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Contribution from the Laboratoire de RMN, URA 464, and URA 500 "Polymères, Biopolymères, Membranes",
Université de Rouen, Faculté des Sciences, BP 118, 76134 Mont-Saint-Aignan, France

^{183}W NMR Studies of Tungstate Complexes of Carbohydrates. 1. Characterization of Two Structural Types in the Alditol Series. Evidence That the Tungstate and Molybdate Threo Complexes Are Not Homologous

Stella Chapelle*,† and Jean-François Verchère*,‡

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Dinuclear tungstate complexes of alditols have been studied in aqueous solution by ^{13}C and ^{183}W NMR spectroscopies. Ligands possessing hydroxyl groups in erythro configuration (erythritol, galactitol) formed a series of tetradentate complexes homologous to the known corresponding molybdate erythro compounds. In contrast, ligands with threo hydroxyl groups (threitol, xylitol) formed tridentate complexes different from the tetradentate molybdate threo species. For all alditols, the ^{183}W NMR spectra showed two sharp tungsten signals separated by 3–7 ppm (erythro series) or $\simeq$60 ppm (threo series). In the erythro complexes, large $^3J_{\mathrm{W,H}}$ coupling constants (8–10 Hz) were measured and allowed the estimation of the corresponding dihedral angles. A structure that accounts for the asymmetry of the chelating site is proposed for the tridentate threo complexes. The structural difference between the molybdate and tungstate complexes of *threo*-alditols is discussed in connection with their stabilities and reactivities.

Introduction

Tungstate complexes of carbohydrates (sugars and alditols) have not been studied as much as their molybdate homologues, presumably because of the expected structural analogy between two elements of column VIB. Accordingly, both elements form 2:1 metal (M = Mo or W)–alditol (L) complexes[1–8]

$$2\mathrm{MO}_4^{2-} + \mathrm{L} + p\mathrm{H}^+ \rightleftarrows (2,1,p)^{(4-p)-} + \mathrm{H_2O} \qquad p = 2, 3$$

and the formation constants of W and Mo complexes are closely correlated[6,9] ($\log K_{\mathrm{W}} - \log K_{\mathrm{Mo}} \simeq 3$). Nevertheless, tungstate species possess specific useful properties. Because alditols complex more strongly tungstate than molybdate, only the former can be determined by acidimetric titration[10] after complexation by xylitol or D-glucitol. For the chromatographic separation of carbohydrates,[1–3,11] solutions of tungstate are superior to molybdate, which can slowly oxidize reducing sugars.

Structures of tungstate complexes are generally assumed to be similar to those of molybdate compounds characterized in the solid state. Recent ^{13}C NMR studies[9,12–14] have brought new support to this belief, because the structures of the ligands appeared very similar in Mo and W species. ^{95}Mo NMR spectroscopy was used for the characterization of molybdate complexes of carbohydrates[9] and alditols,[14,15] although the large signals of this quadrupolar nucleus gave poor information on the nature of the sites of chelation.

Since 1979, ^{183}W NMR spectroscopy has been increasingly used in the study of iso- and heteropolytungstates in solution.[16] This isotope generates narrow signals, due to its nuclear spin $^1/_2$. Moreover, as it is a heavy nucleus, its chemical shifts are very sensitive to the environment and proved helpful in the structural elucidation of polyanions[17] possessing many different types of tungsten atoms. However, no data on carbohydrate complexes could be found in the literature. In continuation of our work on related molybdate complexes, we have undertaken to characterize various types of tungstate–alditol complexes.

Experimental Section

All chemicals were commerical products of reagent grade, used as supplied. Solutions of complexes were prepared by standard methods.[9,13,14]

1D and 2D NMR spectra have been recorded with a Bruker AM 400 spectrometer equipped with 5-mm or 10-mm multinuclear VSP probes. Sample concentrations were 1 M (polyol), 2.5 M (molybdate), and 1.25 M (HCl).

