PREPARATION AND INVESTIGATION OF LEWIS-ACID COMPLEXES, IV*

PREPARATION AND INVESTIGATION OF THE TITANIUM TETRACHLORIDE AND TIN TETRACHLORIDE COMPLEXES OF THE ESTERS OF CYCLOHEXANE DIOLS AND TRIOLS, FURTHER OF MONO- AND OLIGOSACCHARIDES

By

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To our present knowledge, in Friedel—Crafts type reactions catalyzed by Lewis acids, the Lewis acids act by forming a complex with one of the initial substances. The stability of the complex is dependent on the structure of the parent compounds. Owing to polarization, some of the bonds loosen up in the complexes, resulting in an increased reactivity.

The preparation of the complexes of Lewis acids — primarily that of the $AlCl_3$, BF_3, $TiCl_4$ and $SnCl_4$ complexes — has since long been studied. It was found that with various Lewis bases, i.e. with compounds containing atoms suitable to donate electron pairs, i.e. to form dative bonds — such as e.g. oxygen, nitrogen, sulphur or halogen — complexes of different stability are formed and can be isolated. In recent times, the investigation by physical methods of complexes prepared in exactly controlled experimental conditions resulted in some new, important findings.

$TiCl_4$ and $SnCl_4$ differ from the best known Lewis acid, from $AlCl_3$. For the latter, the original definition, interpreting the acid character by a lack of octet, holds true. In $TiCl_4$ and $SnCl_4$, however, the central metal atom is in the hybride state sd^3, and functioning as Lewis acid by forming complexes, it can complete its octet to decet or to dodecet of the hybride state d^2sp^3, while the original tetrahedral steric structure turns into an octahedron, with the four chlorine atoms and the two donor atoms at the corners.

It was assumed [1] that steric structures of the $TiCl_4$ and the $SnCl_4$ complexes differed by the donor atoms assumed at the neighbouring and at the opposite corners of the imaginary octahedron, respectively.

When first studying this problem [2], only the overall composition of the complexes to be obtained from the model compounds at various substrate: Lewis acid molar ratios has been investigated, because at that time, no method suitable to clear the structure of complexes was available.

Besides the given problem, these investigations were thought to be of interest also from another aspect. Earlier it was not studied what kind of complexes were formed, if the substrate contained more than one complex-forming group, that is to say, is polyfunctional from the point of view of electron pair donation. Our model compounds, levoglucosan, glucose and cellobiose esters, contained 3, 5 and 8 ester groups, respectively. The remarkable result was obtained that the number of the bound $TiCl_4$ molecules is less than that of the functional groups: in case of five functional groups (glucosepentaacetate) not more than two, and in case of eight functional groups (cellobiose-octaacetate) not more than three. At that time, the possibility of the formation of the different complexes was interpreted on the basis of charge conditions evolving on the complexes.

About one year after the publication of our results, the work of RIVEST and coworkers [3] reporting on the $TiCl_4$ complexes of dicarboxylic acids has been published. It was found by these authors that the first members of the homologous series yielded only 1 : 1 complexes, while the higher members also 2 : 1 complexes. They assumed that the energetically most stable hexacovalent state was always established, in the 1 : 1 complex with the participation of the carbonyl oxygens of two ester groups, and in the 2 : 1 complex with the participation of the carbonyl and alkyl oxygen of one ester group.

On getting acquainted with the work of RIVEST, we came to think that also the experimental results observed and published by us could be interpreted on the basis of similar considerations. To test this assumption, we set the task to investigate whether the tendency to complex forming of cyclic di- and polyol esters and the composition of the complexes formed were dependent on the relative steric position of the ester groups. Simultaneously, we wished to extend our investigations to the study of the $SnCl_4$ complexes.

With a view to the high sensitivity of Lewis acides and their complexes to even traces of water, complexes were prepared under great care in a "dry box" or in the specially designed apparatus shown in Fig. 1.

According to the general procedure, the solution of the calculated amount of Lewis acid in dry chloroform was added dropwise under stirring to the solution of the substrate in dry chloroform. The precipitate formed spontaneously, or in some cases after dilution with petroleum ether was separated by filtration, washed with a solvent, dried, and tested.

The composition of the complexes was determined by elemental analysis, further by titration with pyridine of the solution in acetonitrile, a method developed earlier [4].

