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A multinuclear NMR spectroscopy characterization of dinuclear tungsten(VI) complexes of tridentate and pentadentate *meso*-D-*glycero*-D-*gulo*-heptitol and D-*glycero*-L-*gulo*-heptitol

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Abstract

The formation of W(VI) complexes of two C-6 epimeric heptitols, namely *meso*-D-*glycero*-D-*gulo*-heptitol and D-*glycero*-L-*gulo*-heptitol, has been studied in aqueous solution. In alkaline medium, both heptitols form two types of dinuclear complexes which have been structurally characterized from multinuclear NMR data. In the first type T, the site of chelation is a tridentate *xylo* system. In the second type P, the site of chelation is a pentadentate system with a central *xylo* triol group. The influence of the nature and orientation of the substituents attached to the lateral carbon atoms of the chelating site upon the complex stability is discussed.

Keywords: *meso*-D-*glycero*-D-*gulo*-Heptitol; D-*glycero*-L-*gulo*-Heptitol; ^{13}C NMR; ^{183}W NMR; Tungstate complexes

1. Introduction

Most sugars and alditols react with tungstate ions in aqueous solution, yielding ionic W(VI)–carbohydrate complexes which are useful for the ion chromatography separation of mixtures of carbohydrates [1–3]. Such complexes are commonly represented by (p,q,r) according to the formation reaction, where L is the carbohydrate:

$$p\mathrm{WO}_4^{2-} + q\mathrm{L} + r\mathrm{H}^+ = (p,q,r) + n\mathrm{H}_2\mathrm{O}$$

The stability constants of a number of W(VI)–carbohydrate complexes have been determined by a potentiometric method and were related to the configurations of the ligands, allowing the establishment of stability–structure correlations [4]. For most compounds, $p = 2$ and $q = 1$, whereas the r value depends on the medium acidity. In acidic solution,

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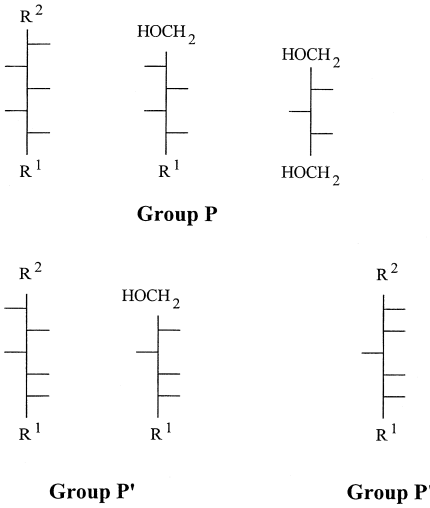
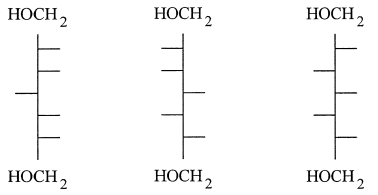
(2,1,2) complexes are formed which are stronger when chelation takes place at erythro sites than at threo sites. Moreover, further NMR studies demonstrated that alditols that possess a site of chelation of *xylo* configuration form three types of W(VI) complexes. Depending on the pH, these complexes differ in the denticity of the ligand [5]. In acidic medium, the major (2,1,2) complexes contain tetradentate ligands whereas in alkaline medium, two types of (2,1,1) complexes contain tridentate (type T) and pentadentate (type P) ligands.

With the smaller alditols, one complex generally prevails, and the site of chelation is identified by experimentally determining the coordination-induced shifts (CIS) for the carbon atoms of the ligand. On the other hand, higher-carbon alditols generally possess several possible chelation sites and may form mixtures of W(VI) complexes, which cannot be easily identified in the crowded carbon spectrum. In such cases, the use of ^{183}W NMR spectroscopy, a technique recently introduced for the study of W(VI) complexes of alditols [5–8] and sugar acids [9,10], allows the structural characterization of the various species formed in aqueous solution. In the tungsten spectrum, the complexes are easily detected, because few signals are present (one or two signals per complex), and these signals are found in specific ranges for each type of complex. Previous studies have shown that two natural heptitols, namely perseitol [7] and volemitol [8], do not form complexes of type P, but mainly (2,1,2) complexes in which tetradentate



Scheme 1. Fischer projection of the pentadentate chelating sites for the three groups of W(VI)–carbohydrate complexes of type P. R^1 and R^2 are non-chelating substituents which may be CH_2OH groups or other groups, such as carboxylate groups.