Coupled 1D ^{13}C spectra were recorded at 100.62 MHz with the following parameters: sweeping range 8500 Hz, acquisition time 1 s, digital resolution 0.5 Hz/pt, relaxation delay 2 s. They were obtained with nuclear Overhauser enhancement by gating off the decoupler during data acquisition. The chemical shifts, referenced to TMSP in $\mathrm{D_2O}$, were determined by the substitution method.[18]

The 1D ^{183}W spectra were measured at 16.65 MHz. Preliminary investigations were made with sweeping range 8000 Hz, acquisition time 2 s, digital resolution 0.5 Hz/pt, relaxation delay 5 s, and a pulse of duration 25 μs, corresponding to a 60-deg pulse angle. Then, coupled spectra were obtained with polarization transfer from proton to tungsten, using a DEPT[19] sequence. The 90-deg ^{183}W pulse was 35 μs and a 45-deg ^{1}H pulse was used to complete the polarization transfer. The reference for chemical shifts was an alkaline $\mathrm{Na_2WO_4}$ solution in $\mathrm{D_2O}$, using the substitution method.

2D NMR ^{13}C–^{1}H heteronuclear shift correlation experiments were made using polarization transfer from ^{1}H to ^{13}C through $^1J_{\mathrm{C,H}}$ couplings.[20] The number of experiments was 64 × 1 K. For 2D NMR ^{183}W–^{1}H experiments, the polarization transfer from ^{1}H to ^{183}W was made via the long-range coupling $^3J_{\mathrm{W,H}}$ (COLOC sequence),[21] the number of experiments being 64 × 256 W.

Results and Discussion

^{13}C NMR Spectroscopy. After addition of tungstate and acidification, the number of signals doubled in the spectra of the alditols, indicating that erythritol, galactitol, DL-threitol, and xylitol formed a single complex each, symbolized hereafter as E, G, T and X, respectively. The signals of the complexed ligands were assigned by 1D proton experiments and 2D heteronuclear ^{13}C–^{1}H correlation shift experiments. Carbons involved in the sites of chelation were revealed by increased values of their chemical shifts and of their coupling constants $^1J_{\mathrm{C,H}}$. Deshielding effects due to the complexation of carbohydrates by borate[22–26] and molyb-

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† Laboratoire de RMN.
‡ URA 500.

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Table I. 100.62-MHz ^{13}C NMR Chemical Shifts δ and $^1J_{C,H}$ Direct Coupling Constants of the Alditol Erythritol and of Its Tungstate and Molybdate Complexes

	carbon position			
param	1	2	3	4
δ, ppm[a]	64.7	74.3	74.3	64.7
δ, ppm[b]	73.1	82.4	92.4	70.8
$^1J_{C,H}$, Hz[b]	148	149	150	146
$\Delta\delta$, ppm	8.4	8.1	18.1	6.1
ΔJ, Hz	7	8	9	5
δ, ppm[c]	74.3	83.5	92.8	71.3
$^1J_{C,H}$, Hz[c]	144	147	147	144
$\Delta\delta$, ppm	9.6	9.2	18.5	6.6
ΔJ, Hz	3	6	6	3

[a] $^1J_{C,H}$ = 141 Hz for all carbons. δ assigned from literature.[30] [b] Tungstate complex. [c] Molybdate complex.[14] Accuracy: $\delta \pm 0.1$ ppm; $J \pm 1$ Hz.

date[9,12-14,27-29] are well documented. Some related examples have been reported for tungstate complexes.[8,9,13]

Erythritol (E) and Galactitol (G) Complexes. Alditols possessing internal erythro groups, erythritol, ribitol, D-arabinitol, D-mannitol, and galactitol, form[12,14] a series of molybdate complexes of related structures, classified by Matulova et al.[12] as types A or C, depending on substitution at lateral carbons of the site of chelation, or more simply by us[14] as type E (for erythro). In this paper, it is referred as type ERY to avoid confusion with complex E. A preliminary ^{13}C NMR study[13] has shown that galactitol and D-mannitol formed complexes of homologous structures with molybdate and tungstate.

Similar results were obtained in the case of erythritol. In the tungstate complex E, the four carbons of the ligand were deshielded in an asymmetric manner, with the same typical pattern as the molybdate complex (Table I). All four carbons showed enhanced coupling constants $^1J_{C,H}$, and the effect of complexation by tungstate was more important than in the molybdate complex. The close analogy between the parameters of the spectra of molybdate and tungstate complexes indicated that no important difference could exist between their structures. Thus, there is strong evidence that alditols of the erythro series form homologous molybdate and tungstate complexes belonging to the same structural type ERY. This series was characterized[12-14] by the ligands being tetradentate and adopting a *sickle* conformation.

