Thermochimica Acta, 191 (1991) 317–322
Elsevier Science Publishers B.V., Amsterdam

Scandium trifluoromethanesulphonate aromatic amine oxide complexes: synthesis, characterisation and thermoanalytical investigation

G. Vicentini, J.D. Ayala and J.R. Matos

Instituto de Química, Universidade de São Paulo, C.P. 20.780, CEP: 01498, São Paulo, SP (Brazil)

(Received 29 March 1991)

Abstract

The preparation and characterisation of the complexes formed between scandium(III) trifluoromethanesulphonates and aromatic amine oxides pyridine-*N*-oxide (pyO), 2-picoline-*N*-oxide, 3-picoline-*N*-oxide, 4-picoline-*N*-oxide (2-, 3- and 4-picNO) and 2,6-lutidine-*N*-oxide (2,6-lutNO), together with their thermoanalytical study, are described.

EXPERIMENTAL

The complexes were prepared by reaction of an ethanolic solution of the hydrated scandium trifluoromethanesulphonate with the ligand in the same solvent (molar ratio 1 : 6), followed by addition of 2,2-dimethoxypropane (dmp). The precipitates were filtered, washed with dmp and dried in vacuo over anhydrous calcium chloride.

The solid complexes are slightly hygroscopic, but the compound with 2,6-lutidine-*N*-oxide is very hygroscopic.

The compounds were characterised by complexometric titration of Sc^{3+} by titration with a 0.02 M EDTA solution, using orthoxylenol orange as indicator and a buffer composed of glycine and hydrochloric acid, according to the method of Tikhonov and Mikhailova [1]. Carbon, hydrogen and nitrogen were determined by the usual microanalytical procedures. Electrolytic conductance measurements were performed at $25.00 \pm 0.02\,^{\circ}C$ using equipment composed of a resistance box, a pointer galvanometer and a Leeds and Northrup Co. cell ($K_c = 0.11597$ cm^{-1}). IR spectra were recorded on an FTIR Bomem, Model MB-102 instrument using KBr windows or pellets. Melting ranges were determined in Carl Zeiss equipment. Thermoanalytical measurements were performed with a Perkin–Elmer TGA-7 system and DSC in a Mettler System TA 4000 using a heating rate of 5 K min^{-1} and air or nitrogen dynamic atmosphere.

RESULTS AND DISCUSSION

The compounds have the formulae $Sc(F_3C{-}SO_3)_3 \cdot 6L$ (L = pyO, and 2-, 3- or 4-picNO) and $Sc(F_3C{-}SO_3)_3 \cdot 5(2,6\text{-lutNO}) \cdot H_2O$. Table 1 contains a summary of the analytical data.

Conductance data in nitromethane and acetonitrile show a 1:3 electrolyte behaviour (Table 2). The bands attributed to ionic trifluoromethanesulphonate are seen in the IR spectra (Table 3). Small ν(NO), δ(NO) and γ(CH) shifts are observed, due to coordination of the amine oxides to the central ions.

Figure 1 shows the TG curves obtained in dynamic air atmosphere (22 ml min^{-1}) using platinum crucibles; Table 4 summarises the thermoanalytical data. The decomposition schemes for each compound, consisting of the elimination of the ligands followed by liberation of $F_3C{-}SO_2F$, SO_2 and COF_2 [2] (in some cases an intermediate oxosalt is formed) with Sc_2O_3 as the residue, are given in Table 5.

TG curves obtained under nitrogen atmosphere show practically the same results, except for the residues which contain small quantities of carbonised material, their percentages being higher than those obtained in air.

TABLE 1

Summary of analytical results (%)

Complex	Scandium		Carbon		Nitrogen		Hydrogen	
	Theor.	Exp	Theor.	Exp	Theor.	Exp.	Theor.	Exp.
$Sc(F_3C{-}SO_3)_3 \cdot 6pyO$	4.23	4.19	37.30	37.30	7.91	7.78	2.85	2.95
$Sc(F_3C{-}SO_3)_3 \cdot 6(2\text{-picNO})$	3.92	4.15	40.84	40.42	7.33	7.40	3.69	3.61
$Sc(F_3C{-}SO_3)_3 \cdot 6(3\text{-picNO})$	3.92	3.87	40.84	40.97	7.33	7.09	3.69	3.71
$Sc(F_3C{-}SO_3)_3 \cdot 6(4\text{-picNO})$	3.92	3.86	40.84	40.83	7.33	7.08	3.69	3.73
$Sc(F_3C{-}SO_3)_3 \cdot 5(2,6\text{-lutNO}) \cdot H_2O$	3.99	3.85	40.54	40.61	6.22	6.28	4.21	4.62