Scheme 2. Fischer projections of *meso*-D-*glycero*-D-*gulo*-heptitol (**1**), D-*glycero*-L-*gulo*-heptitol (**2**) and *meso*-D-*glycero*-L-*ido*-heptitol (**3**).

sites of chelation contain a central erythro diol group. On the contrary, two other carbohydrates containing a sequence of five adjacent CHOH groups with a central xylo triol system, a heptitol [5] and a heptonic acid [10], afford (2,1,1) W(VI) complexes of type P in alkaline medium.

The complexes of type P can be classified into three groups [10], depending on the relative orientations of the five adjacent chelating hydroxyl groups (Scheme 1). Group P corresponds to alditols with an all-threo site of chelation, i.e., the five HO groups define a sequence of four threo diol groups, which can be symbolized by (t–t–t–t). Group P′ corresponds to the (e–t–t–t) sequence and group P″ to the (e–t–t–e) sequence, where *e* and *t* stand for erythro and threo respectively. When one chelating hydroxyl group is a non-chiral CH_2OH group, the configuration of the corresponding $CHOH–CH_2OH$ system is considered, with respect to steric interactions, to be equivalent to a threo system. The reason is that, when both HO groups are oriented syn (which is the case in metal chelates), threo diol systems give rise to much less interaction between the lateral substituents than erythro systems.

Up to now, complexes of group P are known only for alditols [5], whereas complexes of groups P′ and P″ were characterized only for sugar acids, one for D-*glycero*-D-*gulo*-heptonic acid (group P″) [10] and one for L-gulonic acid (group P′). [1] A striking feature was that, in both aldonate complexes, the carboxylate group was not part of the pentadentate chelating site. The search for novel examples of alditol complexes of groups P′ and P″ was prompted by our recent syntheses [11] of two unnatural epimeric heptitols, *meso*-D-*glycero*-D-*gulo*-heptitol (**1**) and D-*glycero*-L-*gulo*-heptitol (**2**), which differ from the previously

[1] M. Hlaïbi, J.F. Verchère, and S. Chapelle, unpublished results.

studied [5] all-threo compound, *meso*-D-*glycero*-L-*ido*-heptitol (**3**), by containing one internal *xylo* triol group surrounded by one or two syn diol groups (Scheme 2). These heptitols were expected to afford mixtures of W(VI) complexes belonging to the three groups P, P′ and P″, accompanied by complexes of type T. Our aim was the comparison of the relative stabilities of the complexes of the tridentate and pentadentate ligands.

2. Experimental

All chemicals were of the highest commercially available purity. Tungsten was introduced as disodium tungstate dihydrate. The heptitols were prepared according to standard procedures [11].

The concentrations for the NMR studies were: 2 M tungstate and 1 M heptitol, in 2 mL D_2O for ^{183}W and ^{13}C spectra or 1 M tungstate and 0.5 M heptitol, in 0.5 mL D_2O for the 2D proton–proton homonuclear (COSY) and proton–carbon heteronuclear (HSQC) correlation experiments. The structural characterization of the complexes was performed by multinuclear NMR spectroscopy [5–8,10]. The ^{13}C and ^{183}W NMR spectra were obtained at 297 K on a Bruker ARX 400 spectrometer equipped with 5- or 10-mm multinuclear probes.

The pH of the solutions of complexes were adjusted by stepwise addition of a concentrated NaOH solution. The pH measurements were made using a Radiometer MI-412 combined glass microelectrode (external diameter 2 mm) and a Metrohm 632 pH meter standardized with commercial buffers.

3. Results

The literature assignments for the ^1H [12] and ^{13}C [13] NMR spectra of the free ligands were redetermined by 2D homo- and heteronuclear experiments (Tables 1 and 2). The results are presented first for *meso*-D-*glycero*-D-*gulo*-heptitol (**1**), which is a symmetrical ligand (Scheme 2) and thus affords simplified NMR spectra.