Threitol (T) and Xylitol (X) Complexes. Contrary to the above series, the spectra of the complexes formed by alditols possessing hydroxyl groups in threo configuration showed that only three vicinal carbons were deshielded: C-1,2,3 in threitol and C-2,3,4 in xylitol (Table II). In both cases, complexation induced the larger chemical shift at the central carbon of the site of complexation and smaller identical variations at the lateral carbons. It indicated that the ligands chelated the ditungstate group in a symmetrical way. This result was not surprising for xylitol but was unexpected for threitol, in which carbons C-1,3 did not appear a priori to be equivalent.

These results contrasted with those obtained for the molybdate complexes of threitol and xylitol, in which the ligands were tetradentate[14] and the C-1,2,3,4 sites of chelation had a symmetrical structure, as similar deshielding effects (Table II) were observed at C-2,3 ($\simeq$10 ppm) and at C-1,4 ($\simeq$12 ppm). The corresponding structures (types B and D[12] or type T for threo[14]) were described as involving the ligands in *zigzag* conformation. Since the symbol T is used now for the tungstate–threitol complex, the series of threo complexes will be referred thereafter as type TH_W for the tridentate tungstate complexes and as type TH_M for the tetradentate molybdate species.

Table II. 100.62-MHz ^{13}C NMR Chemical Shifts δ and $^1J_{C,H}$ Direct Coupling Constants of *threo*-Alditols and of Their Tungstate and Molybdate Complexes

	carbon position				
param	1	2	3	4	5
		DL-Threitol			
δ, ppm[a]	64.8	73.6	73.6	64.8	
δ, ppm[b]	74.3	86.7	83.0	66.6	
$^1J_{C,H}$, Hz[b]	144	149	147	143	
$\Delta\delta$, ppm[b]	9.5	13.1	9.4	1.8	
δ, ppm[c]	77.0	83.4	83.4	77.0	
$^1J_{C,H}$, Hz[c]	144	147	147	144	
$\Delta\delta$, ppm[c]	12.2	9.8	9.8	12.2	
		Xylitol			
δ, ppm[a]	64.8	74.0	72.8	74.0	64.8
δ, ppm[b]	66.7	83.0	86.1	83.0	66.7
$^1J_{C,H}$, Hz[b]	143	147	147	147	143
$\Delta\delta$, ppm[b]	1.9	9.0	13.3	9.0	1.9
δ, ppm[c]	77.1	84.3	83.4	86.6	64.1
$^1J_{C,H}$, Hz[c]	146	148	149	149	142
$\Delta\delta$, ppm[c]	12.3	10.3	10.6	12.6	−0.7

[a] Uncomplexed alditols, $^1J_{C,H}$ = 141 Hz for all carbons. δ assigned from literature.[30] [b] Tungstate complexes. [c] Molybdate complexes. Accuracy: $\delta \pm 0.1$ ppm; $J \pm 1$ Hz.

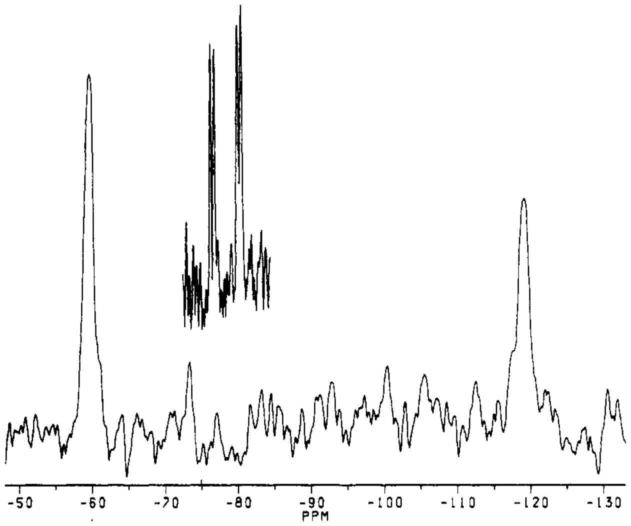

Figure 1. 16.65-MHz ^{183}W NMR spectra of the 2:1 tungstate complexes of erythritol (top, 560 scans, 1 h) and DL-threitol (bottom, 1220 scans, 2 h).

