NMR AND RAMAN SPECTROSCOPIC STUDY OF COMPLEX FORMATION BETWEEN 2-METHYL-2-AZABICYCLO-[2,2,2]-OCTA-3-ONE AND TiCl₄

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ABSTRACT

From analysis of ¹H and ¹³C NMR and Raman spectroscopic data, in CDCl₃ and 1,1,2,2-tetrachloroethane- d_2 solution, the lactam 2-methyl-2-azabicyclo-[2,2,2]-octa-3-one (L) was found to form complexes with TiCl₄ (M) of overall composition M₂L, ML and ML₂. Two forms of the ML₂ complex were observed by NMR. In all these complexes, Ti coordinates to the carbonyl oxygen, and the metal—carbonyl bond is of the same type. The complexes ML and ML₂ contain hexacoordinated Ti; in M₂L the coordination number is probably five. The dynamics of exchange of the lactam between the ML₂ complexes and the uncomplexed form have been characterized and structures are proposed for the four complexes.

INTRODUCTION

Lactams interact strongly with $TiCl_4$ (M) to form very stable complexes. The structure of these complexes in solution is generally unknown. As complexes of lactams with $TiCl_4$ are also formed in the course of $TiCl_4$ -catalyzed cationic polymerization of lactam rings, data on their structure are of importance in studies of the mechanism of such polymerizations.

The interaction of Lewis acids with amides has been studied by NMR and vibrational spectroscopy by a number of authors [1-5]. In these studies it was shown that coordination takes place predominantly via the carbonyl oxygen, and leads to an increase of the double-bond character of the amide bond. For complexes of dimethyl formamide with TiCl₄, spectra of the complexed and free forms could be differentiated in ¹H NMR spectra and the kinetics of exchange between these forms was studied [2]. NMR spectra of 2-azetidones (β -lactams) in the presence of TiCl₄ were measured and assigned by Bose et al. [6, 7], without any attempt at structural correlations. Interaction of seven- and higher-membered lactams with TiCl₄ in solution has not been studied by NMR and vibrational spectroscopy so far.

In our work we have tried to obtain some information on the structure of the complexes of lactams with $TiCl_4$ by analysis of their Raman and NMR

spectra. We have also tried to characterize the transitions between various types of complexes and the free lactam from the temperature dependence of NMR spectra. The rigid molecule 2-methyl-2-azabicyclo-[2,2,2]-octa-3-one (*N*-methylisoquinuclidone, shortened as NMeiQ or L) was chosen as model lactam. This lactam can assume only the *cis*-form of the amide group, and cannot form any conformational isomers. With it the interaction of the lactam *cis*-amide bond with a Lewis acid can be studied without the interference of conformational effects.

EXPERIMENTAL

Synthesis of NMeiQ

2-Azabicyclo-[2,2,2]-octa-3-one was prepared by rapid overheating of p-aminohexahydrobenzoic acid, obtained by hydrogenation of p-aminobenzoic acid (20 g) on Pt catalyst (3.5 g). Lactam (3 g) was transformed to the sodium salt by sodium hydride in a mixture of dry dimethylsulphoxide and benzene; without isolation, the salt was methylated by an excess of methyl iodide. The whole reaction was performed in an argon atmosphere without access of air. After decomposition by water, the reaction mixture was extracted by chloroform. Following evaporation of solvent the crude product was purified by column chromatography on silica gel and distillation at reduced pressure: b.p. 70°C/0.3 torr, m.p. 66.5°C; yield 75%. The purity of the product was controlled by gas chromatography and elemental analysis: found C 68.92%, H 9.34%, N 10.13%; calc. C 69.03%, H 9.41%, N 10.06%. The TiCl₄ was purified by shaking with mercury and by double distillation without access of air. Specific amounts were kept in sealed ampoules under argon. The solvents $CDCl_3$ and 1, 1, 2, 2-tetrachloroethane- d_2 (TCE) were dried by molecular sieves and distilled in an argon atmosphere.