TABLE 2

Conductance data

Complex	Nitromethane		Acetonitrile	
	Conc. (mM l^{-1})	ΛM (Ω^{-1} cm^2 mol^{-1})	Conc. (mM l^{-1})	ΛM (Ω^{-1} cm^2 mol^{-1})
$Sc(F_3C{-}SO_3)_3 \cdot 6pyO$	1.02	216	1.04	361
$Sc(F_3C{-}SO_3)_3 \cdot 6(2\text{-picNO})$	1.07	189	1.10	326
$Sc(F_3C{-}SO_3)_3 \cdot 6(3\text{-picNO})$	1.02	205	1.04	349
$Sc(F_3C{-}SO_30_3 \cdot 6(4\text{-picNO})$	1.01	212	1.14	357
$Sc(F_3C{-}SO_3)_3 \cdot 5(2\text{-lutNO}) \cdot H_2O$	1.05	205	1.19	338

TABLE 3

IR spectra data (cm^{-1})

Compound	ν(NO)	δ(NO)	γ(CH)	$\nu_{as}(SO_3)$	$\nu_s(SO_3)$	$\delta_{as}(SO_3)$	$\delta_s(SO_3)$
PyO	1240vs	835vs	773vs	–	–	–	–
$Sc(F_3C–SO_3)_3 \cdot 6pyO$	1272vs–1231vs [a]	843vs	777vs	1272vs–1231vs [a]	1031vs	638vs	518m
2-PicNO	1232vs	849vs	774vs	–	–	–	–
$Sc(F_3C–SO_3)_3 \cdot 6$(2-picNO)	1222vs	855s	775s	1274vs	1032vs	638vs	518w
3-PicNO	1266vs	797vs	749vs	–	–	–	–
$Sc(F_3C–SO_3)_3 \cdot 6$(3-picNO)	1267vs [a]	798vs	752vs	1267vs [a]	1032vs	638vs	518vs
4-PicNO	1218vs	854s	761vs	–	–	–	–
$Sc(F_3C–SO_3)_3 \cdot 6$(4-picNO)	1269vs–1223vs [a]	859s	780vs	1269vs–1223vs [a]	1029vs	637vs	505vs
2,6-LutNO	1236vs	836vs	780vs	–	–	–	–
$Sc(F_3C–SO_3)_3 \cdot 5(lutNO) \cdot H_2O$	1243vs–1224vs	848s	786vs	1243vs–1224vs	1031vs	635vs	517s

[a] Bands attributed to $\nu(NO) + \nu_{as}(SO_3)$.

TABLE 4

Summary of thermoanalytical data for the trifluoromethanesulphonate amine oxide complexes

Ligand	Temperature range (K)	Weight loss or residue (%) [a]		Melting range (K)	DSC peak temp. (K)	ΔH melt (kJ mol^{-1})
		Theor.	Exp.			
PyO	374– 574	26.85	27.0	359–374	367	+41.6
	574– 730	60.03	59.3			
	730–1113	6.64	8.1			
	Sc_2O_3	6.48	5.6			
2-PicNO	406– 532	19.03	20.1	389–406	398	+40.7
	532– 567	9.51	9.3			
	567– 607	9.52	10.6			
	607–1113	55.93	53.8			
	Sc_2O_3	6.01	6.2			
3-PicNO	423– 584	28.54	27.1	389–407	405	+64.9
	584–1113	65.45	65.7			
	Sc_2O_3	6.01	6.4			
4-PicNO	463– 563	19.03	19.3	446–459	452	+82.3
	563– 617	19.03	18.8			
	617– 779	43.63	42.4			
	779–1113	12.30	13.1			
	Sc_2O_3	6.01	6.4			
$H_2O \cdot$2,6-lutNO	373– 398	1.60	1.9	353–373	365	+88.9
	398– 502	21.88	20.2			
	502– 583	10.94	12.5			
	583– 699	46.93	46.9			
	699–1113	12.53	12.2			
	Sc_2O_3	6.12	6.3			

[a] Dynamic air atmosphere.

