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Lanthanide(III) trifluoromethanesulfonate complexes in anhydrous acetonitrile

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Abstract

Anhydrous solutions of lanthanide(III) trifluoromethanesulfonates (triflates) in acetonitrile have been prepared and studied. Solubility measurements revealed that among the salts considered ($Ln(SO_3CF_3)_3$; Ln = La–Lu) only the heavier ones (Ln = Dy–Lu) are soluble ($S > 150$ mmol dm^{-3}) in strictly anhydrous conditions. Additions of small quantities of water proved that the solubility of lighter salts depends strongly on the presence of this reagent in solution. The ability of the triflate ion to coordinate the tervalent lanthanides in anhydrous solutions has been investigated by means of conductometric and FT-IR techniques. Quantitative IR measurements allowed detection of the main species in solution to be $Ln(SO_3CF_3)_2^+$ and $Ln(SO_3CF_3)_3$. Their apparent equilibrium constants are reported. The competition of perchlorate and triflate for the $Ln(SO_3CF_3)_2^+$ ion has also been studied. Measurements of the formation constant of the mixed complex, $Ln(SO_3CF_3)_2ClO_4$, suggested that the affinity of the perchlorate ion for the $Ln(SO_3CF_3)_2^+$ complex is about ten times lower than that of the third triflate. The effects of added water or dimethyl sulfoxide on the dissociation of the triflate complexes in AN were also obtained.

Introduction

The thermal instability of perchlorates of lanthanides(III) in the presence of organic impurities like grease or traces of acid [1, 2] can lead to serious complications in the preparation of solutions of these salts in acetonitrile (AN) [3]. Considering these hazards we have chosen to use the safer lanthanide trifluoromethanesulfonates (triflates) in our thermodynamic studies in non-aqueous solvents. In these media, perchlorates and triflates are generally considered as noncoordinating anions toward the lanthanide(III) cations [4–7]. However, some recent studies disagree with this assumption. Bünzli and co-workers demonstrated unequivocally that in moderately dissociating solvents such as AN or propylenecarbonate (PC) both lanthanide(III) salts (perchlorates [1] and triflates [8]) behave as 1:2 electrolytes. Moreover, the lighter lanthanides seemed to have appreciable amounts of inner-sphere complexation with more than one anion per cation. Other studies supported similar complexing abilities for triflate and perchlorate in organic solvents [9] although the triflates seem to be less dissociated than the perchlorates in AN [10]. In contrast to these data, a study of the enneahydrated lanthanide(III) triflates gave strong evidence that the salts are completely dissociated in AN [11]. The comparison between this latter observation and the results obtained in anhydrous solvents points out the crucial effect of the presence of water on the solute dissociation.

The purpose of the present study is to assess the nature and the extent of the interactions between the lanthanide(III) cations and the triflate anion in anhydrous AN. This study is preliminary to a series of thermodynamic investigations carried out by using tetraethylammonium triflate as inert electrolyte. Possible complex formation between lanthanide ions and the supporting electrolyte has been often neglected in thermodynamic studies. This may be a source of misinterpretation about the relevant factors in the complexing reactions of these 'hard' cations.

Experimental

Chemicals

Aldrich anhydrous acetonitrile, after further purification by distillation over P_2O_5 and storage over 4 Å

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molecular sieves, had a final water content of 0.2–0.5 mmol dm^{-3} and was used to prepare all the solutions. Lanthanide(III) triflates were prepared from direct reaction of the oxides (Aldrich 99.9%) with a slight stoichiometric deficiency of concentrated triflic acid (Janssen 99%) in H_2O. After the reaction reached completion (*c.* 1 day for most of the elements, 1 week for terbium) the excess of oxide was removed by filtration and the hydrated product obtained by evaporation while maintaining the temperature below 80 °C. The partly anhydrous compounds, $Ln(triflate)_3 \cdot xH_2O$ ($x = 0.1$–0.9), were obtained by heating at 80 °C under high vacuum (10^{-5}–10^{-6} torr) for about two weeks. Stock solutions of the salts, prepared by dissolving weighed amounts of these substances, were subjected to additional dehydration by overnight refluxing in a Soxhlet extractor packed with 4 Å molecular sieves. The final anhydrous solutions so obtained (water content $\leqslant 1$ mmol dm^{-3}) were standardized by complexometry with EDTA and diluted to the final experimental concentration which ranged from ~8 to ~33 mmol dm^{-3}.

