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Synthesis and studies on pyridinium chlorofluoro complexes of indium and bismuth

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Abstract

Pyridinium trichlorotrifluoroindate, $(C_5H_5NH)_3InCl_3F_3$, and pyridinium trichlorofluorobismuthate, $C_5H_5NHBiCl_3F$, have been synthesised by the reaction of pyridinium poly(hydrogen fluoride), PPHF, with $InCl_3$ and $BiCl_3$, respectively. These new complexes have been characterised by chemical and thermal analysis, NMR (^1H and ^{19}F) and infrared spectroscopy, and powder X-ray diffraction methods.

Keywords: Synthesis; Pyridinium trichlorotrifluoroindate; Pyridinium trichlorofluorobismuthate; IR spectroscopy; X-Ray powder diffraction studies; Thermal analysis

1. Introduction

Phosphorus pentachloride, PCl_5, and $TiCl_4$ have been observed to react with PPHF to form the corresponding pyridinium fluoro complexes, $C_5H_5NHPF_6$ and $(C_5H_5NH)_2TiF_6$, respectively [1,2]. Hence, it was of interest to see how indium and bismuth chlorides behave towards PPHF. Preliminary experiments indicated that $InCl_3$ and $BiCl_3$ react with PPHF and complexation then occurs rather than displacement of the chloride, giving rise to the corresponding pyridinium chlorofluoro complexes. For this reason, a detailed study has been undertaken and the results are reported in this paper.

2. Experimental details

2.1. Materials and methods

All reagents were AR (Analar) grade. PPHF was prepared by mixing pyridine and anhydrous hydrogen fluoride in a weight ratio of 3:7 [3]. The fluoride content was determined using a fluoride-ion selective electrode [4] (Orion model 94-09) with a single-junction reference electrode model 90-01 in conjunction with an expandable Ion Analyser model EA™ 940. Infrared spectra were recorded on a Bio-Rad model FTS-7 spectrometer between 4000–225 cm^{-1} as Nujol mulls (CsI discs). NMR (^1H and ^{19}F) spectra were recorded on a Bruker model AC-200F spectrometer at 200 MHz for ^1H and 188.3 MHz for ^{19}F in DMSO-d_6 as solvent. Samples were referenced externally with respect to tetramethylsilane/trifluoromethylbenzene with positive shifts downfield from the standard. Powder X-ray diffraction patterns were recorded on a Philips model PW 1050/70 X-ray diffractometer fitted with a vertical goniometer using Cu Kα radiation. Thermal analysis was carried out in air using a ULVAC SINKU-RICO TA1500 thermal analyser.

2.2. Syntheses

PPHF (35–40 ml) was introduced into a polyethylene flask (100 ml) fitted with a sodium fluoride guard tube (to absorb outgoing HF vapour and avoid the entry of moisture) and the solution stirred with a Teflon-coated magnetic pellet. Indium trichloride (8.66 g) [bismuth trichloride (6.30 g)] was added and stirred for 6–8 d at ambient temperature (24–26 °C). At the end of the reaction (checked by the absence of $BiCl_3/InCl_3$), precipitation was induced by the addition of acetone (≈ 300 ml), the top layer of acetone was decanted and the precipitate washed 2–3 times with dry acetone to remove any adhering PPHF and/or HF, dried in a polyethylene desiccator under vacuum and stored under nitrogen. The products $(C_5H_5NH)_3InCl_3F_3$ (19.87 g) and $C_5H_5NHBiCl_3F$ (8.12 g) were obtained as soft white

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Table 1
Analytical results for pyridinium trichlorotrifluoroindate and pyridinium trichlorofluorobismuthate

Compound	Pyridine (%)		Metal (%)		Chlorine (%)		Fluorine (%)	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$(C_5H_5NH)_3InCl_3F_3$	45.45	45.77	22.33	22.14	20.43	20.51	10.93	10.99
$C_5H_5NBiCl_3F$	19.30	19.09	50.31	50.42	25.17	25.66	4.52	4.58

powders. The yields of the indium and bismuth complex salts (based on the amounts of $InCl_3$ and $BiCl_3$ employed) were 97.9% and 98.7%, respectively.

