.10	1.70	$n\text{-}C_3H_7$ (1.68)	6	3.47	Yellow solid†	1.84 (1.85)	7.60 (7.95)	7.49 (7.67)	340 (352)
3	1.68	1.35	$i\text{-}C_3H_7$ (1.35)	6	2.78	Light yellow solid	1.47 (1.48)	7.82 (7.94)	7.51 (7.67)	—
4	2.05	1.66	$n\text{-}C_4H_9$ (1.78)	4	3.41	Creamish white solid	1.79 (1.81)	7.30 (7.65)	7.03 (7.37)	—
5	1.20	0.97	$i\text{-}C_4H_9$ (1.04)	6	2.12	Yellow solid	1.03 (1.06)	7.48 (7.65)	7.20 (7.37)	—
6	1.92	1.56	$t\text{-}C_4H_9$ (1.67)	6	3.37	Light yellow solid	1.68 (1.70)	7.25 (7.65)	7.26 (7.37)	—
7	1.51	1.22	$-C_6H_5$ (1.37)	6	2.75	Yellow solid	1.32 (1.33)	7.31 (7.48)	7.02 (7.21)	— —
8	1.40	1.13	$o\text{-}C_6H_4CH_3$ (1.45)	6	2.74	Light yellow solid	1.22 (1.23)	6.80 (7.00)	6.45 (6.75)	—
9	1.14	0.92	$m\text{-}C_6H_4CH_3$ (1.18)	6	2.10	Yellow solid	1.07 (1.08)	6.85 (7.00)	6.51 (6.75)	—
10	1.05	0.85	$p\text{-}C_6H_4CH_3$ (1.08)	6	2.00	Yellow solid†	0.91 (0.92)	6.90 (7.00)	6.62 (6.75)	388.5 (400.00)
11	1.42	1.15	$o\text{-}C_6H_4OCH_3$ (1.58)	8	2.90	Yellow solid	1.24 (1.25)	6.50 (6.73)	6.31 (6.49)	—
12	1.04	0.84	$m\text{-}C_6H_4OCH_3$ (1.11)	8	2.00	Light yellow solid	0.91 (0.92)	6.58 (6.73)	6.29 (6.49)	—
13	2.26	1.82	$p\text{-}C_6H_4OCH_3$ (2.51)	8	4.59	Greenish yellow solid	1.98 (1.99)	6.62 (6.73)	6.22 (6.49)	—

†Soluble in benzene.



(III)

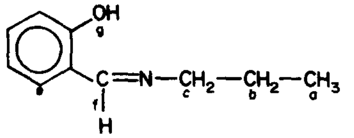
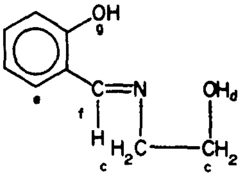
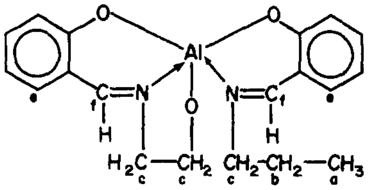
in Table 2) then they are probably 5-coordinate and, as expected, add 1 mol of pyridine.

IR spectra. The IR spectra of the Schiff bases, their corresponding aluminium complexes and the addition products with pyridine have been recorded and the following points appear to be significant:

(i) In the case of Schiff bases, weak and broad absorption bands are observed in the 3500–3300 cm^{-1} region, due to the hydrogen bonding; these bands are absent from the aluminium derivatives, showing chelation through both N and O atoms of the ligands to aluminium.

(ii) A strong band at ~1613 cm^{-1} and ~1625 cm^{-1} is observed in the spectra of salicylidene-ethanolamine and monofunctional bidentate Schiff bases respectively. This is a characteristic of the azomethine ($>C{=}N$) group. In the spectra of the aluminium derivatives containing the

Table 3. PMR spectral data of Schiff base and corresponding aluminium complexes in δ (ppm)

Compound	*a*	*b*	*c*	*d*	*e*	*f*	*g*
	0.5†	1.1‡	2.9†	—	6.1-7.0§	7.62§	12.9
	—	—	3.6†	4.0	6.5-7.8§	8.05¶	8.6
	1.12†	2.85‡	3.68†	—	6.75-7.55§	8.39¶	—

†Triplet, ‡Sextet, §Complex multiplet, and ¶singlet.

above two types of ligands, the same peaks shift to higher frequency (~1620 and ~1640 cm^{-1} respectively). This behaviour indicates that due to the complexing of the nitrogen atom of the ligand, the bond order of the C=N link is increased[8].

(iii) Several new bands of medium intensity in the region 750–630 cm^{-1} are observed in the aluminium derivatives and these may be assigned to Al–O vibrations[6, 9, 10].

(iv) In the complexes bands at ~450 and ~530 cm^{-1} are observed and these may be attributed to ν(Al–N) vibrations[11, 12].

(v) In the addition products of aluminium with pyridine a strong and very sharp peak at 1605 cm^{-1} due to ν (C=N) vibrations and other bands at 1148, 1078, 1030, 1004 and 800 cm^{-1} are observed due to vibrational modes of pyridine[13].

PMR spectra. Assignments are listed in Table 3. On comparison of the PMR spectra of salicylidene-ethanolamine, salicylidene-*n*-propylamine and the corresponding aluminium derivatives, the following points appear to be significant:

(i) The phenolic proton signal at 8.6δ and alcoholic proton signal at 4.0δ in the salicylidene-ethanolamine Schiff base and a phenolic proton signal at 12.9δ in the salicylidene-*n*-propylamine Schiff base were absent in the aluminium complex, showing chelation through oxygen of the –OH group.

(ii) The methine proton signal at 8.05δ in salicylidene ethanolamine and at 7.6δ in salicylidene-*n*-propylamine Schiff bases are shifted to 8.4δ in the aluminium derivative and this shift further supports the view that both nitrogen atoms are coordinated to the central aluminium atom via dative bonds.

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