Synthesis & Characterisation of Binuclear Silicon-Aluminium & Arsenic-Aluminium Complexes with Schiff Bases

VIBHAV CHATURVEDI & J P TANDON*
Department of Chemistry, University of Rajasthan, Jaipur 302004

Received 6 August 1984: revised 10 October 1984: accepted 13 November 1984

Trimethylsilyl acetate or phenylarsonic acid on reaction with aluminium isopropoxide yields two new series of complexes of the types \((\text{CH}_3)_3\text{Si}=\text{O}=\text{Al}(\text{OPr})_2\) and \(\text{C}_8=\text{H}_8\) (\(=\text{O}\)=\(\text{O}\)>\text{Al}(\text{OPr})\). The isopropoxy groups in these derivatives further undergo facile reactions with bidentate Schiff bases giving coloured complexes of the types \((\text{CH}_3)_3\text{Si}=\text{O}=\text{Al}(\text{SB}=\text{H})_2\) and \(\text{C}_8=\text{H}_8\) (\(=\text{O}\)=\(\text{O}\)>\text{Al}(\text{SB}=\text{H})\) respectively, where \(\text{SB}=\text{H}\) is deprotonated form of the Schiff base. The Si-Al type of compounds are monomeric in nature and nonelectrolytes in DMSF and DMSO, whereas the As-Al type of derivatives are insoluble in most of the organic solvents and appear to be polymeric in nature. A few compounds have been found to be quite effective as potential pesticides.

Aluminosiloxanes as well as binuclear complexes of arsenic of the types Si=O=Al and As=O=M (where \(M=\text{Cu}, \text{Ni}, \text{Zn}, \text{Hg}, \text{Co}, \text{Sn}\) and \(\text{Pb}\)) find a number of industrial applications due to their hydrolytic and thermal stabilities. The presence of \((\text{CH}_3)_3\text{Si}=\text{O}\) moiety in the silicon compounds imparts solubility in non-polar solvents.

We report here the preparation and characterization of some binuclear Si=Al and As=Al complexes involving Si=O=Al and As=O=Al linkages with Schiff bases derived from salicylaldehyde or \(\text{o}-\text{hydroxynaphthaldehyde}\) and substituted anilines.

All the chemicals used were of AR grade and the reactions were carried out under anhydrous conditions. Trimethylsilylacetae and aluminium isopropoxide were prepared by the literature methods. Schiff bases were prepared by the condensation of salicylaldehyde or \(\text{o}-\text{hydroxynaphthaldehyde}\) with \(p\)-fluoroaniline, \(p\)-chloroaniline, \(p\)-bromoaniline and \(p\)-nitroaniline. These were further purified by recrystallization from ethanol and analyzed before use. The analytical data of the Schiff bases are given below:

1. N-(\(p\)-fluorophenyl)salicylaldimine: m.p. 118°C. Found C, 76.92. H, 4.50. N, 5.20; Calculated for \(\text{HOC}=\text{H}_8\text{CH}:\text{NC}_8\text{H}_4\text{F}=\text{C}\), 76.98. H, 4.52. N, 5.28. (3) N-(\(p\)-chlorophenyl)salicylaldimine: m.p. 100°C. Found C, 67.30. H, 4.29. N, 6.00; Calculated for \(\text{HOC}=\text{H}_8\text{CH}:\text{NC}_8\text{H}_4\text{Cl}=\text{C}\), 67.38. H, 4.31. N, 6.04. (4) N-(\(p\)-chlorophenyl)-2-hydroxy-1-naphthaldehyde: m.p. 175°C. Found C, 72.42. H, 4.22. N, 9.49; Calculated for \(\text{HOC}=\text{H}_8\text{CH}:\text{NC}_8\text{H}_4\text{Cl}=\text{C}\), 72.46. H, 4.26. N, 9.47. (5) N-(\(p\)-bromophenyl)salicylaldimine: m.p. 105°C. Found C, 62.51. H, 3.60. N, 5.02; Calculated for \(\text{HOC}=\text{H}_8\text{CH}:\text{NC}_8\text{H}_4\text{Br}=\text{C}\), 62.57. H, 3.68. N, 5.07; (6) N-(\(p\)-bromophenyl)-2-hydroxy-1-naphthaldehyde: m.p. 160°C. Found C, 69.82. H, 4.05. N, 4.76; Calculated for \(\text{HOC}=\text{H}_8\text{CH}:\text{NC}_8\text{H}_4\text{NO}_2=\text{C}\), 69.86. H, 4.10. N, 4.79%.

(i) Preparation of complexes having Si=O=Al linkage

Equimolar quantities of aluminium isopropoxide and trimethylsilylacetaet in dry cyclohexane were refluxed under a fractionating column. The progress of the reaction was monitored by estimating isopropylacetate in the azeotrope. The resulting diisopropoxy derivative was then refluxed with Schiff base in 1:2 molar ratio. The reaction could be completed on 18-20 hr. The solvent was then removed and the solid products so obtained repeatedly washed with dry n-hexane. The analytical data of the resulting derivatives have been recorded in Table 1.

