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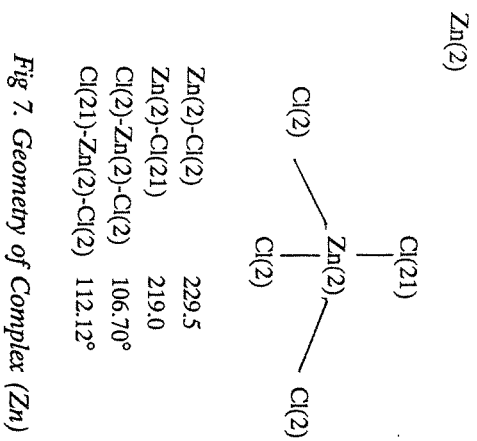
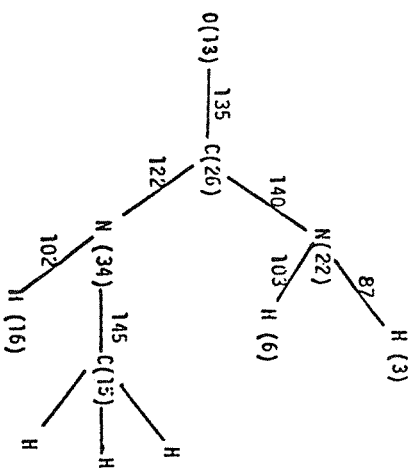
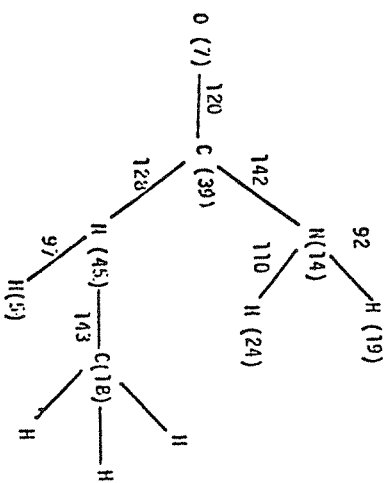
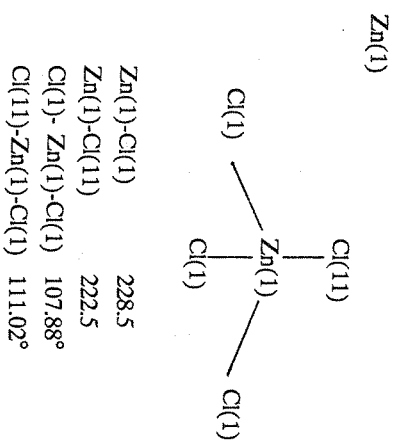
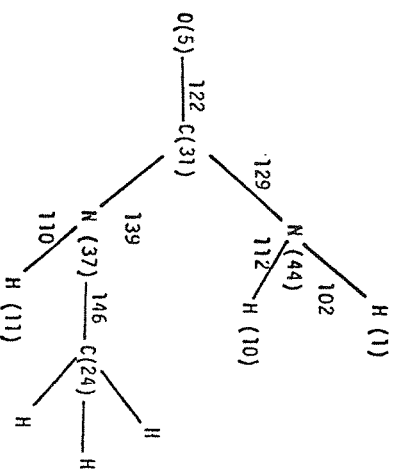
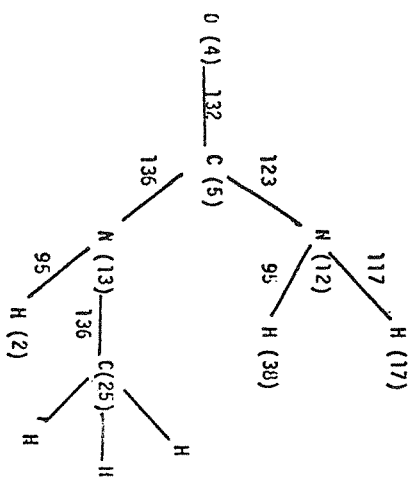


Fig 7. Geometry of Complex (Zn)

Fig 8. Bond Lengths in the Four Distinct Methylurea Ligands

Fig 4. Raman and IR Spectra of  $\{Ti(Meur)_6\} \{ZnI_4\} I$

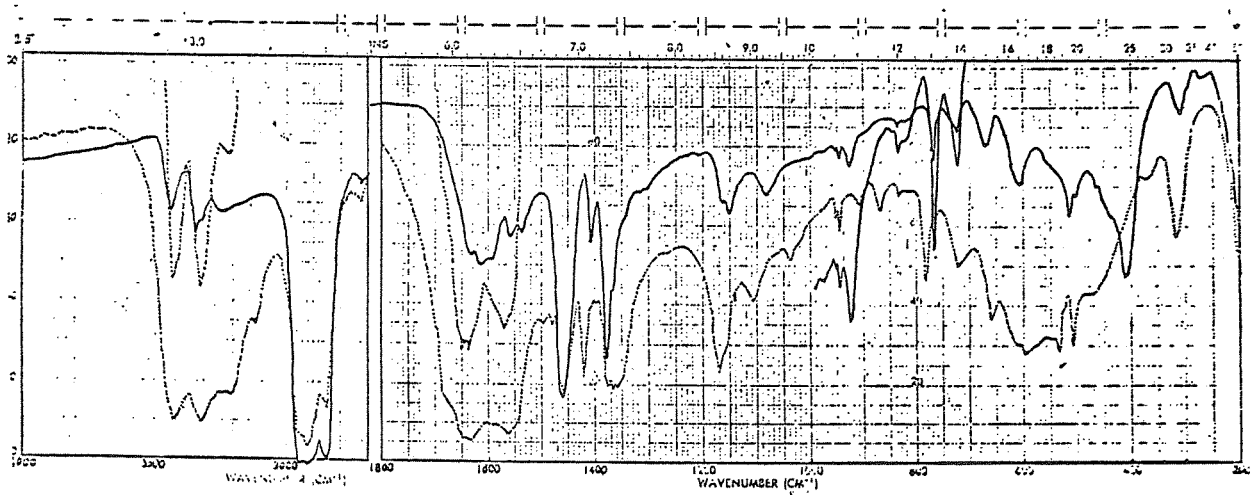
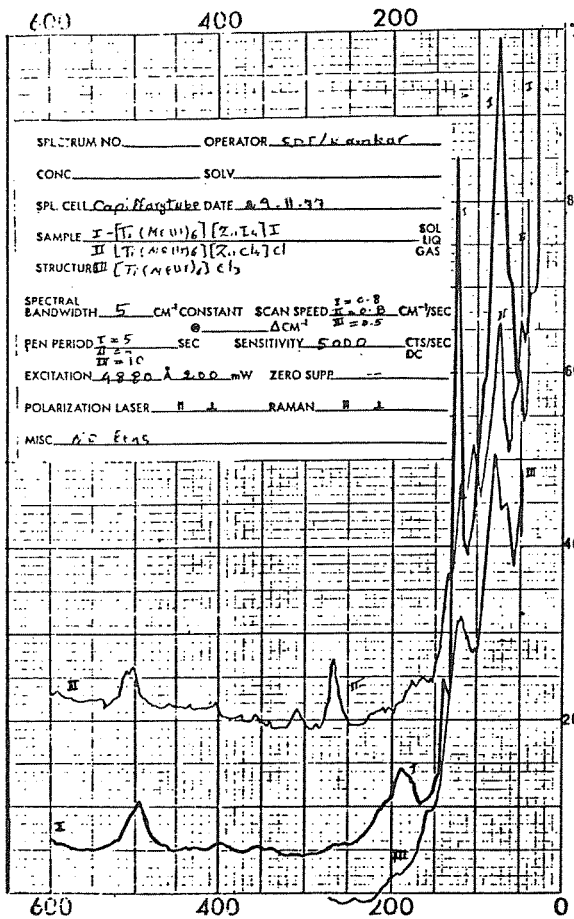
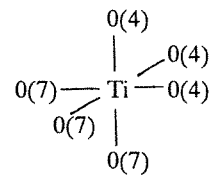