Measurement of spectra

Solutions of the samples were prepared in a mixing vessel equipped with a magnetic stirrer and connected to a vacuum line and to argon. Without access of air they were transferred to the measuring cells (glass tubes of external diameter 5 mm) which were sealed and used both in the NMR and Raman measurements. In the resulting solutions, NMeiQ concentrations were about 20 wt% in CDCl₃ and 9–22 wt% in TCE. In TCE, mixtures of NMeiQ and TiCl₄ could be prepared at molar ratios [L]: [M] = R in the range 0–1 and for R > 2 without any limit. For R values in the range 1–2 a yellow crystalline complex separated from the solution which after washing with chloroform and drying was also studied by Raman spectroscopy. The elemental analysis of this crystalline product (C 29.40%, H 4.20%, N 4.27%) corresponded to the overall composition ML (C 29.12%, H 3.98%, N 4.26%). In CDCl₃, mixtures of NMeiQ and TiCl₄ could only be prepared for R > 2. Raman spectra of the solutions were measured in the above-mentioned NMR cells in the 90° arrangement by means of the Coderg LRDH-800 spectrometer, with excitation by the argon ion laser Coherent CR-3. Spectra were recorded and treated by means of the PDP 11-05 computer in the Tracor system.

¹H NMR spectra were measured at 100 MHz on the JEOL PS-100 spectrometer, ¹³C NMR spectra at 15 MHz on the JEOL FX-60 spectrometer. In all cases chemical shifts were referred to internal TMS. The spectra of the samples were recorded about 30 min after sealing, and their reproducibility was tested by re-measurement of room-temperature spectra after heating to 140°C and cooling, and after 6 weeks. In variable temperature measurements, temperature was calibrated by means of chemical shifts of methanol and ethylene glycol in ¹H NMR spectra [8]. The Tracor TN 4000 Multichannel Analyser was used for spectra simulation.

RESULTS AND DISCUSSION

Raman spectra

Raman spectra of the complexes were measured both in $CDCl_3$ and in TCE solution. After subtraction of the solvent spectrum, Raman spectra of samples with equal molar ratio R = [L]: [M] measured in CDCl₃ and TCE were virtually identical. For studies of samples with R > 2, CDCl₃ solutions were more suitable, because the Raman spectrum of $CDCl_3$ is little affected by the presence of TiCl₄ and the CDCl₃ bands do not seriously overlap the bands of free lactam and the complexes. Solutions with R < 2had to be measured in TCE, in spite of the fact that a Raman spectroscopic study of this system is more complicated, because the conformational equilibrium of TCE is affected by TiCl₄, with resulting changes of some line intensities. Therefore, when working with this solvent, solutions with equal molar concentrations of TiCl_a were used in a series of studies. A further drawback of work with TCE solutions lies in the fact that TCE bands overlap some important bands of the free lactam and the complexes. This can be overcome by digital subtraction of the spectrum of the solvent, but the spectra in the range of the band overlap are of poorer quality.

Raman spectra of solutions of NMeiQ and TiCl₄, with different ratios, R, from which the spectra of the solvents have been digitally subtracted are shown in Fig. 1. As a result of the reaction of NMeiQ with TiCl₄, spectra of solutions with R > 0.42 do not exhibit bands of free TiCl₄ (Fig. 1B, C, E) whereas in spectra of solutions with R < 2.1 some bands characteristic of the Raman spectrum of free NMeIQ are missing (Fig. 1C, E, F, G). The former effect is best observed on the strong band of the Ti—Cl stretching vibration of free TiCl₄ at 396 cm⁻¹ (Fig. 1H) and the latter on the band of free NMeiQ at 598 cm⁻¹ (Fig. 1A). Complex formation is also evidenced by a shift of the frequency of the C=O stretching vibration, from 1644 cm⁻¹ in



Fig. 1. Raman spectra of NMeiQ and its mixtures with TiCl₄. (A) NMeiQ melt; (B) NMeiQ + TiCl₄, R = 6.9, CDCl₃ solution; (C) NMeiQ + TiCl₄, R = 2.1, CDCl₃ solution; (D) solid complex of composition ML, precipitated from the mixture with R = 2 in TCE; (E) NMeiQ + TiCl₄, R = 0.91, TCE solution; (F) NMeiQ + TiCl₄, R = 0.42, TCE solution; (G) NMeiQ + TiCl₄, R = 0.22, TCE solution; (H) TiCl₄. In B, C, E, F, and G solvent peaks were digitally subtracted. x Frequency of solvent peak compensation.

free NMeiQ to about 1613 cm⁻¹ in the complex, and by an appearance of new bands which are most prominent in the range 200-500 cm⁻¹.