2.3. Characterisation

2.3.1. Chemical analysis

The pyridine content of the salts was determined volumetrically [5] and the fluoride content by means of a fluoride-ion selective electrode [4] after converting into soluble sodium fluoride by fusing with a fusion mixture (sodium carbonate and potassium nitrate). The chloride content was determined gravimetrically [6a] by dissolving the compounds in dilute nitric acid and precipitating as silver chloride using silver nitrate. The bismuth content was determined by EDTA titration [6b] using pyrocatechol violet as the indicator after dissolving the compound in dilute nitric acid and adjusting the pH to 2.5–3.5 using dilute ammonium hydroxide solution. The indium compound was digested with dilute sulphuric acid, evaporated almost to dryness, dissolved in water and the indium hydroxide precipitated by the addition of ammonium hydroxide solution. The hydroxide was ignited to 800 °C and finally weighed as indium oxide (In_2O_3). The analytical results obtained are listed in Table 1.

2.3.2. Infrared spectral and proton NMR spectral analyses

The infrared vibrational frequencies (cm^{-1}) of $(C_5H_5NH)_3InCl_3F_3$ were 3255 (m); 3178 (m); 3124 (w); 3081 (m); 3062 (m); 1634 (m); 1609 (s); 1534 (s); 1482 (s); 1326 (w); 1244 (w); 1196 (m); 1161 (m); 1049 (m); 1002 (w); 951 (vw); 892 (vw); 766 (sh); 745 (vs); 672 (vs); 609 (m); 475 (sh); 427 (m); 404 (sh); 339 (m); 316 (m); 281 (m); 241 (m), respectively, and for $C_5H_5NHBiCl_3F$ were 3222 (m); 3159 (m); 3123 (m); 3097 (m); 3067 (m); 1632 (m); 1603 (s); 1530 (s); 1480 (s); 1327 (w); 1239 (m); 1193 (m); 1162 (m); 1049 (m); 1025 (w); 983 (w); 875 (vw); 742 (vs); 670 (vs); 609 (w); 455 (w); 386 (w); 314 (vw); 282 (sh); 241 (s), respectively. These infrared spectral data have been discussed by comparison with the vibrational frequencies of the other pyridinium salts [7], chloroindates [8], fluoroindate [9], chlorobismuthate and mixed halogenobismuthates [10] together with the general trends in vibrational frequencies. Both products show M–F and M–Cl (M = In and Bi) vibrational frequencies along with shoulders which are probably a consequence of the low-site symmetry of the anions [11] because of the presence of two different ligands; in the case of bismuth, another additional factor was the presence of a lone pair of electrons ($6s^2$) which are generally known to remain active in case of four- and five-coordinate anions [12].

The high value of ν_{N-H} vibrational frequencies at 3255 cm^{-1} for $(C_5H_5NH)_3InCl_3F_3$ and at 3222 cm^{-1} for $C_5H_5NHBiCl_3F$ indicates very weak hydrogen bonding or its total absence in the solid phase [7a, 13, 14]. The vibrational frequency at 427 cm^{-1}, along with shoulders in the spectrum of $(C_5H_5NH)_3InCl_3F_3$, has been assigned to In–F stretching modes based on an earlier observed value of 446 cm^{-1} in the case of M_3InF_6 [9]. Other vibrational frequencies in the region 339–241 cm^{-1} can be attributed to the In–Cl stretching mode as reported earlier between 250–266 cm^{-1} in the case of the chloroindates [8]. Similarly, the vibrational frequency at 241 cm^{-1}, along with shoulders in the spectrum of $C_5H_5NHBiCl_3F$, has been assigned to Bi–Cl stretching based on reported values for the chlorobismuthate Et_4NBiCl_4 at 283, 264 and 252 cm^{-1}, for the mixed halogenobismuthate Bu_4NBiCl_3Br at 255 and 269 cm^{-1}, and for Bu_4NBiCl_3I at 284, 274 and 255 cm^{-1} [10]. Based on the trend in vibrational frequencies, the band at 386 cm^{-1} has been assigned to Bi–F stretching.

Evidence for the presence of pyridinium cations in DMSO solution is also obtained from the proton NMR spectra of both compounds, as demonstrated by the characteristic multiplet with downfield chemical shifts [15].