Thus, it is shown that the postulated analogy between the molybdate and tungstate complexes of alditols is verified in the erythro series only. As molybdate complexes of types ERY and TH_M gave ^{95}Mo NMR signals characterized by different chemical shifts,[14,15] we examined the ^{183}W NMR spectra of the corresponding complexes.

^{183}W NMR Spectroscopy. For each complex of *erythro*-alditols, the proton-coupled spectra contained two signals W_1 and W_2 of equal intensities attributed to two nonequivalent tungsten atoms (subscript 1 was given to the more shielded signal). Figure 1 represents the typical spectrum obtained with erythritol. We verified that none of the signals could correspond to remaining uncomplexed tungstate, which in these conditions is present[31] as the heptatungstate ion $[W_7O_{24}]^{6-}$, the ^{183}W NMR spectrum of which shows[17] atoms of three types: one central W (δ = 267 ppm)

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Table III. 16.65-MHz ^{183}W NMR Chemical Shifts δ (ppm) and $^3J_{W,H}$ Coupling Constants (Hz) of Tungstate Complexes of Alditols[a]

param	W_1	W_2
	Erythro Compounds	
δ for erythritol	−76.1	−79.5
$^3J_{W,H}$ for erythritol	9.1	8.8 and 1.0
δ for galactitol	−79.3	−85.8
$^3J_{W,H}$ for galactitol	8.3 and 2	8.3 and 2.2
	Threo Compounds	
δ for DL-threitol	−59.3	−118.3
δ for xylitol	−61.7	−120.8
δ for D-glucitol[b]	−57.7	−121.6

[a] Reference: Na_2WO_4 in alkaline D_2O. Accuracy: $\delta \pm 0.1$ ppm; $^3J_{W,H} \pm 0.5$ Hz. [b] Major complex.

and two sorts of dioxo W ($\delta = -90$ and -180 ppm). In the absence of any published crystal structure, the finding of two signals gave a definitive proof that tungstate complexes are dinuclear. The values of chemical shifts for W_1 and W_2 (Table III) were in the range $\delta = -81 \pm 5$ ppm, in agreement with tungsten being in the +VI oxidation state.[16]

The slight difference between the chemical shifts of the tungsten atoms (3.4 ppm in E, 6.5 ppm in G) was in agreement with a structure close to that of the erythritol–molybdate complex,[32] which can be used as a model for compounds of the ERY series. The environments of the tungsten atoms appeared similar, as both atoms were bound to one doubly bonded and two triply bonded (bridging) oxygen atoms. But one was chelated by three vicinal hydroxyl groups, whereas the second was chelated by only two vicinal and one remote hydroxyl groups. For example, in erythritol (Figure 2a), the bridging oxygen atoms are O-2 and O-4; one tungsten atom is bound to C-2,3,4, and the other one, to C-1,2,4. It indicated conclusively that the structure of the crystalline complex (model of the ERY type) was retained in solution.

The W_1 and W_2 signals appeared as doublets, showing apparently a single coupling ^{183}W–^{1}H with typical J values 8–10 Hz (Table III). Several other couplings might be suspected, because each tungsten atom was chelated by three carbon atoms, each of which possessed at least one hydrogen atom, and a small second coupling was indeed observed in some cases (J = 1–2 Hz). Further experiments were made with polarization transfer from ^{1}H to ^{183}W in order to improve the signal/noise ratio. We observed that polarization transfer took place from proton to W_1, enhancing the corresponding signal. Inversely, the intensity of the W_2 signal dramatically decreased. A possible explanation of these opposite behaviors could have been that the tungsten atoms possessed different relaxation rates. If, contrary to W_1, the transversal relaxation time of W_2 had not been not long enough with respect to the evolution time $(^2J_{W,H})^{-1}$ in the polarization-transfer sequence, the expected transfer would have been decreased. Accordingly, at high magnetic field, heavy nuclei of nuclear spin $^1/_2$ like ^{195}Pt, ^{103}Rh, and ^{183}W relax essentially by chemical shift anisotropy.[33-37] It would have suggested a higher anisotropic character for the bonds surrounding W_2 than for those around W_1. However, this explanation is probably incorrect because the line widths were similar for W_1 and W_2 signals, indicating that the relaxation rates should be equivalent.