Raman spectrum of the complex of overall composition ML_2

From the missing free lactam and free TiCl₄ bands in Raman spectra of solutions of NMeiQ and TiCl₄ in CDCl₃ and TCE with R = 2.1 (Fig. 1C), it is evident that all TiCl₄ and NMeiQ present in the solution is bound in complex form. As only one type of complex is observed, its overall composition must correspond to the formula ML₂. Spectra of solutions with R > 2.1 exhibit bands of free NMeiQ, in addition to the bands observed in the spectrum of the solution with R = 2.1. For all samples with R > 2.1, digital subtraction of the spectrum of the free lactam led to residual Raman spectra practically identical to the spectra of solutions with R = 2.1.

The content of free lactam in CDCl₃ solutions with R > 2.1 was determined from the ratio of the intensities of the CDCl₃ band at 647 cm⁻¹ and the band of the free lactam at 598 cm⁻¹, which was found to be absent in the spectra of the complex forms. The molar content of free lactam determined in this way, $[L_f]$, was subtracted from the total molar content of lactam, [L], in the mixture (Table 1). In this way it was found that for all samples with R > 2.1, the molar ratio of TiCl₄, [M], and NMeiQ bound in the complex, $[L_c]$, is 1:2.1 ± 0.1. Similar values were obtained also when $[L_c]$ was determined from bands characteristic of the complex.

The content of free lactam was also determined from the ratio of the intensities of lactam bands at 812 and 598 cm⁻¹ for all samples with R > 2.1. The intensity of the band at 812 cm⁻¹ is composed of contributions from both free and complexed lactam (see Fig. 1). This determination, which is applicable in both solvents studied, yields values in agreement with the results obtained from the free lactam and CDCl₃ solvent bands. All these measurements lead to the conclusion that for all values of R > 2.1, Raman spectra exhibit the bands of one kind of complex only, of overall composition ML₂.

The complexes of TiCl₄ with NMeiQ are yellow. For the solution of the complex with R = 2.6 in CDCl₃, the Raman spectra were measured with excitation line wavelengths of 4880 Å and 5145 Å (Fig. 2). It was found that the intensities of some lines, as related to the intensities of the solvent bands, are higher for the excitation wavelength 4880 Å than for 5145 Å; this indicates that the spectrum of the complex is affected by the resonance Raman effect. The largest intensity increase is exhibited by the C=O stretching vibration, and by the band at 342 cm⁻¹ which we assigned to the Ti-O stretching vibration. The predominant localization of the resonance Raman effect on these two vibrations of the complex indicates that NMeiQ is coordinated to Ti via the carbonyl oxygen.

TABLE 1

Intensities of Raman lines and molar composition of various samples of NMeiQ and $TiCl_4$ in CDCl₃

Molar composition of samples				Intensity of Raman			Molar composition calc.		
R	[L]	[M]	[CDCl ₃]	lines			trom spectra		
				812 (cm ⁻¹)	647 (cm ⁻¹)	598 (cm ⁻¹)	[L _f]	[L _c]	[L _c]/[M]
2.1	0.167	0.0797	0.754	2165	7540		0	0.167	2.1
4.0	0.174	0.0440	0.783	1873	7830	409	0.081	0.093	2.1
6.9	0.177	0.0257	0.797	1600	7970	620	0.123	0.054	2.1
21.1	0.180	0.0085	0.811	1363	8110	820	0.162	0.018	2.1
80	0.182	0	0.818	1304	8180	966	0.182	0	



Fig. 2. Raman spectra of NMeiQ with TiCl₄ in CDCl₃ solution, R = 2.6. Excitation lines: (A) 5145 Å, (B) 4880 Å, (X) CDCl₃ bands.

Raman spectrum of the complex of overall composition ML

After subtraction of the spectra of solvents, the Raman spectra of the solutions with R = 0.91 and 2.1 are practically identical (Fig. 1E, C). In both cases, bands of free lactam and of free TiCl₄ cannot be detected in these spectra. Therefore in both cases, all TiCl₄ and all NMeiQ must be bound in complexes, while in the former case the overall composition of the complex corresponds to ML, and in the latter case to ML₂. The only difference in the spectra of these two samples is observed in the intensities of the bands of the complex, which are lower for solutions with R = 0.91 than for solutions with R = 2.1. For a quantitative determination, the intensities of the bands of the complex at 433, 391, 342, 294 and 1613 cm⁻¹ have been related to the TCE band at 701 cm⁻¹. For equal concentration of TCE, bands of the complex in solutions with R = 2.1. With regard to the identity of the frequencies of the Raman

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spectra of the complexes ML and ML_2 , it is assumed that both complexes must have the same geometrical arrangement of chlorine atoms and NMeiQ ligands, which is possible only for an equal coordination number of Ti, and that also in both these complexes the site of coordination on the lactam is the carbonyl oxygen.

