X-RAY AND VIBRATIONAL STUDIES OF 1:1 ADDUCT OF NITROMETHANE AND TITANIUM TETRACHLORIDE

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The crystal structure of $Ti_2Cl_8(CH_3NO_2)_2$ has been determined from three dimensional X-ray data. Crystals are monoclinic (space group P 2_1/c) with four $TiCl_4(CH_3NO_2)$ units per unit cell. Lattice constants are:

$a = 9.55$ (1) A $b = 5.93$ (1) A $c = 16.38$ (2) A $\beta = 119.8$ (1)°

Atomic parameters were refined by full matrix least-squares to a final R equal to 0.055 using 1038 non-zero independent reflections. The compound is dimeric with a double chlorine bridge between titanium atoms. Titanium is octahedrally surrounded by five chlorine atoms and one oxygen atom of nitromethane which behaves as a monodentate ligand. IR and Raman spectra are discussed on the basis of the actual structure and assignments are proposed.

INTRODUCTION

Titanium tetrachloride leads to a large number of adducts with either the 1:1 or the 1:2 stoichiometry.[1] In these compounds, the coordination number of titanium is usually 6.[2] If the ligand is monodentate such as benzonitrile, hexacoordination is achieved in a monomeric 1:2 complex or in a 1:1 complex with a chlorine bridged dimeric structure. If the ligand is potentially bidentate and if the complex has the 1:1 stoichiometry, hexacoordination is achieved either in a monomeric structure and two metal–ligand bonds or in a chlorine bridged dimeric structure and one metal–ligand bond only. This is the case of the NO_2 group which can behave as a mono or a bidentate ligand like nitrate group.[3] Some examples are known which show both possibilities: monodentate in $C_6H_5NO_2 \cdot AlCl_3$[4] or bidentate in $CH_3NO_2 \cdot SnCl_4$.[5]

Titanium tetrachloride is reported to give a 1:1 adduct with nitromethane.[6] On the basis of the low melting point and of IR measurements, Norbury and Sinha[6] have concluded to a monomeric structure, nitromethane acting as a bidentate ligand.

This paper deals with the X-ray structure determination of the complex formed by $TiCl_4$ and CH_3NO_2. Our results do not agree with previous conclusions. Therefore IR and Raman spectra have been recorded and discussed on the basis of the actual structure.

EXPERIMENTAL

Preparation

$TiCl_4(CH_3NO_2)$ was prepared according to the procedure described by Norbury.[6] Single crystals suitable for X-ray study were obtained by sublimation under vacuum and all manipulations were carried out under dry argon in a glove box.

Analysis

Microanalysis for Ti, Cl, C, H and N were performed by the "Service Central de Microanalyse du C.N.R.S."

Results lead to the formula $TiCl_4(CH_3NO_2)$.
Found (%): Ti (19.18) — Cl (56.96) — C (4.71) — H (1.20) — N (5.38).
Calculated: Ti (19.08) — Cl (56.59) — C (4.78) — H (1.19) — N (5.58).
Oxygen is obtained by difference.

Infrared and Raman Spectra

IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer and a Grubb-Parsons Cube MK-II interferometer. Powdered samples were examined directly on caesium iodide plates, or as vaseline or polychlorotrifluoroethylene oil mulls on caesium iodide, silicon or polyethylene plates. Cells were

usually sealed with paraffine. Liquid phase was obtained by heating the cell sealed with Araldite epoxyresin in a RIIC variable temperature holder.

Raman spectra were recorded on a Coderg PHO spectrometer equipped with a Spectra Physics argon–krypton laser (5682 and 5145 Å). Solid samples were set in sealed glass capillary tubes. Liquid was obtained by heating the capillary tube to about 50°C in a Coderg "Cryocirc" variable temperature system.