Fig 5. Raman Spectrum of Meurea - Titanium (III) Complexes

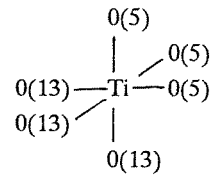


Ti(1)



Ti(1) - 0(4)	202.0
Ti(1)-0(7)	202.3
0(4)-Ti(1)-0(4)	91.06°
0(7)-Ti(1)-0(7)	91.04°
0(4)-Ti(1)-0(7)	179.62° ; 88.69° ; 89.22°

Ti (2)



Ti(2)-0(5)	202.5
Ti(2)-0(13)	201.2
0(5)-Ti(2)-0(5)	89.72°
0(13)-Ti(2)-0(13)	91.42°
0(5)-Ti(2)-0(13)	178.27° ; 88.55° ; 90.32°

Fig 6. Coordination Geometry of Complex (Ti)

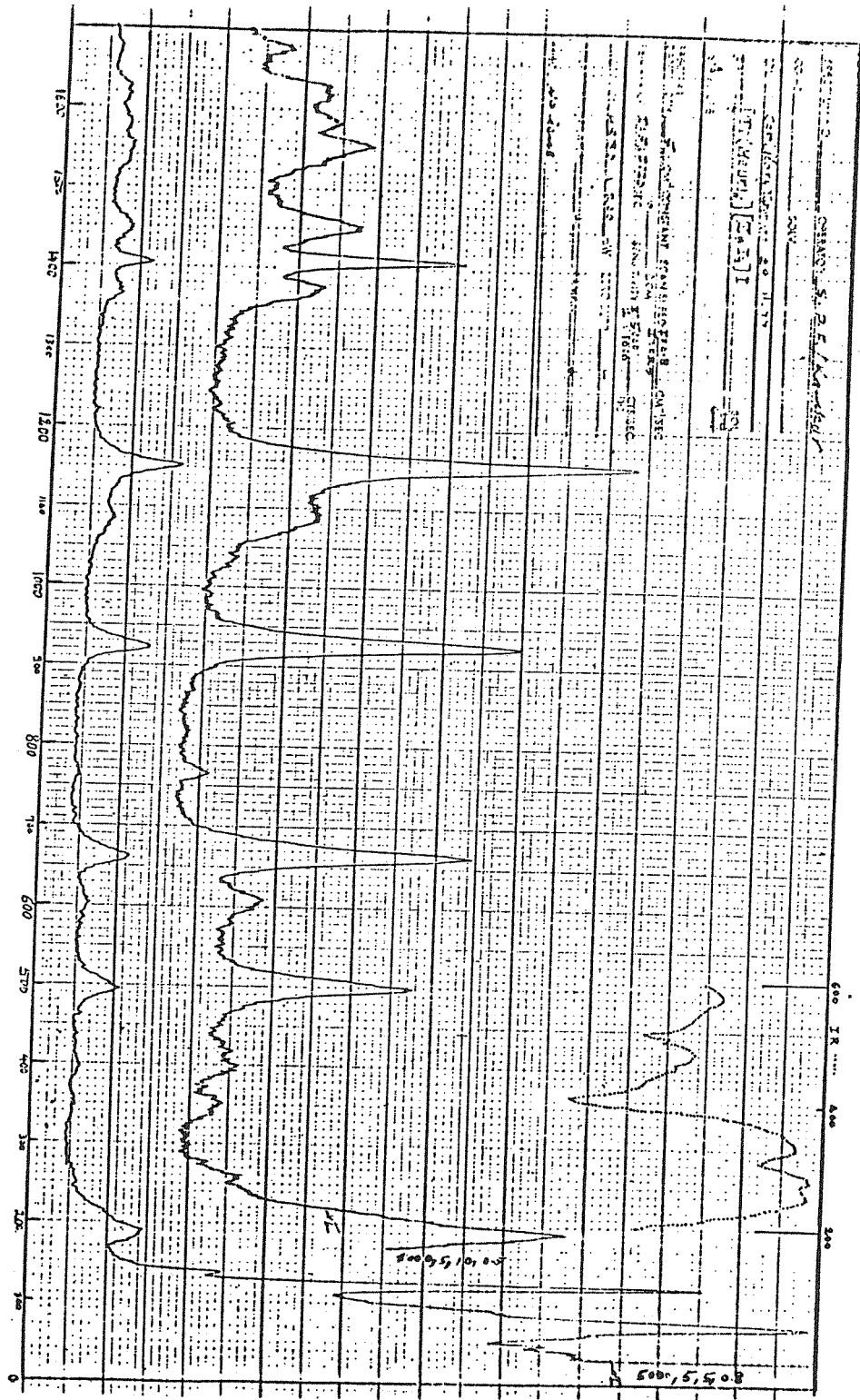


Fig. 3. Infrared Spectra of {Ti(Meur)<sub>6</sub>} {ZnI<sub>4</sub>} I (---) and Meurea (.....)

