Compounds of L(+)-ascorbic acid with metals VIII. Titanium(IV) complexes of L(+)-ascorbic acid and 5,6-*O*-isopropylidene-L-ascorbic acid

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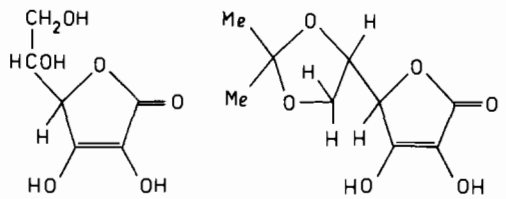
Abstract

The reactions of titanium(IV) halogen compounds with the monoalkali and dialkali metal salts of L(+)-ascorbic acid and 5,6-*O*-isopropylidene-L-ascorbic acid, respectively, in EtOH or THF as solvent, generally result in the formation of complexes of the appropriate dianions. Whereas the ascorbate dianion exclusively forms an ate-complex, this is not observed in the case of the 5,6-*O*-isopropylidene-L-ascorbate dianion. The results of our spectroscopic studies show the ene-diolate group to be the coordination site for both of the dianions. However, for the 5,6-*O*-isopropylidene-L-ascorbate dianion an additional weak interaction between one of the O atoms of its dioxolane ring and Ti(IV) cannot be excluded.

Introduction

Up to this time, our studies of the complex formation of the ascorbate system have mainly dealt with the isolation and characterization of complexes of the ascorbate monoanion ($Hasc^-$) in aqueous solution [1–4]. The results of UV–Vis, IR, ^1H NMR spectroscopic and magnetic studies of these complexes of the general type $M(Hasc)_n \cdot xH_2O$, M being TiO^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, have shown the ene-diolate group to be the coordination site of $Hasc^-$ with the anionic oxygen as the donor atom. Some of these results suggest the formation of a chelate ring structure by $Hasc^-$ using its non-deprotonated OH group at the C(2) atom. For the ascorbate dianion (asc^{2-}) chelation should be the normal kind of coordination. However, the isolation of analytically pure complexes of the dianion from aqueous solution was expected to be very difficult, if not impossible, because of its high basicity and instability. For this reason in these studies we used organic solvents, i.e. EtOH or THF. To overcome the problem of solubility to be expected in these solvents in the case of L(+)-ascorbic acid (H_2asc, see Fig. 1(a)) and especially its metal compounds, we also used its 5,6-*O*-ketal, i.e. the 5,6-*O*-isopropylidene-L-ascorbic acid (H_2Iasc, see Fig. 1(b)). According to Kurbatova [5] there is no difference



(a) (b)

Fig. 1. L(+)-ascorbic acid (a) and 5,6-*O*-isopropylidene-L-ascorbic acid (b).

in the ligand behaviour between H_2asc and its derivative H_2Iasc, because the glycolic side chain and the dioxolane ring, respectively, are not engaged in the complex formation. The following results show similarities as well as significant differences in the complex formation of the two dianions, asc^{2-} and $Iasc^{2-}$, with Ti(IV).

Experimental

L(+)-ascorbic acid and solvents were purchased from commercial sources, purified, and dried by standard procedures before using. $TiCl_4 \cdot 2THF$ and Cp_2TiCl_2 were prepared using standard methods. The preparation of 5,6-*O*-isopropylidene-L-ascorbic acid, its monoalkali and dialkali metal salts as well as those of L(+)-ascorbic acid will be described elsewhere [6]. Reactions were carried out under Ar

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TABLE 1. Analytical data for the new compounds

Compound	Found (%)			Calculated (%)		
	Ti	C	H	Ti	C	H
I	7.5	32.8	2.9	7.39	33.34	2.80
II	10.5	45.6	4.1	10.06	45.39	4.23
III	12.0	57.9	5.0	12.21	58.18	5.14

atmosphere and precautions were taken to avoid the presence of oxygen at every stage.

Preparations

$K_2Ti(C_6H_6O_6)_3$ (I)

To a mixture of $TiCl_4 \cdot 2THF$ (2,50 g, 7,5 mmol) and $K_2C_6H_6O_6$ (7,56 g, 30 mmol) 60–80 ml EtOH were added. The suspension so formed was heated under reflux for 16 h with magnetic stirring. The brownish red product was filtered off, extracted several times with hot MeOH, and dried *in vacuo*. The same complex has been obtained using $TiCl_4 \cdot 2THF$ and $KC_6H_7O_6$ in the molar ratio 1:6.