At pH < 7.5, the ^{13}C NMR spectrum of **1** was not modified after the addition of two equivalents of disodium tungstate. Complex formation began at pH 7.5, but only broad signals were observed in the spectrum, indicating exchange phenomena between several complexes and the free heptitol. The nature of these complexes was determined as follows. The presence of two characteristic signals in the δ, 91–92 range is the ‘fingerprint’ for the formation of a pair of dinuclear complexes involving the *arabino* O-1,2,3,4 or O-4,5,6,7 sites of **1**. Such complexes were

Table 1
100.62-MHz ^{13}C NMR data (δ, in ppm and $^1J_{C,H}$, in Hz) for the W(VI) complexes of *meso*-D-*glycero*-D-*gulo*-heptitol (**1**) and D-*glycero*-L-*gulo*-heptitol (**2**)

Carbon atom	C-1	C-2	C-3	C-4	C-5	C-6	C-7
1, u, δ	63.1	71.8	73.5	69.0	73.5	71.8	63.1
1, u, $^1J_{C,H}$	143	140	145	141	145	140	143
P″, δ	63.9	86.1	82.2	69.5	82.2	86.1	63.9
P″, $\Delta\delta$	0.8	14.3	8.7	0.5	8.7	14.3	0.8
P″, $^1J_{C,H}$	143	145	144	142	144	145	143
T, δ	64.7	73.0	82.5	84.2	82.5	73.0	64.7
T, $\Delta\delta$	1.6	1.2	9.0	15.2	9.0	1.2	1.6
T, $^1J_{C,H}$	143	144	144	150	144	144	143
2, u, δ	63.7	71.5	71.8	70.7	72.7	72.0	63.8
2, u, $^1J_{C,H}$	141	143	140	141	140	140	141
P′, δ	64.0	87.7	83.4	83.3	79.8	85.5	64.0
P′, $\Delta\delta$	0.3	16.2	11.6	12.6	7.1	13.5	0.2
P′, $^1J_{C,H}$	143	145	146	146	144	143	143
P, δ	64.7	73.5	88.0	82.8	86.7	83.0	77.9
P, $\Delta\delta$	1.0	2.0	16.2	12.1	14.0	11.0	14.1
P, $^1J_{C,H}$	143	141	143	145	145	146	144
T, δ	64.6	71.8	74.9	82.2	84.5	82.5	63.4
T, $\Delta\delta$	0.9	0.3	3.1	11.5	11.8	10.5	−0.4
T, $^1J_{C,H}$	141	141	144	147	143	145	141

u, Uncomplexed. $\delta \pm 0.01$ ppm, $^1J_{C,H} \pm 1$ Hz.

Table 2
400.13-MHz ^{1}HNMR chemical shifts (δ, in ppm) for the W(VI) complexes of *meso*-D-*glycero*-D-*gulo*-heptitol (**1**) and D-*glycero*-L-*gulo*-heptitol (**2**)

Carbon atom	H-1	H-2	H-3	H-4	H-5	H-6	H-7
1, u, δ	3.55/3.70	3.67	3.63	3.90	3.63	3.67	3.55/3.70
P″, δ	3.64/3.76	4.38	4.36	4.01	4.36	4.38	3.64/3.76
T, δ	3.76/3.89	3.69	4.36	5.37	4.36	3.69	3.76/3.89
2, u, δ	3.69/3.73	3.58	3.65	3.85	3.65	3.70	3.69/3.73
P′, δ	3.50/3.50	4.35	4.68	4.57	3.87	3.86	3.51/3.51
P, δ	3.49/3.49	3.64	4.19	4.68	4.36	4.79	4.16/4.30
T, δ	3.72/3.84	3.93	3.74	4.38	5.52	4.32	3.69/3.77

u, Uncomplexed. $\delta \pm 0.01$ ppm.

already characterized for many alditols and are referred to as type E in the literature [5,7,8]. Other signals for deshielded carbons near δ 83 revealed the presence of a third complex formed at the *xylo* O-3,4,5 site, which is fully characterized below as type T. Since W(VI) complexes of type E are well-known [5–7], no other attempts were made for further characterization of these species at pH 7.5.

