Vol. 45, No. 1
Jan. 5, 1976]

DIIODOSALICYLATES OF THE RARE EARTHS

D. K. KOPPIKAR AND S. SOUNDARARAJAN
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

ABSTRACT

Rare earth diiodosalicylates of the general formula, $Ln(I_2Sal)_3 \cdot xH_2O$, where $x = 5$ when Ln = La, Ce, Pr, Nd ; $x = 4$ when Ln = Sm, Ho, Yb and Y, and $I_2Sal = I_2C_6H_2$ (OH) COO^-, have been prepared and characterised by chemical analyses, infrared, conductance and differential thermal analyses. The infrared data show that the bonding of the carboxylate group to the metal is bidentate. The infrared and thermal studies reveal that one molecule of water is coordinated to the metal in all the chelates.

INTRODUCTION

THE compounds of salicylic and substituted salicylic acids with metals are of interest because the salicylate ion can attach itself to the metal in a number of ways. A number of salicylates of the rare earths has been synthesised in the past[1,2]. Although studies on a few compounds of rare earths with substituted salicylic acids have been carried out[3,4], no studies have been reported on the preparation and characterisation of the rare earth compounds of 3, 5-diiodosalicylic acid. A few salts of diiodosalicylic acid that have been prepared have been shown to be of considerable biological importance. Bismuth diiodosalicylate has been used in antisyphilitic therapy[5]. The sodium salt has been shown to possess antitoxic properties[6], and has been used for protection from hyperthyreosis[7]. The copper complexes possess pronounced antimicrobial properties[8]. The visible and ultraviolet spectra of copper complexes[9], as also the effect of the lithium salt on the melting points of gelatins[10] have been studied. The present paper deals with the preparation, infrared, conductance and DTA studies on the rare earth diiodosalicylates.

EXPERIMENTAL

Materials.—Diiodosalicylic acid was recrystallised from ethanol before use. Rare earth oxides, 99·9% purity (American Potash and Chemical Corporation, U.S.A.), were treated with aqueous hydrochloric acid and evaporated to dryness to obtain the hydrated rare earth chlorides. Hydrated $CeCl_3$ was prepared similarly by using cerium hydroxide.

Preparation of the Complexes.—Diiodosalicylic acid (2·5 g) was dissolved in ethanol and ethanolic ammonia added drop by drop with stirring, when the ammonium salt of the acid separated out. To a warm aqueous solution of the ammonium salt was added with stirring, an aqueous solution of the rare earth chloride (0·3 g oxide). The thick flocculent precipitate which separated out was filtered, washed with water, dried first in air and then over calcium chloride under reduced pressure.

Analyses.—The metal content of the compounds was estimated by igniting a known weight of the compound to the metal oxide. Carbon and hydrogen in a few complexes were estimated by microanalytical methods by way of verification.

Physical Methods.—The infrared spectra, in Nujol mull, were recorded with a Carl-Zeiss UR-10 automatic spectrophotometer. The molar conductance in acetone was determined by a Siemens conductivity bridge, and the concentration of the solutions was *ca.* 0·001 M. The differential thermograms were recorded on an automatic instrument fitted with chromel-alumel thermocouples, and using calcined alumina as the reference material. The conductance and the infrared data are presented in Table I and Table II respectively.

RESULTS AND DISCUSSION

Analytical results of the compounds conform to the general formula, $Ln(I_2Sal)_3 \cdot xH_2O$, where $x = 5$ when Ln = La, Ce, Pr, Nd and $x = 4$ when Ln = Sm, Ho, Yb and Y. The compounds are quite stable and are unaffected in air. They are insoluble in water, dimethyl formamide, dimethyl sulphoxide and non-polar solvents, but are slightly soluble in ethanol, methanol and acetone.

Unlike the sodium and ammonium diiodosalicylates which are soluble in water, all the rare earth metals form insoluble diiodosalicylates. This may be due to an appreciable covalent character of the metal-carboxylate bond, water being unable to sever this bond. The covalency of the metal-carboxylate bond in these compounds is further confirmed by their conductance measurements in acetone which show their non-electrolyte nature in this solvent.