Tetraethylammonium triflate was prepared by adding a solution of tetraethylammonium hydroxide (Janssen) to a diluted solution of triflic acid until neutrality was reached. After water evaporation, the crude salt was purified by dissolution in acetone and precipitated with benzene. The dry substance was obtained by heating at 60 °C for 24 h under high vacuum. Tetraethylammonium perchlorate (Fluka purum) was purified as described previously [12].

All the solutions were prepared, handled and stored in a stainless steel glovebox filled with dry nitrogen and provided with a gas purification system (water content < 1 ppm). The water content of the chemicals was measured using a Metrohm 684 KF Coulometer.

FT-IR measurements

FT-IR spectra were recorded under nitrogen purge at 25 ± 1 °C on a Nicolet 5 SX spectrometer with a 4 cm^{-1} resolution and 256 scans. For these measurements a single cell with barium fluoride windows and 28 μm thickness, determined by the method of the interference fringes [13], was used. The cell was filled in the glovebox, tightly closed, and transferred into the spectrometer cavity with a sealed container. The solvent and the solution spectra were recorded separately, ratioed against the background and converted to absorbance units. Successively, the solvent spectrum was numerically subtracted from the solution spectra in order to obtain the difference spectra. For quantitative measurements the absorbances of the peaks were evaluated by deconvolution of the difference spectra. The decomposition into the individual line bands used a Marquardt non-linear regression program, assuming Lorentzian lineshapes.

Conductometric measurements

The measurements were performed at 25 ± 0.2 °C by means of an Amel model 134 conductivimeter under a controlled atmosphere.

Results and discussion

In contrast to previous reports [11, 14], difficulties were encountered in dissolving some of the anhydrous salts during the initial experiments. For this reason we decided to carry out a preliminary study on the solubilities of the lanthanide(III) triflates in AN. These measurements, performed in order to obtain an operative, not a thermodynamic, solubility value, revealed that only the heavy (Dy–Lu) lanthanide triflates are soluble ($S > 150$ mmol dm^{-3}) in strictly anhydrous conditions while the solubility of the lighter triflates decreases greatly as the atomic weight of the lanthanide decreases. These latter salts are moderately soluble when the water-to-lanthanide(III) concentration ratios are relatively high but their solubilities decrease drastically as water is removed from the solution. For the neodymium compound, for example, the solubility is almost three times the value reported in Table 1 when the water concentration is raised to 45 mmol dm^{-3}. The values of the solubilities reported in Table 1 were obtained after the amount of water introduced to obtain a saturated solution was removed by refluxing with a Soxhlet extractor. This strong influence of water on the solubility of the lanthanide triflates can be explained by the high affinity of these ‘hard’ cations towards water. They, in fact, are preferentially solvated by water even in acetonitrile containing small quantities of water [1, 15].

Based on this strong effect on solubilities, the presence of water can be expected to exert also some influence on the dissociation of the triflates in AN. Preliminary measurements of the molar conductivities of anhydrous solutions containing 1.0 and 10.0 mmol dm^{-3} of Yb(III) triflate (136 and 58 Ω^{-1} mol^{-1} cm^2, respectively) disagree with a previous report [11] indicating lanthan-

TABLE 1. Solubility of $Ln(CF_3SO_3)_3$ (Ln = La–Lu) in anhydrous acetonitrile at 25 ± 0.5 °C

Ln(III)	S (mmol dm^{-3})
La	0.9
Pr	1.9
Nd	2.6
Sm	5.9
Eu	10.9
Gd	18.1
Tb	75.7
Dy–Lu	> 150

ide(III) triflates are present as 1:3 electrolytes in AN. The conductivity value in the 1.0 mmol dm^{-3} solution is in good agreement with the accepted value for 1:1 electrolytes in AN (140 Ω^{-1} mol^{-1} cm^2 [16]), while the value obtained for the more concentrated solution indicates the presence of even greater association between the triflate and the trivalent lanthanide ions.