At pH 8.5, the signals in the ^{13}C NMR spectrum became sharper than at pH 7.5, showing that the rate of exchange was noticeably slower, and at pH 9.9 and 10.4, three sets of four well-defined signals were observed in 2:2:2:1 ratio. Such an intensity pattern demonstrates that the three corresponding species are symmetrical. One of them is the free ligand (proportion 15%). The other species are two W(VI) complexes (proportions 70% and 15%). The carbon and proton assignments given in Tables 1 and 2 show that the major complex (type T) contains the tridentate ligand (O-3,4,5). The ^{183}W NMR spectrum of the solution at pH 9.9 showed four signals, one for free tungstate at $\delta \approx 0$ and three signals for the two complexes. As in other complexes of type T [5,6], none of the tungsten atoms is coupled to the ligand protons. The smaller signal at δ, 96 was attributed to the minor species, whereas two larger signals of equal intensities found at δ, −54 and −124 correspond to the major complex (Table 3). The latter pattern is characteristic for a species of type T [5,6], the structure of which is represented in Fig. 1.

The identification of the minor complex of **1** began from the observation that the single signal found at δ, 96 in the ^{183}W NMR spectrum lies in the range characteristic for complexes of type P [5,10]. The structure of such complexes, containing the pentadentate ligand, is represented in Fig. 2. Complexes of type P generally display two separate tungsten signals in the δ, 82–108 range, but only one signal is observed when both tungsten atoms are magnetically equivalent because the ligand is symmetrical, as is

Table 3
16.67-MHz ^{183}WNMR chemical shifts (δ, in ppm) for the W(VI) complexes of tridentate (type T) and pentadentate (type P) carbohydrate ligands[a]

Ligand	Type	Site	W-1	W-2
1	T	O-3,4,5	−54.2	−124.5
2	T	O-4,5,6	−56.6	−118.9
1	P″	O-2,3,4,5,6	96.1	96.1
2	P′	O-2,3,4,5,6	95.6	93.1
2	P	O-3,4,5,6,7	93.1	83.3
Xylitol [5]	P	O-1,2,3,4,5	93.3	93.3
L-Iditol [5]	P	O-1,2,3,4,5	93.4	82.3
L-Gulonate[b]	P′	O-2,3,4,5,6	105.4	91.1
D-*glycero*-D-*gulo*-Heptonate [10]	P″	O-2,3,4,5,6	108.1	102.3

[a] Relative to Na_2WO_4 in alkaline D_2O.
[b] M. Hlaïbi, J.F. Verchère, and S. Chapelle, unpublished results.
$\delta \pm 0.1$ ppm.
1, *meso*-D-*glycero*-D-*gulo*-heptitol; **2**, D-*glycero*-L-*gulo*-heptitol.

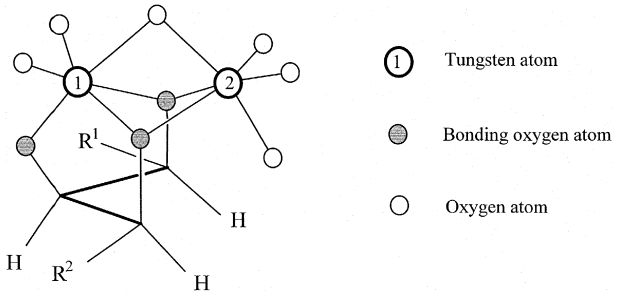


Fig. 1. Structures of W(VI)–heptitol complexes of type T. **1**, $R^1 = R^2 = CHOH–CH_2OH$. **2**, $R^1 = CH_2OH$; $R^2 = CHOH–CHOH–CH_2OH$.

the case for xylitol (Table 3). Therefore, the observation of a single signal for the complex of **1** indicates that the site of chelation can only be the symmetrical O-2,3,4,5,6 system. This assumption is in agreement with the symmetry of the ^1H and ^{13}C NMR spectra (Tables 1 and 2). However, the CIS patterns do not agree with the expected observation of five deshielded adjacent carbon atoms or protons. Only C-2,3,5,6 are deshielded to the normal extent, while C-4 is not ($\Delta\delta = 0.5$). In the same way, H-4 exhibits a very small deshielding ($\Delta\delta = 0.11$), contrary to H-2,3,5,6. This finding was not a complete surprise, as large variations of the CIS for the central carbon atom of the ligand are known to occur in complexes of type P [5,10]. For example, in the heptonate complex [10], $\Delta\delta = 5$ for C-4, which is smaller than in other reported complexes of type P ($\Delta\delta > 10$). Since the stereochemistry of the postulated site in **1** (O-2,3,4,5,6) is the same as that in the heptonate ligand, both complexes belong to group P″ (Schemes 1 and 2).