$Ti(C_9H_{10}O_6)_2$ (II)

A suspension of $TiCl_4 \cdot 2THF$ (1,67 g, 5 mmol) and $Na_2C_9H_{10}O_6$ (3,9 g, 15 mmol) in 50 ml THF was shaken at room temperature for 6–8 h. The white precipitate of NaCl was filtered off; the deep red solution was concentrated *in vacuo* to a volume of about 15 to 20 ml. Dropwise addition of about 200 ml Et_2O afforded the reddish brown compound **II**, which was collected by filtration and dried *in vacuo*. Complex **II** has also been obtained by using $TiCl_4 \cdot 2THF$ and $NaC_9H_{11}O_6$ in the molar ratio 1:6. In this case the product had to be redissolved and precipitated several times.

$(\eta^5\text{-}C_5H_5)_2Ti(C_9H_{10}O_6)$ (III)

$(\eta^5\text{-}C_5H_5)_2TiCl_2$ (1,25 g, 5 mmol) was extracted into about 50 ml THF containing $NaC_9H_{11}O_6$ (2,38 g, 10 mmol). The resulting suspension was refluxed under magnetic stirring for a further 4 h. Then the NaCl precipitate was filtered off. The deep red solution was shaken at room temperature for several h. The deep red crystals of **III** were collected by filtration and dried *in vacuo*.

The analytical data are summarized in Table 1.

Results and discussion

From the reactions of $TiCl_4 \cdot 2THF$ with the alkali metal ascorbates MHasc and M_2asc, in THF as solvent, no analytically pure products were obtained. After refluxing the reaction mixtures containing an excess of the alkali metal ascorbates for several days and repeated extraction of the isolated products with hot MeOH, the brown–red reaction products in any case contained various amounts of chloride. The reason for this seems to be a problem of solubility: presumably, even the partially substituted products are highly insoluble in THF so that the exchange of Cl^- can take place only very slowly. However, using EtOH as solvent and an excess of the ascorbate ligands, the ligand exchange can be completed. Surprisingly, the reaction products with the ascorbate mono- and dianion are identical, namely $K_2Ti(asc)_3$ (**I**). In the case of the ascorbate dianion the reaction course expected according to eqn. (1) is really observed. But the monoanion must previously be deprotonated to form the dianion complex and the free acid according to eqn. (2). Indeed, the free H_2asc could be isolated from the reaction mixtures.

$$TiCl_4 + 3K_2asc \longrightarrow K_2Ti(asc)_3 + 4KCl \quad (1)$$

$$TiCl_4 + 6KHasc \longrightarrow K_2Ti(asc)_3 + 4KCl + 3H_2asc \quad (2)$$

The same effect has been observed in the reactions of $TiCl_4 \cdot 2THF$ with the alkali metal salts of H_2Iasc, MHIasc and M_2Iasc, in THF as solvent. Similarly, an excess of the alkali metal salts was necessary for completing the ligand exchange. The reactions follow the courses given in eqns. (3) and (4).

$$TiCl_4 + 2Na_2Iasc \longrightarrow Ti(Iasc)_2 + 4NaCl \quad (3)$$

$$TiCl_4 + 4NaHIasc \longrightarrow Ti(Iasc)_2 + 4NaCl + 2H_2Iasc \quad (4)$$

The remarkable difference in the reactions of the asc^{2-} and $Iasc^{2-}$ dianions is the formation of an ate-complex with the former ligand and its failure with the latter, despite a sufficient excess in this case also.