The determination of the composition of the complexes permitted to establish the maximum number of molecules of Lewis acid, which could be bound by the tested model compound. The determination of the composition,

however, did not furnish information on the kind of linkage, or whether also for this case the concept of RIVEST [3] is valid.

A study of the infrared spectra of these complexes was to furnish information on these structural characteristics.
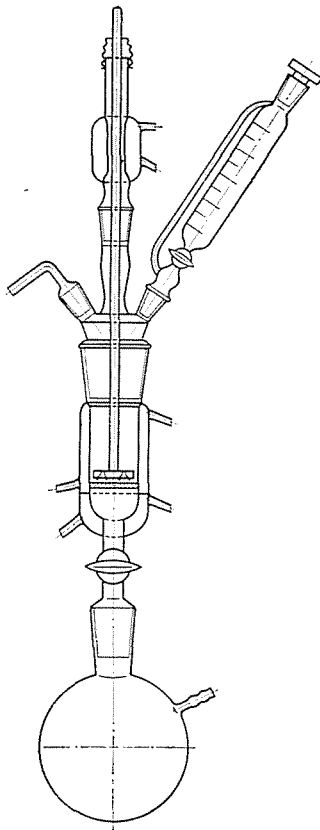

Fig. 1

The IR spectra of Lewis acid complexes of esters were first studied by LAPPERT [6], who investigated the complexes of ethylacetate and BF_3, BCl_3, $TiCl_4$, $SnCl_4$, $SnBr_4$, $ZrCl_4$ and $FeCl_3$.

These investigations proved unequivocally that the complex formed is linked to the carbonyl oxygen of higher electron density, since the carbonyl frequency occurs at a lower and the $C—O—C$ stretching frequency at a higher wave number with the complexes than in the case of the basic compound.

It is remarkable that while only an inflection was observed at the band sides with increasing wave numbers in the spectra of $TiCl_4$, $TiBr_4$, and TiI_4, the carbonyl band in the spectrum of $ZrCl_4 \cdot 2EtOAc$ splitted, and two distinct bands appeared at wave numbers 1637 and 1613.

The two kinds of carbonyl bands are indicative of the fact that for the 1 : 2 complexes of Ti-halogenides and of $ZrCl_4$-ethyl acetate, configurations are trans octahedral and cis octahedral, respectively.

Indeed, the C—O stretching vibrations of the carbonyl groups are coupled through the central metal atom to one another, and in case of trans configuration, vibrations of the same phase are infrared-inactive.

This finding is contradictory to the concept mentioned in the introduction and lacking experimental evidence [1], that titanium tetrachloride complexes exclusively have a cis-configuration.

It was hoped on the basis of the investigations of LAPPERT that the IR spectra of the complexes of the polyesters, selected as model substances, will be helpful in clearing their structure.

Since the complexes decompose on dissolution, the KBr disc or the paraffin oil suspension methods were the choice for recording the spectra. Owing to the instability of the substances, naturally also the test samples were prepared in a dry box. In the preliminary experiments, the KBr-method was found to be unsuitable, since the complexes were partly decomposed during recording, and only diffuse, inevaluable bands appeared in the pictures. The technique using paraffin oil suspension proved to be satisfactory, so that this method was adopted in the further work for recording the IR spectra of the complexes.

After the development of experimental and analytical methods, the complexes of the selected model compounds have been prepared. Their compositions and decomposition points were determined, and the infrared spectra recorded.

The cis- and trans-cyclohexane-1,2-diol-diacetates were selected as the first model compounds. As is known, the cis-diol contains OH-groups of a, e, or e, a position. In the trans-diol the same groups are in e, e or a, a position, but it is a generally accepted opinion that energetically the position e, e is more favourable. The distance between the OH-groups in a, e and e, e position being identical, the possibility that the trans-diol reacted in the form a, a, that is to say there might be a difference in the complexing tendency of the acetoxy groups including an angle of 60° and 180°, respectively, was to be investigated on the cis- and trans-cyclopentane-diol-diacetates.

The already mentioned model compounds were prepared further for purposes of comparing cyclohexane-1,3- and -1,4-diol-diacetate, and the composition of the complexes possible to prepare was determined. In general, the complexes were prepared from each compound at three different ratios of $TiCl_4$: substrate, taking equimolar quantities, or double as much from $TiCl_4$ or from the substrate.