Contrary to heptitol **1**, D-*glycero*-L-*gulo*-heptitol

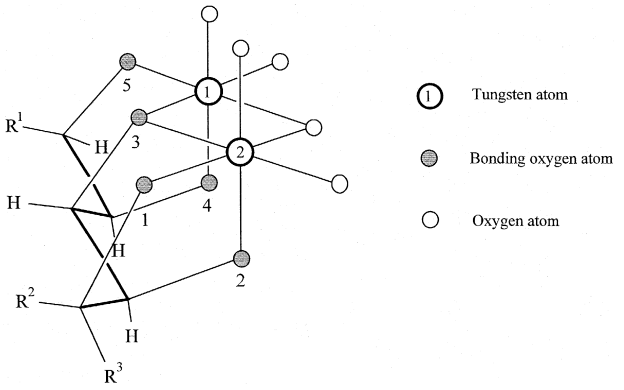


Fig. 2. Structures of W(VI)–heptitol complexes of type P. **1**, Group P″, $R^1 = R^2 = CH_2OH$, $R^3 = H$. **2**, Group P, $R^1 = R^2 = H$; $R^3 = CHOH–CH_2OH$. **2**, Group P′, $R^1 = R^3 = CH_2OH$, $R^2 = H$.

(**2**) is not a symmetrical ligand (Scheme 2). The carbon and proton assignments for free **2**, made as above, are reported in Tables 1 and 2. In the presence of two equivalents of disodium tungstate, the ^{13}C NMR spectrum could not be resolved at pH < 10.6, owing to exchange phenomena. At pH 10.6, however, the carbon signals are much sharper and allow the identification of three complexes (proportions 27% each) in addition to the free ligand (19%). At pH 11.7, the proportion of free ligand is larger (40%), while those of the three complexes are 30, 25 and 5%. The complexes were characterized from their ^{183}W NMR spectra at pH 11.7 and 10.6. At pH 11.7, three signals lie in the 83–96 ppm range, specific for complexes of type P (Table 3). The spectrum was analyzed as containing two pairs of signals, since the larger central peak is due to overlapping of two signals. The CIS patterns reported in Tables 1 and 2 show that the corresponding sites of chelation are O-3,4,5,6,7 (group P) and O-2,3,4,5,6 (group P′). By analogy with the ^{183}W and ^{13}C NMR spectra of the W(VI)–iditol complex [5], one pair of tungsten signals (δ, 93.1 and 83.3) was assigned to the complex of group P. The other pair of signals (δ, 95.6 and 93.1) was thus attributed to the complex of group P′ (Scheme 1). The third complex present at pH 10.6 gives rise to an additional pair of small signals at δ, −57 and −119, characteristic for a complex of type T. The assignments for the carbon spectrum, detailed in Table 1, show that this complex contains the tridentate ligand bound at the xylo O-4,5,6 site (Fig. 1). No coupling could be detected between the tungsten atoms and the ligand protons.

The magnitude of the proton–carbon coupling constants in the complexes warrants some comments. Although previous studies have reported a significant increase in the $^1J_{C,H}$ values for all carbon atoms of the chelating site in many tungsten–carbohydrate complexes [5–8], the data in Table 1 do not show such large variations. In our opinion, this result must be attributed to the heptitols being bound to tungsten in zigzag conformation, with negligible resulting steric strain. Examination of molecular models confirmed that the pentadentate ligands fit easily, without any twisting, with the dinuclear tungsten core, as shown in Figs. 1 and 2.

As is common in the aqueous chemistry of W(VI), kinetic variations were noticed for the complexes of **2**. At pH 10.6, the proportion of complex T is lower (5%) in the carbon and tungsten spectra, recorded after a long accumulation (27 h), than in the carbon spectrum carried out after 10 min (27%). It indicates

that complex T slowly gives complexes of type P and is a very minor species at equilibrium. At pH 11.7, no T type complex appeared in the tungsten and carbon NMR spectra recorded after 15 h. Moreover, the relative proportions of the complexes of groups P and P′ also changed with time. The proportion of complex P (initially 25%) increased at the expense of complex P′ (initially 30%). It may suggest that like T, P′ is a kinetic product and P is the thermodynamic product of the complex-forming reaction. However, previous studies have established that the proportions of complexes T, P and P′ do not change with pH and that their kinetic variations do not reflect different protonation states [5].