The deprotonation of the monoanions $Hasc^-$ and $HIasc^-$ in the coordination sphere of Ti(IV) takes place under the influence of the high ionic potential of the highly charged central atom. The basic mono-

TABLE 2. UV–Vis spectral data of the new and some relevant ascorbate compounds[a]

Compound	CT Band		Inner-ligand band	
	max (nm)	log ε_{max}	max (nm)	log ε_{max}
II[b]	360.3	3.4	265.1	4.0
III[b]	476.0		243.0	4.3
$Cp_2Ti(Hasc)_2$[c,e]			252.0	
$TiO(Hasc)_2 \cdot 2H_2O$[c,d]	364.4	3.1	264.6	4.5
TiO(OH)(Hasc)[c,d]	344.8	2.8	263.9	4.1
NaHasc[c]			268.2	4.2
Na_2Iasc[b]			270.7	4.1

[a]Spectra were recorded by using quartz cells of 1 cm path length with a Specord UV–Vis spectrophotometer (VEB Carl Zeiss Jena). [b]In MeOH. [c]In H_2O. [d]From ref. 2. [e]From ref. 7.

anions, which are present in at least an equivalent amount, serve as proton acceptor. The formation of stable chelate rings with the dianions can be considered as a supporting factor for the deprotonation reaction. Whether this reaction takes place or not seems to be a question of the nature of the solvent. Recently, Cardin and Roy [7] described the formation of a bis(monoanion) complex, $Cp_2Ti(Hasc)_2$, in the reaction of Cp_2TiCl_2 with NaHasc in aqueous solution. In the analogous reaction of Cp_2TiCl_2 with NaHIasc in THF as solvent we have obtained a complex of the dianion, namely $Cp_2Ti(Iasc)$ (III), according to eqn. (5). We have briefly described this complex elsewhere [8].

$$Cp_2TiCl_2 + 2NaHIasc \longrightarrow Cp_2Ti(Iasc) + 2NaCl + H_2Iasc \quad (5)$$

Deprotonation of the ascorbate monoanion was also observed by Cardin and Roy in the case of diorganotin(IV) compounds, and these reactions were carried out in an organic solvent, too. Thus it can be concluded that the deprotonation of ascorbate monoanions in the coordination sphere of atoms with strong acceptor properties take place only in organic solvents without any or with only a weak protolytic character solving the free acids without deprotonation. In general, under these conditions it seems to be a characteristic reaction.

The deep red colour of complexes I–III and their solutions is the result of an intensive charge transfer in the Vis region which was already observed in the spectra of the earlier described titanyl ascorbates $TiO(Hasc)_2 \cdot 2H_2O$ and TiO(OH)(Hasc) [2]. The UV–Vis spectral data are summarized and compared with some other metal compounds of H_2asc and H_2Iasc in Table 2. However, complex I is nearly insoluble in all common organic solvents and, therefore, we could not obtain its UV–Vis spectrum.

The changes of the position of the absorption band in the Vis region show the effect of the co-ligands OH^- and Cp^- on the energy of the charge transfer from the ascorbate anion to Ti(IV) as expected. The position of the inner-ligand band of the ascorbate anions in the UV region depends on the co-ligands, too, but the observed shifts are smaller and generally take place to lower wavelengths.

By using the Cauchy–Gauss product and/or sum function for a numerical approximation of the experimental absorption envelopes between 1800 and 1500 cm^- in the IR spectra of H_2asc, its alkali metal salts, and its transition metal complexes we were able to deconvolute these complex regions of the stretching vibrations of double bonds. Despite the deformation vibration of the water molecule in the spectra of the transition metal ascorbate hydrates we found four single bands (A to D in the order of decreasing wavenumber) in this region for all compounds. The positions itself as well as the systematic changes of position and intensity of the individual bands in the series free acid–free anions–coordinated anions clearly show that A and

TABLE 3. IR spectral data (cm^{-1}) of the new and some relevant Ascorbate compounds[a]

Compound	ν(C=O) (I)	ν(C=O) (II)	ν(C=C)
I	1705s[b]	1591s	1528s
H_2asc	1752vs	1675s	1610w
NaHasc	1701vs	1632s	1579s
K_2asc	1703s	1589s	1524s
$Cp_2Ti(Hasc)_2$[c]	1725m	1603vs	
II	1746s	1696m	1579s
III	1740s	1730m	1617s
H_2Iasc	1757vs	1665vs	1603w
Na_2Iasc	1739vs	1717s	1581s

[a]Spectra were recorded on Perkin-Elmer 180 IR spectrophotometer as nujol mulls. [b]vs, very strong; s, strong; m, medium; w, weak. [c]From ref. 7.

