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Synthesis and Characterization of Aluminium(III) Complexes with Schiff Bases Obtained from Salicylaldehyde Derivatives and Alkylamines

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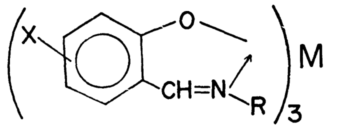
Aluminium(III) complexes with Schiff bases (abbreviated as X–sal–R) obtained from salicylaldehyde derivatives and amines (RNH_2) have been synthesized by a method starting from aluminium(III) isopropoxide. Complexes of the type Al(X–sal–*n*-alkyl)$_3$ have been isolated, but any attempt to obtain complexes of the types Al(X–sal–*i*-C_3H_7)$_3$ and Al(X–sal–aryl)$_3$ has not been successful. The tris-complexes obtained show similar electronic absorption spectra, regardless of R. Proton magnetic resonance spectra indicate that the aluminium(III) complexes may have a *fac*-configuration.

Tris(*N*-alkyl- or *N*-aryl-salicylideneaminato)-complexes of tervalent 3d transition elements, such as vanadium(III),[1)] chromium(III),[2,3)] cobalt(III),[4,5)] and iron(III),[6)] were studied previously. It seems interesting to study the corresponding complexes (abbreviated as M(X–sal–R)$_3$, I) of other tervalent metal ions having no d-electrons and compare the results with those previously reported for the complexes of the 3d ions. Along that line, yttrium(III) complexes with these ligands were examined in a previous paper.[7)]



(I)

As extension of the previous studies, aluminium(III) was taken up as the central metal ion in the present work. No aluminium(III) complexes with these Schiff bases have ever been isolated.

Experimental

Materials. *Tris(*N *- alkylsalicylideneaminato) aluminium(III)*: To a suspension of aluminium(III) isopropoxide (0.01 mol) in 1-butanol or 2-propanol was added a Schiff base (0.033 mol), and the mixture was heated on an oil-bath at about 90 °C for 5 h. The solution was filtered and allowed to stand in a refrigerator overnight. A yellow, crystalline precipitate was collected by filtration and recrystallized from methanol or ethanol to yield pale-yellow crystals of Al(X–sal–R)$_3$. Difficulty was sometimes encountered in the recrystallization, since the complexes often undergo decomposition in the solution. The compounds are soluble in chloroform, methanol and ethanol, but insoluble in benzene. They undergo decomposition in water very readily. Analytical data of the complexes are shown in Table 1.

Measurements. Electronic absorption spectra were measured on a Shimadzu MPS-50L spectrophotometer. Infrared spectra were obtained from Nujol mulls using a Hitachi EPI-S2 infrared spectrophotometer.

Proton magnetic resonance spectra were recorded on a JEOL Model C-NMR spectrometer using tetramethylsilane as an internal reference. Measurements at a temperature lower than −4 °C were not possible because of too low solubility.

Since the complexes underwent decomposition in solution, the spectral measurements were carried out as quickly as possible. Moreover, measurements were repeated after the spectra had once been determined, to see if any spectral change due to decomposition during the measurements occurred or not.

Results and Discussion

The reaction in ethylene glycol at a temperature higher than 100 °C was reported to be suitable in synthesizing the chromium(III) tris-complexes.[3,8)] This method was employed successfully in the preparation of the tris(*N*-alkylsalicylideneaminato)iron(III) complexes, but did not yield the corresponding aluminium(III) complexes. The reaction of aluminium(III) isopropoxide with a Schiff base in a suitable anhydrous solvent, such as 1-butanol or 2-propanol, proved to be appropriate for synthesizing tris(*N*-alkylsalicylideneaminato)aluminium(III). This method may be considered to be applicable to preparation of the tris-complexes of other metal ions in high oxidation states.

It was not possible to synthesize complexes of the type Al(X–sal–*t*-C_4H_9)$_3$. The complexes of this type have never been reported for 3d elements, owing possibly to steric hindrance arising from the bulky *t*-butyl groups. Any attempt to isolate complexes of the type M(X–sal–*i*-C_3H_7)$_3$ has so far been unsuccessful

TABLE 1. ANALYTICAL DATA OF THE Al(X–sal–R)$_3$ TYPE COMPLEXES

X	R	Calcd, %			Found, %			Mp °C	ν (C=N)	ν (C–O)
		C	H	N	C	H	N			
H	CH_3	66.66	5.59	9.72	66.77	5.61	9.58	205	1620	1540
H	C_2H_5	68.77	6.41	8.91	68.58	6.55	8.72	155	1620	1540
H	*n*-C_3H_7	70.15	7.07	8.18	69.65	6.96	8.04	187	1620	1540
5-Br	CH_3[a)]	41.94	3.81	6.11	42.11	3.42	5.92	238	1620	1535
3-CH_3O	CH_3[a)]	60.33	6.00	7.82	60.29	5.68	7.58	181	1625	1540

ν: cm^{-1}. a) With 1 H_2O.