Recently FT-IR investigations have been successfully employed to investigate the interaction between perchlorate and trivalent lanthanide ions in anhydrous AN [1]. The concentration of free ionic triflate, which strongly absorbs in the range 1400–1000 cm^{-1} [17], can be obtained with this experimental technique. In Fig. 1 the transmittance spectrum of acetonitrile in this IR spectral window is reported. In the same Fig. are also reported, as examples of uncoordinated and coordinated triflates (*vide infra*), the difference spectra of tetraethylammonium triflate 100 mmol dm^{-3} and of lutetium triflate 33.3 mmol dm^{-3} solutions. Acetonitrile shows a remarkable transparency in the region where the free and coordinated $CF_3SO_3^-$ ions show the strongest absorptions. This fact allows simple subtraction of the solvent spectrum from the sample spectra, with only a very small uncertainty introduced by this subtraction.

Generally the tetraethylammonium salts are considered to be completely dissociated in apolar solvents [16], so we have chosen the tetraethylammonium triflate as a source of free ionic triflate for the calibration experiments. The complete dissociation of this salt in AN was further shown by the following experimental evidence: (i) the molar conductivities of 1.0 and 10.0 mmol dm^{-3} tetraethylammonium triflate solutions, 173 and 136 Ω^{-1} mol^{-1} cm^2, respectively, were in good agreement with the values reported for the 1:1 electrolytes [16]; (ii) no significant differences in the bandshape were observed upon variation of the $Et_4NSO_3CF_3$ concentration from 10 to 175 mmol dm^{-3}; (iii) the increase of the absorbance of the peak centered at 1270 cm^{-1} with the concentration of $Et_4NSO_3CF_3$ was very linear ($A^{max}_{1270} = 5.542 \times C_{triflate}$; r factor = 0.9998) up to a salt concentration of 125 mmol dm^{-3}.

Comparison between the spectrum of the tetraethylammonium triflate solution, presented in Fig. 1, and the assignments reported in ref. 18 for the ionic $AgSO_3CF_3$ in the solid state allows one to assign the bands at 1270, 1223, 1155 and 1032 cm^{-1} to the triflate stretching modes $\nu_{as}(SO_3)$, $\nu_s(CF_3)$, $\nu_{as}(CF_3)$ and $\nu_s(SO_3)$, respectively. The large differences between the absorbance spectra in Fig. 1 reflect an extensive complexation of the triflate anion by Lu^{3+}. The relatively simple IR spectrum of the lutetium(III) salt is indicative of the presence in solution of at least two types of triflate groups. Apart from the observed weak band at 1270 cm^{-1} and the shoulder at ~1155 cm^{-1} assigned to the stretching modes of ionic triflate present in solution, the three strong bands at ~1330, ~1210 and ~1030 cm^{-1} and the remaining absorptions near 1235 and 1180 cm^{-1} can be assigned, on the basis of a previous report [17], to the SO_3 and CF_3 stretching modes of triflate coordinated to the metal ion. All the lanthanide(III) triflate solution spectra we have recorded show only small differences among them (Table 2) so the lutetium(III) spectrum reported in Fig. 1 can be considered as representative of all the lanthanide complexes.

Observation of Fig. 1 suggested that the vibration $\nu_{as}(SO_3)$ at 1270 cm^{-1} was the most suitable for quantitative measurements of the concentration of free triflate in solution. In fact it has the highest molar absorption coefficient (*c.* 2000 dm^{-3} mol^{-1} cm^{-1}) among all the vibrations of the free triflate ion and it appears