We have also measured the Raman spectra of the precipitate formed when mixing $TiCl_4$ with NMeiQ in R ratios between 1 and 2. The spectra of this precipitate, which according to elemental analysis has an overall composition ML, differ from the spectra of the complex ML (and also ML_2) in solution to such an extent (Fig. 1D) that a completely different structure must be assumed for the precipitate.

Raman spectrum of the complex with overall composition M_2L

In samples with R < 1, additional bands appear next to lines characteristic of the complexes ML_2 and ML. In the range 200–500 cm⁻¹, the lines at 420, 386 and 317 cm^{-1} evidently correspond to a different type of complex. The spectrum of the sample with R = 0.42 does not exhibit any bands typical of the ML₂ and ML complexes, and shows only weak bands of free TiCl₄ next to the bands of a new complex (Fig. 1F). The contents of free TiCl₄ in samples with R = 0.42 and 0.22 were calculated from the ratio of intensities of the TiCl₄ band at 396 cm⁻¹ and of the TCE band at 349 cm⁻¹. In both these samples an identical spectrum was obtained after subtraction of the spectra of solvent and of free TiCl₄, and according to the determined ratio of bound TiCl₄ and NMeiQ this spectrum corresponds to a complex of overall composition M_2L . The carbonyl frequency of this complex does not differ significantly from that of the complexes ML and ML₂, indicating that also in this complex coordination takes place via the carbonyl oxygen. As the difference between the Raman spectra of the complexes M_2L and ML_2 in the range 200-500 cm⁻¹ is profound, it must be assumed that the complex of overall composition M₂L has a different geometrical structure and a different coordination number on Ti.

NMR spectra

¹H NMR spectra of complexes of NMeiQ with TiCl₄ in tetrachloroethaned₂ corresponding to various values of R, together with the spectrum of the free lactam, are shown in Fig. 3. In Table 2 the chemical shifts of the lactam proton groups are summarized for samples with various values of R in TCE and CDCl₃. In the spectrum of the free lactam, the bands at highest field correspond to the protons of the four CH₂ groups, with the CO–CH band at 2.47 ppm, the N–CH₃ band at 2.90 ppm and the N–CH band at lowest field, at 3.46 ppm. With increasing content of Ti, the bands of all proton groups shift to lower field, the magnitude of the low-field shifts differing for different proton groups. Largest low-field shifts are experienced by the

TABLE 2

$\overline{R^a}$	Form	δ					
		N-CH ₃	N-CH	СОСН			
In TCE	-						
\$	b	2.90	3.46	2.47			
	F	2.90	3.48	2.46			
4.7	Cr	3.48	3.98	3.77			
	Сп	3.34	3.93	3.56			
2.05	Cī	3.44	3.86	3.76			
	Cπ	3.30	3.80	3.54			
0.91	ML	3.44	4.02	3.52			
0.49	M ₂ L	3.46	4.06	3.50			
In CDCl	1						
~	c	2.93	3.49	2.50			
	F	3.00	3.60	2.62			
4.0	Cr	3.52	4.03	3.81			
	с _п	3.39	3.98	3.60			
2.1	$\overline{C_{I}}$	3.52	4.05	3.80			
	$\mathbf{c}_{\mathbf{n}}$	3.38	3.98	3.61			

Chemical shifts δ of proton groups of NMeiQ and its various forms in mixtures with TiCl₄ (ppm from TMS)

 ${}^{a}R = [\text{NMeiQ}]:[\text{TiCl}_{4}]$. b Pure NMeiQ in TCE solution. c Pure NMeiQ in CDCl₃ solution.

bands of the CO–CH group which in the spectra of the complexes appear below the $N-CH_3$ band. This is in agreement with the generally accepted idea that Lewis acids are predominantly coordinated to the carbonyl oxygen in amides [3-5]. Spectra (a) and (b) in Fig. 3, corresponding to R values of 0.49 and 0.91, are very similar and exhibit the same number of bands as the spectrum of free lactam, in spite of the fact that in this composition range the existence of two different complexes has been demonstrated by Raman spectra. On the other hand, in Fig. 3 the spectra (c) and (d), with R > 2, exhibit a larger number of bands than the spectrum of the free lactam. Considering chemical shifts and integrated band areas, for spectrum (c) with R = 2.05, the bands at 3.30 and 3.44 ppm can be assigned to two different N-CH₃ groups, and the partly overlapping bands at 3.54, 3.76 and 3.86 ppm to two different CO–CH groups and two corresponding N–CH groups. Spectrum (d), corresponding to R = 4.7, exhibits bands at the same frequencies as spectrum (c), and besides that also bands only slightly shifted with respect to the bands of the free lactam. This leads to the conclusion that in systems with R > 2, in the complex of NMeiQ with TiCl₄, the lactam is bound in two different ways, in spite of the fact that Raman spectra seemed to indicate the presence of only one type of complex in this composition range.

