Synthesis & Characterization of Aluminium(III) Complexes of Amidoximes & N-Substituted Arylbenzamidoximes

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The synthesis and spectral characterization of a number of new crystallizable amidoximates and N-arylbenzamidoximates of aluminium(III) (I to IV) are reported. Ebulloscopic molecular weight measurements of these complexes show that derivatives of N-arylbenzamidoximes are less associated (with average molecular complexity of 1.9-1.5) as compared to their simple amidoxime analogues (with average molecular complexity of the order 3-4).

RECENTLY derivatives of amidoximes, \([RNH_2C=NOH]\) with some non-transition elements (like, B, Si and Sn) have been prepared and characterised by Gupta and Goel. However, aluminium(III) derivatives of amidoximes and N-arylbenzamidoximes do not appear to have been prepared. In this paper we report the synthesis and characterization of some Al(III) complexes with these ligands.

The reactions of aluminium isopropoxide with amidoximes \(R(NH_2)C=NOH\) and N-arylbenzamidoximes \(Ph(ArN)C=NOH\), in equimolar ratios in benzene at ambient temperature (~30°C) yield the products of the type (I) in around 90% yield. The characterization data of these products are given in Table 1 (Eq. 1). However, under refluxing conditions in benzene, the products of the type (II) are obtained. These products are listed in Table 2 (Eq. 2).

At ambient temperature, only hydroxy group of amidoxime appears to be reactive (Eq. 1) resulting in O-substituted products (I). Under refluxing conditions, the \(-NH_2\) group of the ligand also takes part in the replacement reaction and leads to cyclic products (II).

Products of the type (III) are obtained when the reaction of aluminium isopropoxide with amidoximes is carried out in 2 : 3 molar ratios in refluxing benzene. Under these conditions, all the isopropoxy groups can be replaced by ligand moieties (Eq. 3). The characterization data of the products are given in Table 3.
Molecular weight measurements (ebullioscopically in benzene) of simple amidoximes of the type (IVa-d) and (IIa-d) exhibit oligomeric behaviour in boiling benzene with average molecular complexity of the order of 3-4. Derivatives of the type (I) and (III) are insoluble in most of the common organic solvents suggesting their polymeric nature and complex structures for these.

The effect of ramification on increasing the volatility and lowering the degree of molecular association of metal derivatives has been well established. The derivatives of N-arylbenzamidoximes are much less associated compared to those of the corresponding simple benzamidoximes. Thus, the monoisopropoxide N-arylbenzamidoxime derivatives of aluminium exhibit an average molecular complexity of the order of 1.5, compared to the observed tri/tetra-meric nature of the analogues with simple unsubstituted amidoximes. Again the 2:3 products (III e-f) and tert-butoxy derivatives (IV e-f) of N-arylbenzamidoximes show monomeric behaviour in refluxing benzene.

IR spectral data of Al(III) derivatives — A strong band at 3650-3570 cm⁻¹ due to ν (OH) of parent amidoximes disappears in newly synthesized derivatives, indicating chelation of aluminium atom to oxygen. This is further supported by the appearance of a number of new bands in the region 590–730, which are assignable to ν (Al-O) vibrations. The O-substituted derivatives(I) show the presence of a doublet due to ν (NH) in the regions 3300–3320 and 3400–3430, confirming O-substitution. However, an appreciable lowering in the position of this doublet (Δ ν 60 cm⁻¹) in comparison to parent ligands reveal the possibility of internal coordination via amino nitrogen also. In the cyclic derivatives of simple amidoximes, this doublet gets replaced by a broad band at 3300–3320 cm⁻¹ in oxime derivatives of aluminium. The position of ν (Al-N) varies largely and it has been reported at different positions by various authors. On the basis of existing data, two new bands appearing in the region 435–470 cm⁻¹ in Al(III) complexes of amidoximes may be assigned to ν(Al-N). A band of medium intensity observed in the region 1620–1675 cm⁻¹ in free ligand and are shifted to lower region (Δ ν 30–40 cm⁻¹) in the complexes, indicating coordination via azomethine nitrogen also. Similar lowerings in ν (C = N) bands have been reported by Mehrotra et al. in oxime derivatives of aluminium.

It has not been possible to observe any complexation effect on ν (CO) frequency in the region 1175–1135. The position of ν (Al-N) varies largely and it has been reported at different positions by various authors. On the basis of existing data, two new bands appearing in the region 435–470 cm⁻¹ in Al(III) complexes of amidoximes may be assigned to ν(Al-N). A band of medium intensity observed in all compounds in the region 920-940 cm⁻¹ appears to arise due to ν (N-O).
PMR spectral data† of monoalkoxy N-arylbenzamidoximates(II) — In general, the absence of signals due to —OH and NH protons in these complexes indicate deprotonation from both these sites or bonding of aluminium to oxygen as well as nitrogen atoms. Besides the typical aromatic (phenyl) protons which appear as a multiplet in the region 7.80 to 6.80, the derivatives of N-m-tolyl benzamidoxime exhibit a sharp three-proton singlet at 2.5 due to methyl protons. The isopropoxy and t-butoxy groups show typical signals in the expected region of the spectrum around 1.5 and 1.38 respectively.

The isopropoxy derivatives of the type(II) having molecular complexity between monomeric and dimeric species (with average molecular complexity of the order 1.5) are likely to exist as an equilibrium mixture of low species (A and B).

On the basis of these suggested structures (A and B), one could expect separate signals due to terminal and bridging isopropoxy groups attached to aluminium. An interesting feature in the PMR spectra (run at room temperature) of these compounds is the appearance of only one kind of isopropoxy protons (8 1.5) inspite of the expected two signals. The existence of only one kind of alkoxy proton signals can be attributed to the fact that there is a fast exchange between monomeric and dimeric species which cannot be recorded at the PMR time scale.

Experimental Procedure

All experiments were conducted in hermetically sealed apparatus. Aluminium isopropoxide was distilled before use (b.p., 105°/5 mm). Solvents (benzene, n-hexane) were dried by standard methods. Amidoximes† and N-arylbenzamidoxime14,15 were prepared by the reported methods.

Reaction between aluminium isopropoxide and amidoximes/N-arylbenzamidoximes in 1:1 molar ratio in benzene at 30-35° — Formation of products (I) — Aluminium isopropoxide in benzene (~50 ml) was heated under reflux for 6-14 hr with amidoximes or N-arylbenzamidoximes in molar ratios 1:1 and 2:3. Isopropanol was separated azeotropically and analyzed. After removal of benzene under reduced pressure (35-40°/3-4 mm), the compounds of the type (II) and (III) respectively were obtained. Products (II) were recrystallized from benzene or benzene/n-hexane mixture (Table 2), while the products (III) were separated as white insoluble solids (Table 3).

Reactions between (II) and excess of t-butanol in refluxing benzene — Formation of products of type (IV) — Compounds of the type (II) were heated under reflux in excess t-butanol for 12-14 hr. Isopropanol was fractionated out azeotropically and analyzed. After removal of solvent and excess t-butanol and drying the residue at 35° for 12-14 hr, products of the type IV were obtained as white solids. The analytical data are summarized in Table 4.

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References