Fig. 2. Raman and IR Spectra of  $\{Ti(Meur_6)\} \{ZnCl_4\} Cl$

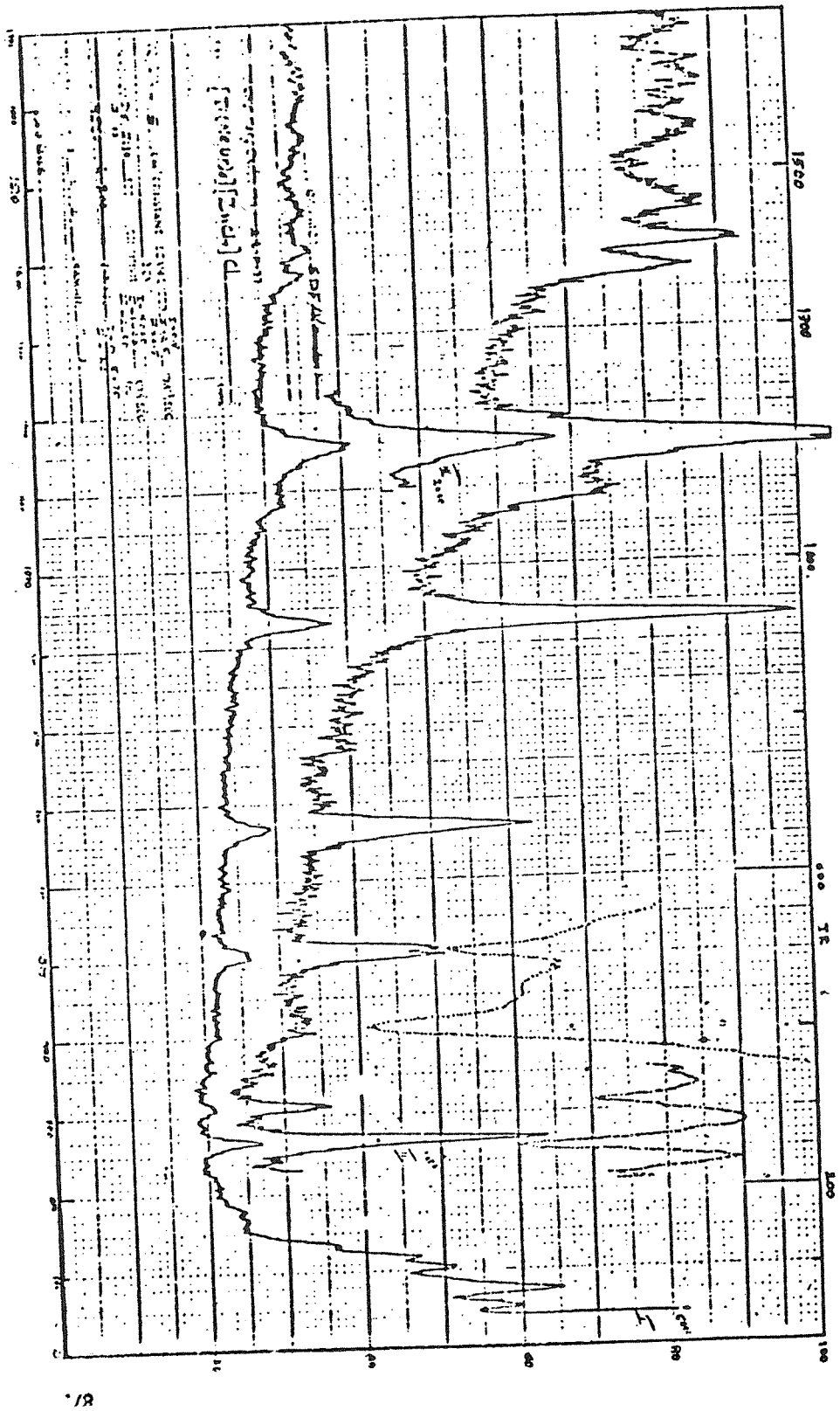


Table 3. Raman Frequen.

$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	Ref
$\{ZnCl_4\}^{2-}$				
268?	105	268	118	this work
		255(i.r)		
282	--	277	--	25
282	82	298	116	27
282	82	276(i.r)	116	29
288(s)	116(w)	298(w)	130(w)	30
280	82-116	280	82	22
278	110	278	110	31
275	79	306	104	23
290	112	290	140	32
		279(i.r)		
$\{ZnI_4\}^{2-}$				
122	48	190	60	this work
122	44	170	64	23
122	44	170	62	22
122	--	170	--	25
122	--	--	--	27
130	60	172	70	30

Fig 1. Infrared Spectra of  $\{Ti(Meur)_6\} \{ZnCl_4\} Cl$  (---) and Meurea (.....)