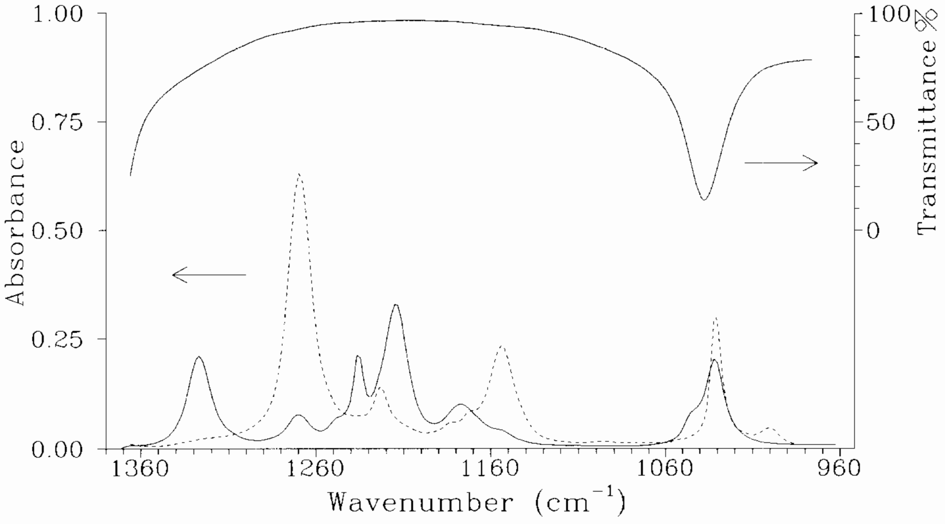

Fig. 1. IR difference spectra of tetraethylammonium triflate (– – –) and lutetium triflate (——) solutions in the spectral range of the main triflate vibrations. The upper trace represents the spectrum of acetonitrile in transmission units.

TABLE 2. IR frequencies observed for the difference spectra of tetraethylammonium (100 mmol dm^{-3}) and lanthanide(III) (~33 mmol dm^{-3}) triflate solutions in the range 2350–960 cm^{-1}

Freq. (cm^{-1})	Assignment[a]	Et$_4$N$^+$	Gd^{3+}[b]	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
2293	$\nu_3+\nu_4$(CH$_3$CN)	n.o.[c]	2312	2312	2312	2313	2314	2314	2314	2315
2253	ν_2(C–N)	n.o.[c]	2283	2284	2285	2285	2285	2287	2286	2288
			1328	1328	1328	1329	1328	1329	1329	1329
1270	ν_{as}(SO$_3$)	1270	1270	1270	1270	1270	1270	1270	1270	1270
			1248[d]	1248[d]	1249[d]	1249[d]	1249[d]	1249[d]	1249[d]	1250[d]
1237	ν_s(CF$_3$)	1223	1236	1236	1236	1236	1236	1237	1237	1237
			1213	1213	1213	1213	1214	1215	1215	1215
			1179	1179	1180	1179	1179	1179	1179	1179
1167	ν_{as}(CF$_3$)	1155	1155[d]	1155[d]	1155[d]	1155[d]	1155[d]	1155[d]	1155[d]	1155[d]
			1044[d]	1044[d]	1044[d]	1045[d]	1045[d]	1046[d]	1046[d]	1047[d]
1043	ν_s(SO$_3$)	1032	1028	1029	1030	1031	1032	1032	1032	1033

[a] The assignments for CH$_3$CN frequencies are taken from ref. 19, those for triflate from ref. 18. [b] Solubility limited the Gd solution to ~18 mmol dm^{-3}. [c] Not observed. [d] Shoulder.

in a spectral range almost free from interferences. As neighbouring bands can anyhow interfere to a certain degree on the relatively small absorbance of the peak at 1270 cm^{-1} we used the following curve fitting procedure to perform quantitative analyses.

Firstly, we decomposed the experimental spectra of free triflate solutions. They were simulated by three Lorentzian curves in the range 1000–1360 cm^{-1}; ν_{as}(SO$_3$) at 1270 cm^{-1}, full width at half height (fwhh) = 15 cm^{-1}; ν_s(CF$_3$) at 1222 cm^{-1}, fwhh = 8 cm^{-1}; ν_{as}(CF$_3$) at 1153 cm^{-1}, fwhh = 18 cm^{-1}. Successively, a calibration curve was obtained by plotting the calculated absorbance at 1270 cm^{-1} versus the analytical concentration of the salt in solution. Finally, the concentration of free triflate in the solutions containing the metal ions was calculated by using the calibration curve and the value of the absorbance of the peak at 1270 cm^{-1} obtained after spectral decomposition ($A^{\max}_{1270}$). The result of such a decomposition for a lutetium(III) triflate solution is given in Fig. 2. The experimental spectrum is simulated by eight Lorentzian curves of which for three, those representing the free triflate vibrations, both the linewidth and the band positions were kept constant during the deconvolution. A similar procedure was used for the other Ln(III) ions.