(ii) Preparation of complexes having As=O=Al type of linkage

The preparation was carried out in two steps. In the first step phenylarsonic acid was reacted with aluminium isopropoxide in equimolar ratio in the presence of dry toluene. In the second step the monoisopropoxy derivatives was reacted with bidentate Schiff base in 1:1 molar ratio.

Silicon was estimated as silicon dioxide and aluminium as aluminium oxinate. Arsenic was estimated iodometrically and nitrogen by Kjeldahl's method. Carbon and hydrogen analyses were carried out by microanalytical methods.
The reactions of trimethylsilyl acetate, aluminium isopropoxide and monobasic bidentate Schiff base ($\text{NOH}$) in the molar ratio of 1:1:2 may be represented by the following equations:

$$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{OPr})_2 + \text{C}_3\text{H}_7\text{OCCCH}_3 \rightarrow (\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{OPr})_3 + \text{C}_3\text{H}_7\text{OCCCH}_3$$

$$= \ldots (1)$$

$$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{OPr})_3 + 2\text{NOH} \rightarrow (\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{ON})_2 + 2\text{C}_3\text{H}_7\text{OH} \rightarrow \ldots (2)$$

The resulting complexes are coloured solids with sharp melting points and these are soluble in benzene, chloroform, DMF and DMSO. The complexes are nonelectrolytes in DMF and DMSO and are monomeric in nature. The binuclear Schiff base complexes of arsenic and aluminium were found to be insoluble in most of the organic solvents; therefore, their molar conductances and molecular weights could not be determined. These compounds decompose on heating. Thus a polymeric structure can be tentatively proposed for such type of complexes as has been reported earlier in the literature.\(^7\)\(^8\)\(^9\).

The broad absorption bands in the region, 3300-2850 cm\(^{-1}\) in the infrared spectra of the ligands have been assigned to the hydrogen bonded $\text{OH}$. These bands disappear in the binuclear complexes, showing coordination through phenolic oxygen after deprotonation. A strong band observed at $\sim 1600 \pm 10$ cm\(^{-1}\) in the spectra of ligands is characteristic of the azomethine ($\geq C = N$) group. This gets shifted to the higher wave number side in the corresponding complexes and is observed at $\sim 1610 \pm 10$ cm\(^{-1}\).

---

**Table 1 — Analytical Data of Binuclear Complexes**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour</th>
<th>m.p. °C</th>
<th>Analysis, Found (Calc.) %</th>
<th>Mol Wt Found (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOF})_2$</td>
<td>Light yellow</td>
<td>240</td>
<td>C 63.91, H 4.91, Si/As 5.10, Al 4.90, N 5.10</td>
<td>540</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOF})_2$</td>
<td>-do-</td>
<td>220</td>
<td>(63.97) (4.96) (5.14) (4.96) (5.14)</td>
<td>(344)</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOCl})_2$</td>
<td>Dark yellow</td>
<td>165</td>
<td>(60.25) (4.61) (8.00) (4.60) (4.79)</td>
<td>560</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOCl})_2$</td>
<td>-do-</td>
<td>185</td>
<td>(60.31) (4.67) (8.5) (4.67) (4.85)</td>
<td>(577)</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOCI})_2$</td>
<td>Light yellow</td>
<td>125</td>
<td>C 52.40, H 4.02, Si/As 4.00, Al 4.00, N 4.00</td>
<td>670</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOCI})_2$</td>
<td>-do-</td>
<td>140</td>
<td>(52.42) (4.06) (4.21) (4.06) (4.21)</td>
<td>(664)</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOBr})_2$</td>
<td>Dark yellow</td>
<td>145</td>
<td>C 58.10, H 4.45, Si/As 4.60, Al 4.45, N 4.64</td>
<td>755</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOBr})_2$</td>
<td>-do-</td>
<td>165</td>
<td>(58.19) (4.51) (4.68) (4.51) (4.68)</td>
<td>(598)</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOBr})_2$</td>
<td>Orange</td>
<td>180</td>
<td>C 65.54, H 4.52, Si/As 4.10, Al 4.10, N 4.79</td>
<td>677</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOBr})_2$</td>
<td>Dark yellow</td>
<td>220</td>
<td>C 60.25, H 4.61, Si/As 4.30, Al 4.30, N 4.79</td>
<td>677</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOBr})_2$</td>
<td>Orange</td>
<td>250</td>
<td>C 57.90, H 4.01, Si/As 3.60, Al 3.60, N 3.50</td>
<td>755</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOBr})_2$</td>
<td>Dark yellow</td>
<td>270</td>
<td>C 57.96 (4.04) (3.65) (4.51) (4.68)</td>
<td>(766)</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOBr})_2$</td>
<td>Orange</td>
<td>290</td>
<td>C 56.32 (4.4) (4.01) (3.86) (4.01)</td>
<td>(698)</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOBr})_2$</td>
<td>Red</td>
<td>320</td>
<td>C 54.34 (3.35) (14.76) (5.32) (2.75)</td>
<td>(598)</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{C}_3\text{H}_7\text{NOBr})_2$</td>
<td>Orange</td>
<td>340</td>
<td>(49.79) (3.05) (16.35) (5.89)</td>
<td>(305)</td>
</tr>
</tbody>
</table>

d = Decomposition

**NOTES**

IR spectra were recorded in the form of KBr pellets in the range 4000-200 cm\(^{-1}\) on a Perkin-Elmer 577 grating spectrophotometer. PMR spectra were recorded on a Perkin-Elmer RB-12 spectrometer in DMSO-$d_6$ at room temperature using TMS as an internal reference. Molar conductance of the complexes were determined in dry DMF using a Systronics conductivity bridge Model 305. Molecular weight determinations were carried out cryoscopically.