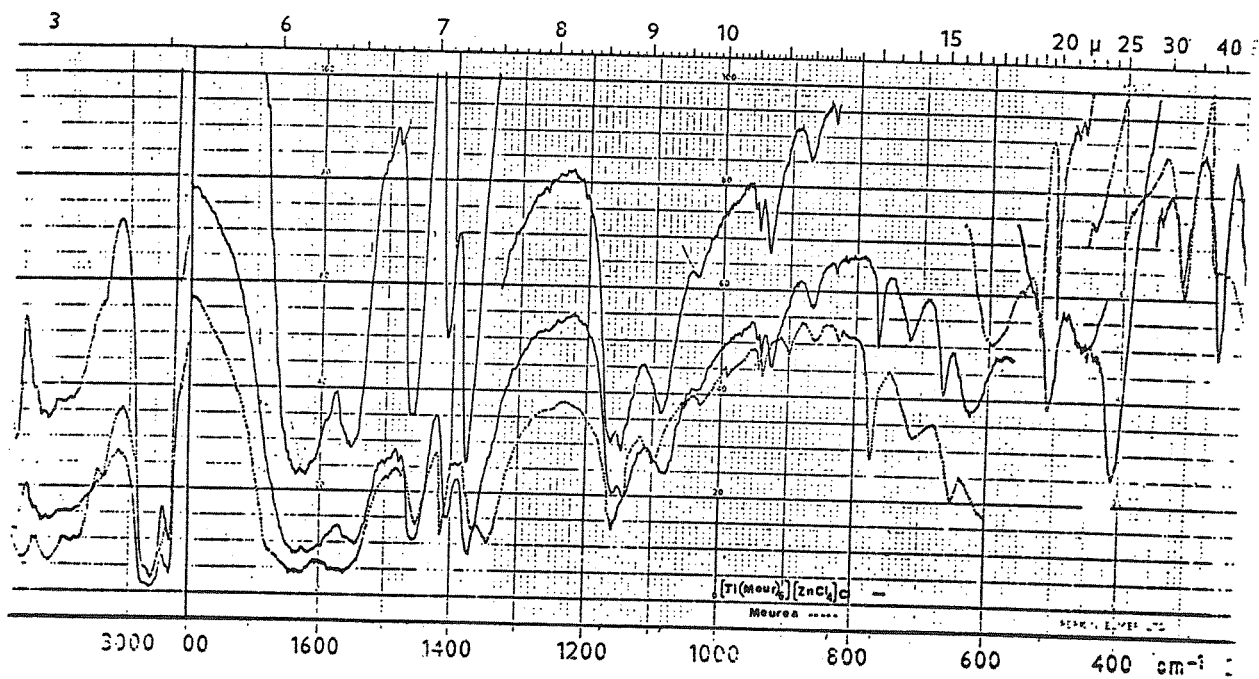


Table 2. Observed I.R. and Raman Frequencies of Hexamethylureatitanium  
(III) Complexes and the Ligand

(li(ur) <sub>6</sub> )Cl <sub>3</sub>		Methylurea		(li(Meur) <sub>6</sub> )Cl <sub>3</sub>		(Ti(Maur) <sub>6</sub> ) (ZnCl <sub>4</sub> )Cl		(Ti(Meur) <sub>6</sub> ) (ZnI <sub>4</sub> )I		
I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman	
3440s		3420s		3440s		3430s		3435m		a $\nu$ NH <sub>2</sub>
3320s		3320s		3310s		3320s		3340m		s- $\nu$ NH <sub>2</sub>
3180s		3210s.sh		3220b		3220b		3230b		$\nu$ NH <sub>2</sub> (bond)+ $\nu$ CH
--		3120s.sh		3170b		3100sh		3160sh		$\nu$ NH <sub>2</sub> (bond)+ $\nu$ CH
1655sh	--	1640s	1645m	1635s	--	1640s	1685m	1635sh	1675v.w	$\nu$ C=O+ $\delta$ NH
1630	--	--	--	--	--	1620s	1615m	1615s	1620w	$\delta$ NH+ $\nu$ C=O
1580sh	--	1570b.s	1574m	1575s	1590s	--	1585m	1595sh	1580v.w	$\delta$ NH <sub>2</sub>
1550s	--	--	--	--	1560v.w	1550s	1560m	1560s	1550w	$\delta$ NH+ $\delta$ CN
1490sh	1505w	--	--	--	--	--	1505m	1538s	--	$\delta$ N'H+ $\nu$ C=O
1480m	--	1460s	1455m	1455s	1465s	1460m	1460m	1460a	1450w	a+ $\delta$ CH <sub>3</sub>
--	--	1420v.s	1420m	1410a	1425s	1410v.s	1410m	1408v.s	1408w	$\delta$ CH
1375s	--	1375s.sh	1365w	--	--	1375v.s	1380m	1378v.s	1378w	s- $\delta$ CH <sub>3</sub> +a- $\nu$ CN <sub>2</sub>
1365sh	--	1355b.s	--	--	--	--	--	1370sh	--	$\nu$ CN
1350sh										
1160b.s	1175v.w	1168s	1170s	1165s	1178s.sh	1170s	--	1175sh	--	$\delta$ CH+ $\delta$ N'C'H
--	--	--	1150s	1150s	1160s	1150s	1155v.sp	1150s	1155m	$\nu$ CN'
1090w	1100w	1110w	1115sh	1100s	1118m	1060s	1095sh	1080s	1085sh	$\nu$ C=O..
1030s	1040s	1035w	--	--	--	1035sh	--	--	--	$\nu$ C-N'+ $\omega$ CH <sub>3</sub> $\sigma$ $\nu$ CH <sub>3</sub>
940s	950sh	950w	--	940s	--	940s	--	945s	--	s- $\nu$ CN <sub>2</sub> + $\rho$ CH <sub>3</sub>
--	--	910w	916s	920s	935s	925s	930sp	925s	924	$\nu$ C=O+ $\nu$ C-N'
--	830w	870w	--	--	--	865s	--	833w	--	$\nu$ CN'+ $\nu$ CN+ $\gamma$ CH <sub>3</sub>
						830sh				
768m	770sh	780v.s	--	760s	775w	765v.w	765v.w	768v.s	765w	$\delta$ NH <sub>2</sub> + $\rho$ NH <sub>2</sub>
720w	--	720b	--	720s	--	720s	--	722	--	$\delta$ C=O
--	--	660s	660m	640m	665s	668v.s	668s	670s	663s	$\nu$ C-N'+ $\delta$ NCO+ $\delta$ CN'C'
					658s					
620s	620m	610b.sh	--	610w	--	625b.s	--	610s	610w	$\tau$ NH <sub>2</sub> + $\gamma$ OCNN'
	610sh									
--	--	595b	--	580v.w	575w	--	--	--	--	$\delta$ C=O
				565sh						
555m	555m	535v.s	532sp.sh	525v.s	530s	510v.s	510s	515s	498w	$\delta$ NCN'+ $\nu$ CN+ $\delta$ CN'C'
535m	500w	510v.s	519s	490s	480sh		502s	505sh		+ $\rho$ C=O+ $\gamma$ OCN <sub>2</sub>
445v.b	480w	--	--	420v.s	420v.w	410v.s	410v.w	410v.s	420sh	$\nu$ Ti+O
	465w								395v.w	$\nu$ Ti=O
350m	--	375sh	--	375s	340m	--	--	--	350v.w	$\delta$ NCO+ $\delta$ CN'C'
--	310v.w	310v.s	310w	320vw.sh	395w	310v.s	310w	310s	260w.sh	$\delta$ NCN'
--	205sh	--	--	--	277m	255v.s	268sp	270v.w	--	$\delta$ <sub>3</sub> Zn-Cl+ $\delta$ CN'C
					242m					+ $\delta$ NCN'
--	155w.sh	--	195sh	--	195sh	--	180sh	--	190m	
--	182w.sh	--	148m	--	170sh	--	133sh	--	138sp.sh	
--	140sh	--	--	--	120s	--	118m	--	122s.sp	
--	--	--	95s	--	--	--	105s	--	90sh	
--	--	--	73s	--	89s	--	75v.s	--	73v.s	
--	--	--	--	--	70sh	--	--	--	60sh	
--	--	--	47s	--	52s	--	52s	--	48s	

Table 3. Raman Frequen.

