

Some Chelates of Al(III) & Their Reactions*

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Bidentate chelating ligands, viz. salicylaldehyde, acetylacetone, benzoylacetone, benzoylphenyl hydroxylamine and 8-hydroxyquinoline react with aluminium alkoxides (ethoxide, isopropoxide and *t*-butoxide) forming chelated aluminium compounds without undergoing any molecular rearrangement. These chelated aluminium compounds react with thionyl/sulphuryl chloride, to give bis-chelated chloro-aluminium compounds and form addition complexes with $TiCl_4$, $SnCl_4$ and $AlCl_3$.

MUCH work has been reported on organic derivatives and chelates of aluminium¹⁻⁴. Addition complexes of organo-aluminium compounds with nitrogen bases and of aluminium alkoxides with organotin compounds have also been reported^{5,6}. This paper deals with the reaction of aluminium alkoxides with bidentate ligands, viz. salicylaldehyde, acetylacetone, benzoylacetone, acetoacetanilide, benzoylphenyl hydroxylamine and 8-hydroxyquinoline. The chelated aluminium compounds thus obtained form addition compounds with a number of Lewis acids like $TiCl_4$, $SnCl_4$ and $AlCl_3$.

Results and Discussion

Aluminium alkoxides (ethoxide, isopropoxide and *t*-butoxide) were found to react almost quantitatively with salicylaldehyde giving *tris*-salicylaldehyde aluminium. The same compound has also been obtained by reacting anhydrous aluminium chloride with sodio salicylaldehyde. The products obtained from different aluminium alkoxides and aluminium chloride were identical with respect to their colour, m.p., analysis and IR spectra. Acetylacetone, benzoylacetone, acetoacetanilide, *N*-benzoyl-*N*-phenylhydroxylamine and 8-hydroxyquinoline also formed similar *tris*-chelates with aluminium alkoxides (Table 1). These aluminium chelates were yellow of solids, sparingly soluble in benzene and many of them melted with decomposition above 200°. Attempts to make chelated chloro-aluminium compounds by the disproportionation reaction between the *tris*-chelate and anhydrous aluminium chloride did not give the expected products. Chlorination of the *tris*-chelate using acetyl chloride, benzoyl chloride or chlorine gas also failed to give the chloro-chelates. *Bis*-chelated chloro-aluminium compounds were however obtained from the *tris*-chelates by the action of thionyl or sulphuryl chloride; a mixture of the two acid chlorides gave better results (Table 1). The chlorination process did not affect rest of the molecule or the coordination as indicated by their IR spectra.

Another interesting property of aluminium chelates was the formation of addition compounds with Lewis acids, viz. $TiCl_4$, $SnCl_4$ and $AlCl_3$. The aluminium chelates formed with titanium tetrachloride 1:1.5 adducts while with stannic chloride and aluminium chloride 1:1 adducts were obtained. (Table 1). These compounds were non-melting solids, sparingly soluble in common solvents. They decomposed into a mixture of compounds when reacted with a further amount of the chelating ligand. The adduct formation, however, did not affect the original coordination of the ligands around aluminium atom as seen from their IR spectra. Because of their insolubility, properties such as molecular weight, conductivity, etc., could not be determined. Therefore, the exact nature of these complexes could not be ascertained.