The values of $A^{\max}_{1270}$ and of the free triflate concentration for all the systems studied are given in Table 3. In all the solutions examined, the concentration of uncoordinated triflate was less than one third of the total triflate. For this reason we assumed that eqn. (1) could represent the prevalent equilibrium in solution in the range of concentrations investigated

$$\mathrm{Ln(SO_3CF_3)_2{}^+ + CF_3SO_3{}^-} \overset{K_3}{\rightleftharpoons} \mathrm{Ln(SO_3CF_3)_3} \qquad (1)$$

By simple calculations we obtained the concentrations of all the species present in the lanthanide solutions along with an estimate of the apparent equilibrium constants, K_3. All these results are presented in Table 3. In column 9 of Table 3 the absorbances of the IR vibration previously assigned to the coordinated triflate, $A^{\max}_{\sim 1330}$, are reported. When the values of $A^{\max}_{\sim 1330}$ are divided by the total amount of associated triflate (i.e. 3[Ln(CF$_3$SO$_3$)$_3$] + 2[Ln(CF$_3$SO$_3$)$_2{}^+$]) and by the thickness of the cell, rather constant values of the molar absorbance ($\epsilon_{\sim 1330}$) are obtained for all the lanthanides investigated. This gives a measure of the quality of internal consistency in the data.

Within the experimental uncertainties, the log K_3 values in Table 3 show a consistent small decrease with increasing atomic number. Since the cationic radius is decreasing with Z, the charge density is increasing which would suggest that log K_3 should increase with Z. It seems probable that the observed decrease is a result of increased steric crowding as the third ligand is added to Ln(CF$_3$SO$_3$)$_2{}^+$. In Fig. 3, plots of log K_9 for the coordination of the ninth dimethyl sulfoxide (DMSO) molecule to the [Ln(DMSO)$_8$]$^{3+}$ complex in anhydrous AN [20] and log K_3 of triflate (present work) are shown. The curves are almost parallel, suggesting a common explanation. Since solvation effects are not expected to be similar in these systems, the simplest common factor would seem to be steric crowding.

Spectra in the region where absorptions of coordinated acetonitrile occur gave results in good agreement with the data already published by Bünzli and coworkers. The shifts of the frequencies ν_2 and $\nu_3+\nu_4$ in respect to the bulk vibrations have values between those observed for the solutions containing lanthanide(III) nitrates [21] and those for the solutions con-