The dependence of ¹H NMR spectra on composition in the range R =

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Fig. 3. ¹H NMR spectra of NMeiQ with TiCl₄ in TCE solution. (a) R = 0.49; (b) R = 0.91; (c) R = 2.05; (d) R = 4.7; (e) NMeiQ only.

Fig. 4. 'H NMR spectra of NMeiQ with TiCl₄ in CDCl₃ solution, range of N-CH₃, N-CH and CO-CH groups. (a) R = 2.1; (b) R = 2.6; (c) R = 4.0; (d) R = 6.9.

2.1-6.9 in CDCl₃ solution is shown in detail in Fig. 4. In the range 2.8-3.5 ppm these spectra exhibit three N-CH₃ bands. Of these, the two N-CH₃ bands at lower field do not change their shift and only slightly change their shape in dependence on composition. In the following the N-CH₃ band at lowest field will be designated as corresponding to complex I (C₁), the N-CH₃ band at higher field as corresponding to complex II (C₁). The shift and shape of the third N-CH₃ band at highest field change profoundly with composition of the mixture. At R = 6.9, its shift corresponds to that of the N-CH₃ band of free lactam, at R = 2.1 it almost coincides with the N-CH₃ band of complex II. While shifting to lower field, this band also undergoes broadening. It is assumed that this behaviour is a consequence of exchange of molecules of free NMeiQ with lactam molecules in various solvation sphere of complexes I and II. For simplicity, in the following, the third N--CH₃ band at highest field will be designated as the band of "free" lactam (F). Because of band overlap, it is not easy to determine quantitatively the relative populations of the two complexes. From the measured spectra it can be only qualitatively stated that the relative populations of the two complexes either do not change, or change only slightly with composition of the mixture, and that the relative amounts of the two complexes are approximately equal. As will be shown in greater detail later on, their relative populations do not even change with temperature.

Relatively good quantitative measurement is possible for the ratio of areas of the N-CH₃ and CO-CH bands of the "free" lactam to the total integrated intensity of all bands of the spectrum for various R values. We have tried to apply these data for a determination of the composition of the complexes corresponding to the N-CH₃ signals of C_I and C_{II}. Our determination of the overall composition of the complexes C_I and C_{II} was based on the total molar concentrations of TiCl₄, [M], and of NMeiQ, [L]. If the solution contains, in addition to "free" lactam, complexes of overall composition ML_m and ML_n, then the fraction of "free" lactam in this solution is

$$x_{\mathrm{F}} = \frac{[\mathrm{F}]}{[\mathrm{L}]} = 1 - \frac{m[\mathrm{ML}_m]}{[\mathrm{L}]} - \frac{n[\mathrm{ML}_n]}{[\mathrm{L}]}$$

where $[ML_m] + [ML_n] = [M]$.

If the relative populations of the two complexes are independent of the composition of the solution, then

$$\frac{[ML_m]}{[ML_n]} = K; [ML_m] = \frac{K[M]}{1+K}; [ML_n] = \frac{[M]}{1+K}$$

Rearranging

$$x_{\rm F} = 1 - \frac{[M]}{[L]} \left(\frac{mK + n}{1 + K} \right) = 1 - a \frac{[M]}{[L]}$$

A plot of x_F vs. $[M] : [L] = R^{-1}$ gives a straight line yielding, by linear regression, $a = 1.96 \pm 0.05$, with correlation coefficient R = 0.999. The finding that the dependence of x_F on R^{-1} is really linear confirms the assumption that the ratio $[ML_m] : [ML_n] = K$ is constant in the range studied. If it is assumed that the complexes C_I and C_{II} are of simple stoichiometry with n and m corresponding to small integers, and since the value of K is near to unity (from dynamic analysis discussed later, K = 1.15), then the relation found experimentally

$$a = (mK + n)/(1 + K) = 2$$

can be most simply fulfilled for m = n, i.e. for the case where both complexes C_{I} and C_{II} have the same overall composition ML_{2} . This result agrees with the findings obtained from Raman spectra analyzed with the assumption that only one type of complex is present.