STRUCTURAL DETERMINATION

Crystal Data

The single crystal used was a 1 x 0.3 x 0.5 mm prism set in a sealed Pyrex capillary. Precession X-ray photographs show monoclinic symmetry with space group $P\,2_1/c$ and lattice constants:

$$a = 9.55\,(1)\,\text{Å}$$
$$b = 5.93\,(1)\,\text{Å}$$
$$c = 16.38\,(2)\,\text{Å}$$
$$\beta = 119.8\,(1)^\circ$$

Based upon four molecules of $TiCl_4(CH_3NO_2)$ per unit cell, the calculated density is 2.07 g/cm³, in good agreement with 2.03 g/cm³ measured by flotation in a methyl iodide and ethyl iodine mixture.

Data were recorded on an automatic four circle diffractometer using molybdenum K_α radiation (graphite monochromator). 1119 independent reflections, including 78 zeros, with a Bragg angle less than 23° were recorded at room temperature. All reflections were corrected for counting losses[7] and for Lorentz polarisation.

For every structure factor F, a standard deviation σ is computed by $\sigma = ERR/2\,F$, where

$$ERR = \left[I_{obs} + CORPER + FC\left(\frac{BAL}{TFC}\right)^2 \right]^{1/2},$$

in which I_{obs} is the integrated intensity, CORPER is the counting loss, FC is the background count, BAL is the scan time and TFC is the background duration. No absorption corrections were made because of the relatively low absorption coefficient (22.9 cm⁻¹).

Structure Solution and Refinement

The structure was solved by direct methods using MULTAN[8] and refined by full matrix least squares.[9] The quantity minimized is $\Sigma\,W(|Fo| - |Fc|)^2$ where Fo and Fc are the observed and calculated structure factors put on the same scale and the weights W are taken as the reciprocal of σ^2.

TABLE I

Final atomic fractional ($\times 10^4$) and thermal ($\times 10^4$) parameters with estimated standard deviations in parentheses

atome	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl_1	−75(2)	2827(3)	527(1)	250(9)	293(10)	376(10)	−4(8)	125(8)	66(9)
Cl_2	3920(2)	2393(4)	1706(1)	316(10)	440(13)	472(13)	76(10)	85(9)	115(10)
Cl_3	1984(2)	2463(4)	−637(1)	449(12)	368(12)	440(11)	−9(10)	228(9)	−78(10)
Cl_4	4037(2)	7009(4)	544(2)	309(10)	421(12)	554(13)	−92(10)	212(10)	−23(10)
Ti	2275(1)	4600(2)	536(1)	221(7)	273(8)	333(8)	3(6)	101(5)	−1(6)
O_1	2165(6)	6925(10)	1552(4)	342(27)	377(31)	334(30)	−33(24)	130(23)	−54(25)
O_2	1943(9)	4849(13)	2556(5)	862(52)	562(48)	591(50)	−79(39)	385(39)	90(35)
N	2051(8)	6638(13)	2273(5)	367(38)	477(48)	401(41)	−32(33)	194(33)	11(18)
C	2000(12)	8743(18)	2759(7)	581(59)	587(63)	475(53)	−77(49)	268(46)	−207(49)

Anisotropic temperature factors in the form:
$$\exp[-2\pi^2(U_{11}a^2h^2 + U_{22}b^2k^2 + U_{33}c^2l^2 + 2U_{12}abhk + 2U_{13}achl + 2U_{23}bckl)]$$

TABLE II

Bond distances with their standard deviations for $[TiCl_4(CH_3NO_2)]_2$,[a] $[TiCl_4(CH_3COOC_2H_5)]_2$[b] and $[TiCl_4(POCl_3)]_2$[c]

	$[TiCl_4(CH_3NO_2)]_2$ distances A	$[TiCl_4(CH_3COOC_2H_5)]_2$ distances A	$[TiCl_4(POCl_3)]_2$ distances A
Ti_1Cl_1 (bridge)	2,471 (3)	2,500 (2)	2,44 (1)
$Ti_1Cl'_1$ (bridge)	2,478 (4)	2,497 (2)	2,54 (1)
Ti_1Cl_4	2,203 (3)	2,224 (2)	2,24 (1)
Ti_1Cl_2	2,206 (4)	2,220 (2)	2,23 (1)
Ti_1Cl_3	2,202 (3)	2,232 (2)	2,20 (1)
Ti_1O_1	2,204 (6)	2,029 (3)	2,10 (2)
O_1N	1,250 (9)		
O_2N	1,18 (1)		
NC	1,50 (1)		

[a]This paper.