TABLE I

Analytical and conductance data

Compound	% Metal Found	% Metal Calc.	% Carbon Found	% Carbon Calc.	% Hydrogen Found	% Hydrogen Calc.	Molar Conductance λ, mho cm^2 mol^{-1}
La $(I_2Sal)_3 . 5H_2O$	9·95	9·96	18·20	18·05	1·58	1·36	8·2
Ce $(I_2Sal)_3 . 5H_2O$	9·93	10·02	..	..	..	..	15·4
Pr $(I_2Sal)_3 . 5H_2O$	9·98	10·08	18 14	18·02	1·24	1·36	7·8
Nd $(I_2Sal)_3 . 5H_2O$	10·18	10·30	..	..	..	..	13·9
Sm $(I_2Sal)_3 . 4H_2O$	10·90	10·81	18·32	18·13	1·45	1·22	13·9
Ho $(I_2Sal)_3 . 4H_2O$	11·80	11 76	..	..	..	..	8·2
Yb $(I_2Sal)_3 . 4H_2O$	12·23	12·26	17·92	17·84	1·34	1·20	11·2
Y $(I_2Sal)_3 . 4H_2O$	6·64	6·70	19·30	18·98	1·56	1·28	9·6

Note.– Carbon and hydrogen have been estimated only for a few representative compounds.

TABLE II

Infrared spectral data

I_2SalH	$La(I_2Sal)_3 . 5H_2O$	Na-Salt	Assignments
3520			O–H stretch
	3480		H_2O stretch
	3200		H_2O stretch
1706			C=O stretch
1625	1620	1638	ring C–C stretch
1580			
	1558	1575	asym. COO^- stretch
1445	1450	1450	ring C-C stretch
1420	1430	1430	
1400	1420		
	1370	1368	sym. COO^- stretch
1305			C–O stretch (of COOH)
1240			
1230	1250	1270	C–O stretch (phenolic O)
885			O–H out-of-plane bending (of COOH)
	882	881	C–H out-of-plane bending

Note.—The i.r. spectra of the other diiodosalicylates are quite similar.

The i.r. spectrum of diiodosalicylic acid has not been so far reported in literature. Hence, the frequency assignments for the ligand and the rare earth compounds have been made on the basis of the i.r. data available for benzoic and salicylic acids[11,12]. Of the three possible internally hydrogen bonded forms of salicylic acid, Tsuzuki *et al.*[13] have preferred the one where the phenolic group forms a hydrogen bond with the carbonyl oxygen atom of the cis-carbonyl structure, on the basis of the observation of the bands for carbonyl, carboxylic –OH and phenolic –OH groups at 1690 cm^{-1}, 3530 cm^{-1} and 3200 cm^{-1} respectively, in the i.r. spectrum of salicylic acid. In the present investigation, i.r. bands have been observed for diiodosalicylic acid at 1706 cm^{-1} and 3520 cm^{-1} attributed to the carbonyl and carboxyl –OH stretching vibrations, and another somewhat broadened band in the region 3080–3200 cm^{-1} attributed to the phenolic –OH group. Hence, it can be inferred that diiodosalicylic acid also exists in an internally bonded form which is similar to the one present in salicylic acid.

The two bands at 1706 cm^{-1} and 1310 cm^{-1} which are due to ν C=O and ν C—O of the carboxyl group of the ligand are absent in the rare earth compounds. The rare earth compounds show bands at $\sim$ 1560 cm^{-1} and $\sim$ 1370 cm^{-1} which can be attributed, respectively, to the asymmetric ν COO^- and symmetric ν COO^- vibrational frequencies of the carboxylate group. The corresponding bands for the sodium salt are observed at 1575 cm^{-1} and 1368 cm^{-1}, respectively. Thus the difference between the two ν COO^- frequencies ($\Delta \nu$) is less in the rare earth compounds than in the sodium salt. This shows that, in the compounds investigated, the bonding of the carboxylate group to the metal is not monodentate; if it were so the frequency separation, $\Delta \nu$, would be more than that in the sodium salt. In the case of a bidentate mode of coordination there are two factors influencing the symmetric and asymmetric carboxylate frequencies. Due to the bidentate mode