4. Discussion

Structures of the complexes.—In the three types of W(VI)–alditol complexes, E, T and P, the ligands exhibit various denticities and the structure of the ditungstate core is different. At pH ≤ 7, the ligands are tetradentate and bind a W_2O_5 metal core made of two WO_6 octahedra sharing a face. In alkaline medium, the ligands are either tridentate and bind a W_2O_6 metal core in which two WO_6 octahedra share a face (type T), or pentadentate and bind a W_2O_5 metal core in which two WO_6 octahedra share an edge (type P) [5,10]. The latter mode of bonding between WO_6 octahedra resembles that observed in many inorganic iso- and hetero-polytungstate anions [14]. The present results show that, in alkaline medium, both heptitols **1** and **2** afford W(VI) complexes of types T and P.

The complexes of type T are similar to their shorter homologues [5]. In the structure represented in Fig. 1, W-1 (δ, ≈ -60) is bound to three adjacent oxygen atoms, whereas W-2 (δ, ≈ -120) is bound to both side oxygen (bridging) atoms.

Few examples of dinuclear W(VI)–carbohydrate complexes of type P have been reported, since they require ligands with at least five adjacent hydroxyl groups, including three central CHOH groups in *xylo* configuration. The complexes of xylitol and iditol have been characterized by multinuclear NMR spectroscopy, whereas two complexes of *meso*-D-*glycero*-L-*ido*-heptitol (**3**) were studied by ^{13}C NMR spectroscopy only [5]. The general structure of complexes of type P is represented in Fig. 2, showing that the central oxygen atom of the pentadentate chelating site bridges the tungsten atoms, and that each tungsten atom is bound to three adjacent oxygen atoms. If the site of chelation is numbered O-1,2,3,4,5, as shown in Fig. 2, the four C-1,2,4,5 atoms are deshielded by 9–15 ppm, but for the central C-3, the deshielding effect $\Delta\delta$ lies between 0 and 14 ppm. Such variations of the CIS may reflect the existence of steric strain in the pentadentate site, due to the interaction of the central C-3 with the substituents attached to C-1 and C-5 (only when HO-1,2 and/or HO-4,5 are erythro) [10]. Accordingly, the deshielding effect on C-3 decreases in the order: P > P′ > P″ (Table 1). If it is admitted that the complex stability is related to the number and strength of the C–O–W bonds, then weakening the central bond should make the complex weaker. Thus, the stabilities of complexes of type P would follow the order indicated by the deshielding of C-3, since the steric strain is larger in group P″ than in group P′, and nil in group P (Scheme 1).

Ranges of ^{183}W NMR chemical shifts in the complexes.—The various complexes of W(VI)–alditol complexes can be characterized by ^{183}W NMR spectroscopy, since each type of complex gives signals that appear in a specific range. For example, complexes of type T display two signals near δ, -60 and -120, whereas complexes of type P show one or two uncoupled signals with positive chemical shifts (δ, 82–108) [5]. The available data for all known complexes of type P, collected in Table 3, suggest that when the chelating site contains a deprotonated CH_2OH group, the W atom bound to this oxygen atom gives a signal near δ 93. On the contrary, W atoms bound to three adjacent deprotonated CHOH groups give a signal in the 82–108 range. There seems to be no apparent relationship between the tungsten chemical shifts and the complex group (P, P′ or P″). Thus, the steric effects responsible for the small CIS for the central carbon in complexes of groups P′ and P″ do not seem to influence the tungsten chemical shifts, which do not show specific values for complexes of groups P, P′ and P″.

The present data obtained for heptitol complexes and previous results for aldonate complexes [10] [1] allow a comparison of the influence of CH_2OH or COO^- substituents on the tungsten chemical shifts in the complexes of type P (Table 3). For complexes of alditols, $\delta < 100$ ppm are found for the three groups, whereas for complexes of aldonates, $\delta > 100$ ppm are observed at least for one tungsten atom. It suggests that the presence of the unbound carboxylate group is responsible for the enhancement of the tungsten chemical shifts in aldonate complexes.