$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	Ref
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		255(i.r)		
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278	110	278	110	31
275	79	306	104	23
290	112	290	140	32
		279(i.r)		
$\{\text{ZnI}_4\}^{2-}$				
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122	44	170	64	23
122	44	170	62	22
122	--	170	--	25
122	--	--	--	27
130	60	172	70	30

Fig 1. Infrared Spectra of  $\{\text{Ti}(\text{Meur})_6\} \{\text{ZnCl}_4\} \text{Cl}$  (---) and Meurea (.....)

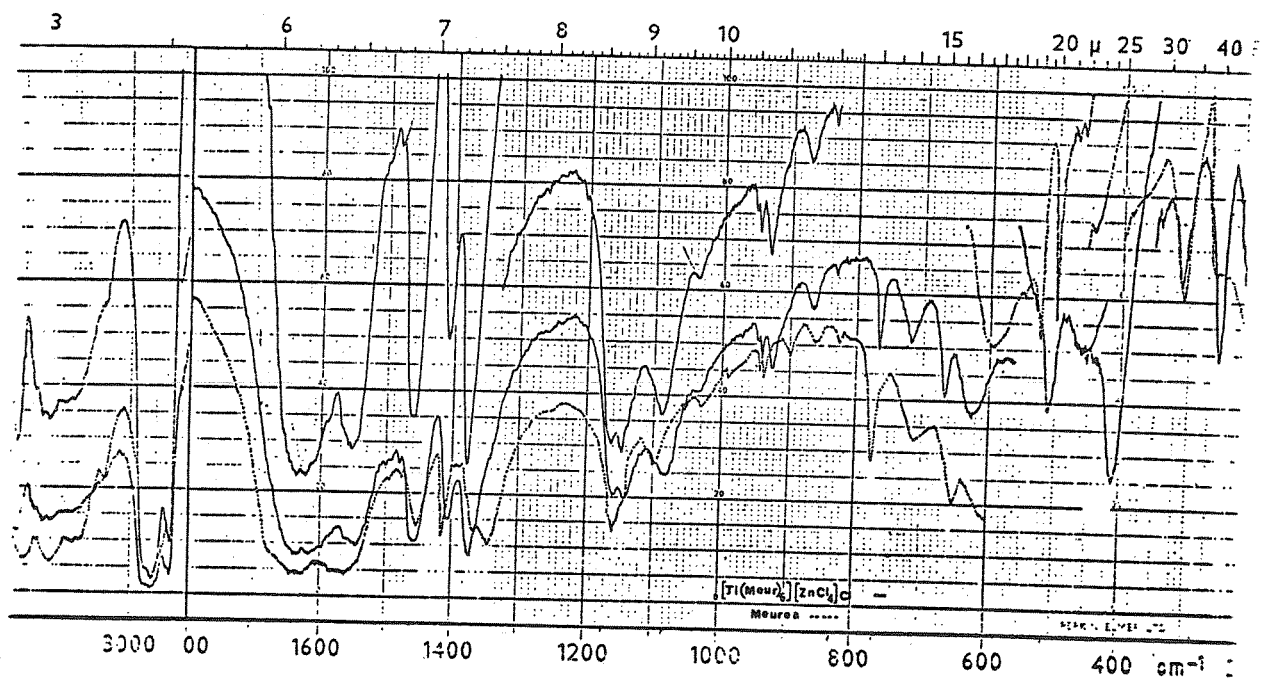




Table 2. Observed I.R. and Raman Frequencies of Hexamethylureatitanium  
(III) Complexes and the Ligand