Results are contained in Table I. It can be seen from data in Table I that with the exception of trans-cyclopentane-1,2-diacetate and trans-cyclo-

hexane-1,2-diacetate, in all the other cases also the 2 : 1 complexes can be prepared under suitable conditions. From trans-cyclopentane-1,2-diacetate, one of the exceptions, only the 1 : 1 complex can be prepared, while the other exception, trans-cyclohexane-1,2-diacetate yields, at a molar ratio of 2 : 1, the 3 : 2 complex.
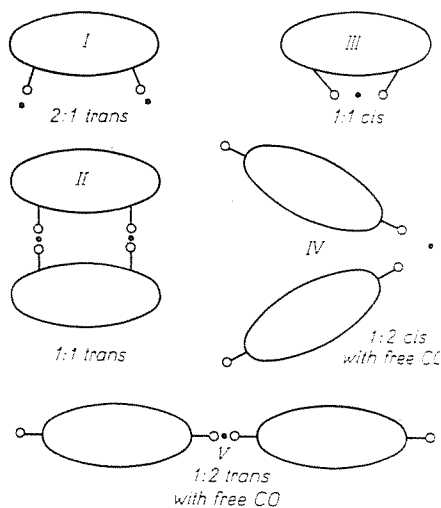
Fig. 2
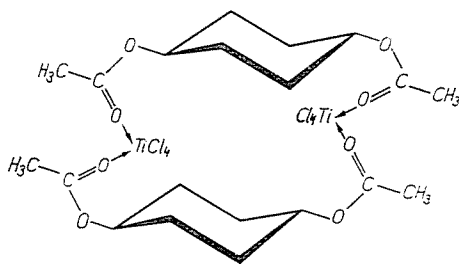
Fig. 3

In Table I also the most characteristic data of the spectra of the complexes are listed.

Though it is not possible to determine the molecular weight of the complexes, the types shown in Fig. 2 may be deduced from their composition, spectra and steric arrangement as possible structures.

On the simplified diagrams the cyclohexane skeleton is marked with an oval, the acetyl groups with blank circles, and titanium tetrachloride with blackened circles.

Table I

Substrate(s)	In IR spectra		Ratio of substrate to $TiCl_4$	
	νCO cm^{-1}	ν_{as} C—O—C cm^{-1}	at preparing	in the complex
Ethyl acetate	1740	1240	1 : 1	1 : 1
Cyclohexyl acetate	1740	1250/1240	1 : 1	1 : 1
trans-Cyclopentane-1,2-diol diacetate	1745	1250	1 : 1	1 : 1
cis-Cyclopentane-1,2-diol-diacetate	1745	1250	1 : 1	1 : 1
			1 : 2	1 : 2
trans-Cyclohexane-1,2-diol diacetate	1740	1250/1240	1 : 1	1 : 1
			1 : 2	1 : 1.5
			2 : 1	2 : 1
cis-Cyclohexane-1,2-diol diacetate	1740	1250/1230	1 : 1	1 : 1
			1 : 2	1 : 2
trans-Cyclohexane-1,3-diol diacetate	1740	1240	1 : 1	1 : 1
			1 : 2	1 : 2
			2 : 1	2 : 1
Cyclohexane-1,4-diol diacetate	1720	1240	1 : 1	1 : 1
			1 : 2	1 : 2
γ-Cyclohexane-1,2,3-triol triacetate	1740	1240	1 : 1	1 : 1
			1 : 3	1 : 2
α-Cyclohexane-1,2,3-triol triacetate	1740	1240	1 : 3	1 : 2
3,4-Diacetoxy-tetrahydrofuran	1750	1250	1 : 1	
			1 : 2	2 : 1
			2 : 1	
α-D-Xylose-tetraacetate	1750	1220	1 : 2	1 : 1
β-D-Xylose-tetraacetate	1760	1220	1 : 2	1 : 1
2,3,4-Triacetyl-1-α-methyl glucoside	1755	1230/1250	1 : 1	compound
2,3,4-Triacetyl-levoglucosane	1760, 1740, 1730	1250, 1235, 1220	1 : 1	1 : 1
2,3,4-Tribenzoyl-levoglucosane	1725	1260	1 : 1	1 : 1
			1 : 3	1 : 2
2,3,4,6-Tetraacetyl-β-D-glucose	1760	1245	1 : 1	compound
			1 : 3	1 : 2
α-D-Glucose-pentaacetate	1755/1745	1250, 1235, 1225	1 : 1	1 : 1
			1 : 3	1 : 2
β-D-Glucose-pentaacetate	1760	1220	1 : 1	1 : 1
			1 : 3	1 : 2
α-D-Cellobiose-octaacetate	1750	1230	1 : 2	1 : 2
			1 : 6	1 : 3
β-D-Cellobiose-octaacetate	1760/1750	1230	1 : 1	1 : 1
			1 : 2	1 : 2
			1 : 5	1 : 3
Raffinose-hendecaacetate	1760	1230	1 : 1	1 : 1
			1 : 5	1 : 4