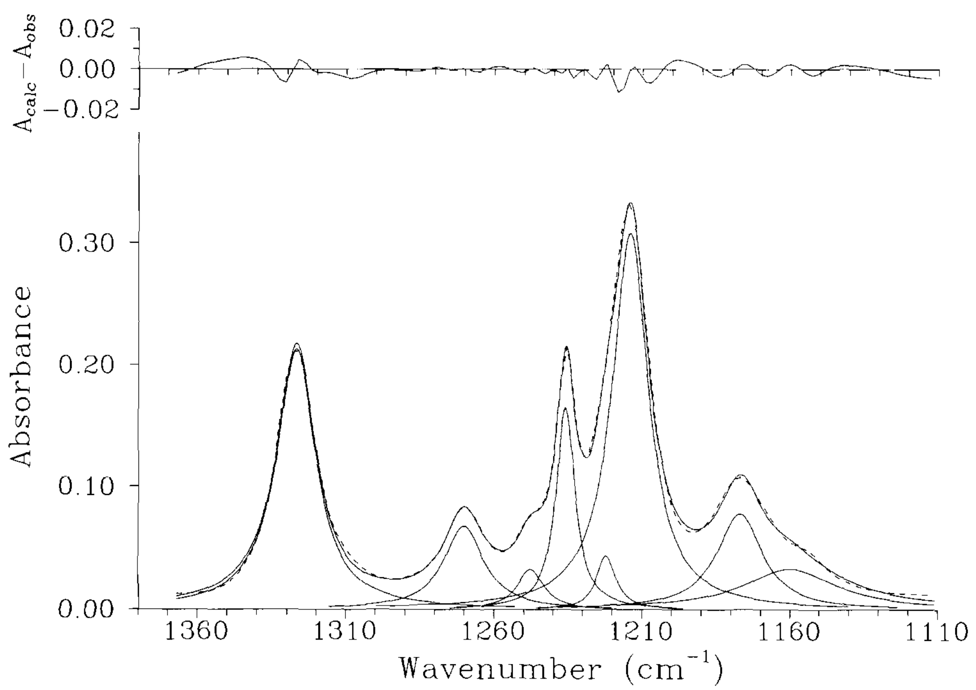

Fig. 2. Result of a spectral deconvolution. Experimental (– – –) and calculated (——) spectra for a 33.9 mmol dm^{-3} lutetium(III) triflate solution. Eight Lorentzian functions were employed to simulate the experimental spectrum. The residuals are reported in the top of the Figure.

TABLE 3. The concentrations in mmol dm^{-3} of free triflate, [L$^-$], and of lanthanide(III) triflate complexes in solutions containing different amounts of the salts, C_{ML_3}. The log $\bar{K}_3$ values represent the average of two or three independent measurements of the apparent constant for the formation of tris-triflate complex, K_3. $\epsilon_{\sim 1330}$ is the calculated molar absorbance of the coordinated triflate at ~1330 cm^{-1} in l mol^{-1} cm^{-1}. The estimated errors for [L$^-$] are of the order of 5%

M^{3+}	C_{ML_3}	A^{max}_{1270}	[L^-]	[ML_2^+]	[ML_3]	K_3	log $\bar{K}_3$	$A^{max}_{\sim 1330}$	$\epsilon_{\sim 1330}$
Gd	9.19	0.0229	3.80	3.80	5.39	372	2.52	0.0463	696
	18.38	0.0389	6.45	6.45	11.93	286		0.1040	763
Tb	11.14	0.0260	4.32	4.32	6.82	366		0.0639	784
	21.12	0.0366	6.08	6.08	15.04	408	2.58	0.1267	790
	33.41	0.0494	8.19	8.19	25.22	376		0.2011	780
Dy	10.67	0.0254	4.22	4.22	6.45	362		0.0632	812
	21.37	0.0397	6.59	6.59	14.75	339	2.53	0.1329	825
	32.01	0.0516	8.56	8.56	23.45	320		0.2014	822
Ho	11.07	0.0266	4.41	4.41	6.66	343		0.0640	794
	22.13	0.0410	6.80	6.80	15.33	332	2.53	0.1328	796
	33.20	0.0506	8.40	8.40	24.80	351		0.2006	786
Er	11.18	0.0282	4.68	4.68	6.50	297		0.0637	788
	22.35	0.0440	7.31	7.31	14.04	281	2.45	0.1373	821
	33.53	0.0562	9.34	9.34	24.19	277		0.2109	825
Tm	11.02	0.0293	4.86	4.86	6.16	260		0.0644	816
	22.03	0.0456	7.58	7.58	14.45	252	2.41	0.1343	820
	33.05	0.0581	9.65	9.65	23.40	252		0.2040	814
Yb	11.23	0.0314	5.22	5.22	6.01	221		0.0629	789
	22.45	0.0486	8.06	8.06	14.39	221	2.32	0.1287	775
	33.68	0.0665	11.05	11.05	22.63	185		0.1993	791
Lu	11.30	0.0316	5.24	5.24	6.06	220		0.0623	776
	22.61	0.0483	8.01	8.01	14.60	227	2.33	0.1292	771
	33.91	0.0662	10.98	10.98	22.93	190		0.1973	776

