# AZOMETHINE DERIVATIVES OF ALUMINIUM CONTAINING Al-O-SiMe<sub>3</sub> GROUPS

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Abstract—The synthesis of azomethine derivatives of aluminium containing Al—O—SiMe<sub>3</sub> groups and resistant to hydrolysis is described. These have been prepared either by the equimolar reactions of bibasic tridentate or bibasic tetradentate azomethines, viz. N-(2-mercaptoethyl) salicylaldimine, N-(2-mercaptophenyl) salicylaldimine, salicylaldehyde sulphisoxazole, salicylaldehyde azine, salicylaldehyde semicarbazone, salicylaldehyde thiosemicarbazone, o-hydroxyacetophenone azine N,N'1,3-propylene-bis(salicylaldimine) and diacetyl bis(2-mercaptoanil), or of 1:2 molar reactions of monobasic bidentate imines viz. N-(2-mercaptophenyl) benzaldimine, benzaldehyde semicarbazone and benzaldehyde thiosemicarbazone with Me<sub>3</sub>Si—O—Al(OPr<sup>1</sup>)<sub>2</sub> in the medium of dry benzene. The resulting derivatives are coloured solids with sharp m.ps, non-volatile, non-electrolytes, soluble in chloroform, dimethylformamide and dimethylsulphoxide, and monomeric in nature. Their IR, 'H NMR and electronic spectral data have been presented in support of the proposed structures.

Frisch<sup>1</sup> synthesized some binuclear compounds of arsenic containing the Si-O-As linkage by the interaction of alkyl or aryl chlorosilanes with arsonic acids, and which on hydrolysis yield polymers containing arsenic and silicon in the molar ratio 1:2. A number of patents concerning the complexes having Si-O-As type bonding appear in the literature.<sup>2,3</sup> Bradley and Thomas<sup>4</sup> were the first to utilize the transesterification method for the preparation of silvloxides of Ti(IV), Zr(IV), Nb(V) and Ta(V). A few reactions of alkoxides of lanthanides and trimethyl acetoxysilane with a variety of tridentate azomethines, possessing the ONS donor sequence have been reported from these laboratories.<sup>5</sup> However, reactions of aluminium isopropoxide and trimethylacetoxysilane with azomethins having NS, ON, ONS, ONN, ONNO and SNNS donor sequences do not seem to have been studied earlier. The present paper describes the synthesis and characterization of few heteronuclear derivatives of а type.  $Me_3Si - O - Al(SB)$ ,  $Me_3Si - O - Al(S'B')$ and Me<sub>3</sub>Si—O—Al(S"B")<sub>2</sub> (where SB<sup>2-</sup>, S'B'<sup>2-</sup> and S"B"<sup>1-</sup> = anions of different Schiff bases).

## **RESULTS AND DISCUSSION**

The equimolar reaction of trimethylacetoxysilane  $Me_3SiOOCCH_3$  with aluminium isopropoxide  $Al(OPr')_3$  can be represented by the following equation:

$$(CH_3)_3 SiOOCCH_3 + Al(OPr^i)_3$$
  

$$\rightarrow (CH_3)_3 Si - O - Al(OPr^i)_2 + OPr^i OCCH_3.$$

The liberated isopropylacetate in the above reaction was simultaneously fractionated off as an azeotrope with cyclohexane and its estimation at regular intervals oxidimetrically indicated the extent to which the reaction had proceeded.

To the resulting solution of silyloxide of aluminium, an appropriate amount of azomethine [equimolar in the case of bibasic tri- (HON  $\chi$ H) or tetradentate (H $\chi$  N  $\chi$  XH), and 1:2 in the case of monobasic bidentate (N  $\chi$ H) was added. The liberated isopropanol was again fractionated

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off till the reaction was complete (8-12 h):



(where HO N XH = SBH<sub>2</sub> HX N N SH = S' B'H<sub>2</sub> and N XH = S" B"H)

These reactions take place in two consecutive steps and the following reaction mechanism can possibly be advanced.