In the case of salicylaldehyde derivatives, the $C=O$ absorption band found at 1650 cm^{-1} in the free ligand shifts to 1630 and 1600 cm^{-1} respectively in the *tris*-chelate and the chloro-compound. In the addition complexes of *tris*-salicylaldehyde aluminium with $TiCl_4$, $SnCl_4$ and $AlCl_3$ the $\nu C=O$ occurs between 1600 and 1615 cm^{-1} indicating strong chelation. As expected, the coordination of ligand to metal is found to be stronger in the chloro-aluminium chelates than in the *tris*-chelates. In acetylacetone compounds, the doublet at 1710 \pm 15 cm^{-1} present in the unchelated keto-form of the pure ligand, disappeared completely indicating strong coordination. In 8-hydroxyquinolino complexes, the single peak at 1587 cm^{-1} in the ligand is split into two sharp peaks, probably as a result of augmentation of the $\nu C=N$ which was previously hidden on the ring $C=C$ vibrations. The $\nu O-H$ found in benzoylphenyl hydroxylamine at 3105 cm^{-1} is completely absent in the complexes. The $\nu C=O$ at 1630 cm^{-1} found in benzoylphenyl hydroxylamine appear at 1600 cm^{-1} in the *tris*-chelate, chloro-chelate and the complexes with $TiCl_4$, $SnCl_4$ and $AlCl_3$ which may as well be superimposed on one of the $C=C$ vibrations. The $\nu N-O$ which appears in the free ligand at 920 cm^{-1} shifts towards 935 cm^{-1} upon complexing. These effects are nearly the same for all the three types of derivatives of this ligand.

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TABLE 1 — CHELATED ALUMINIUM COMPOUNDS

Sl. No.	Reactants		Molar ratio (A: B)	Product	Colour
	A	B			
1	AlCl ₃	Salicylaldehyde sodium	1: 4	Al(C ₇ H ₅ O ₂) ₃	Deep yellow
2	Al(OPri) ₃	Salicylaldehyde	do	Al(C ₇ H ₅ O ₂) ₃	do
3	do	Acetylacetone	do	Al(C ₆ H ₇ O ₂) ₃	Light yellow
4	do	Benzoyl acetone	do	Al(C ₁₀ H ₉ O ₂) ₃	do
5	do	Acetoacetanilide	do	Al(C ₁₀ H ₁₀ O ₂ N) ₃	do
6	do	Benzoylphenyl hydroxylamine	do	Al(C ₁₃ H ₁₀ O ₂ N) ₃	White
7	do	8-Hydroxyquinoline	do	Al(C ₉ H ₆ ON) ₃	Yellow
8	Al (Sal) ₃	SOCl ₂ + SO ₂ Cl ₂	Excess of B	(C ₇ H ₅ O ₂) ₂ AlCl	Deep yellow
9	Al (Bpha) ₃	do	do	(C ₁₃ H ₁₀ O ₂ N) ₂ AlCl	White
10	Al (8-Hq) ₃	do	do	(C ₉ H ₆ ON) ₂ AlCl	Yellow
11	Al (Sal) ₃	TiCl ₄	1: 2	Al(C ₇ H ₅ O ₂) ₃ .1.5TiCl ₄	Red
12	do	SnCl ₄	1: 1.5	Al(C ₇ H ₅ O ₂) ₃ .SnCl ₄	Yellow
13	do	AlCl ₃	do	Al(C ₇ H ₅ O ₂) ₃ .AlCl ₃	do
14	Al (Acac) ₃	TiCl ₄	1: 2	Al(C ₅ H ₇ O ₂) ₃ .1.5TiCl ₄	Red
15	do	SnCl ₄	1: 1.5	Al(C ₅ H ₇ O ₂) ₃ .SnCl ₄	Yellow
16	do	AlCl ₃	do	Al(C ₅ H ₇ O ₂) ₃ .AlCl ₃	do
17	Al (Bpha) ₃	TiCl ₄	1: 2	Al(C ₁₃ H ₁₀ O ₂ N) ₃ .1.5TiCl ₄	Red
18	do	SnCl ₄	1: 1.5	Al(C ₁₃ H ₁₀ O ₂ N) ₃ .SnCl ₄	Yellow
19	do	AlCl ₃	do	Al(C ₁₃ H ₁₀ O ₂ N) ₃ .AlCl ₃	do
20	Al (8-Hq) ₃	TiCl ₄	1: 2	Al(C ₉ H ₆ ON) ₃ .1.5TiCl ₄	Red
21	do	SnCl ₄	1: 1.5	Al(C ₉ H ₆ ON) ₃ .SnCl ₄	Yellow
22	do	AlCl ₃	do	Al(C ₉ H ₆ ON) ₃ .AlCl ₃	do

SalH = salicylaldehyde; BphaH = benzoylphenyl hydroxylamine; 8-HqH = 8-hydroxyquinoline; and AcacH = acetylacetone.