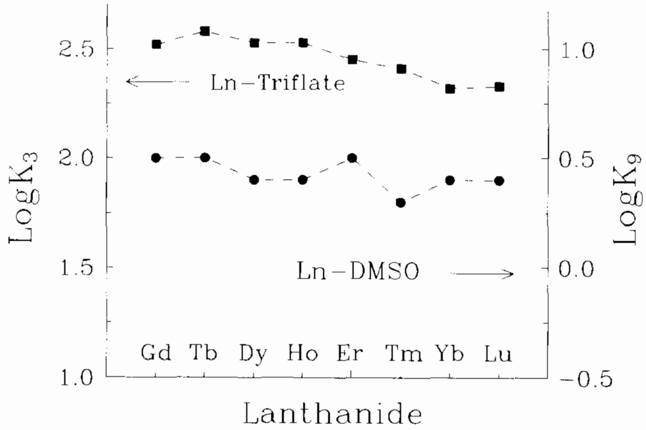

Fig. 3. Plots of log K for the formation of Ln(Triflate)$_3$ and [Ln(DMSO)$_9$]$^{3+}$ complexes in anhydrous acetonitrile.

taining perchlorates [1]. This trend reflects the different electron density of the lanthanide(III) ion in the nitrate, triflate and perchlorate complexes.

It has been suggested that perchlorate and triflate ions exhibit similar affinity toward the lanthanide(III) cations in methanol [9]. The present data suggest that $CF_3SO_3^-$ does coordinate the metal ions stronger than ClO_4^- in AN since in similar experimental conditions a larger number of triflate ions (2 or 3) than perchlorate (1 or 2, ref. 1) are bonded to each Ln^{3+}. A quantitative evaluation of the relative complexing ability of $CF_3SO_3^-$ and ClO_4^- versus Lu^{3+} and Tb^{3+} was obtained by the FT-IR spectra of solutions containing known concentrations of lanthanide(III) triflate and different amounts of tetraethylammonium perchlorate. Three independent experiments for each of the metal ions were carried out. In each experiment the concentration of perchlorate varied from ~20 to ~80 mmol dm^{-3}. Due to the competition between perchlorate and triflate, the spectra of the solutions revealed an increase of free triflate concentration upon addition of perchlorate (Fig. 4). The values of the concentrations of free triflate, determined by the deconvolution method illustrated above, along with the apparent equilibrium constant K_3 and the mass balance equations of perchlorate, triflate and metal ion, allowed us to calculate an apparent formation constant for the mixed complexes of Tb and Lu according to the equation:

$$Ln(SO_3CF_3)_2^+ + ClO_4^- \overset{K_{mix}}{\rightleftharpoons} Ln(SO_3CF_3)_2ClO_4 \quad (2)$$

The values of log K_{mix} obtained are 1.64±0.10 (Tb) and 1.59±0.10 (Lu) which agree within experimental error. The similarity of the values for these metal ions indicates that perchlorate bonds equally to the metal, regardless of the ionic radius of the cation. A comparison between the values of these equilibrium constants and the K_3 values suggests that the affinity of the perchlorate ion for the lanthanide(III) bis-triflate complex is approximately ten times lower than the one of the triflate itself. Perhaps, the steric crowding is balanced by the increased charge density to result in the similar values of K_{mix}.

Based on these constants, the percentages of $Ln(SO_3CF_3)_2ClO_4$ and $Ln(SO_3CF_3)_3$ complexes in a solution containing 10 mmol dm^{-3} of lutetium triflate and 70 mmol dm^{-3} of tetraethylammonium perchlorate are quite similar, 40.2 and 42.1%, respectively. More-