* $\Delta\nu CO = \nu CO_s = \nu CO_c$
$\Delta\nu C=O=C = \nu C=O=C_c - \nu C=O=C_s$

It is remarkable that according to the evidence of the spectrum also in the 1 : 1 complex of cyclohexane-1,4-diol-diacetate both of the carbonyl-oxygens participate in the formation of the coordinative bond to the central titanium. This finding can best be interpreted by assuming the development of the cyclic structure shown in Fig. 3.

Decomposition point —°C	In IR spectra		Notes**	Type of complex
	$\Delta\nu\cdot CO^{\pm}$ cm^{-1}	$\Delta\nu_{as}C{-}CO{-}^{*}$ cm^{-1}		
80—107	120	85		pentacovalent (?)
94— 97	130	65/70		pentacovalent (?)
135	95	50	v.w.o.b.	trans
115—130	85/115	50	v.w.o.b.	cis
138—140	120	50		trans
125—135	120	50		trans
160—163	100	60/65		trans
163—167	60/110	50	s.o.b.	cis
177—178	80/120	50/70	v.w.o.b.	cis (?)
153—154	120	50/70		trans
100—102	120	70	v.w.o.b.	trans
135—137	130	70, 90		trans (?)
99	120	60	s.o.b.	trans
198	50/100	70		cis
167—168	120	75		trans
178—180	70/100	50	s.o.b.	cis
168—173	100	50	v.w.o.b.	trans
107—108	120	40	v.w.o.b.	trans
105—115	90	60	v.s.o.b.	trans
99—101	100	70	s.o.b.	trans
98—102	100	70	s.o.b.; at 1540 cm^{-1}: new band	trans
143—145	80	70	s.o.b.; at 1540 cm^{-1}: new band. νOH at 3520 cm^{-1} disapp.	trans
120—137	75/105	55	s.o.b.	cis
130—138	85/95, 50/55	20	s.o.b.	cis
133—140	80/90, 50	30	v.w.o.b.	cis
114—135	90	50	s.o.b.; at 1150 cm^{-1}: new band, νOH at 3480 cm^{-1} disapp.	trans
125—150	95	50	the same as above	trans
99—120	80	50	s.o.b.	trans
121—147	80	50	w.o.b.	trans
100—118	90	80	s.o.b.; new band at 1540 cm^{-1}	trans
119—150	90	80	w.o.b.; new band at 760 cm^{-1}	trans
135—152	80	70	s.o.b.	trans
148—154	80	70	w.o.b.	trans
120—130	75	75	v.s.o.b.; new band at 1540 cm^{-1}	trans
143—150	75	70	s.o.b.; new band at 760 cm^{-1}	trans
149—160	75	70	w.o.b.	trans
111—116	90	70	v.s.o.b.	trans
151—156	90	70	w.o.b.	trans

** v.w.o.b.: very weak original band
v.s.o.b.: very strong original band

The probable structure shown in Fig. 3 calls the attention to the fact that in the determination of the structure of complexes consideration must be given to the possibility of intermolecular linkages.