[b]Ref. 13.

[c]Ref. 14.

TABLE III

Bond angles with their standard deviations for $[TiCl_4(CH_3NO_2)]_2$,[a] $[TiCl_4(CH_3COOC_2H_5)]_2$[b] and $[TiCl_4(POCl_3)]_2$[c]

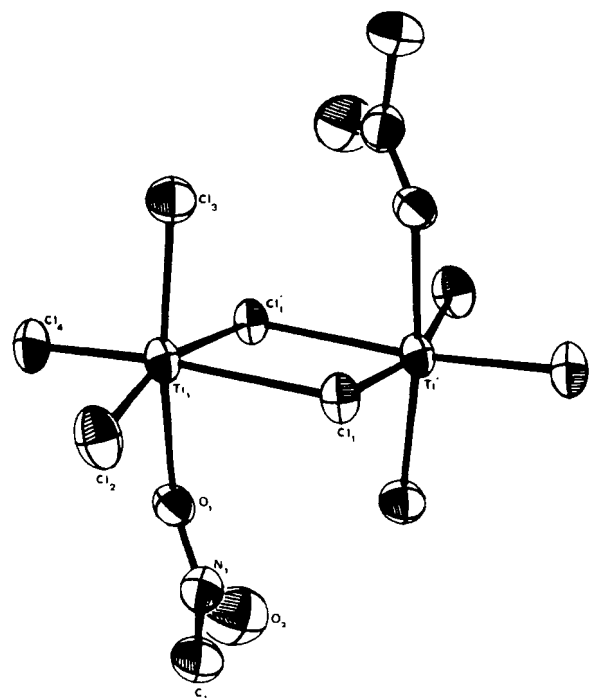|	$[TiCl_4CH_3NO_2)]_2$	$[TiCl_4(CH_3COOC_2H_5)]_2$	$[TiCl_4(POCl_3)]_2$
$Cl_1Ti_1Cl'_1$	78,9 (1) °	79,08 (5) °	78,5 (3) °
$Cl_1Ti_1Cl_4$	164,8 (1)	166,28 (5)	165,0 (4)
$Cl_1Ti_1Cl_2$	90,3 (1)	89,95 (6)	92,8 (4)
$Cl_1Ti_1Cl_3$	91,7 (1)	90,99 (6)	92,2 (4)
$Cl_1Ti_1O_1$	83,5 (1)	80,42 (10)	83,0 (6)
$Cl'_1Ti_1Cl_4$	89,0 (2)	89,85 (6)	89,1 (4)
$Cl'_1Ti_1Cl_2$	164,9 (1)	167,55 (5)	167,5 (4)
$Cl'_1Ti_1Cl_3$	92,6 (2)	89,34 (6)	91,7 (4)
$Cl'_1Ti_1O_1$	78,7 (2)	83,60 (9)	82,6 (6)
$Cl_2Ti_1Cl_4$	99,6 (2)	100,23 (7)	98,2 (4)
$Cl_4Ti_1Cl_3$	98,2 (1)	97,01 (7)	96,2 (4)
$Cl_4Ti_1O_1$	85,0 (2)	90,40 (10)	87,4 (6)
$Cl_2Ti_1Cl_3$	98,3 (2)	96,57 (6)	97,4 (4)
$Cl_2Ti_1O_1$	89,7 (2)	89,02 (9)	88,1 (6)
$Cl_3Ti_1O_1$	170,7 (3)	169,77 (10)	173,0 (6)
Ti_1O_1N	133,4 (5)		
O_1NO_2	124,0 (8)		
O_1NC	115,6 (8)		
O_2NC	120,5 (7)		
$Ti_1Cl'_1Ti'$	101,1 (5)		

[a] This paper.