Stabilities of the complexes.—The proportions, at equilibrium, of W(VI)–heptitol complexes of types T

and P are dependent on their relative stabilities. The observed trend is that from **1** to **3**, which differ only by their C-2,6 configurations, the proportion of complexes of type P increases at the expense of complexes of type T. This trend is probably related to the different stabilities of complexes of groups P, P′ and P″, since the proportion of complex of type P increases when the ligand changes from **1** (complex of group P″) to **2** (complexes of groups P and P′) and **3** (complexes of group P only). It is in agreement with the stability order: P > P′ > P″.

Three important factors that influence the stabilities of W(VI) complexes of alditols have been considered in the literature [4,5,15,16]. The first one is the denticity of the ligand, since the complex stability increases with the number of W–O–C bonds. The second factor is the steric strain created when two lateral substituents of the chelating site may interact, as a result of their unfavorable orientation. The third factor is the involvement of one CH_2OH group instead of a CHOH group in the site of chelation. Since a free CH_2OH group has a higher degree of freedom than a CHOH group [17], complexes which involve one or two primary HO groups are weaker than similar species involving only CHOH groups. The influence of these three factors was examined for complexes of types T and P.

According to the first factor, complexes of type P, involving pentadentate ligands, should be intrinsically stronger than those of type T, involving tridentate ligands. It must be stated here that the notion of intrinsic stability implies that the chelating sites are $(CHOH)_n$ systems ($n = 3$ or 5). In fact, our results show that complexes of type T are weaker than complexes of groups P and P′ (ligand **2**), but stronger than the complex of group P″ (ligand **1**). This finding may be accounted for by examining the influence of the second factor on both types of complexes. Steric strain is probably of little importance for species of type T, in which the lateral substituents R^1 and R^2 are always well-separated (Fig. 1). On the contrary, it may play a role in species of type P, since groups R^1 and R^2 are located closer than groups R^3 and H (Fig. 2). Hence, the observed stability order, P > P′ > P″, agrees with the variations of the magnitude of the interaction between substituents R^1 and R^2.

The third factor is probably responsible for the relative stabilities of the W(VI) complexes of **2** and **3**. Complexes of group P are expected to be stronger than those of group P′, but for alditol **2**, complex P (O-3,4,5,6,7) involves the primary HO-7 group, whereas complex P′ (O-2,3,4,5,6) involves only CHOH groups. Thus, the complex of group P is weaker than 'normal' complexes of group P formed by a ligand containing a $(CHOH)_5$ chelating site, explaining the similar stabilities of both complexes P and P′. The relative stabilities of both complexes of group P formed by **3** have also been rationalized by consideration of this third factor, since the minor complex contains a binding CH_2OH group [5].

Other complexes of type P have also been reported with aldonate ligands [10] [1]. These complexes, in which the carboxylate group is not part of the chelating site, may thus be compared with the above heptitol complexes. The L-gulonate complex [1] belongs to group P′, but its site of chelation (O-2,3,4,5,6) involves a binding CH_2OH group, which makes it weaker than a 'normal' complex of group P′. The D-*glycero*-D-*gulo*-heptonate complex [10] is formed at the O-2,3,4,5,6 site and thus belongs to group P″, like the complex of **1**. However, no complexes of type T have been reported for both aldonates, showing that their complexes of type P are much stronger than those of type T. This result is especially surprising for the heptonate ligand, whose chelating site has the same configuration as alditol **1** and was therefore expected to react in a similar manner. This finding may indicate either a peculiar stability of the aldonate complexes of type P, or a peculiar instability of their complexes of type T. A possible reason may be associated with the presence of the carboxylate substituent, but available data is not sufficient for the interpretation of this interesting result.

5. Conclusions

Epimeric C-2,6 heptitols **1**–**3** form well-characterized W(VI) complexes of two types in alkaline medium. Complexes of type T involve the tridentate ligands, whereas complexes of type P involve the pentadentate ligands. Depending on the configurational sequence in the chelating sites, complexes of type P can be separated into three groups, P (t–t–t–t), P′ (e–t–t–t) and P″ (e–t–t–e). The stability order, P > P′ > P″, is due to steric strain that appears when the lateral diol groups of the chelating site are erythro. The observation of large variations in the CIS of the central carbon supports this assumption. Complexes of type T are stronger than complexes of group P″, but are weaker than complexes of groups P′ and P.

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