Table II

Substrate (s)	In IR spectra		Ratio of substrate to SnCl$_4$	
	νCO cm^{-1}	r_{as} C—O—C cm^{-1}	at preparing	in the complex
Ethylene glycol diacetate	1750	1240	1 : 1	1 : 1
Ethylene glycol dibenzoate	1725	1265	1 : 2	1 : 1
Cyclohexyl acetate	1740	1250/1240	1 : 1	2 : 1
			2 : 1	2 : 1
trans-Cyclopentane-1,2-diol diacetate	1745	1250	1 : 2	1 : 1
cis-Cyclopentane-1,2-diol diacetate	1745	1250	1 : 2	1 : 1
trans-Cyclohexane-1,2-diol diacetate	1740	1250/1240	1 : 2	1 : 1
cis-Cyclohexane-1,2-diol diacetate	1740	1250/1230	1 : 2	1 : 1
trans-Cyclohexane-1,3-diol-diacetate	1740	1240	1 : 2	1 : 1
trans-Cyclohexane-1,4-diol diacetate	1720	1240	1 : 2	1 : 1
cis-Cyclohexane-1,4-diol dibenzoate	1715	1280	1 : 2	1 : 2
γ-Cyclohexane-1,2,3-triol triacetate	1750	1240	1 : 3	1 : 1
β-Cyclohexane-1,2,3-triol triacetate	1750	1260/1240	1 : 3	1 : 1
3,4-Diacetoxy tetrahydrofuran	1750	1250	1 : 2	1 : 1
α-D-xylose tetraacetate	1750	1220	1 : 2	1 : 1
β-D-Xylose tetraacetate	1760	1220	1 : 2	1 : 1
2,3,4-Triacetyl-1-α-methylglucoside	1755	1250/1230	1 : 1	1 : 1
2,3,4-Triacetyl-levoglucosane	1760, 1740, 1730	1250, 1235, 1220	1 : 3	1 : 1
2,3,4,6-Tetraacetyl-β-D-glucose	1760	1245	1 : 2	1 : 1
α-D-Glucose pentaacetate	1755, 1745	1250, 1235, 1225	1 : 2	1 : 1
α-D-Cellobiose octaacetate	1750	1230	1 : 1	1 : 1
β-D-Cellobiose octaacetate	1760/1750	1230	1 : 1	1 : 1
			1 : 3	1 : 2
Raffinose hendecaacetate	1760	1230	1 : 1	1 : 1
			1 : 4	1 : 2

* $\Delta \nu CO = \nu CO_s - \nu CO_c$

$\Delta \nu C{=}O{=}C = \nu C{=}O{=}C_c - \nu C{=}O{=}C_s$

The next step in our work was the investigation of the complexing ability of cyclohexane-triol-triacetates. The three possible steroisomers of the compound were prepared.

The so-called α-pyrogallitol of tri-equatorial conformation was studied in greatest detail. For the 1 : 1 complex (see Table I) two new bands appeared at wave numbers 1640 and 1665 cm^{-1} besides the original carbonyl band (1750 cm^{-1}), indicative of a cis structure.

On preparing the complexes with titanium tetrachloride in excess, the 2 : 1 complex is formed, which already has a trans configuration, because it has only one band with an inflection at 1640 cm^{-1}. Presumably, the two complexes have the structures shown in Fig. 4.

Thus an excess of titanium tetrachloride does not produce the expected effect, i.e. the attachment of a further mole of Lewis acid to the still free acetoxy group, but a completely new structure is formed.

Decomposition point °C	In IR spectra		Notes**	Type of complex
	$\Delta\nu$ CO* cm^{-1}	$\Delta\nu_{as}$ C–O–C* cm^{-1}		
120—124	90/130	60		cis
84— 97	45	20	new band at 1738 cm^{-1}, 1625 cm^{-1}	
95— 97	130	55	v.w.o.b.	trans
93— 97	130	55	v.w.o.b.	trans
116	85/125	55	new strong band at 1725 cm^{-1}	trans
128	110/140	55		cis
140	100/130	50	new band at 1715 cm^{-1}	cis
144	120	65		trans
115—116	110/130	70		cis
148—149	90/110	70		cis
122—125	30	40		trans
125—128	120	60	s.o.b.	trans
70— 82	120	60	s.o.b.; new band at 1710 cm^{-1}	trans
115—120	110	60	strong new band at 1760 cm^{-1}	trans
45— 50	90	70	new bands at 1770 cm^{-1}, 1640 cm^{-1}	trans
60— 70	70	70	new bands at 1770 cm^{-1}, 1630 cm^{-1}	
148—150	75	~50	s.o.b.; new band at 1775 cm^{-1}	
113—117	110	~50		trans
65— 77	120	~65	s.o.b.; strong new band at 1720 cm^{-1}	trans
78— 93	120	~60	s.o.b.; new band at 1720 cm^{-1}	trans
90— 95	100	80	v.s.o.b.	trans
76— 95	110	80		
71— 93	110	80	v.s.o.b.; new band at 1720 cm^{-1}	trans
72— 95	120	80		
80— 98	120	70	new band at 1720 cm^{-1}	trans