^{19}F NMR spectral analysis of both $(C_5H_5NH)_3InCl_3F_3$ and $C_5H_5NHBiCl_3F$ demonstrated the existence of broad singlets at δ 96.8 and 98.7 ppm, respectively, probably as a consequence of fluoride exchange.

2.3.3. Powder X-ray diffraction pattern

The observed d (Å) values (relative intensities) for $(C_5H_5NH)_3InCl_3F_3$ were 8.7824 (34), 7.3096 (100), 5.1557 (56), 4.0303 (43) and 3.9884 (32), respectively, and for $C_5H_5NHBiCl_3F$ were 9.6841 (48), 6.1237 (48), 4.8399 (61), 3.8564 (65) and 3.4891 (100), respectively.

2.3.4. Thermal analysis

During melting point determinations it was found that $(C_5H_5NH)_3InCl_3F_3$ decomposed before melting. For this reason, simultaneous TG–DTA thermograms of both products were recorded in air. The thermogram for pyridinium chlorofluoroindate showed that decomposition commenced at ca. 115 °C and proceeded with major weight losses up to 325 °C, exhibiting three clear endotherms at 129, 233 and 291 °C, and weak endotherms at 155, 183 and 325 °C which probably arise as a consequence of decomposition and evaporation of pyridine and HF. Above 325 °C, the weight loss continued (with very weak endotherms at 409 and 520 °C) but only very slowly and to a small extent as a consequence of the conversion of the intermediates formed, i.e. InOCl and InOF, to In_2O_3 with the weight becoming constant at ca. 540 °C.

A separate pyrolysis experiment on pyridinium trichlorotrifluoroindate in air showed that decomposition started at ca. 115 °C. It was found that the product decomposed by evolution of pyridine and HF. A part of the pyridine combined with HF and condensed as a white solid on the cooler zones of the apparatus. The remaining pyridine was identified by its characteristic smell and later confirmed via the IR spectrum of the gas evolved. On pyrolysis at 325 °C, the residual product was found to be InOF ($>90\%$) [16a] together with a small amount of InOCl and In_2O_3 ($<10\%$) [16b,c] (based on powder X-ray diffraction peak intensity analysis). On further heating up to 540 °C, the residual product was found to be In_2O_3 [16c]. The thermogram showed an experimental weight loss of 73.81% which agrees well with the calculated weight loss of 73.28% based on $(C_5H_5NH)_3InCl_3F_3$.

The thermogram for pyridinium chlorofluorobismuthate showed that the decomposition commenced at ca. 163 °C and proceeded with major weight losses up to 340 °C, exhibiting three endotherms at 207, 233 and 335 °C. After 340 °C, the weight loss continued but only very slowly as a consequence of the conversion of the oxochloride (BiOCl) formed to the oxide (Bi_2O_3). During trials to determine the melting point of the solid it was found that $C_5H_5NHBiCl_3F$ decomposed before melting. In another separate pyrolysis experiment in air, it was found that a white solid containing bismuth was deposited on the cooler zones (checked by passing H_2S into an acidic solution of the deposited compound which led to a dark brown precipitate of Bi_2S_3), indicating that the intermediate formed had partially evaporated. The residual product at 340 °C was identified as BiOCl by comparison of its powder X-ray diffraction pattern [16d]. The thermogram of pyridinium chlorofluorobismuthate showed an experimental weight loss of 52.71% up to 340 °C. This experimental loss is much higher than the expected weight loss, i.e. 37.16% (assuming that all the bismuth is retained and converted to BiOCl). This discrepancy in weight loss is attributed to the partial evaporation of the intermediate formed, i.e. bismuth chloride ($BiCl_3$, m.p. 232 °C, b.p. 447 °C), before its conversion to BiOCl as observed in the separate pyrolysis experiment.

3. Results and discussion

The above results show that the products formed were $(C_5H_5NH)_3InCl_3F_3$ and $C_5H_5NHBiCl_3F$ and not a mixture of hexachloroindate ($InCl_6{}^{3-}$) [8] and hexafluoroindate ($InF_6{}^{3-}$) [9] or halogenobismuthates [10] as their characteristic frequencies [8–10] were not observed in the IR spectra.

The reaction trends in the cases of indium(III) and bismuth(III) chlorides are different from those of phosphorus(V) and titanium(IV) chlorides which form pyridinium hexafluorophosphate, $C_5H_5NHPF_6$ [1], and pyridinium hexafluorotitanate, $(C_5H_5NH)_2TiF_6$ [2], respectively.