Some information on the manner of binding of the lactam in the two ML_2 complexes, C_1 and C_{11} , and also in the ML and M_2L complexes, may be obtained from the ¹³C NMR spectra shown in Table 3 and Fig. 5. From these it is seen that in ¹³C NMR spectra separate signals of "free" and bound lactam can be observed at R > 2.1. For the bound lactam, the C=O, N--CH₃ and $N-CH_2$ carbon atoms exhibit low-field shifts, and the other carbon atoms exhibit high-field shifts. Largest shifts occur for the C=O band, in agreement with the assumption about Ti coordination being predominantly via the carbonyl oxygen. These shifts are of similar magnitude to those cited by Bose and Srinivasan [6] for the complexes of TiCl₄ with some β -lactams. The low-field shifts of the C=O, N-CH₃ and N-CH carbon atoms are somewhat smaller in $CDCl_3$ than in TCE solution, and in contrast the high-field shifts of the other carbon atoms are larger in $CDCl_3$. This indicates some differences in the electronic structure of the complex-bound lactam in the two solvents. In TCE solution, the chemical shift of the C=O band of complex-bound lactam is practically unchanged in the whole studied composition range, corresponding to complexes of composition ML_2 , MLand M_2L , thus indicating that the manner of binding of the lactam carbonyl is very similar in all these complexes. The downfield shifts of the NCH₃ and N-CH carbon atoms for the M₂L complex are larger than for the other com-

TABLE 3

R ^a	Form	Δ ^b						
_		C=0	N—CH ₃	N—CH	СО-СН	CH, ^c		
In TCE		·				_		
	F	1.6	0.9	0.3	-0.6	0.0, 0.1		
4.2	CI	71	4.7	2.9		_08_03		
	C_{II}	1.1	4.2	2.6	2.9	0.0 - 0.0		
2.05	CI	73	5.0	3.2		-05 -01		
2.00	$\mathbf{C}_{\mathbf{II}}$	1.0	0.0	2.9	2.0	0.0, 0.1		
0.91	ML	7.4	5.0	2.9	-2.9	-0.5, -0.1		
0.49	M ₂ L	7.0	6.0	5.1	-1.7	-0.7, 0.3		
In CDCl ₃								
_	F	0.7	0.6	0.6	-0.4	0.0, 0.1		
4.0	C_{I}	65	4.4	28	3.0	_07_03		
	$\mathbf{C}_{\mathbf{\Pi}}$	0.0	3.9	2.0	-0.0	-0.7, -0.5		
2.1	CI	63	4.4	2.6	9 8	-08-04		
	$\mathbf{C}_{\mathbf{II}}$	0.0	3.8	2.2	2.0	0.0, -0.4		

Differences of ¹³C chemical shifts Δ of NMeiQ and its various forms in mixtures with TiCl₄ (ppm)

 $^{a}R = [\text{NMeiQ}]:[\text{TiCl}_{4}].$

 ${}^{b}\Delta$ = Difference between chemical shift of pure NMeiQ in solution and of the forms F, C_I, C_{II}, ML and M₂L in the same solvent. Positive Δ corresponds to downfield shift on TiCl₄ addition.

^cUnassigned.



Fig. 5. ¹³C NMR spectra of NMeiQ with TiCl₄ in CDCl₃ solution (a) R = 2.1; (b) R = 4.0; (c) NMeiQ only.

plexes. This indicates some participation of the nitrogen atom in the Ti coordination for the M₂L complex. In the composition range of the ML and both ML₂ complexes, both the CO, and the N—CH₃ and N—CH carbon shifts remain constant. The existence of the two complexes C_I and C_{II} manifested in ¹H NMR spectra at R > 2.1, leads in ¹³C NMR spectra to small splittings of the N—CH₃ and N—CH bands, but the carbonyl band of the complex-bound lactam remains a narrow singlet and exhibits the same chemical shift at all values of R. Therefore the manner of binding of the carbonyl is evidently equal in both ML₂ complexes. The large difference in the ¹H NMR spectra and small difference in ¹³C NMR spectra of both ML₂ complexes could be explained, for example, by the assumption that these two complexes differ by the orientation of the bound lactams in space.