** v.w.o.b.: very week original band
v.s.o.b.: very strong original band

It became clear already from these investigations that contrary to the statements in literature, unsupported by experiments, titanium tetrachloride, in dependence on the structure of the substrate and the composition of the complex, was able to form complexes of both cis and trans structure. A study of the SnCl$_4$ complexes gave similar results (see Table II).

In the best known anhydro-carbohydrate, in triacetyl-levoglucosane, the steric arrangement of the acetoxy groups is the same as described above for triol-triacetate. The fact that even at a high excess of titanium tetrachloride a complex of a maximum ratio of 2:1 can be prepared from levoglucosane, represents a further similarity. In the 1:1 complex the new band, shifted by a wave number of about 120 cm^{-1}, appears beside the original carbonyl band. In the 2:1 complex this new band is still to be observed, but a second new band occurs at 1700 cm^{-1} instead of the original carbonyl band.

Thus, the situation is different from that found for triol-triacetates, the spectra of their 2 : 1 complexes presenting a single shifted band.

With more than three functional groups, the pattern becomes still more complicated. Namely, from o-xylose acetate (from both the alpha and the beta anomer), containing already four acetoxy groups, only the 1 : 1 complex can be prepared with a trans structure. Since in this case at most two acetyl groups can be attached to titanium tetrachloride, the question arises, how many free carbonyl groups are contained in the complex: two or three? In
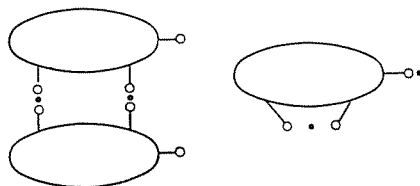

Fig. 4

the spectrum the intensity of the band of the bonded carbonyl group is slightly higher than that of the free carbonyl group. Taking into consideration the observation that the intensity of the complexed carbonyl band is always increased, it may be assumed that two of the four carbonyl groups are bonded. As the spectrum shows the complex to be of trans type, presumably it has the structure shown in Fig. 5.
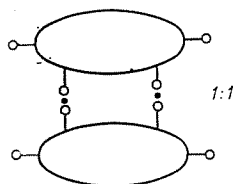

Fig. 5

In the case of glucose pentaacetates, which are able to form also 2 : 1 complexes, such estimation becomes already impossible. All the complexes have trans structures, and the formation of the complexes with different ratios is easy to follow on the basis of the change in intensity of the bands.

The complexes of the acetylated derivatives of disaccharide cellobiose and trisaccharide raffinose do not furnish much further information. From cellobiose acetate and from raffinose acetate the 3 : 1 and 4 : 1 complex, resp., can be prepared. This is indicative of the fact that the degree of complex formation is considerably influenced by steric factors. This is substantiated also by observations made on the tin tetrachloride complexes of benzoic acid

esters. As contrary to cyclohexane-1,4-diol-dibenzoate, neither the 1,2-diol-dibenzoate, nor levoglucosane-tribenzoate and glucose-pentabenzoate form complexes. This shows that benzoyl groups of great space requirement in neighbouring position form a steric hindrance to the development of the complex. Owing to its greater flexibility, no such hindrance is met with ethylene-glycol-dibenzoate.

As may be seen from Table II, tin tetrachloride generally yields 1 : 1 complexes. Besides the already mentioned 1,4-dibenzoate, exceptions are also cellobiose-acetate and raffinose-acetate, from which also complexes containing two molecules of Lewis acid can be prepared. Also these results are indicative of the important effect of steric hindrance.

Our further investigations were extended to model compounds containing besides the ester group also hydroxyl groups. Results of these investigations were to be used in clearing the mechanism of a carbohydrate chemistry reaction, studied earlier, namely the conversion of levoglucosane-triacetate to 2,3,4-tri-O-acetyl-α-D-glucosyl chloride, catalyzed by titanium tetrachloride [5].