[b] Ref. 13.

[c] Ref. 14.

FIGURE 1   ORTEP drawing of dimer $[TiCl_4(CH_3NO_2)]_2$ (thermal ellipsoids contain 50% of the electronic density).[12]

The R factors are defined by

$$R = \frac{\Sigma(|Fo| - |Fc|)}{\Sigma|Fo|}$$

and by

$$Rw = \left[\frac{\Sigma W(|Fo| - |Fc|)^2}{\Sigma WFo^2} \right]^{1/2}$$

Values of the atomic scattering factors were those published by Cromer and Waber.[10]

After correction of the secondary extinction effect according to Larson and Cromer,[11] the final refinement gave:

    non weighted R including 78 zeros 0.059
    non weighted R excluding 78 zeros 0.055
        weighted R including 78 zeros 0.059
        weighted R excluding 78 zeros 0.058

$F(000)$ and the secondary extinction parameter are respectively equal to 858 and 0.15×10^{-5}. A Fourier difference map did not show the hydrogen atoms.

Atomic parameters with their standard deviations are given in Table I, bond lengths and bond angles in

Tables II and III†, ORTEP drawing in Figure 1.

RESULTS AND DISCUSSION

The complex between $TiCl_4$ and CH_3NO_2 has a dimeric structure, as shown in Figure 1, with two chlorine bridges typical of 1:1 adducts such as $[TiCl_4(CH_3COOC_2H_5)]_2$,[13] $[TiCl_4(POCl_3)]_2$[14] and $[TiCl_4(NCCOOC_2H_5)]_2$[15] in which the titanium atom is hexacoordinated.

The titanium, chlorine and oxygen frameworks are very similar in $[TiCl_4(CH_3NO_2)]_2$, $[TiCl_4(CH_3COO C_2H_5)]_2$ and $[TiCl_4(POCl_3)]_2$. The Ti—Cl and Ti—O bond lengths and the Cl Ti Cl' and Cl Ti O bond angles of the three compounds are compared in Tables II and III.

The Ti—O distances in the three compounds are consistent with the relative orders of donor strength of the ligands, characterized by their donor number DN_{SbCl_5} as defined by Gutmann[16] (Table IV). There is an increase in the bond length correlated to a decrease in the donor character of the ligand. The average length of a bridging Ti—Cl bond (2.47 Å) is typically longer than a non-bridging Ti—Cl bond (2.20 Å). The hexacoordination of the titanium atom in the complex leads to a weakening of the bond forces between titanium and terminal chlorine atoms in comparison with pure titanium tetrachloride.[17] This results in a difference between the two bond lengths respectively equal to 2.20 and 2.18 Å.

Only one of the nitromethane oxygen atoms is bonded to titanium. The decrease in the electronic density on this atom leads to a lengthening of the nitrogen-bridged oxygen bond length and a shortening of the other O—N distance, while the ONO angle decreases (Table V).[18]

TABLE IV

Comparison between donor numbers of $CH_3COOC_2H_5$, $POCl_3$ and CH_3NO_2 and TiO distances in their complexes with $TiCl_4$

	$CH_3COOC_2H_5$	$POCl_3$	CH_3NO_2
DN_{SbCl_5}	17,1	11,7	2,7
Ti–O distances (Å)	2,03[a]	2,10[b]	2,20[c]

[a] Ref. 13.
[b] Ref. 14.
[c] This paper.

† A table of observed and calculated structure factors is available from the Editor upon request.

TABLE V
Comparison of bond distances and bond angles of free
CH_3NO_2 and coordinated CH_3NO_2

	Free CH_3NO_2 (Ref. 18)	CH_3NO_2 in the complex
$N-O_1$	1,21 (2) Å	1,25 (1) Å
$N-O_2$	1,21 (2) Å	1,18 (1) Å
$C-N$	1,46 (2) Å	1,49 (1) Å
$\widehat{O_1NO_2}$	127°	123,9°

The other bond lengths and bond angles of free
and coordinated nitromethane do not differ signifi-
cantly.