(li(ur) <sub>6</sub> )Cl <sub>3</sub>		Methylurea		{li(Meur) <sub>6</sub> }Cl <sub>3</sub>		{Ti(Maur) <sub>6</sub> } {ZnCl <sub>4</sub> }Cl		{Ti(Meur) <sub>6</sub> } {ZnI <sub>4</sub> }I		
I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman	
3440s		3420s		3440s		3430s		3435m		$\nu_{\text{NH}_2}$
3320s		3320s		3310s		3320s		3340m		$s-\nu_{\text{NH}_2}$
3180s		3210s.sh		3220b		3220b		3230b		$\nu_{\text{NH}_2}(\text{bond})+\nu_{\text{CH}}$
--		3120s.sh		3170b		3100sh		3160sh		$\nu_{\text{NH}_2}(\text{bond})+\nu_{\text{CH}}$
1655sh	--	1640s	1645m	1635s	--	1640s	1685m	1635sh	1675v.w	$\nu_{\text{C}=\text{O}}+\delta_{\text{NH}}$
1630	--	--	--	--	--	1620s	1615m	1615s	1620w	$\delta_{\text{NH}}+\nu_{\text{C}=\text{O}}$
1580sh	--	1570b.s	1574m	1575s	1590s	--	1585m	1595sh	1580v.w	$\delta_{\text{NH}_2}$
1550s	--	--	--	--	1560v.w	1550s	1560m	1560s	1550w	$\delta_{\text{NH}}+\delta_{\text{CN}}$
1490sh	1505w	--	--	--	--	--	1505m	1538s	--	$\delta_{\text{N}'\text{H}}+\nu_{\text{C}=\text{O}}$
1480m	--	1460s	1455m	1455s	1465s	1460m	1460m	1460a	1450w	$a+\delta_{\text{CH}_3}$
--	--	1420v.s	1420m	1410a	1425s	1410v.s	1410m	1408v.s	1408w	$\delta_{\text{CH}}$
1375s	--	1375s.sh	1365w	--	--	1375v.s	1380m	1378v.s	1378w	$s-\delta_{\text{CH}_3}+a-\nu_{\text{CN}_2}$
1365sh	--	1355b.s	--	--	--	--	--	1370sh	--	$\nu_{\text{CN}}$
1350sh										
1160b.s	1175v.w	1168s	1170s	1165s	1178s.sh	1170s	--	1175sh	--	$\delta_{\text{CH}}+\delta_{\text{N}'\text{C}'\text{H}}$
--	--	--	1150s	1150s	1160s	1150s	1155v.sp	1150s	1155m	$\nu_{\text{CN}'}$
1090w	1100w	1110w	1115sh	1100s	1118m	1060s	1095sh	1080s	1085sh	$\nu_{\text{C}=\text{O}}$
1030s	1040s	1035w	--	--	--	1035sh	--	--	--	$\nu_{\text{C}-\text{N}'}+\omega_{\text{CH}_3}+\rho_{\text{YCH}_3}$
940s	950sh	950w	--	940s	--	940s	--	945s	--	$s-\nu_{\text{CN}_2}+\rho_{\text{CH}_3}$
--	--	910w	916s	920s	935s	925s	930sp	925s	924	$\nu_{\text{C}=\text{O}}+\nu_{\text{C}'\text{N}'}$
--	830w	870w	--	--	--	865s	--	833w	--	$\nu_{\text{CN}'}+\nu_{\text{CN}}+\gamma_{\text{CH}_3}$
						830sh				
768m	770sh	780v.s	--	760s	775w	765v.w	765v.w	768v.s	765w	$\delta_{\text{NH}_2}+\rho_{\text{NH}_2}$
720w	--	720b	--	720s	--	720s	--	722	--	$\delta_{\text{C}=\text{O}}$
--	--	660s	660m	640m	665s	668v.s	668s	670s	663s	$\nu_{\text{C}'\text{N}'}+\delta_{\text{NCO}}+\delta_{\text{CN}'\text{C}'}$
					658s					
620s	620m	610b.sh	--	610w	--	625b.s	--	610s	610w	$\tau_{\text{NH}_2}+\gamma_{\text{OCNN}'}$
	610sh									
--	--	595b	--	580v.w	575w	--	--	--	--	$\delta_{\text{C}=\text{O}}$
				565sh						
555m	555m	535v.s	532sp.sh	525v.s	530s	510v.s	510s	515s	498w	$\delta_{\text{N}'\text{CN}'}+\nu_{\text{CN}}+\delta_{\text{CN}'\text{C}'}$
535m	500w	510v.s	519s	490s	480sh	480sh	502s	505sh		$+\rho_{\text{C}=\text{O}}+\gamma_{\text{OCN}_2}$
445v.b	480w	--	--	420v.s	420v.w	410v.s	410v.w	410v.s	420sh	$\nu_{\text{Ti}=\text{O}}$
	465w								395v.w	$\nu_{\text{Ti}=\text{O}}$
350m	--	375sh	--	375s	340m	--	--	--	350v.w	$\delta_{\text{NCO}}+\delta_{\text{CN}'\text{C}'}$
--	310v.w	310v.s	310w	320vw.sh	395w	310v.s	310w	310s	260w.sh	$\delta_{\text{N}'\text{CN}'}$
--	205sh	--	--	--	277m	255v.s	268sp	270v.w	--	$\delta_3\text{Zn}-\text{Cl}+\delta_{\text{CN}'\text{C}'}$
					242m					$+\delta_{\text{N}'\text{CN}'}$
--	155w.sh	--	195sh	--	195sh	--	180sh	--	190m	
--	182w.sh	--	148m	--	170sh	--	133sh	--	138sp.sh	
--	140sh	--	--	--	120s	--	118m	--	122s.sp	
--	--	--	95s	--	--	--	105s	--	90sh	
--	--	--	73s	--	89s	--	75v.s	--	73v.s	
--	--	--	--	--	70sh	--	--	--	60sh	
--	--	--	47s	--	52s	--	52s	--	48s	

by all other workers (22-23) (Table3). However, the assignment of the two very weak shoulders at 60 and 90  $\text{cm}^{-1}$  to  $\nu_2$  and  $\nu_4$  modes, or even the band at 48  $\text{cm}^{-1}$  to the  $\nu_2$  mode, is rather uncertain, as is the assignment of the band at 190  $\text{cm}^{-1}$  to the  $\nu_3$  mode.

### the Structure of $\{\text{Ti}(\text{Meur})_6\} \text{ZnCl}_5$

The crystal and molecular structure of this compound was determined by X-ray diffraction.

The structure contains two formula-weights of  $\text{Ti}(\text{OC}(\text{NHCH}_3)\text{NH}_2)_6\text{ZnCl}_5$  in the unit cell. The two non-equivalent titanium atoms are surrounded approximately octahedrally by six oxygen atoms from the ligands, with the following bond lengths (pm) and angles: (Fig.6)

This co-ordination geometry is similar to that observed <sup>(18)</sup> for  $\{\text{Tiur}_6\}^{3+}$  (in the iodide), and would not seem to be sufficiently distorted from regular octahedral to generate the observed electronic splitting ( $2722 \text{ cm}^{-1}$ ) of the visible region absorption band. (This splitting has been given in Ref.(1) the alternative explanation of a Jahn - Teller effect on the  $^2 E_g$  excited state).

The structure contains the discrete anions  $\text{Cl}^-$  and  $\text{ZnCl}_4^{2-}$ , these being two non - equivalent and somewhat distorted tetrahedral  $\text{ZnCl}_4$  groups (Points symmetry  $c_{3v}$ ) per unit cell (and two  $\text{Cl}^-$  ions also).

The existence of a discrete tetrahedral  $\text{ZnCl}_4^{2-}$  ion and separate  $\text{Cl}^-$  was also deduced from the Raman spectrum of this compound, (Fig.7) and this type of structure may be assumed for the other complexes with similar stoichiometry ( $\text{Co}(\text{NH}_3)_6\text{ZnCl}_5$  which was shown <sup>(33)</sup> to have a similar structure).

The four crystallographically distinct methylurea molecules have surprisingly different bond lengths (Figure 8). This presumably accounts (in part) for the splitting (e.g. C=O stretch) of ligand bands in coordination of the ligand to the titanium atom (the four C-O bond lengths are: 135, 132, 122, 120 pm). In each case, the free- $\text{NH}_2$  group shows two widely different N-H bond lengths, one  $> 100$  pm, one  $< 100$  pm. In each case, the hydrogen atom with the shorter N-H bond appears (from the structure) to be H-bonded to the O-atom in another ligand.