(i) The first step involving the reaction between aluminium isopropoxide and trimethylacetoxysilane is almost similar to the one suggested for the transesterification reaction and it may be illustrated as below : The resulting complexes are coloured solids, nonvolatile and soluble in chloroform, dimethylformamide and dimethylsulphoxide. Their resistance to hydrolysis may be due to the water repellent properties of the organo-silicon group present in these derivatives. The molar conductance in dry dimethylformamide has been found to be below

$$(CH_3)_3 Si - 0 + Al - OPr^i \longrightarrow (CH_3)_3 Si - 0 - Al OPr^i + OPr^i OCCH_3$$

(ii) The trimethylsilyloxide of aluminium diisopropoxide subsequently reacts with a bibasic tri- or tetradentate azomethine probably by an  $SN^2$  type of mechanism as depicted below :



 $15 \,\Omega^{-1} \, \text{cm}^2 \, \text{mol}^{-1}$  at  $10^{-3} \, \text{M}$  concentration, which is indicative of the non-ionic nature of these derivatives. The molecular-weight determinations indicate their monomeric nature.

It may, therefore, be inferred that in these newly synthesized complexes, the silicon atom is in the tetracoordinated environment,<sup>5</sup> whereas the aluminium atoms possibly are in tetra- or penta-coordination states as shown at top of next column.

The proposed structures of the imine complexes are further supported by the IR, electronic and <sup>1</sup>H NMR spectral studies.

A strong and broad band in the 3400–3100-cm<sup>-1</sup> region is observed in the IR spectra of the ligands and this may be due to the hydrogen-bonded OH or NH stretching vibrations. Further, the absence of v(SH) in the 2600–2500-cm<sup>-1</sup> region along with a v(C=N) band at ~ 1600 cm<sup>-1</sup> in the ligands *N*-(2-mercaptoethyl) salicylaldimine (C<sub>9</sub>H<sub>11</sub>ONS), *N*-(2-mercaptophenyl)salicylaldimine (C<sub>13</sub>H<sub>11</sub>ONS) and diacetylbis(2-mercaptoanil) (C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>) is strong evidence for the existence of benzothiazoline ring and not the imine form in these ligands.<sup>6</sup>

The IR spectra of aluminium complexes do not.



show any band in the 3400-3100-cm<sup>-1</sup> region, indicating the chelation of the phenolic oxygen and azomethine nitrogen of the ligands to the aluminium atom.<sup>5</sup> Further, the C=N stretching vibration at 1635 cm<sup>-1</sup> in the case of the ligand salicylaldehyde azine shifts towards a lower wavelength in the corresponding aluminium complex, which suggests the coordination of the azomethine nitrogen to the aluminium atom.<sup>7</sup>

In the case of complexes derived from N-(2-mercaptophenyl) salicylaldimine and diacetylbis(2mercaptoanil), a strong band appearing at 1600 cm<sup>-1</sup> may be assigned to the coordinated  $\Sigma = N$ group which supports very well the fact that the resulting complexes are metal-imine complexes due to the rearrangement of the benzothiazoline structure<sup>8</sup> to give the imine form, which finally acts as a bibasic tri- or tetradentate ligand.

The C—O stretching modes of the phenolimine form of the ligands occur at  $\sim 1280 \text{ cm}^{-1}$  and shift towards a higher frequency ( $\sim 1300 \text{ cm}^{-1}$ ) due to complexation through the phenolic oxygen of the ligand moiety.

A band of medium intensity is observed in all the trimethylsilyloxide aluminium-bonded imine complexes in the 1250-1260-cm<sup>-1</sup> region which may be

assigned to the presence of a  $-Si(CH_3)_3$  group, as also reported by Barraclough<sup>9</sup> in the case of trimethylsilanol.