INFRARED AND RAMAN STUDIES

General Considerations

An infrared study of $[TiCl_4(CH_3NO_2)]$ has been
carried out by Norbury and Sinha.[6] They proposed a
monomeric structure, with hexacoordinated titanium
and nitromethane acting as a bidentate ligand. The
dimeric structure proved by X-ray diffraction dis-
agrees with their conclusions. It was then interesting
to reexamine the spectra on the basis of the actual
structure.

As pointed out above, different IR sampling tech-
niques were used. The results show that the yellow
complex partly dissociates in vaseline mulls. It turns
orange, and a strong band at 498 cm^{-1}, characteristic
of $TiCl_4$[19], appears in the spectrum, together with
typical nitromethane bands. Norbury et al. performed
IR measurements with Nujol mulls and their results
could be consistent with the spectrum of a mixture.
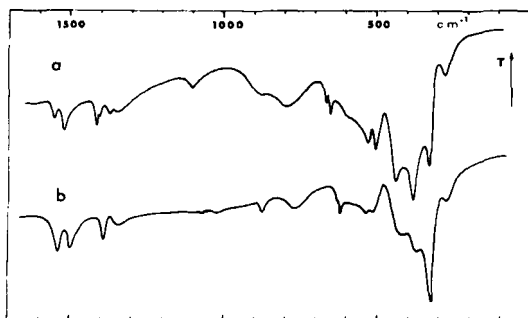On the contrary the IR spectrum obtained with the

FIGURE 2   Infrared spectra of solid complexes: a =
$[TiCl_4(CH_3NO_2)]_2$; b = $[TiCl_4(CD_3NO_2)]_2$.

powdered compound on CsI plates seems characteris-
tic of the pure complex. The discussion will be based
only upon this spectrum.

The IR and Raman spectra of $[TiCl_4(CH_3NO_2)]_2$
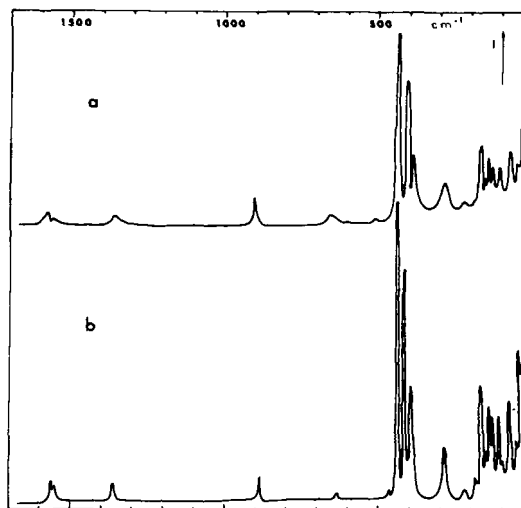and of its deuterated homologue are shown in Figures
2 and 3.

FIGURE 3   Raman spectra of solid complexes: a =
$[TiCl_4(CH_3NO_2)]_2$; b = $[TiCl_4(CD_3NO_2)]_2$.

Classification of Vibrations

The dimer $[Ti_2Cl_8(CH_3NO_2)_2]$ has C_i molecular
symmetry. Assuming a point mass model for the
methyl groups, the expected 48 fundamental vibra-
tions are classified as:

$$\Gamma_{vib} = 24\ A_g\ (R) + 24\ A_u\ (IR)$$

Since the unit cell contains two dimers, a crystal
effect is to be expected, each A_g mode (or each A_u)
giving rise to one A_g mode and one B_g mode (or one
A_u and one B_u) in the C_{2h} factor group.
However not all expected bands are observed.
It seems more convenient to consider separately the
assignments of frequencies corresponding to the
coordinated nitromethane and to the $Ti_2Cl_8O_2$
skeleton. Terminal chlorine atoms are referred to as
Cl_t and bridged chlorine atoms as Cl_b.