The spectra of threo complexes T (Figure 1) and X differed considerably from those of the erythro species, as they showed two unresolved multiplets of equal intensities, in which no coupling constants could be determined. The more important feature was that the W_1 and W_2 signals were separated by $\Delta\delta \simeq 60$ ppm (Table III), a much higher value than for complexes E and G ($\Delta\delta$ = 3.4 or 6.5 ppm). It implied that the environments of the tungsten atoms, which were similar in the ERY series, should considerably differ in the TH_W series.

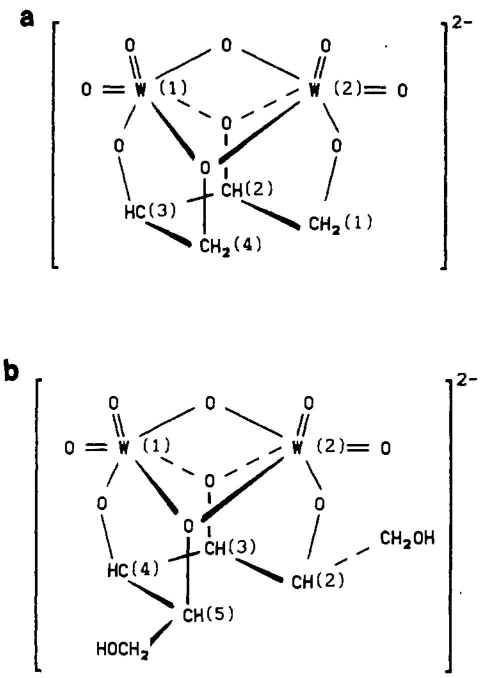

Figure 2. Proposed structures for the tetradentate tungstate complexes of *erythro*-alditols (ERY series) in aqueous solution, showing numbering of the tungsten and carbon atoms: (a) erythritol; (b) galactitol. A similar structure has been characterized[32] in the solid molybdate–erythritol complex and is attributed[12,14,15] to all molybdate complexes of the ERY type.

Discussion

Structures of the Erythro Complexes. Analysis of the ^{183}W–^{1}H couplings gave important information on the geometries of the complexes. They could only correspond to $^3J_{W,H}$ coupling constants, because each tungsten atom was separated by three bonds at least from any hydrogen atom. Each tungsten atom was mainly coupled to only one hydrogen atom, although it could have been coupled to at least three (complex G) or four (complex E) hydrogen atoms.

It is known that $^3J_{W,H}$ coupling constants depend, by a relation of the Karplus type,[38] on the values of the dihedral angle θ formed by the planes of the bonds W–O–C–H involved in the coupling path. The coupling constant is maximum for $\theta = 180°$ and minimum when $\theta = 90°$. Other $^3J_{W,H}$ values reported in the literature[39,40] were in the range 1.5–8 Hz. The higher values (8 Hz) were found[40] in complexes of W(II) with aromatic nitrogen ligands, in which the couplings were transmitted through double bonds, corresponding thus to $\theta = 180°$. Hence, such values are probably close to the maximum possible value for $^3J_{W,H}$. This is why we assumed that, in the alditol complexes, the higher $^3J_{W,H}$ values (8–10 Hz) were close to a maximum, corresponding to θ values close to 180°. On the contrary, the smaller values (1–2 Hz) were close to the expected minimum and should correspond to θ values approaching 90°.