The appearance of some new bands of strong to weak intensities in the spectra of metal imine complexes in the 900–920(s)-, 760–620(m,s)-, 570– 430(m,w)- and 410–300(w)-cm<sup>-1</sup> regions are due to v(Si-O-Al), v(Al-O),<sup>10</sup>  $v(Al\leftarrow N)^{10-12}$  and v(Al-S),<sup>13</sup> respectively. Barraclough *et al.*<sup>9</sup> have similarly assigned a strong band at 900 cm<sup>-1</sup> in the case of a number of monomeric metal trialkylsilyloxides to Si-O stretching vibrations.

The electronic spectra of ligands derived from oaminothiophenol show two bands at 250 and 310 nm, and these are fully consistent with the typical spectrum of benzothiazolines.<sup>14</sup> These transitions, which arise due to  $\phi - \phi^*$  and  $\pi - \pi^*$  benzenoid rings, remain unchanged in all the silyloxide aluminiumbonded imine complexes, whereas an additional band is also observed at ~ 415 nm due to  $n-\pi^*$ electronic transitions of the azomethine group, indicating the isomerization of the ligand on complexation.

However, the electronic spectra of other azomethines used in these investigations exhibit three bands around 245, 295 and 400 nm. The bands around 245 and 295 nm are possibly due to  $\phi$ - $\phi^*$  and  $\pi$ - $\pi^*$  transitions of the benzenoid ring in conjugation with the double bond of the azomethine group, and the band around 400 nm may be due to n- $\pi^*$  transitions of bonding electrons present on the nitrogen of the azomethine group. In the corresponding complexes, there is no shift in the positions of the first two bands. However, the band around 400 nm undergoes a bathochromic shift of 20 nm in the complexes and this may be due to the coordination of the nitrogen of the azomethine group to the central aluminium atom.

Further, to confirm the bonding modes in these complexes, the <sup>1</sup>H NMR spectra of salicylaldehyde azine and its 1:1 complex with metal silyloxide have been recorded in CDCl<sub>3</sub> and the chemical-shift values [ $\delta$  (ppm)] for different protons reveal the following salient point.

In the ligand, the hydrogen-bonded NH proton signal appears as a broad signal centred at  $\delta$  13.40 ppm which disappears in the corresponding azinate complex, showing the chelation of both phenolic oxygens of the ligand moiety to the aluminium atom after the deprotonation of both phenolic groups.

The proton signal for the azomethine proton (-C=N)

 $(-C=N) | is observed at \delta 7.95 ppm in the ligand, H$ 

and it shifts downfield to  $\delta$  8.40 ppm in the spectrum of the aluminium complex due to the deshielding as