Nitromethane Frequencies

A comparison of the IR spectra of $[TiCl_4(CH_3NO_2)]_2$
and $[TiCl_4(CD_3NO_2)]_2$ allows NO_2 stretching modes
to be separated from CH_3 bending modes (see Table

VI). Each NO_2 stretching mode splits into two components; the ν_{as} NO_2 mode at 1553 cm^{-1} and 1520 cm^{-1}, and the ν_s NO_2 mode at 1405 cm^{-1} and 1350 cm^{-1} (free nitromethane: 1565 cm^{-1} (ν_{as}) and 1385 cm^{-1} (ν_s)).[20] In the δ ONO bending region (655 cm^{-1} in free ligand), two bands are also observed at 662 and 650 cm^{-1}.

As shown above by X-ray diffraction, the geometry of CH_3NO_2 is only slightly modified by coordination (Table V). The decrease of ONO angle is consistent with the observed decrease of ν_{as} NO_2 and increase of ν_s NO_2.[21]

The occurrence of two bands for ν_{as} NO_2, ν_s NO_2 and δ ONO, instead of one (C_i molecular symmetry) can be explained by a crystal effect. In this assumption, only one band should occur for the complex in the liquid phase or in solution.

The Raman spectrum of the liquid phase clearly exhibits the characteristic lines of free CH_3NO_2 and free $TiCl_4$ and, below 450 cm^{-1}, some extra lines (Figure 4). The characteristic bands of free CH_3NO_2 and free $TiCl_4$ are also present in the IR spectrum of the liquid phase, as well as in the IR and Raman spectra of a benzene solution of the complex. Because

of this dissociation of the complex, the NO_2 bands of free nitromethane hinder the observation of the NO_2 bands of the complex. The crystal effect cannot be proved by this way; however it is likely to cause the bands to split.

For the solid complex a slight decrease of the ν C–N stretch is observed, in agreement with the slight lengthening of the C–N bond in the complex (Table V).

$Ti_2Cl_8O_2$ Skeleton Frequencies

The bands at 525–502 cm^{-1} in the IR spectrum are assigned to ν Ti–O stretch, as observed for oxygenated compounds of hexacoordinated titanium.[22]

Ti–Cl$_t$ stretching frequencies in titanium complexes usually occur in the 350–450 cm^{-1} region.[23-26] For [$Ti_2Cl_8(CH_3NO_2)_2$], three ν Ti–Cl$_t$ are expected in the IR spectrum (A_u type) and in the Raman spectrum (A_g type). It is then reasonable to assign the strong IR bands at 438, 380 and 328 cm^{-1} and the strong Raman lines at 435, 409 and 391 cm^{-1} to the ν Ti–Cl$_t$ stretching modes.

Bridging Ti–Cl$_b$–Ti stretching frequencies are

TABLE VI
Infrared frequencies (cm^{-1})

[TiCl$_4$(CH$_3$NO$_2$)]$_2$	[TiCl$_4$(CD$_3$NO$_2$)]$_2$	Assignments
1553	1542	} ν_{as} NO$_2$
1520	1500	
1412		δ_{as} CH$_3$
1405	1396	ν_s NO$_2$
1370		δ_s CH$_3$
1350	1350	ν_s NO$_2$
1100		ρ CH$_3$
	1069	δ_{as} CD$_3$
	1028	δ_s CD$_3$
880	880	ν C–N (+ρCD$_3$)
790	770	
662		
650	622	δ ONO
595	540	ρ NO$_2$
{525 502	515	ν Ti–O
438	425	ν Ti–Cl$_t$
380	380	ν Ti–Cl$_t$
328	325	ν Ti–Cl$_t$
275	280	ν Ti–Cl$_b$–Ti

(ν = stretching; δ = bending; ρ = rocking).