A tentative assignment of the hydrogen atoms involved in the different couplings was made by performing 2D heteronuclear ^{183}W–^{1}H shift correlation experiments via long-range coupling. For complexes E and G, the W_1 atom gave a strong cross-correlation peak (due to the large coupling) with the hydrogen atom bound to the most deshielded carbon atom, i.e. C-3 in erythritol and C-4 in galactitol. It gave also weak cross-correlation peaks

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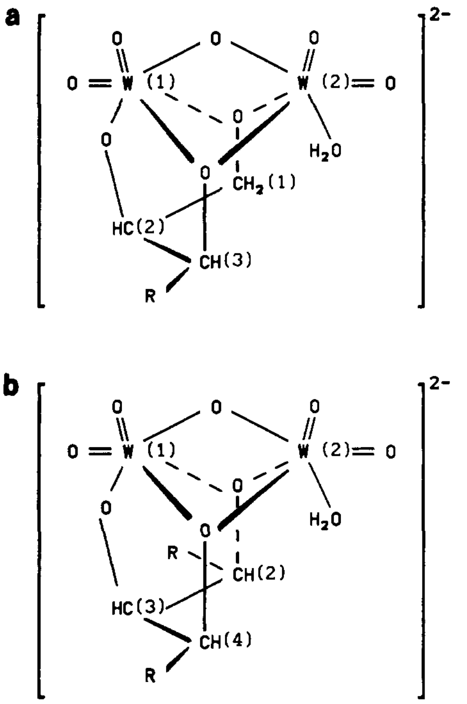

Figure 3. Proposed structures for the tridentate tungstate complexes of *threo*-alditols (TH_W series) in aqueous solution, showing numbering of the tungsten and carbon atoms (R = CH_2OH): (a) DL-threitol; (b) xylitol.

with the erythritol H-2 and H-4 responsible for the smaller couplings. Besides, the W_2 atom gave only weak cross-correlation peaks, which did not allow the identification of the coupled hydrogen atoms.

It is therefore demonstrated that, in erythritol, the W_1 atom is chelated by HO-2,3,4 (Figure 2a). The value of the dihedral angle W_1,O-3,C-3,H-3 is close to 180°. The other angles W_1,O-*n*,C-*n*,H-*n* ($n = 2$ and 4) have values close to 90°. It should be remarked that O-2,4 are bridging, triply bonded oxygen atoms, whereas O-3 is bound to only one tungsten atom. Consequently, the W_2 atom must be chelated by the HO-1,2,4 system. In the homologous galactitol complex (Figure 2b), the most deshielded carbon atom is C-4, the bridging oxygen atoms are O-3,5, and the W_1 atom is chelated by HO-3,4,5, and the W_2 atom, by HO-2,3,5. The angle values are similar in complexes E and G.

The above data for the erythritol–tungstate complex were matched to the known[32] crystal structure of its molybdate homologue. The locations of the hydrogen atoms at C-2,3,4 were determined with simple geometric assumptions, considering the carbons as tetrahedral. It showed that the H-3 atom was coplanar with the Mo_1, O-3, and C-3 atoms, in agreement with the angle value found in the tungstate species, $\theta \simeq 180°$. In contrast, the only possible location for H-2 was almost perpendicular to the plane Mo_1,O-2,C-2.

Structures of the Threo Complexes. ^{13}C NMR data indicated that the sites of chelation in complexes T and X involved three vicinal hydroxyl groups bound in a symmetrical way, with a highly deshielded central carbon and two equivalent lateral carbons. Examination of models showed that such a site could not accommodate identically two tungsten atoms, since one atom could be bound to three vicinal hydroxyl groups, whereas the second could not and was only chelated by two hydroxyl groups. This finding agreed with the large difference observed between the W_1 and W_2 chemical shifts.

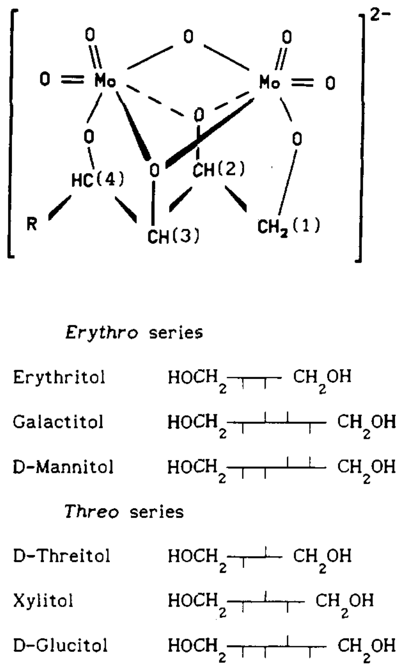

Figure 4. Top: Structure of the tetradentate molybdate complexes of *threo*-alditols (TH_M series) according to ref. 14 (DL-threitol, R = H; xylitol, R = CH_2OH). Bottom: formulas of alditols used. Following the rules adopted for carbohydrate chemistry, carbons are always numbered starting from the right-hand side.