TABLE 4. ^{1}H NMR data of the new and some relevant ascorbate compounds[a]

Compound	δC(4)–H	δC(5,6)–H	δC(8,9)–H	δC(Cp)–H
II	1.75m	3.97m, 3.57m	1.26d	
III	2.45m	4.0–4.6m	1.29d	6.4–6.6m
Na_2Iasc	1.75m	3.92m, 3.58m	1.24d	
Cp_2TiCl_2				6.55s
$Cp_2Ti(Hasc)_2$[b]	4.79d	3.90m, 3.69m		6.67s
KHasc	4.24d	3.72m, 3.41d		

[a]Spectra were recorded in D8 THF solution using internal TMS standard with a KRH 100 R spectrometer (ZWG of AdW of GDR); all shifts are in ppm downfield from TMS. [b]From ref. 7.

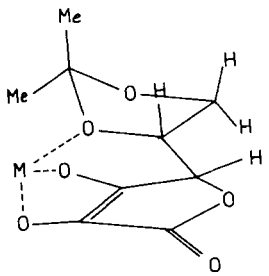

Fig. 2. Possible coordination mode of the 5,6-*O*-isopropylidene-L-ascorbate dianion.

B can be interpreted as ν(C=O) (I) and ν(C=O) (II), respectively. D can be assigned to ν(C=C). The individual band C, the origin of which could not be clarified till now, shows no systematic changes in position and intensity (for further details see refs. 3 and 9). The numerical analysis of the 1800–1500 cm^{-1} region of the IR spectra of H_2Iasc and its metal compounds afforded the same results.

The results of our IR spectroscopic studies which are summarized in Table 3 clearly suggest that the coordination site of the ascorbate dianions in the new complexes **I–III** is their ene-diolate group with the anionic oxygens as donor atoms

The ^{1}H NMR data of complexes II and **III** which are given in Table 4 together with some other results likewise prove the coordination type of the $Iasc^{2-}$ dianions characterized above. However, instead of the sharp singlet for the ten equivalent protons of the Cp^- ring system in Cp_2TiCl_2 the ^{1}H NMR spectrum of **III** is characterized by a very complex multiplet in this region. Within this multiplet a single resonance signal at 6.5 ppm corresponding to about five protons can be observed. From this it can be concluded that the unhindered rotation of one of the two Cp^- rings is prevented by steric hinderance. An overcrowded coordination sphere of Ti(IV) in the presence of the two Cp^- rings and the $Iasc^{2-}$ ligand would be plausible if the lactone ring and the dioxolane ring of the latter are directed toward the central atom as shown in Fig. 2. In this case an additional, but only weak interaction between one of the O atoms of the dioxolane ring, presumably C(5)–O, and Ti(IV) cannot be excluded. Such a weak interaction may contribute to the observed splitting of the singlet of the Me protons into a doublet in the spectrum of **III** which can also be observed in the spectra of **II** and of all other metal compounds of H_2Iasc. At the same time, this orientation of the dioxolane ring and the resulting steric hinderance give rise to a plausible explanation for the ate-complex formation with the asc^{2-} dianion contrary to the behaviour of the $Iasc^{2-}$ dianion. It is interesting to note that a splitting of the Cp^- proton resonance signal to a small extent is also mentioned by Cardin and Roy for $Cp_2Ti(Hasc)_2$. According to these authors, however, the multiplet is due to the presence of small amounts of other isomers [7].

References

1 W. Jabs and W. Gaube, *Z. Anorg. Allg. Chem., 514* (1984) 179.
2 W. Jabs and W. Gaube, *Z. Anorg. Allg. Chem., 514* (1984) 185.
3 W. Jabs and W. Gaube, *Z. Anorg. Allg. Chem., 538* (1986) 166.
4 W. Jabs, W. Gaube and B. Jurkutat, *Z. Chem., 27* (1987) 301.
5 G. T. Kurbatova, *Zh. Neorg. Khim., 25* (1980) 2725.
6 W. Jabs, W. Gaube and C. Fehl, *Z. Chem.*, submitted for publication.
7 C. J. Cardin and A. Roy, *Inorg. Chim. Acta, 107* (1985) L37.
8 W. Jabs, W. Gaube and R. Lukowski, *Z. Chem., 28* (1988) 412.
9 W. Jabs, *Dissertation B*, University of Greifswald, 1989.