TABLE VII
Raman frequencies (cm^{-1})

$[TiCl_4(CH_3NO_2)]_2$	$[TiCl_4(CD_3NO_2)]_2$	Assignments
1576	1562	$\nu_{as}\ NO_2$
1558	1558	
1360	1365	$\nu_s\ NO_2$
908	890	$\nu C{-}N$
657	630	δONO
603		ρNO_2
508	464	
435	435	$\nu Ti{-}Cl_t$
409	409	$\nu Ti{-}Cl_t$
391	391	$\nu Ti{-}Cl_t$
286	287	$\nu Ti{-}Cl_b{-}Ti$
222	220	
188	187	
170	170	$\nu Ti{-}Cl_b{-}Ti$
156	156	and
144	143	$\delta Ti{-}Cl_b{-}Ti$
132	133	and
110	109	$\delta Cl_t{-}Ti{-}Cl_t$
76	76	
52	51	
37	39	

(ν = stretching; δ = bending; ρ = rocking)

expected at lower frequencies than ν Ti—Cl_t modes.[23] We observe an IR band at 275 cm^{-1} and a Raman line at 286 cm^{-1} which could be assigned to a ν Ti—Cl_b—Ti stretch.

At lower frequencies, bending modes involving terminal chlorine atoms, as well as stretching and bending modes involving bridging chlorine atoms may occur. Many Raman lines which appear in this low-frequency region correspond to these modes.

The assignments are summarized in Table VI and VII.

Nature of the Liquid Phase

As reported above, the Raman spectrum of the liquid phase contains the characteristic lines of free CH_3NO_2, free $TiCl_4$ and of another unknown species (Figure 4). The relative intensity of the 419 cm^{-1} and 360 cm $^{-1}$ lines, with respect to that of the 387 cm^{-1} line of $TiCl_4$, increases when the temperature decreases; it is possible to follow the phenomenon to room temperature, since the phase easily remains undercooled. All these observations suggest an equilibrium between

this species and its two constituents, namely $TiCl_4$ and CH_3NO_2. The easy dissociation of the complex can be related to the long Ti—Cl_b distances, as well as to the long Ti—O distances.

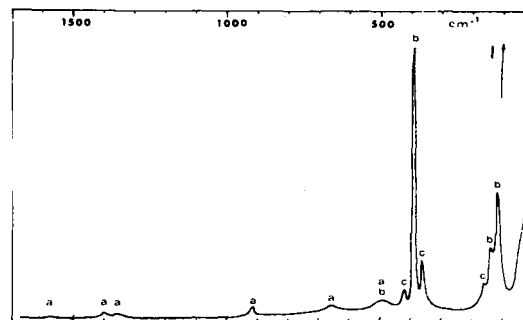The Raman spectrum of this unknown species in the liquid phase is characterized by the lines labelled

FIGURE 4   Raman spectrum of $[TiCl_4(CH_3NO_2)]_2$ heated above 50°C (homogeneous liquid). a) lines of free nitromethane; b) lines of free titanium tetrachloride; c) lines of a complex species.

c on Figure 4. These lines do not appear in the spectrum of the pure solid complex, suggesting a difference between their structures. Since there is no line in the region characteristic of Ti—Cl$_b$—Ti stretch, it can be assumed that the liquid phase species does not contain bridging chlorine atoms. There is not enough information to propose either a pentacoordination with monodentate nitromethane, or a hexacoordination with bidentate nitromethane for this species.

CONCLUSION

X-ray structure determination shows that CH_3NO_2 and $TiCl_4$ give a 1:1 dimeric complex where nitromethane behaves as a monodentate ligand. The hexacoordination of titanium atom is achieved by a double chlorine bridge.

The long titanium—oxygen distance is in good agreement with the low donor character of nitromethane. Modifications in bond distances and bond angles of nitromethane are weak. This is correlated with slight modifications in characteristic frequencies of coordinated nitromethane. Splittings of $\nu_{as}NO_2$, $\nu_s NO_2$ and δ ONO are explained by a crystal effect. Assignments of ν Ti—Cl$_t$ and ν Ti—Cl$_b$—Ti are proposed.

In the liquid phase, or in benzene solution, IR and Raman spectra show the occurrence of another complex in equilibrium with $TiCl_4$ and CH_3NO_2. From Raman data it seems that this complex is monomeric, since no ν Ti—Cl$_b$—Ti is observed.

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