

NOTE

Synthesis and Characterization of Some Dicarboxylato and Salicylato Derivatives of Bismuth(III) Nitrate

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The interaction of sodium salts of dicarboxylic acids and salicylic acid with bismuth(III) nitrate in non-aqueous solvent resulted in coordination complexes with the general composition $\text{Bi}(\text{NO}_3)_2 \cdot \text{LL} \cdot 2 \text{DMF}$ (where LL is the bidentate ligand, namely oxalato, succinato, adipato, tartarato, phthalato and salicylato). Their physical characteristics and IR, UV spectra are reported. The nature of the metal-carboxyl group linkage is discussed.

Bismuth(III) nitrate on treatment with sodium salts of dicarboxylic acids and salicylic acid in 1 : 1 molar ratio gave the corresponding dicarboxylato and salicylato derivatives in which two nitrate group of the bismuth trinitrate molecule are substituted by the dicarboxylate or the salicylate residue. The $\nu_{\text{sym}}(\text{O}-\text{C}-\text{O})$ and $\nu_{\text{asym}}(\text{O}-\text{C}-\text{O})$ values are helpful in establishing the nature of the metal-carboxylato group bonding.

Bismuth(III) nitrate was obtained from BDH (AR grade). Sodium salts of dicarboxylic acids and salicylic acid were prepared in the laboratory. All the complexes were synthesized by the following general method. Bismuth(III) nitrate and sodium salts of respective dicarboxylic acids were kept for 6-8 h, in equimolar ratios in dimethyl formamide at ca. 60°C. The reaction mixture were allowed to cool slowly. In some cases, the precipitates were obtained immediately and in some cases gradual precipitation took place. The complexes were then filtered, washed thoroughly with petroleum ether and dried.

The complexes prepared in the present study are either white or light coloured solids and stable in dry atmosphere. They do not sublime or melt but decompose above 150°C. They decomposed on heating with dilute acids or alkalis. The analytical data of the complexes are given in Table-1. Their magnetic susceptibilities are low (ca. 0.05 BM) indicating that they are diamagnetic. Their molar conductivities are low (1.0-2.5 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) showing non-ionic character. The monomeric nature of these complexes was confirmed by the molecular weight determinations by Rast's camphor method.

The aliphatic carboxylato groups showed the usual alkane vibrations¹, the phthalato and salicylato complexes showed the bands expected for an *ortho* substituted benzene derivative². In all the dicarboxylato and salicylato complexes the $\nu_{\text{sym}}(\text{O}-\text{C}-\text{O})$ and $\nu_{\text{asym}}(\text{O}-\text{C}-\text{O})$ are of interest since their position and

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separation helps in determination of the nature of bonding of the carboxylato group to bismuth. The $\nu_{\text{sym}}(\text{O}-\text{C}-\text{O})$ and $\nu_{\text{asym}}(\text{O}-\text{C}-\text{O})$ for various complexes are assigned at 1390 cm^{-1} and 1590 cm^{-1} respectively for oxalato complex, 1360 cm^{-1} and 1620 cm^{-1} for succinato complex, 1250 cm^{-1} and 1650 cm^{-1} for adipato complex, 1380 cm^{-1} and 1600 cm^{-1} for tartarato complex, 1390 cm^{-1} and 1660 cm^{-1} for phthalato complex, 1385 cm^{-1} and 1600 cm^{-1} for salicylato complex. A comparison of these two frequencies with the ionic salts on one hand and covalent esters on the other hand shows that the carboxylate metal bond is covalent in nature. Absorption bands at *ca.* 900 cm^{-1} and 1020 cm^{-1} indicate a metal to carboxylate link.³

TABLE-I
ANALYTICAL DATA OF DICARBOXYLATO AND SALICYLATO DERIVATIVES OF BISMUTH(III) NITRATE

Complex	Mol. wt. Found (Calcd)	Analysis, Found (Calcd.) %		
		Bi	C	N
$\text{C}_2\text{O}_4\cdot\text{Bi}(\text{NO}_3)[\text{HCON}(\text{CH}_3)_2]_2$ (Oxalato)	501 (505)	41.61 (41.38)	18.75 (19.00)	8.53 (8.31)
$\text{C}_4\text{O}_4\text{H}_4\cdot\text{Bi}(\text{NO}_3)[\text{HCON}(\text{CH}_3)_2]_2$ (Succinato)	5.29 (533)	38.87 (39.21)	22.83 (22.51)	7.68 (7.87)
$\text{C}_6\text{O}_4\text{H}_8\cdot\text{Bi}(\text{NO}_3)[\text{HCON}(\text{CH}_3)_2]_2$ (Adipato)	557 (561)	37.63 (37.25)	25.42 (25.66)	7.70 (7.48)
$\text{C}_4\text{O}_6\text{H}_4\cdot\text{Bi}(\text{NO}_3)[\text{HCON}(\text{CH}_3)_2]_2$ (Tartarato)	559 (565)	36.51 (36.98)	21.59 (21.23)	7.31 (7.43)
$\text{C}_8\text{O}_4\text{H}_4\cdot\text{Bi}(\text{NO}_3)[\text{HCON}(\text{CH}_3)_2]_2$ (Phthalato)	578 (581)	35.76 (35.97)	29.20 (28.91)	7.50 (7.22)
$\text{C}_7\text{O}_3\text{H}_4\cdot\text{Bi}(\text{NO}_3)[\text{HCON}(\text{CH}_3)_2]_2$ (Salicylato)	548 (553)	37.20 (37.79)	27.93 (28.20)	7.37 (7.59)

The shift in carbonyl frequencies of the tartarato complexes may be due to intramolecular hydrogen bonding between OH group and oxygen of the $\text{C}=\text{O}$ group. This is supported by the appearance of a medium intensity band at *ca.* 1600 cm^{-1} and a broad but weak band at *ca.* 2800 cm^{-1} indicating that the second carbonyl group is involved in hydrogen bonding which is further supported by the lowering of $\nu(\text{O}-\text{H})$ to *ca.* 3200 cm^{-1} .^{4,5} The frequency shift of $\nu_{\text{asym}}(\text{O}-\text{C}-\text{O})$ and $\nu_{\text{sym}}(\text{O}-\text{C}-\text{O})$ from normal values in the phthalato complexes may be due to aryl conjugation⁵. The lowering of $\nu(\text{C}=\text{O})$ from *ca.* 1650 to 1590 cm^{-1} indicates that dimethyl formamide molecule is attached through oxygen atom to bismuth atom in the complexes.^{6,7} This is supported by the fact that the aldehyde $\nu(\text{C}-\text{H})$ at *ca.* 2700 cm^{-1} is absent in the IR spectra of the complexes⁸. The bands at *ca.* 2800 and 2750 cm^{-1} may be assigned to $\nu(\text{CH}_3)$. The $\nu(\text{C}-\text{N})$ appears at *ca.* 1390 cm^{-1} . All the complexes showed bands for the NO_3 group at *ca.* 1400 and *ca.* 1250 cm^{-1} which may be assigned to $\nu_{\text{asym}}(\text{O}-\text{N}-\text{O})$ and $\nu_{\text{sym}}(\text{O}-\text{N}-\text{O})$ respectively.⁹ The $\nu(\text{Bi}-\text{O})$ appear as 2-3 bands in

the range 450–370 cm^{-1} indicating difference in $\nu(\text{Bi—O})$ in nitrate group, $\nu(\text{Bi—O})$ in carboxylate group and $\nu(\text{Bi—O})$ in DMF complexes.

The peaks at *ca.* 260 and 210 nm in the UV spectra of all the complexes may be due to charge transfer.

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