Two hypotheses were made for the coordination of the second tungsten atom, depending on whether it was chelated by two vicinal or alternated hydroxyl groups. In the first case, the lateral carbons of the chelating site should differ, because one would be bound to both tungsten atoms and the other to only one. As these carbons showed similar variations of their chemical shifts, this hypothesis was dismissed. In the second case, each lateral carbon would be coordinated in the same way to both tungsten atoms and the central carbon would be specifically bound to only one tungsten atom, in agreement with NMR data.

Taking into account the above requirements, possible structures for the tridentate threo TH_W complexes were drawn (Figure 3a,b). They differ largely from that proposed previously (Figure 4) for the corresponding tetradentate molybdate complexes TH_M.[14,15] The origin of the difference is probably the larger size of the ditungstate moiety, which cannot be properly accommodated by the tetradentate ligand, contrary to the smaller dimolybdate group. Assignment of the tungsten signals was made by comparing the proposed structures and the chemical shifts of the erythro and threo complexes. It was assumed that the triply bound atom must show the smallest variation in chemical shifts and corresponded to the W_1 signal at $\delta \simeq -60$ ppm in the TH_W complexes, compared to $\delta \simeq -78$ ppm in the ERY type. The threo W_2 signal at $\delta \simeq -120$ ppm was assigned to the atom chelated by two hydroxyl groups, which showed the higher variation from the erythro W_2 signal at $\delta \simeq -83$ ppm.

The above results allowed us to explain a surprising difference noticed previously between the reactivities of various alditols toward tungstate. It had been reported, in a study of the titration of tungstate complexed by alditols,[10] that threo compounds such as threitol, xylitol, and D-glucitol reacted faster than erythro compounds like erythritol, D-mannitol, and galactitol. At the time, no correlation could be found with the known stabilities of these complexes. The above results led us to the hypothesis that the higher reaction rates could be associated with the formation of tridentate complexes. It was checked by performing complementary experiments with D-glucitol, which possesses CHOH groups in erythro (HO-4,5) and threo (HO-2,3 and HO-3,4) configurations (terminal CH_2OH groups have low tendency to chelation). ^{183}W NMR spectroscopy indicated the formation of several complexes in D-glucitol–tungstate mixtures, and the chemical shifts measured for the major species established it to be of the TH_W type (Table III). Although the exact nature of the other species is currently under study, it confirmed that alditols reacting rapidly with tungstate are those that form mainly tridentate complexes. Alditols that can form the more stable erythro tetradentate species react at a slower rate, presumably because of stringent steric requirements for the formation of the fourth bond.

Table IV. Comparison of the Formation Constants[a] of Molybdate and Tungstate Complexes of Alditols

	erythro series			threo series		
	erythritol	galactitol	D-mannitol	DL-threitol	xylitol	D-glucitol
log K_W[b]	18.00	20.10	19.65	16.95	18.50	19.15
log K_{Mo}[c]	15.20	17.30	16.70	14.60	16.25	16.60
Δ	2.80	2.80	2.95	2.35	2.25	2.55

[a] Formation constant for the equilibrium (M = Mo or W, L = alditol) $2MO_4^{2-} + L + 2H^+ \rightleftarrows (2,1,2)^{2-} + H_2O$. Potentiometric values: *t*, 25 °C; *I* (KCl), 0.1 M. Δ is the difference log K_W − log K_{Mo}. [b] Reference 10. [c] Reference 14.