Fig. 6. Temperature dependence of 'H NMR spectra of NMeiQ with TiCl₄ (R = 4.9) in TCE. (a) Measured; (b) simulated.

We have also attempted to obtain further data on the structure of the complexes, and simultaneously also on the dynamics of exchange of NMeiQ between the complexes C_I , C_{II} and "free" lactam from an analysis of the temperature dependence of ¹H NMR spectra of mixtures of NMeiQ and TiCl₄ in TCE. Thanks to the high boiling point of TCE this dependence can be measured in a broad temperature range (-20 to + 140°C). Best quantitative data could be obtained from the solution with comparable populations of free and complexed lactam (R = 4.9). The temperature dependence of ¹H NMR spectra of this solution is shown in Fig. 6(a). From this figure it is evident that two main processes can be observed in this system: exchange of NMeiQ between the complex C_{II} and "free" lactam F (above 41°C), and at higher temperatures the exchange between the complex C_I and the

averaged system ($C_{II} \leftrightarrow F$). At temperatures below 70°C the N–CH₃ signal of the complex C_I remains sharp, while coalescence of all lactam bands of complex C_{II} and "free" lactam is observed. At intermediate temperatures, between 70 and 90°C, spectra of all components of the system are affected by exchange. At 122°C, the signals of all components are completely averaged for all proton groups.

As has already been mentioned above, the component designated as "free" lactam is itself a complicated system in which exchange is taking place between unbound lactam molecules and molecules weakly bound in the solvation spheres of the complexes. In the temperature range of the measurements shown in Fig. 6 it may be assumed that exchange in this system is so rapid that "free" lactam may be treated as a single substance. Under these circumstances the system corresponding to Fig. 6(a) can be analyzed in terms of an equilibrium reaction $C_I \leftrightarrow C_{II}$. For this three-component

system, theoretical spectra have been calculated similarly as in our previous paper [9], for exchange between three sites [10]. The spectra of the three components, as used in the calculation, were constructed from Lorentzian lines with chemical shifts and line widths giving best fit with experimental spectra at negligible exchange. On the screen of the computer, the simulated spectra were visually compared with the experimental shapes, and the rate constants and populations of components were varied to obtain best agreement between measured and calculated spectrum. These best spectra for the given system, with $K = [C_1] : [C_{11}] = 1.15$, are shown in Fig. 6(b). It is seen that by this procedure a good agreement between theoretical and experimental spectra may be obtained. Small differences in shape may be due to the fact that all signal shapes were approximated as Lorentzian, even though the N -CH and CO--CH bands are multiplets split by spin-spin interaction, and to the three-component approximation of a possibly more complicated process. At the same time, however, the experimental data are not of the quality warranting a more complicated calculation. By visual shape comparison, the rate constants for the temperatures shown in Fig. 6(a) could be determined with an accuracy better than 10%. The temperature dependence

of the rate constants for the reactions $C_{II} \stackrel{k_{23}}{\longleftrightarrow} F$ and $C_{I} \stackrel{k_{12}}{\longleftrightarrow} (C_{II} \leftrightarrow F)$ is shown in Fig. 7. The reaction $C_{I} \stackrel{k_{13}}{\longleftrightarrow} F$ is evidently so slow that it does not appreciably affect the shape of the spectra.

For intermolecular exchange reactions, thermodynamic parameters can be simply obtained from the rate constants, divided by the appropriate statistical factors, by means of the Eyring equation in the case of a monomolecular mechanism; in more complicated cases the rate constants are functions of the concentrations of reactants depending on the type of the reaction mechanism [10]. It can be shown that the free energy of activation ΔG^{\neq} , is relatively insensitive to the choice of the reaction mechanism (e.g. in our case ΔG^{\neq} values calculated for a monomolecular and bimolecular mechanism differ by a few %), but the activation enthalpies and entropies may be much more



Fig. 7. Temperature dependence of the rate constants of the reactions (a) $C_{II} \stackrel{R_{23}}{\longleftrightarrow} F$; (b) $C_{I} \stackrel{R_{12}}{\longleftrightarrow} (C_{II}, F)$.

severely affected. As the mechanism of the exchange reactions studied is unknown, only the ΔG^{\neq} values were evaluated from the rate constants, which were regarded as those of a monomolecular reaction, with statistical factors $f_{23} = 0.5$ and $f_{12} = 1$, $\Delta G_{23}^{\neq} = 64.5$ kJ mol⁻¹ and $\Delta G_{12}^{\neq} = 78.1$ kJ mol⁻¹ at 356 K.

