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Heterocarboxylates of Al(III)

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Heterocarboxylates of Al(III) were prepared by the reactions of aluminium isopropoxide with 2-furoic and 2-thenoic acid in presence of benzene. The following three types of new compounds have been isolated: $Al(OPr^i)_2(X)$, $Al(OPr^i)(X)_2$ and $Al(X)_3$ (where X is the anion of 2-furoic or 2-thenoic acid). Only monosubstituted derivatives were soluble in benzene. The IR spectral studies of these derivatives have been made.

Introduction

A considerable amount of work has been carried out on the carboxylic acid [1], hydroxy carboxylic acid [2] and thio carboxylic acid [3–4] derivatives of Al(III). An extensive search though the literature reveals that no study has been made on the heterocarboxylate derivatives of aluminium. During the course of the present investigation a systematic study of the reactions of aluminium isopropoxide with 2-furoic (FH) and 2-thenoic acid (TH) in different stoichiometric ratios have been carried out in benzene medium.

Experimental

Aluminium isopropoxide (Riedel) was distilled under reduced pressure (108 °C/2 mm) and analysed before use. Benzene (BDH) was dried over sodium wire followed by azeotropic fractionation in presence of ethanol. 2-Furoic acid and 2-thenoic acid (Riedel) were dried on pump at room temperature. All the reactions were carried out under anhydrous conditions.

Aluminium was analysed as aluminium oxinate. Isopropanol was estimated by oxidation with normal dichromate solution in 12.5% sulphuric acid [5]. Infrared spectra were recorded on a Perkin-Elmer 180 Spectrophotometer using KBr pellets.

Reaction of Aluminium Isopropoxide with 2-Furoic Acid (1:1 Molar Ratio)

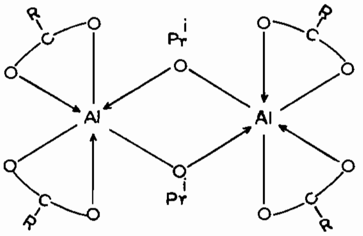
To aluminium isopropoxide (0.86 g) in benzene was added the calculated quantity of 2-furoic acid (0.47 g). The contents were refluxed and the liberated isopropanol was fractionated out azeotropically with benzene. Progress of the reaction was ascertained by estimating the amount of isopropanol in the azeotrope. A white microcrystalline solid, soluble in benzene, was obtained after distilling of excess solvent under reduced pressure (yield 1.05 g).

For brevity the reactions of aluminium isopropoxide with 2-furoic and 2-thenoic acid are summarised in Table I.

Results and Discussion

A systematic study of reactions of $Al(OPr^i)_3$ with 2-furoic and 2-thenoic acid in different stoichiometric ratios in refluxing benzene yielded products of the type $Al(OPr^i)_2(X)$, $Al(OPr^i)(X)_2$ and $Al(X)_3$ (where X is the anion of acid), which are white to cream-colored solids. Monosubstituted derivatives are soluble in benzene while di- and trisubstituted derivatives are insoluble in benzene. All these derivatives are soluble in dimethylformamide and pyridine. All the FH derivatives do not melt but the TH derivatives show sharp melting points.

Aluminium is tetracoordinated in monosubstituted derivatives, considering it monomeric in benzene. The structure of $Al(OPr^i)_2(X)$ is probably similar to those of $Al(OPr^i)_2(acac)$ (acac = anion derived from acetyl acetone) [6]. The probable dimeric structure of the disubstituted product $Al(OPr^i)(X)_2$ having coordination number six may be indicated as



(I)

R=FURAN OR THIOPHENE RING

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TABLE I. Reactions of $Al(OPr^i)_3$ with 2-Furoic (FH) and 2-Thenoic Acid (TH).