The first problem to be decided was, whether 2,3,4-tri-O-acetyl-α-D-glucosyl chloride was the primary product, or formed only in a secondary process, by the decomposition of some adduct of $TiCl_4$ and the compound. Data in literature, according to which alkyl halogenide and alkoxy aluminium dichloride are formed in the decomposition of ethers with $AlCl_3$, are indicative of this latter possibility. However, it must be remembered that in the case of levoglucosane-triacetate not ether, but semiacetal bonds are ruptured. It was assumed that in the reaction product the OH group in position 6 is not free, but attached to $TiCl_3$. To clear the position of the band which is to be assigned to the C—O—Ti bond in the IR spectrum of the complex to be isolated as final reaction product, ethoxy-titanium chloride was prepared and its IR spectrum recorded. The spectrum unambiguously showed that the strong characteristic band in the region of 1100 cm^{-1} was to be assigned to the C—O—Ti valency vibration. Next, the $TiCl_4$ complex of 2,3,4-tri-O-acetyl-α-D-glucosyl chloride was prepared (molar ratio of $TiCl_4$: substrate 2 : 1).

In the spectrum of the complex a very broad carbonyl band occurs with a minimum in the region of wave number 1680, and at the same time, a band appears at wave number 1105, which can be co-ordinated to the asymmetric C—O—Ti vibration of the C—O—Ti(Cl_3) group. Such bond can form at the hydroxyl group on the carbon atom in position 6. Indeed, in the so-called LiF region of the spectrum there is no stretching vibration band, as contrary to the spectrum of the starting material (2,3,4-tri-O-acetyl-α-D-glucosyl chloride). Since the band characteristic of the free carbonyl groups (1755 cm^{-1}) appears only as impurity, and only two titanium atoms fall according to analysis to one sugar molecule, it is to be assumed that also the titanium atom

of the C—O—TiCl$_3$ moiety of the molecule participates in the formation of the complex.

The study of the complexes of model compounds containing hydroxyl groups permitted to evaluate the differences in the properties of TiCl$_4$ and SnCl$_4$ complexes, having apparently similar molecular structures. The model substance in these investigations was 1-β-methyl-triacetyl-glucoside. It was established that with 1 mole of TiCl$_4$ a complex, containing by 1 chlorine less according to analysis, was formed, and the strong gamma-OH band exhibited at 3520 cm^{-1} by the basic compound, was also in this case absent in the so-called LiF region.

The composition of the 1 : 1 complex prepared with SnCl$_4$ indicates a complex formation in the absence of the former reaction. It is interesting to note that the νOH band of gamma-OH at 3520 cm^{-1} lacks, however, a broad band ranging from 3200 cm^{-1} to about 2200 cm^{-1} is to be observed in the spectrum. Since the absorption due to paraffin oil obscured the picture, the spectrum was recorded also in perfluor-kerosene. In this picture, a broad band, with its centre between the range 2400 to 2500 cm^{-1}, was distinctly discernible, and obviously was to be attributed to the OH group in chelate bonding.

Subsequently, the complex resulting as the final product of the ring-splitting reaction was isolated. As the band at 1105 cm^{-1} due to C—O—Ti was present in the IR spectrum of this complex, this substantiated our earlier presumption, according to which the hydroxyl in position 6 in the primary reaction product is attached to TiCl$_3$, and the free hydroxyl is formed only in the hydrolysis of the complex.

Summary

From compounds containing several complex-forming groups, i.e. from compounds polyfunctional from the point of view of electron pair donation, thus from cyclopentane- and cyclohexane-diol-diacetates, cyclohexane-triol-triacetates, xylose-tetraacetates, glucose-pentaacetates, cellobiose-octaacetates and raffinose-acetate, the corresponding Lewis acid complexes were prepared with titanium tetrachloride and tin tetrachloride, respectively. The possible structure of the complexes was inferred on the basis of the IR spectra. It was assumed that, depending on the structure of the substrate and on the composition of the complex, the donor atoms are sited in two neighbouring or two opposite corners of the imaginary octahedron. It was established that titanium tetrachloride reacted with substrates containing also a hydroxyl group, to form, under elimination of HCl, the corresponding derivative of trichloro-ortho-titanic acid. In this compound, titanium is bonded with a coordinative bond intra- or intermolecularly to the carboxyl-oxygen of the ester group. With tin tetrachloride, no such compound is formed.

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