for M=aluminium(III) and iron(III),[9] whereas the corresponding chromium(III),[3] manganese(III),[9] and cobalt(III)[10] complexes were obtained previously. The failure in isolating the aluminium(III) complexes of this type may be due mainly to the steric factor, since the ionic radius of Al^{3+} (0.57 Å) is much smaller than the other three ions. On the contrary, the radius of Fe^{3+}(0.67 Å) is slightly larger than those of Cr^{3+} (0.65 Å), Mn^{3+}(0.66 Å) and Co^{3+}(0.65 Å). Consequently, the reluctance of iron(III) to form the Fe(X-sal-*i*-C_3H_7)$_3$ type complexes may be due not to the steric factor alone, but to weaker iron(III)-to-ligand bond, as compared with that for chromium(III), manganese(III), and cobalt(III).

It may also be interesting to note that any aluminium(III) complexes with the neutral *N*-alkyl- or *N*-arylsalicylideneamines have not been isolated in the present work, in contrast to the yttrium(III) complexes.[7]

Main electronic absorption bands of the complexes Al(X-sal-alkyl)$_3$ are shown in Table 2. It is found that the electronic absorption bands due to internal transitions within the ligands are shifted very slightly toward higher frequencies on formation of the aluminium(III) complex. This slight band shift seems to show the weak aluminium(III)-to-ligand bond.

TABLE 2. ELECTRONIC ABSORPTION BANDS OF Al(X-sal-R)$_3$ IN CHLOROFORM

Compound	ν(log ε)
Al(H-sal-CH_3)$_3$	24.6 (2.74), 31.8 (4.10)
Al(H-sal-C_2H_5)$_3$	24.6 (2.71), 31.8 (4.10)
Al(H-sal-*n*-C_3H_7)$_3$	24.5 (2.74), 31.8 (4.10)
(H-sal-CH_3)H[a]	24.5 (2.20), 31.6 (3.58)

ν: 10^3 cm^{-1}. a) Free Schiff base.

The complexes show an infrared ν(C=N) band at about 1620 cm^{-1}, indicating that the ligands are coordinated as bidentates in their deprotonated form with the metal ion. Previous studies have shown that the bidentate *N*-substituted salicylideneaminate anion bound with a metal ion exhibits the corresponding band at about 1610—1620 cm^{-1}, whereas the neutral salicylideneamines coordinated to a metal ion show the corresponding band at about 1640 cm^{-1}.[11]

The *fac* and *mer* isomers are possible in tris(chelate)-metal complexes, if the bidentate ligands are not symmetric. Pairs of such isomers have indeed been obtained with ligands, such as amino acids[12] and β-diketonates.[13] For the complexes of the type M-(X-sal-R)$_3$, however, only the *mer* form has so far been isolated, and the *mer* form was found to be an exclusively predominant species in their solutions as well.[14] This result was ascribed to the steric disposition of the nitrogen substituents on one hand and to the electrostasic repulsion among the three oxygen atoms in the *fac* form on the other.

Main PMR spectral data of the complexes Al(X-sal-CH_3)$_3$ in chloroform-*d* are shown in Table 3. The N-CH_3 resonance appears as a sharp singlet at about 6.78 and 6.84 τ for X=H and 5-Br, respectively, at 50, 20, and −4 °C. It should be noted that the N-CH_3 resonance at 50 °C is as sharp as at −4 °C. The *mer* isomer, which has a lower symmetry than the *fac* isomer, would be unambiguously identified by three equally intense signals for the N-CH_3 groups, as was found to be the case with the corresponding cobalt(III) and vanadium(III) complexes.[1,14,15] Hence, the spectra of Al(H-sal-CH_3)$_3$ and Al(5-Br-sal-CH_3)$_3$ are found to be consistent with the *fac* form having three-fold symmetry, although their low solubility did not allow PMR spectral measurements at lower temperatures. A recent X-ray structural study[16] has revealed that Al(H-sal-CH_3)$_3$ consists of six-coordinate aluminium(III) complexes having a *fac* configuration. These aluminium(III) complexes seem to be the first examples of tris(*N*-substituted salicylideneaminato)metal(III) complexes having a *fac* configuration to be isolated.

TABLE 3. CHEMICAL SHIFTS, τ(N-CH_3), OF Al(X-sal-CH_3)$_3$ AT DIFFERENT TEMPERATURES

Compound	−4 °C	20 °C	50 °C
Al(H-sal-CH_3)$_3$	6.78	6.78	6.78
Al(5-Br-sal-CH_3)$_3$	6.84	6.84	6.84
(H-sal-CH_3)H[a]	—	6.87	—

a) Free Schiff base.

It is not clarified at the moment why the *fac* form of these aluminium(III) complexes is obtained much more readily than the *mer* form, in contrast to many 3d metal complexes. However, it may be true that the present finding would give rise to renewed controversies over the stability of the *mer* and *fac* isomers of the tris(bidentate)-metal complexes.

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