The reactions of trimethylsilyl acetate, aluminium isopropoxide and monobasic bidentate Schiff base ($\text{NOH}$) in the molar ratio of 1:1:2 may be represented by the following equations:

$$(\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{OPr})_3 + 2\text{NOH} \rightarrow (\text{CH}_3)_3\text{Si} - \text{O} - \text{Al}(\text{ON})_2 + 2\text{C}_3\text{H}_7\text{OH} \rightarrow \ldots (2)$$

The resulting complexes are coloured solids with sharp melting points and these are soluble in benzene, chloroform, DMF and DMSO. The complexes are nonelectrolytes in DMF and DMSO and are monomeric in nature. The binuclear Schiff base complexes of arsenic and aluminium were found to be insoluble in most of the organic solvents; therefore, their molar conductances and molecular weights could not be determined. These compounds decompose on heating. Thus a polymeric structure can be tentatively proposed for such type of complexes as has been reported earlier in the literature.\(^7\)\(^8\)\(^9\).

The broad absorption bands in the region, 3300-2850 cm\(^{-1}\) in the infrared spectra of the ligands have been assigned to the hydrogen bonded $\text{OH}$. These bands disappear in the binuclear complexes, showing coordination through phenolic oxygen after deprotonation. A strong band observed at $\sim 1600 \pm 10$ cm\(^{-1}\) in the spectra of ligands is characteristic of the azomethine ($\geq C = N$) group. This gets shifted to the higher wave number side in the corresponding complexes and is observed at $\sim 1610 \pm 10$ cm\(^{-1}\).
indicating coordination of azomethine nitrogen to the aluminium atom. In the phenylarsenic acid, vOH occurs in the region 2750-2250 cm⁻¹ whereas in the spectra of complexes, these bands are absent, indicating the chelation of both the oxygens of AS-O group with aluminium. A band of medium intensity at ~1250 cm⁻¹ in silicon-aluminium complexes may be attributed to (CH₃)₂Si group. Further, several new bands of strong to medium intensity occurring in the region 750-400 cm⁻¹ in the spectra of complexes may be attributed to the different vibrational modes of Al−O and Al−N bonds.

The proton magnetic resonance spectra of N-p-chlorophenylsalicylaldimine and its binuclear silicon-aluminium complex have been recorded in DMSO-d₆ and these further substantiate the proposed mode of coordination of the ligands. The ligand spectrum shows the signal due to OH proton at δ 12.85 ppm; on complexation this signal disappears indicating the deprotonation of the ligand and the chelation of oxygen to aluminium atom. A sharp singlet due to the azomethine proton (≥C=N) at δ 8.2 ppm in the ligand gets shifted downfield (δ 8.40 ppm) in the corresponding complex showing the coordination of azomethine nitrogen to the aluminium atom. A multiplet, due to phenyl protons is observed at δ 6.80-7.70 ppm in the spectra of both the ligand and its corresponding complex.

On the basis of above studies, it can be concluded that in the Si−Al binuclear complexes these atoms are in tetra and penta coordinated environments respectively as shown in structure I. As −Al complexes contain Al atom in 4-coordinated environment.

The toxicity of four of the representative compounds, (CH₃)₂Si−O−Al (C₁₃H₉NOF-p)₂ (A), (CH₃)₂Si−O−Al (C₁₃H₉NOCI-p)₂ (B), (CH₃)₂Si−O−Al (C₁₃H₉NOBr-p)₂ (C) and (CH₃)₂Si−O−Al (C₁₃H₉NNO₂-p)₂ (D) was studied against Aedes aegypti 3rd instar larvae. The compounds were dissolved in DMSO to obtain 0.12, 0.25 and 0.5% solutions of the compounds. 0.5 ml of each of the solution was mixed with 100 ml of water and in each solution ten 3rd instar larvae of Aedes aegypti were put from the inbred colony. Replicates and controls were also run simultaneously and the mortality was observed after 24 hr. Similarly, the ligands were also tested for their biological activity.

No mortality was observed in ligands treated against larvae instar. In the case of complexes no mortality was observed with 0.12% concentration but mortality was 100% with 0.5% solution. In the case of 0.25% solutions, the mortality data were 100%, 40%, 10% and 100% for compounds (A), (B), (C) and (D) respectively.

One of the authors (VC) is thankful to the CSIR, New Delhi for financial support.

References
10 Busch D H & Bailar J C (Jr), J Am chem Soc. 78 (1956) 1137.