Thermal decomposition of $(C_5H_5NH)InCl_3F_3$ proceeds via InOF as the major intermediate product, while in the case of $C_5H_5NHBiCl_3F$ the intermediate formed is BiOCl. This difference in product formation could be due to the higher dissociation energy of the In–F bond compared to the In–Cl bond in $(C_5H_5NH)_3InCl_3F_3$ and the reverse (Bi–Cl > Bi–F bond) in $C_5H_5NHBiCl_3F$, as can be seen from the bond dissociation energy trend of diatomic molecular chlorides and fluorides (bond energies expressed in kcal mol^{-1}), i.e. In–Cl, 105 ± 2; In–F, 121 ± 3.5: Bi–Cl, 72 ± 1; Bi–F, 62 ± 7 [17].

This extra stability of the Bi–Cl bond in the case of $C_5H_5NHBiCl_3F$ might arise as a result of the contribution of the available outer orbital $6s^2$ lone-pair electron in bismuth bonding, due to its relatively high polarisability. Such a situation does not occur in the case of indium(III).

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References

[1] K.S. Mohamed, D.K. Padma, R.G. Kalbandkeri and A.R.V. Murthy, *J. Fluorine Chem., 23* (1983) 509.

[2] K.S. Mohamed and D.K. Padma, *J. Fluorine Chem., 35* (1986) 411.

[3] G.A. Olah, J.T. Welch, Y.D. Vankar, M. Nojima, I. Kerckes and J.A. Olah, *J. Org. Chem., 44* (1979) 3832.

[4] Y. Koryta, *Anal. Chim. Acta, 61* (1972) 329.

[5] P.A. Van der Meulen and H.A. Heller, *J. Am. Chem. Soc., 54* (1932) 4404.

[6] A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 3rd edn., Longman Green, London, UK, 1969, (a) p. 486, (b) p. 445.

[7] (a) D. Cook, *Can. J. Chem., 39* (1961) 2009; (b) N.S. Gill, R.H, Nuttall, D.E. Scaife and D.W.A. Sharp, *J. Inorg. Nucl. Chem., 18* (1961) 79; (c) N.N. Greenwood and K. Wade, *J. Chem. Soc.*, (1960) 1130; (d) V.P. Petrosjan and A.A. Ennan, *Zh. Neorg. Khim., 24* (1979) 1562.

[8] (a) T. Barrowcliffe, I.R. Beattie and K. Livingston, *J. Chem. Soc. A,* (1967) 1810; (b) A.W. Atkinson and B.O. Field, *J. Inorg. Nucl. Chem., 32* (1970) 2615; (c) J. Gislason, M.H. Lloyd and D.G. Tuck, *Inorg. Chem., 10* (1971) 1907.

[9] R.D. Peacock and D.W.A. Sharp, *J. Chem. Soc.*, (1959) 2762.

[10] G.Y. Ahlijah and M. Goldstein, *J. Chem. Soc. A,* (1970) 326, 2590.

[11] R.S. Halford, *J. Chem. Phys., 14* (1946) 8.

[12] (a) L.E. Orgel, *J. Chem. Soc.*, (1959) 3815; (b) J.D. Smith, in J.C. Bailer, H.J. Emeleus, R. Nyholm and A.F. Trotman-Dickenson (eds.), *Comprehensive Inorganic Chemistry*, Pergamon, Oxford, 1973, Vol. 2, p. 645.

[13] B. Chenon and C. Sandorfy, *Can. J. Chem.*, *36* (1958) 1181.

[14] R.H. Nuttall, D.W.A. Sharp and T.C. Waddington, *J. Chem. Soc.*, *(1960) 4965.*

[15] J.C. Smith and W.G. Schneider, *Can. J. Chem.*, *39* (1961) 1158.

[16] *Powder Diffraction File, Inorganic Phases,* International Center for Diffraction Data, Swarthmore, PA, 1990, (a) 19-584, (b) 11-510, (c) 6-416, (d) 6-249.

[17] R.C. West (ed.), *CRC Handbook of Chemistry and Physics*, 67th edn., CRC Press, Boca Raton, FL, 1986–87, pp. F167–176.