						АсОН Реон		Analyses (%)	
					Compound formed,	(g)	Si	AI	z
	Me <sub>3</sub> SiOAc	Al(OPr') <sub>3</sub>	Ligand	Molar	characteristics and	Found	Found	Found	Found
No.	(g)	(g)	(g)	ratio	yield (g)	(calc.)	(calc.)	(calc.)	(calc.)
1	0.75	1.16	C <sub>9</sub> H <sub>11</sub> ONS	1:1:1	Me <sub>3</sub> Si—O—Al(C <sub>9</sub> H <sub>9</sub> ONS),	0.34, 0.68	9.6	9.1	4.8
			(1.02)		brown solid, 1.52	(0.34, 0.68)	(6.5)	(9.2)	(4.8)
2	0.64	0.99	C <sub>13</sub> H <sub>11</sub> ONS	1:1:1	Me <sub>3</sub> Si—O—Al(C <sub>13</sub> H <sub>9</sub> ONS),	0.28, 0.58	8.1	7.9	4.1
			(1.11)		yellow solid, 1.49	(0.29, 0.58)	(8.2)	(0.7)	(4.0)
e	0.52	0.80	C <sub>16</sub> H <sub>17</sub> O₄N <sub>3</sub> S	1:1:1	$Me_{3}Si - O - Al(C_{16}H_{15}O_{4}N_{3}S),$	0.23, 0.45	5.8	5.4	8.7
			(1.46)		dark yellow solid, 1.65	(0.23, 0.46)	(5.7)	(2.2)	(8.6)
4	0.60	0.94	$C_{14}H_{12}O_2N_2$	1:1:1	Me <sub>3</sub> Si—O—Al(C <sub>14</sub> H <sub>10</sub> O <sub>2</sub> N <sub>2</sub> ),	0.27, 0.54	8.0	7.5	7.9
			(1.10)		shining yellow solid, 1.45	(0.27, 0.54)	(6.7)	(1.6)	(6.7)
ŝ	1.18	1.82	$C_8H_9O_2N_2$	1:1:1	$Me_3Si - O - Al(C_8H, O_2N_3)$ ,	0.51, 1.05	9.6	9.1	14.1
			(0.69)		light yellow solid, 1.57	(0.53, 1.06)	(9.5)	(9.2)	(14.3)
9	0.88	1.36	C <sub>8</sub> H <sub>9</sub> ON <sub>3</sub> S	1:1:1	Me <sub>3</sub> Si—O—Al(C <sub>8</sub> H <sub>7</sub> ON <sub>3</sub> S),	0.39, 0.81	9.1	8.8	13.5
			(0.67)		light brown solid, 1.36	(0.40, 0.80)	(0.6)	(8.7)	(13.6)
2	0.56	0.86	$C_{16}H_{16}O_2N_2$	1:1:1	Me <sub>3</sub> Si—O—Al(C <sub>16</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> ),	0.25, 0.50	7.4	6.9	7.2
			(1.13)		yellow solid, 1.45	(0.25, 0.50)	(1.3)	(1.0)	(7.3)
<b>90</b>	0.76	1.17	$C_{17}H_{18}O_2N_2$	1:1:1	$Me_{3}Si-O-AI(C_{1},H_{16}O_{2}N_{2}),$	0.34, 0.68	7.1	6.6	7.0
			(0.84)		dim yellow solid, 1.46	(0.34, 0.68)	(0.()	(6.8)	(1.0)
6	0.67	1.03	$C_{16}H_{16}N_2S_2$	1:1:1	Me <sub>3</sub> Si-O-Al(C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> S <sub>2</sub> )	0.29, 0.61	5.8	5.6	8.9
			(0.94)		yellow solid, 1.44	(0.30, 0.60)	(5.9)	(5.7)	(8.8)
10	0.44	0.68	C <sub>13</sub> H <sub>11</sub> NS	1:1:2	$Me_{3}Si-0-Al(C_{13}H_{10}NS)_{2}$	0.19, 0.38	4.9	4.5	4.8
			(1.55)		brownish yellow solid, 1.68	(0.19, 0.38)	(4.7)	(4.6)	(4.8)
11	0.52	0.80	C <sub>8</sub> H <sub>9</sub> ON <sub>3</sub>	1:1:2	$Me_3Si-O-Al(C_8H_8ON_3)_2$	0.23, 0.46	9.9	6.0	18.9
			(1.28)		light brown solid, 1.80	(0.23, 0.46)	(6.4)	(6.1)	(19.1)
12	0.72	1.11	C <sub>8</sub> H <sub>9</sub> N <sub>3</sub> S	1:1:2	$Me_{3}Si-O-Al(C_{8}H_{8}N_{3}S)_{2}$	0.32, 0.64	6.0	5.6	17.6
			(1.50)		yellow solid, 1.5	(0.32, 0.64)	(5.9)	(5.7)	(17.8)
" Sati	sfactory carbon	and hydrogen a	nalyses were also obta	ained. Ligands	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 are N	-(2-mercaptoethyl) s	alicylaldimir	ie, N-(2-merc	aptophenyl)

salicylaldimine, salicylaldehyde sulphisoxazole, salicylaldehyde azine, salicylaldehyde semicarbazone, salicylaldehyde thiosemicarbazone, o-hydroxyacetophenone azine, N,N'-1,3-propylanebis(salicylaldimine), diacetylbis(2-mercaptoanil), N-(2-mercaptophenyl)benzaldimine, benzaldehyde semicarbazone and benzaldehyde thiosemicarbazone,

respectively.