Table 1. Summary of Titanium Complexes Prepared

Complex	colour	Solubility		
		H <sub>2</sub> O	EtOH	Acetonitrile
$\{\text{Ti}(\text{ur})_6\}\text{I}_3$	d - blue	s	s	i
$\{\text{Ti}(\text{ur})_6\}\text{Cl}_3$	c - blue	s	sl	i
$\{\text{Ti}(\text{Meur})_6\}\text{Cl}_3$	c - blue	s	sl	i
$\{\text{Ti}(\text{DMeur})_6\}\text{Cl}_3$	v - blue	s	sl	i
$\{\text{Ti}(\text{DMeur})_6\} \{\text{ZnI}_4\}\text{I}$	d - blue	s	sl	i
$\{\text{Ti}(\text{Meur})_6\} \{\text{ZnI}_4\}\text{I}$	d - blue	s	sl	i
$\{\text{Ti}(\text{Meur})_6\} \{\text{ZnCl}_4\}\text{Cl}$	c - blue	s	i	i
$\{\text{Ti}(\text{Meur})_6\}\text{I}_3$	d - blue	s	sl	i
$\{\text{Ti}(\text{DMeur})_6\}\text{I}_3$	d - blue	s	sl	i
$\{\text{Ti}(\text{Etur})_6\} \text{Cl}_3$	c - blue	s	i	i
$\{\text{Ti}(\text{Etur})_6\}\text{I}_3$	d - blue - s	-	-	-
$\{\text{Ti}(\text{DEtur})_6\}\text{Cl}_3$	c - blue	s	i	i
$\{\text{Ti}(\text{DEtur})_6\}\text{I}_3$	d - blue	s	sl	i
$\{\text{Ti}(\text{Phur})_6\}\text{Cl}_3$	g - blue	s	i	i
$\{\text{Ti}(\text{phur})_6\}\text{I}_3$	d - blue - s	-	-	-
$\{\text{Ti}(\text{Dphur})_6\}\text{Cl}_3$	c - blue - s	-	-	-
$\{\text{Ti}(\text{Dphur})_6\}\text{I}_4$	y and w	-	-	-
$\{\text{Ti}(\text{pr - ur})_6\}\text{I}_3$	d - blue - s	-	-	-
$\{\text{Ti}(\text{Bt - ur})_6\}\text{I}_3$	d - blue	s	sl	i
$\{\text{TiCl}_3, \text{tetmeur}\}$	green	s	s	sl
$\{\text{Ti}(\text{acetamide})_6\}\text{I}_3$	d - blue	s	s	sl

2d = dark, v = violet, c = clear, g = grey, y = yellow, blue - s = blue solution, s = soluble, sl = slightly soluble, i = insoluble, w = white

## Raman Spectra

Raman spectra were measured on a Model Cary 82 Laser - Raman spectrophotometer, using Argon - Ion or Helium - Neon lasers. The samples were finely powdered and contained in 2 mm I.D. capillary tubes. The spectral range covered extended from the Rayleigh line to  $1700\text{ cm}^{-1}$

## Results and Discussion

### Infrared and Raman Spectra of Hexakis (Methylurea) Titanium (III) Complexes

There are three types of hydrogen bonds ( $\text{NH}\dots\text{O}$ ,  $\text{N}\overset{\text{H}\dots\text{I}}{\text{H}\dots\text{I}}$  and  $\text{N}\dots\text{I}$ ) in the crystal structure of hexakis titanium (III) iodide. Also, from the four hydrogens in one molecule of urea, three are involved in hydrogen-bonding. <sup>(17,18)</sup> In the structure of the methylurea of the complex, it may be supposed that the methyl group takes the place of the fourth hydrogen, while the hydrogen atoms of the methyl group are probably involved in more hydrogen - bonding. Observed vibrational frequencies and assignments of hexamethyl ureatitanium (III) complexes and the ligand ( Figs. 1-5) are Presented in Table 2. The assignments, as before the urea complexes, are made by comparison with different organic compounds and previous complexes. For these complexes the Raman spectra are also given, and the most interesting region is that below  $600\text{ cm}^{-1}$ .

### The Structure of the Anion, $\{\text{Zn X}_4\}^{2-}$

Before considering the assignment of the spectra of complexes containing these anions, a brief summary of the structure of this species will be given.

X-ray diffraction studies (20,21) have shown solid  $\text{Cs}_2\text{ZnBr}_4$  and  $\text{Cu}_2\text{ZnCl}_4$  to contain tetrahedral  $\{\text{Zn X}_4\}^{2-}$  species. Raman studies by Delwalle<sup>(22)</sup> and others <sup>(23,24)</sup> have established a tetrahedral structure for  $\text{ZnI}_4^{2-}$  and  $\text{ZnBr}_4^{2-}$  in aqueous solution. The single-crystal X-ray results show that the point group symmetry of the  $\text{ZnCl}_4^{2-}$  ion in the cobalt complexes,  $\{\text{Co}(\text{NH}_3)_6\}\{\text{ZnCl}_4\}\text{Cl}$ , is not  $T_d$  but  $m$  ( $C_s$ ).

Four fundamental Raman- active internal vibrations are expected for a tetrahedral  $\text{XY}_4$  molecule,

namely the two stretching modes,  $A_1$  and  $T_2$  and the two bending modes,  $E$  and  $T_2$ . For  $\{\text{ZnX}_4\}^{2-}$  ions, the former modes would be expected in the  $200\text{-}400\text{ cm}^{-1}$  region, and the latter below  $200\text{ cm}^{-1}$ . This is the region where vibrations attributable to the titanium-oxygen and to the zinc - chloride and iodide bonds should occur. The only pattern observed is one identical with that of the  $\text{ZnCl}_4^{2-}$  and  $\text{ZnCl}_4^{2-}$  ions in their salts, clearly indicative of the presence of tetrahalogenozincate (II) as the principal zinc-containing species. (see Table 3)

The bands around  $410\text{ cm}^{-1}$  are assigned to the titanium-oxygen frequencies; the shift to lower wave numbers is expected because the molecule is more complicated and the ligand is heavier.

The Raman spectra of this region for the complexes are given in Fig.5. The assignment is given in Table 3 with the results of others for comparison (22-23).

The infrared spectrum of hexamethylureatitanium (III) tetrachlorozincate (II) chloride shows a strong band at  $410\text{ cm}^{-1}$  which is assigned to the Ti-O vibrations. In the Raman spectrum it is a weak broad band. The band at  $310\text{ cm}^{-1}$ , which is present in all the spectra involving the ligand is assigned to the  $\delta_{\text{NCN}}$  mode. The band at  $268\text{ cm}^{-1}$  in the Raman spectrum, which is seen at  $255\text{ cm}^{-1}$  in the infrared spectrum, is assigned to the Zn-Cl vibration ( $\nu_3$  or  $\nu_1$ ). The bands at  $118$  and  $105\text{ cm}^{-1}$  are assigned to the  $\nu_4$  and  $\nu_2$  modes, respectively. The very strong band at  $75\text{ cm}^{-1}$  which is seen in the spectrum of the ligand ( $73\text{ cm}^{-1}$ ) and the other complexes, should be assigned to vibrations within the ligand, as should the band at  $52\text{ cm}^{-1}$ .