of coordination of the carboxylate group to the metal, there is a decrease of both the COO^- stretching frequencies, as compared to the corresponding value for the sodium salt, due to the drainage of the electron density from the carboxylate group to the metal. But at the same time the O–C–O angle is decreased due to an increase in the metal-oxygen bond strength. This decrease in the O–C–O angle results in a decrease in the frequency separation, $\Delta\nu$[14-16]. These two factors have a unidirectional effect on the asymmetric νCOO^- frequency and an opposite effect on the symmetric νCOO^- frequency. Hence, when the bonding of the carboxylate group is bidentate, the asymmetric frequency decreases and the symmetric frequency shows only small shifts, thus making, $\Delta\nu$, less than that in the sodium salt. Thus the bonding of the carboxylate group, in the compounds investigated, must be bidentate, as $\Delta\nu$ has been found to be less in these compounds than in the sodium salt. However, in the present chelates, the shift of the asymmetric frequency is less than the corresponding shift in the rare earth salicylates[2], suggesting that the metal-carboxylate bond has more ionic character in the former than in the latter.

The –COOH group gives bands at 3520 cm^{-1} (s) and 2600 cm^{-1} (w) due to the –OH stretching vibrations and another broad band at 885 cm^{-1} due to the –OH out-of-plane vibration. These bands are absent in the chelates.

The rare earth chelates show bands in the 3000–3600 cm^{-1} region due to the stretching modes of water molecules. The bands in this region can be assigned to the lattice water ($\sim$ 3475 cm^{-1}) and to the coordinated water ($\sim$ 3,200 cm^{-1}).

Differential thermograms were obtained for La, Nd and Sm diiodosalicylates. They show similar behaviour for the three compounds studied and the same behaviour can be expected for the other rare earth compounds as well. An endotherm in the region 70–100° C shows the removal of water. Heating of the samples at 100° C for 4–5 hours showed that four water molecules were removed in the case of La, Ce, Pr and Nd chelates, and three water molecules in the case of the Sm, Ho, Yb and Y chelates. Thus one molecule of water is coordinated in all the chelates, the rest of them being only lattice held. There is no endotherm in the differential thermograms showing the removal of the coordinated water. The removal of the coordinated water is probably accompanied by the decomposition of the compound which gives a strong and broad exotherm centered around 300° C.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. A. K. Sundaram (B.A.R.C., Bombay) for his help in getting the differential thermograms. One of the authors (D. K. K.), thanks U.G.C. (India) for a fellowship.

1. Misra, S. N., *Indian J. Chem.*, 1967, 5, 508.
2. Kanekar, C. R., Marathe, V. R. and Thakur, N. V., *Proc. Chem. Symp., DAE India*, 1969, 2, 265.
3. Spacu, P., Antonescu, E., Mavrodin, M. and Serban, S., *Acad. Rep. Populare Romine, Studii. Cercetari. Chim.*, 1963, 11, 385.
4. Shestakova, M. T. and Pirkes, S. B., *Zh. Neorg. Khim.*, 1970, 15, 993.
5. Pollano, F., *Minerva med.*, 1930, 1, 786.
6. Velluz, L., *Compt. rend.*, 1931, 193, 372.
7. Marsal, A., *Rev. Soc. Argentina Biol.*, 1936, 12, 151.
8. Gershan, H., Parmegiani, R. and Nickerson, W. J., *Appl. Microbiol.*, 1962, 10, 556.
9. Schulman, S. G., Kilroy, W. P. and Gershan, H., *J. Phys. Chem.*, 1968, 72, 3372.
10. Bello, J., Riese, H. C. A. and Vinograd, J. R., *Ibid.*, 1956, 60, 1299.
11. Taylor, M. D., Carter, C. P. and Wynter, C. I., *J. Inorg. Nucl. Chem.*, 1968, 30, 1503.
12. Green, J. H. S., Kynaston, W. and Lindsey, A. S., *Spectrochim. Acta*, 1961, 17, 486.
13. Mori, N., Asano, Y., Irie, T. and Tsuzuki, Y., *Bull. Chem. Soc. Jap.*, 1969, 42, 484.
14. Spinner, E., *J. Chem. Soc.*, 1964, p. 4217.
15. Grigor'ev, A. I., *Russ. J. Inorg. Chem.*, 1963, 8, 407.
16. —, and Maksimov, V. N., *Ibid.*, 1964, 9, 580.