Table 1. Reactions of Al(OPr'), with Me<sub>3</sub>SiOAc and azomethines

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a result of coordinate bond formation between the nitrogen and aluminium.

The signal observed at  $\delta$  1.05 ppm in the complex is attributable to the methyl protons of the -Si(CH<sub>3</sub>)<sub>3</sub> groups. Further, a downfield shift in the resonance signal of aromatic protons of the ligand has also been observed in the case of the metal complex as a result of the deshielding of the aromatic protons due to the coordination of the azomethine nitrogen to the aluminium atom.

### EXPERIMENTAL

Throughout these investigations, a glass apparatus fitted with interchangeable standard ground joints was used.

The different Schiff bases used as ligands in the present investigations were prepared by the usual condensation<sup>6,7</sup> of a carbonyl compound (ketone/aldehyde) with the appropriate amine, amino-thiol, sulphonamide or diamine. The ligands were further purified either by recrystallization or by distillation under reduced pressure.

Aluminium isopropoxide was prepared by the direct reaction of aluminium metal with isopropanol in the presence of mercuric chloride as a catalyst and distilled before use  $(85^{\circ}C/0.6 \text{ mm})$ . Found: Al, 13.2; OPr<sup>*i*</sup>, 86.7. Calc.: Al, 13.2; OPr<sup>*i*</sup>, 86.8%.

Trimethylacetoxysilane was obtained by the reaction between anhydrous sodium acetate and trimethyl chlorosilane in ether. The product was distilled before use (b.p.  $103^{\circ}$ C/740 mm). Found : Si, 21.1; OAc, 44.3, Calc. : Si, 21.2; OAc, 44.7%.

The binuclear Schiff base complexes of aluminium containing Al-O-SiMe<sub>3</sub> groups were synthesized by the reactions of aluminium isopropoxide in an equimolar ratio with trimethylacetoxysilane, (CH<sub>3</sub>)<sub>3</sub>SiOOCCH<sub>3</sub>, in dry cyclohexane medium. The aluminium isopropoxide was refluxed under a fractionating column and the calculated amount of trimethylacetoxysilane diluted with dry cyclohexane was added. The reaction led to the liberation of isopropylacetate,  $C_3H_7^iCOOCH_3$  which was continuously fractionated off azeotropically with cyclohexane at regular intervals for 8-10 h. When the liberated isopropanol/acetic acid corresponded to 1 mol, an equimolar amount of bibasic tri- or tetradentate azomethine was added to the resulting product,  $(CH_3)_3Si - O - Al(OC_3H_7)_2$ . However, in the case of monobasic bidentate ligands, the azomethine was added in a 1:2 molar ratio.

The reaction mixture was further refluxed for 8–14 h and the isopropanol liberated was again fractionated off and estimated oxidimetrically. The

liberation of almost the theoretical amount of isopropanol in the azeotrope is an indication of the completion of the reaction. The excess of the solvent was then stripped off by distillation and the last traces of the volatile materials were removed under reduced pressure. The solid products so obtained were washed several times with anhydrous *n*-hexane and finally dried at 50–60°C/0.25 mm for about 4 h. The experimental details of these reactions along with the analyses of the products are recorded in Table 1.

The apparatus and instruments used for conductance measurements, molecular-weight determinations and electronic, IR and <sup>1</sup>H NMR spectral studies were the same as reported in our previous communications.<sup>5,7</sup> Silicon and aluminium were estimated gravimetrically as silicon dioxide and aluminium oxinate, respectively. Isopropanol was estimated oxidimetrically.<sup>15</sup> For the determination of the acetoxy group, a weighed amount of the compound was hydrolyzed and then titrated against a 0.05 N solution of sodium hydroxide using phenolphthalein as an indicator.

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