TABLE 5

Decomposition schemes

$4Sc(F_3C{-}SO_3)_3(pyO)_6 \rightarrow 4Sc(F_3C{-}SO_3)_3(pyO)_3 + 12pyO$ $4Sc(F_3C{-}SO_3)_3(pyO)_3 \rightarrow 2ScO(F_3C{-}SO_3) + Sc_2O_3 + 12pyO + 5F_3C{-}SO_2F + 5COF_2 + 5SO_2$ $2ScO(F_3C{-}SO_3) + Sc_2O_3 \rightarrow 2Sc_2O_3 + F_3C{-}SO_2F + COF_2 + SO_2$	(1)
$2Sc(F_3C{-}SO_3)_3(2\text{-}picNO)_6 \rightarrow 2Sc(F_3C{-}SO_3)_3(2\text{-}picNO)_4 + 4(2\text{-}picNO)$ $2Sc(F_3C{-}SO_3)_3(2\text{-}picNO)_4 \rightarrow 2Sc(F_3C{-}SO_3)_3(2\text{-}picNO)_3 + 2(2\text{-}picNO)$ $2Sc(F_3C{-}SO_3)_3(2\text{-}picNO)_3 \rightarrow 2Sc(F_3C{-}SO_3)_3(2\text{-}picNO)_2 + 2(2\text{-}picNO)$ $2Sc(F_3C{-}SO_3)_3(2\text{-}picNO)_2 \rightarrow 2Sc_2O_3 + 4(2\text{-}picNO) + 3F_3C{-}SO_2F + 3COF_2 + 3SO_2$	(2)
$2Sc(F_3C{-}SO_3)_3(3\text{-}picNO)_6 \rightarrow 2Sc(F_3C{-}SO_3)_3(3\text{-}picNO)_3 + 6(3\text{-}picNO)$ $2Sc(F_3C{-}SO_3)_3(3\text{-}picNO)_3 \rightarrow Sc_2O_3 + 6(3\text{-}picNO) + 3F_3C{-}SO_2F + 3COF_2 + 3SO_2$	(3)
$2Sc(F_3C{-}SO_3)_3(4\text{-}picNO)_6 \rightarrow 2Sc(F_3C{-}SO_3)_3(4\text{-}picNO)_4 + 4(4\text{-}picNO)$ $2Sc(F_3C{-}SO_3)_3(4\text{-}picNO)_4 \rightarrow 2Sc(F_3C{-}SO_3)_3(4\text{-}picNO)_2 + 4(4\text{-}picNO)$ $2Sc(F_3C{-}SO_3)_3(4\text{-}picNO)_2 \rightarrow 2ScO(F_3C{-}SO_3) + 4(4\text{-}picNO) + 2F_3C{-}SO_2F + 2COF_2 + 2SO_2$ $2ScO(F_3C{-}SO_3) \rightarrow Sc_2O_3 + F_3C{-}SO_2F + COF_2 + SO_2$	(4)
$2Sc(F_3C{-}SO_3)_3(2,6\text{-}lutNO)_5 \cdot H_2O \rightarrow 2Sc(F_3C{-}SO_3)_3(2,6\text{-}lutNO)_5 + 2H_2O$ $2Sc(F_3C{-}SO_3)_3(2,6\text{-}lutNO)_5 \rightarrow 2Sc(F_3C{-}SO_3)_3(2,6\text{-}lutNO)_3 + 4(2,6\text{-}lutNO)$ $2Sc(F_3C{-}SO_3)_3(2,6\text{-}lutNO)_3 \rightarrow 2Sc(F_3C{-}SO_3)_3(2,6\text{-}lutNO)_2 + 2(2,6\text{-}lutNO)$ $2Sc(F_3C{-}SO_3)_3(2,6\text{-}lutNO)_2 \rightarrow ScO(F_3C{-}SO_3) + 4(2,6\text{-}lutNO) + 2F_3C{-}SO_2F + 2COF_2 + 2SO_2$ $2ScO(F_3C{-}SO_3) \rightarrow Sc_2O_3 + F_3C{-}SO_2F + COF_2 + SO_2$	(5)

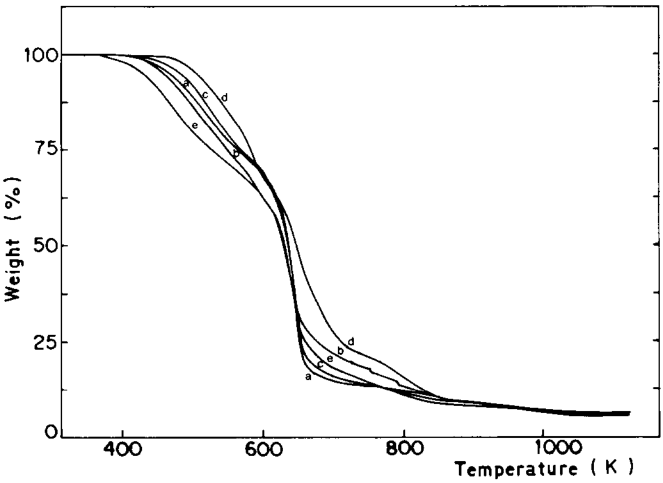

Fig. 1. TG curves obtained in dynamic air atmosphere for the complexes containing: (a) pyO, (b) 2-picNO, (c) 3-picNO, (d) 4-picNO, and (e) 2,6-lutNO.

ACKNOWLEDGEMENTS

J.D.A. is much indebted to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for a fellowship at the University of São Paulo. The authors thank the following for financial support: CNPq, Financiadora de Estudos e Projetos (FINEP) and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

REFERENCES

1 V.N. Tikhonov and O.A. Mikhailova, J. Anal. Chem. USSR, 38 (1983) 1522.
2 J.E. Roberts and J.S. Bykowski, Thermochim. Acta, 25 (1978) 233.