It prompted us to question the already mentioned remark[9] that the stabilities of tungstate and molybdate complexes of carbohydrates, including alditols, varied in parallel relationship (tungstate species are always more stable). For this purpose, we calculated the difference Δ between the logarithms of the formation constants, K_W or K_{Mo}, determined for the $(2,1,2)^{2-}$ complexes involving two tungstate or molybdate groups, one alditol, and two protons, using literature data[9,10,14] obtained in comparable conditions. That comparison (Table IV) showed that the claimed invariance of Δ was a rough approximation, as the Δ values could be separated into two groups corresponding to the erythro or threo series of alditols. Erythro ligands, including D-mannitol, were characterized by Δ values between 2.80 and 2.95. Comparable values, 3.00–3.15, were also reported for aldoses of lyxo-manno configuration.[9] Besides, threo compounds exhibited lower Δ values, typically 2.25 and 2.35. The higher value obtained for D-glucitol, Δ = 2.55, was probably biased by the side formation of minor ERY complexes and should be higher than the true difference between pure TH species. Thus, in the threo series, the stability enhancement due to the replacement of Mo by W is smaller than in the erythro series. It appears clearly that the existence of several structural series of complexes can explain the differences observed between the stabilities of molybdate and tungstate complexes of various alditols.

Conclusion

^{183}W NMR spectroscopy proved a powerful tool for the study of anionic tungstate complexes of carbohydrates in aqueous solution. Contrary to the ^{95}Mo NMR spectra, in which the resonances of both Mo atoms were confused in a single broad signal, ^{183}W NMR spectroscopy showed, for each dinuclear complex, two sharp signals coupled to protons via large long-range $^3J_{W,H}$ couplings, which allowed the estimation of the dihedral angles in the ERY type complexes. It demonstrated that their structures in solution were closely related to that reported in a X-ray study of the molybdate–erythritol complex.

On the other hand, we found that alditols of the threo species formed distinct types of complexes with molybdate (tetradentate) and tungstate (tridentate). The ^{183}W NMR signals were assigned to the structurally different W atoms (triply or doubly chelated) on the basis of comparison with the triply chelated atoms present in the erythro complexes.

Contribution from the Department of Chemistry,
Howard University, Washington, D.C. 20059

Mercury(II) Reactions with Water-Soluble Porphyrins

Louis R. Robinson and Peter Hambright*

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Below pH 1 at 25 °C, equilibrium constants were measured for the reaction of Hg^{2+} with the free base of tetrakis(*N*-methyl-2-pyridiniumyl)porphyrin, the monocation of tetrakis(*N*-methyl-4-quinoliniumyl)porphyrin, and the diacid of tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin, all of which produce complexes of the composition $Hg_2\text{–}P^{2+}$ which have the presumed structure $[Hg\text{–}P\text{–}Hg]^{2+}$. Near neutral pHs, the free bases of the pyridiniumylporphyrins form 1:1 adducts with mercury(II), formulated as $(HO)_2Hg\text{–}P^{2-}$ or $O\text{–}Hg\text{–}P^{2-}$, and the corresponding equilibrium constants are reported. Kinetic studies of the reaction of M(II) (M = Zn, Cu) with several of the Hg_2–Ps gave evidence for [M–P–Hg] intermediates, which either react with Hg^{2+} to re-form $Hg_2\text{–}P^{2+}$ or decompose to the final M(II)–P adduct. The catalysis of M(II)–P formation by added Hg(II) ions is traced to the extremely rapid formation of mercury–porphyrin intermediates.

Certain metal ions participate in labile equilibria with porphyrin molecules to form metalloporphyrins:

$$M^{2+} + H_2\text{–}P = M\text{–}P + 2H^+ \qquad (1)$$

Equilibrium constants for such 1:1 complexes have been measured in aqueous solutions for Zn(II),[1] Cd(II),[2] and Pb(II)[3] ions and in DMSO–water[4] mixtures for Zn(II) and Cu(II). Such Cd(II) and Pb(II) porphyrin intermediates[3,5] catalyze the incorporation of Zn(II), Co(II), Ni(II), and Mn(II) into porphyrins, where for example activated complexes of the composition [Zn–P–Cd] lead to Zn(II)–P production 10^2–10^3 times faster than the reaction of Zn(II) with H_2–P itself. The situation is rather more complicated for Ag(I)[6] and Hg(II) interactions with porphyrins. Along with Hg–P, Smith and co-workers have demonstrated in nonaqueous solution the existence of homodinuclear Hg–P–Hg species[7] and "double-sandwich" porphyrins[8] of the structure Hg–P–Hg–P–Hg. Adeyemo and Krishnamurthy[9] investigated certain of these re-

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