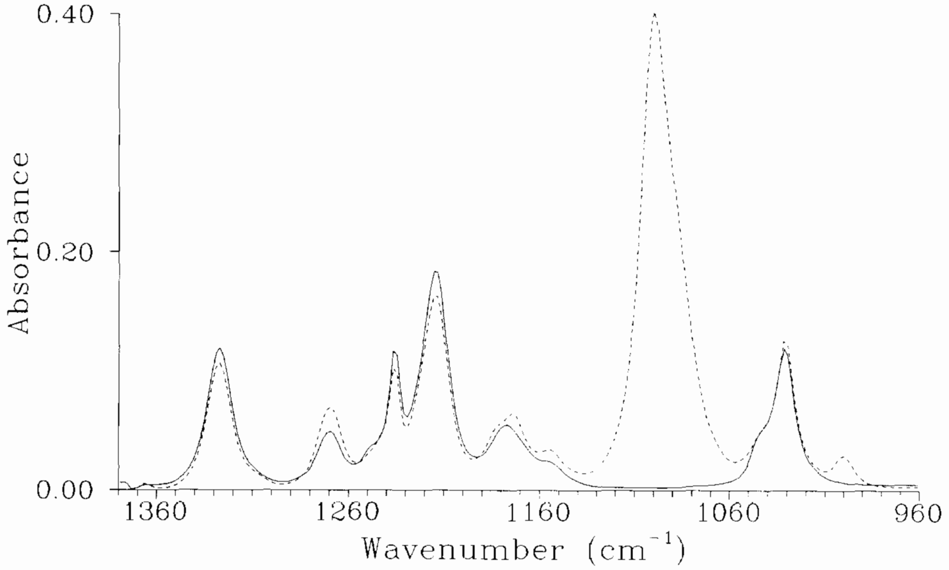

Fig. 4. Difference spectra of solutions containing 33.9 mmol dm^{-3} of Lu(SO$_3$CF$_3$)$_3$. The dashed line represents the absorbance of a solution containing 80 mmol dm^{-3} of tetraethylammonium perchlorate.

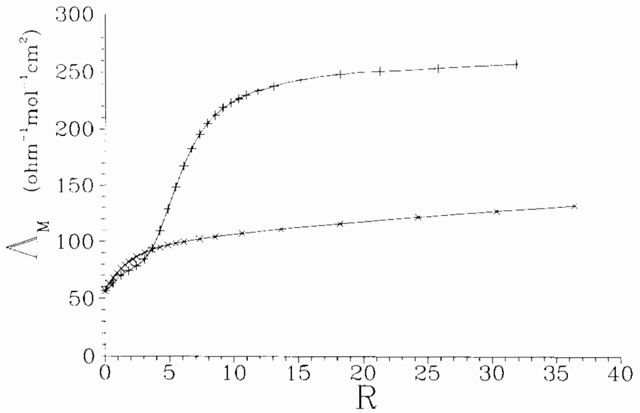

Fig. 5. Molar conductance of solutions containing 10 mmol dm^{-3} of $Lu(SO_3CF_3)_3$ and different amounts of water (x) and dimethyl sulfoxide (+). *R* denotes the ratio between the moles of water or dimethyl sulfoxide and the moles of metal ion in solution.

over, if the lutetium concentration is increased to 20 mmol dm^{-3} and the concentration of the alkylammonium salt to 40 mmol dm^{-3}, the percentages change drastically to 58.2 and 23.4%. These differences in the composition of the solution can play a non-negligible role when the tetraalkylammonium perchlorates are employed to adjust the ionic medium in thermodynamic studies involving lanthanide(III) triflates.

The preferential solvation of lanthanide ions by water in AN has been mentioned earlier. A question arises as to how much the preferential solvation by a neutral ligand influences the dissociation of the triflate complexes. We obtained a qualitative answer to this question by conductivity measurements. In Fig. 5 the values of the molar conductivity of a 10 mmol dm^{-3} solution of lutetium triflate, containing different concentrations of water and dimethyl sulfoxide, are reported. The different dissociating power of the substances considered in respect to the lanthanide complexes is quite evident. When the ratio between the competing species (water or DMSO) and the metal ion is higher than 20 the curves reach two distinct plateaux in the range expected for 1:1 electrolytes (120–160 Ω^{-1} cm^2 mol^{-1} [16]) if water is the competing ligand. By contrast, dissociation continues until a second triflate is released when DMSO is employed (molar conductances accepted for 1:2 electrolytes: 220–300 Ω^{-1} cm^2 mol^{-1} [16]). No interaction between trivalent lanthanides and perchlorate ions was detected in anhydrous solutions of acetonitrile containing DMSO and metal ions in a concentration ratio higher than 7:1 [20]. This last observation and the previous finding reflect the stronger donating power toward the lanthanide cations of triflates in comparison to perchlorate ions.

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