Experimental Procedure

All the reactions were carried out using pure, thoroughly dried solvents and reagents under N₂ atmosphere. Extensive care was taken to use dry nitrogen and to keep away moisture. All filtrations were done in apparatus fitted with sintered glass using a positive pressure of nitrogen.

Preparation of tris-salicylaldehyde aluminium — Salicylaldehyde (4.27 g; 0.35 mole) was added to aluminium isopropoxide (2.04 g; 0.01 mole) in warm benzene (100 ml) and the mixture refluxed for 1 hr. A yellow precipitate obtained was filtered, washed with cold benzene and then with pet. ether (40-60°) and dried *in vacuo* at 60° as deep yellow powder, m.p. 202-4°; yield 3.51 g (90% of theory). [Found: Al, 6.90; C, 64.12; H, 3.91; Al(C₇H₅O₂)₃ requires Al, 6.92; C, 64.62; H, 3.85%] sparingly soluble in benzene, hexane and carbon tetrachloride, but soluble in alcohol.

Identical products were obtained by the reaction of aluminium ethoxide and *t*-butoxide with salicylaldehyde. Tris-chelates of aluminium with acetylacetone, benzoylacetone, acetoacetanilide, benzoyl phenyl hydroxylamine and 8-hydroxyquinoline were similarly prepared from aluminium isopropoxide and the chelating ligand.

Preparation of bis-salicylaldehyde chloro-aluminium — Tris-salicylaldehyde aluminium (3.9 g; 0.01 mole) and a mixture of freshly distilled thionyl and sulphuryl chlorides (5 ml each; excess) were mixed and kept at 25° for 2 hr. Petroleum ether (50 ml) was then added and the precipitate obtained filtered, washed with pet. ether and dried at 60° *in vacuo* as deep yellow non-melting solid; yield 2 g (65% of theory) (Found: Al, 8.91; Cl, 11.75; C, 55.03; H, 3.40. Al(C₇H₅O₂)₂Cl requires Al, 8.87; Cl, 11.64;

C, 55.17; H, 3.38%). It is sparingly soluble in benzene, hexane and carbon tetrachloride. Other tris-chelates of aluminium behaved similarly.

Reaction with titanium tetrachloride — Tris-salicylaldehyde aluminium (3.9 g; 0.01 mole) and TiCl₄ (2.2 ml; 0.02 mole) were mixed in benzene (50 ml) and refluxed for 2 hr. A brown solid formed was filtered, washed with benzene and dried *in vacuo* at 60°; yield 6 g (85% of theory) (Found: mixed oxide, 25.48; Cl, 31.15; C, 38.01; H, 2.52. Al(C₇H₅O₂)₃.1.5 TiCl₄ requires mixed oxide, 25.33; Cl, 31.56; C, 37.34; H, 2.22%). Other aluminium chelates gave similar addition products with titanium tetrachloride.

Reaction with stannic chloride — Tris-salicylaldehyde aluminium (3.9 g; 0.01 mole) and stannic chloride (1.7 ml; 0.015 mole) were mixed in benzene (50 ml) and refluxed for 1 hr. A brownish yellow solid separated was filtered, washed with benzene and dried *in vacuo* at 60°, yield 6 g (92% of theory) [Found: mixed oxide, 31.25; Cl, 22.14; C, 39.07; H, 2.76%. Al(C₇H₅O₂)₃.SnCl₄ requires mixed oxide, 31.03; Cl, 21.81; C, 38.71; H, 2.30%]. Other aluminium chelates behaved similarly.

Addition products of aluminium trichloride were prepared similarly using a solution of it in benzene.

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