The spectrum of the zinciodide salt shows also a strong band at  $410\text{ cm}^{-1}$  which is assigned to Ti-O frequencies, and two bands, at  $48$  and  $73\text{ cm}^{-1}$  which are seen in the spectrum of the ligand at  $42$  and  $73\text{ cm}^{-1}$ . The assignment of the sharp band at  $122\text{ cm}^{-1}$  in this spectrum (Fig.4) to Zn-I vibration ( $\nu_1$ ) is unambiguous because this band is characteristically sharp and strong, is seen only in the spectrum of this complex, and has been assigned to  $\nu_1$

## INTRODUCTION

The majority of coordination compounds of titanium (III)<sup>(1-17)</sup> are highly unstable with respect to oxidation and many hydrolyse rapidly in the presence of moisture. This is one of the reasons why there is a lack of accurate structural information from X-ray measurements on their detailed stereochemistry in the solid state. Among the titanium (III) complexes the urea complex is unusually stable and its crystal-structure has been reported (18,19).

There have been remarkably few vibrational studies of urea and N- substituted urea Ti (III) complexes, and stretching frequency of Ti-O in the complex and hydrogen bonded molecular structures.

The complex technic and unstability of Ti(III) complexes with some ligands are the reasons that the spectroscopical and structural studies and their properties are rather rare.

Preparation a series of these complexes<sup>(1)</sup> gave us this chance - that to study the Ti (III) ion in special symmetry groups. This especial situation appears more a little with the present of species such as  $Zn \times 4^{2-}$  that give a new coordination sphere and configuration, and establish the molecular frequencies.

This work reports the preparation and characterisation of some titanium (III). complexes with N-substituted urea ligonds. The complexes were studied by infrared and Raman spectroscopy, and X-ray crystallography.

## Experiment

Starting material - titanium trichloride solution (~15%  $TiCl_3$ ) from B.D.H. chemicals Ltd. This solution contains zinc chloride and is presumably produced by the reduction of titanium (IV) by zinc and hydrochloric acid (see refernce 1).

### I. Complex $Ti [CO(NHME) NH_2]_6 ZnCl_5$

Methylurea was added to  $TiCl_3$  solution (~ 15%  $TiCl_3$ ) contains zinc chloride in a schlenk tube, under nitrogen and room temperature. The solution was vacuum evaporated over about 2 hours, down to  $\frac{2}{3}$  volume. A mixed solvent ethanol and chloroform

( $\frac{2v}{15v}$ ) with 1g ligand was added to the solution. The dark-blue solution was warmed and stirred for a few minutes and adding some dichloromethane and placed in a refrigerator (-10°C) and then at room temperature, after two months there were some crystals which were filtered off and washed with ethanol twice and dried under vacuum. Analysis<sup>(1)</sup> (calculated for  $Ti (CO (NHMe) NH_2)_6 ZnCl_5$ ) :

%	C	H	N	Cl	Ti	Zn	O
Calc.	19.6	4.9	22.9	24.1	6.5	8.9	13.1
Found	19.6	5.0	22.0	23.8	7.0	8.9	-

### II. Complex $[Ti (MeUr)_6] [ZnI_4] I$

Also prepared as the same method for chloride salt, except potasium iodide was added to the blue solution, and potasium chloride crystals were filtered off, but did not add dichloromethane to the solution.

%	C	H	N	I	Ti	Zn	O
Calc.	12.1	3.1	14.1	53.2	4.0	5.5	8.1
Found	12.5	3.2	14.7	51.8	4.0	5.2	-

### III. Complex $[Ti(NN' DMeUr)_6] [ZnI_4] I$

This complex also prepared as the choride salt of Methyl complex. But with addition of chloroform and without dichloromethane. After drying crystals, some of them dissolved in ethanol and they recrystalized from ethanol solution. (Found 2)

%	C	H	N	I	Ti	Zn	O
Calc.	16.9	3.8	13.2	49.7	3.8	5.1	7.5
Found1	16.2	3.4	11.0	40.3	3.1	5.0	-
Found2	16.9	4.1	12.7	48.2	4.0	5.1	-

The complexes were formulated as  $[TiL_6] [ZnX_4] X$  on the basis of an X-ray crystal structure determination.

## Infrared Spectra

Infrared spectra were measured on Perkin Elmer Infrared spectrophotometers model 557, and model 225, sodium chloride and caesium iodide plates being used for the ranges 4000, 1000  $cm^{-1}$ , and 1000 - 200  $cm^{-1}$  respectively.

# Synthesis and Molecular Structure of Hexakis (N-Methylurea) Titanium (III) Tetrachlorozincate (II) Monochloride. And Similar Complexes of Iodide Salts

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## ABSTRACT

*During synthesis of Ti (III), N - substituted urea and acetamide complexes<sup>(1)</sup>, the complex Ti [CO(NHMe) NH<sub>2</sub>]<sub>6</sub> Zn Cl<sub>5</sub> was synthesized using the N- methylurea and TiCl<sub>3</sub> solution (~ 15% TiCl<sub>3</sub> solution contains zinc chloride) and the crystal and molecular structure of this compound was studied by X - ray diffraction and infrared and Raman Spectroscopy.*

*X-ray diffraction study has shown the structure contains two formula - weight of Ti (OC ( NHCH<sub>3</sub> )NH<sub>2</sub> )<sub>6</sub> ZnCl<sub>5</sub> in the unit cell. The two non - equivalent titanium atoms are surrounded approximately octahedrally by six oxygen atoms from the ligands, with the following bond lengths (pm) and angles (see fig 6).*

*The structure contains the discrete anions Cl<sup>-</sup> and ZnCl<sub>4</sub><sup>2-</sup>, these being two non - equivalent and somewhat distorted tetrahedral ZnCl<sub>4</sub> groups. (Point symmetry C<sub>3v</sub>) per unit cell (and two Cl<sup>-</sup> ions also).*

*Key Words: Titanium (III), Zinc (II), Methylurea and Dimethylurea Complexes of Ti (III), and Zn (II), X-ray and Spectroscopic Studies*

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