Structure of the complexes

The above analysis of Raman and NMR spectra leads to the conclusion that, in CDCl₃ and TCE solutions of mixtures of NMeiQ and TiCl₄, four types of complexes of overall composition M_2L , ML and ML_2 (with forms C_I and C_{II}) are formed. The shift of the frequency of the CO band in Raman spectra, detection of a pronounced resonance Raman effect on the carbonyl and Ti—O stretching vibrations, and the shift of the CO band in ¹³C NMR spectra provide evidence that TiCl₄ is coordinated to NMeiQ via the carbonyl oxygen, and that the manner of bonding of the carbonyl to Ti is the same in all four types of complexes. In view of the different overall composition of the four complexes this also means that only one atom of Ti is bound to one carbonyl in all these complexes.

The complexes with the overall composition ML_2 contain 6 ligands per 1 atom of Ti. It is therefore simplest to assume that their structure corresponds to the coordination number 6 which is customary in titanium compounds, with the usual octahedric arrangement of the ligands [12]. The two forms C_I and C_{II} which can be differentiated in ¹H and ¹³C NMR spectra exhibit the same Raman spectrum and the same frequency of the CO band in

the ¹³C NMR spectrum. This shows that they have the same octahedric arrangement of ligands on Ti, and the same type of carbonyl—Ti bonding. The great difference in their ¹H NMR spectra indicates that these two forms of the ML₂ complex differ by orientation of the bonded lactams in space. Two possible structures compatible with these observations and with the assumed hexacoordination and octahedric arrangement of ligands on Ti are octahedra with the two lactams coordinated at the two opposite vertices (*trans*, Fig. 8a) and with the two lactams coordinated at two neighbouring vertices (*cis*, Fig. 8b). It may be expected that the *cis*-form would be less stable than the *trans*-form [13]. As in a parallel study of a series of lactams it has been found [14] that the relative population of the complex C_{II} decreases with increasing size of the lactam ring, it is assumed that the spectrum of the complex C_{II} corresponds to the *cis*-form, and the spectrum of the complex C_{I} to the *trans*-form of ML₂.

The complex of overall composition ML contains 5 ligands per 1 atom of Ti. The simplest model of this complex, with the coordination number 5 on Ti, is in conflict with the close similarity of Raman and also of ¹³C NMR spectra of the complexes of overall composition ML and ML₂. It seems highly improbable that a complex with the coordination number 5 and geometrical structure completely differing from that corresponding to the coordination number 6 could have the same Raman spectrum. Further evidence for the structure of the ML complex comes from the similarity of its ¹H NMR spectra with those of the *trans* ML₂ complex C_I (Fig. 3, Table 3). Therefore for the complex of overall composition ML we propose the structure.





α



С

Fig. 8. Proposed structures of NMeiQ—TiCl₄ complexes. (a,b) ML_2 ; (c) ML (the two lactams can assume any of the four positions marked X, the remaining two are occupied by Cl).

ture of the adduct $ML_2 \cdot M$ (Fig. 8c), with hexacoordination on Ti. This adduct would have an increased tendency to form ionic structures, which might explain the weaker intensity of Raman lines of the complex ML as compared to ML_2 . This is also in agreement with the fact that for some lactams, electrical conductivity in solutions with $R \sim 1$ is much higher than in solutions with $R \ge 2$. The tendency toward formation of ionic structures is probably because, in the range of R values 1-2 the complexes are not stable in solution, and with the observation that the structure of the precipitated solid complex of composition ML differs profoundly from the structure of the complex with the same composition in solution.

The complex of the overall composition M_2L exhibits a Raman spectrum quite different from the spectra of the complexes ML and ML₂. In view of the observed identical type of Ti—carbonyl bonding in all complexes, the difference in Raman spectra must be a consequence of a difference in the geometric arrangement of the ligands on Ti; the coordination number of Ti in the M₂L complex must therefore be different from 6. For composition M₂L, with 9 ligands per 2 Ti atoms, the structure with the coordination number 5 on both metal atoms must contain one ligand shared by two atoms of Ti:



The observation of equal bonding of the carbonyl in all complexes studied seems to exclude the possibility of the presence of a lactam bicoordinated through two oxygen electron pairs in M_2L and would favour the structure with a shared Cl atom. If the ¹³C NMR shift of the N—CH carbon in the M_2L complex is interpreted as indicating coordination both on C=O and on N, the structure with a bicoordinated lactam should be preferred.

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