$Al(OPr^i)_3$ (g)	Ligand (g)	Molar Ratio	Reflux Time (hr)	Product and Characteristics (Yield g)	Isopropanol in Azeotrope (g) Found (calcd)	Metal % Found (calcd)	Melting Point
0.86	(FH) 0.47	1:1	6	$Al(OPr^i)_2(F)$ (1.05) White microcrystalline solid	0.248 (0.253)	10.4 (10.5)	Does not melt up to 250 °C
0.71	(FH) 0.77	1:2	8	$Al(OPr^i)(F)_2$ (1.06) White solid	0.408 (0.418)	8.6 (8.7)	Decomposes at 220 °C
1.02	(FH) 1.68	1:3	10	$Al(F)_3$ (1.80) White solid	0.901 (0.904)	7.5 (7.4)	Decomposes at 235 °C
0.77	(TH) 0.48	1:1	6	$Al(OPr^i)_2(T)$ (1.02) Cream colored microcrystalline solid	0.217 (0.229)	9.8 (9.9)	167–170 °C
0.84	(TH) 1.06	1:2	8	$Al(OPr^i)(T)_2$ (1.41) White solid	0.487 (0.499)	7.8 (7.9)	271–272 °C
1.29	(TH) 2.43	1:3	10	$Al(T)_3$ (2.56) White solid	1.093 (1.141)	6.4 (6.6)	Softens at 152 °C and decomposes at 220 °C

Unfortunately the dimeric nature of the complex (1) could not be ascertained by the molecular weight determination because of its limited solubility. However, Tandon and Prasad have also reported molecular association ~2 for monoisopropoxy aluminium Schiff base derivatives [7]. Stable coordination number six is given to the central aluminium atom of the trisubstituted derivatives, considering the bidentate carboxylate group symmetrically bonded which is further supported by infrared spectra of these derivatives.

Infrared Spectra

The $\nu C{=}O$ frequencies in the 2-furoic (FH) and 2-thenoic acid (TH) occur as strong absorptions at 1685 and 1675 cm^{-1} respectively. The bands at 1420 and 1300 cm^{-1} for FH and at 1428 and 1275 cm^{-1} for TH are probably due to the C–O stretching vibrations which are coupled with the in-plane bending vibration of the OH group ($\nu C{-}O + \delta OH$). In all these compounds all the above bands are absent. The strong $\nu C{=}O$ band in the free FH and TH splits into asymmetric and symmetric COO^- vibrations in these derivatives. In the FH derivatives, strong absorption at 1600–1570 cm^{-1} can be assigned to asymmetric COO^- stretching and bands at 1435 cm^{-1} arising from the symmetric COO^- stretching vibration while in TH derivatives strong bands at 1575–1525 cm^{-1} arise from asymmetric COO^- stretching and bands at 1440–1435 cm^{-1} arise from the symmetric COO^- stretching vibration.

The separation $\Delta\nu(COO^-)$ between the ν_{asy} COO^- and ν_{sym} COO^- frequency is generally taken as an indication of the nature of coordination of the carboxylate ion to metal [8]. The bidentate coordination of the carboxylate group to the metal results in a lowering of both the νCOO^- frequencies due to the drainage of electron density from the carboxylate group to the metal. At the same time, the O–C–O angle is expected to decrease when the metal–oxygen bond becomes stronger. Decrease in the O–C–O angle results in a decrease in the frequency separation $\Delta\nu$. The separation $\Delta\nu$ which is small (~135 cm^{-1}) and remains constant for these derivatives suggests that the bonding of the carboxylate group to the metal is bidentate in these derivatives.

The FH derivatives showed the usual 2-substituted furan IR vibrations [9] with the ring breathing mode in the region 1012–1010 cm^{-1} which appears at 1017 cm^{-1} for free acid. The TH derivatives showed the usual 2-substituted thiophene IR vibrations [10] with the ring breathing vibration in the region 860–858 cm^{-1} which appears at 855 cm^{-1} for free TH.

The mono and diisopropoxy derivatives of both acids show characteristic frequencies of isopropyl group at 1170, 1145–1135, 955–945 and 820–755 cm^{-1} [11]. The strong bands in the region 1010–1000 cm^{-1} in mono and diisopropoxy derivatives can be assigned to the C–O stretch mode of Al–O–C group [12]. The band at 1375 cm^{-1} may be assigned to asymmetric CH_3 bending in isopropoxy group in these isopropoxy derivatives which is further supported by the strong skeletal vibration at 1170 cm^{-1}. The value of C–O stretch vibration in mono-isopropoxy derivatives (*ca.* 1010 cm^{-1}) agrees with C–O vibrations of bridging alkoxy group [13]. This result further supports the dimeric structure proposed for the disubstituted monoisopropoxy derivatives involving the bridging alkoxy group.

Absorption bands in the region 650–500 cm^{-1} indicate metal to carboxylate linkage νAl–O [12]. Two to four νAl–O stretching vibrations have been found in all these derivatives.

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