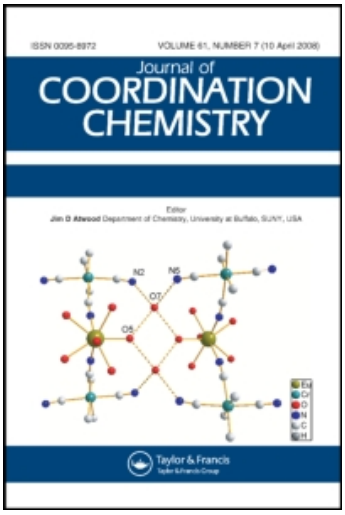

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CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDIES OF OXOTUNGSTEN(VI) COMPLEXES WITH AMINOPOLYCARBOXYLIC ACID LIGANDS

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Complex formation between tungsten and aminopolycarboxylic acids is found to require facial, tridentate orientation of ligand dentates. Coordination of hydroxyl groups is found to result in loss of the hydroxyl proton and formation of a W_2O_5 core structure. Hydroxyl coordination is found to be only slightly less favored than carboxylate coordination, but the resulting alkoxy bond is much less labile than that of carboxylate. Different coordinating ability is found for the two nitrogens of 1,2-PDTA and the formation of a "proton chelate" is proposed for this molecule.

INTRODUCTION

Periodic tendencies are quite pronounced in group VIB. Tungsten is the heaviest member and, like its lighter congeners chromium and molybdenum, exists as monomeric or polymeric oxoanions in solution when in the +6 oxidation state.[1] Many similarities exist in the solution chemistries of these ions; however, standard potentials become markedly more negative in descending the column. Molybdenum is especially important as the redox center of many biological and artificial catalysts.[2,3] Because tungsten(VI) analogs can be used to investigate mechanisms without electron transfers occurring, details of aqueous tungsten chemistry are highly relevant. Previous studies[4–9] have mapped out numerous aspects of the coordination chemistry of Mo(VI) and W(VI) oxo species and, while the behavior of tungsten parallels that of molybdenum in many ways, specific differences exist.[4,9]

We report here the results of an investigation of the coordination of W(VI) in pH ~5 aqueous solution to a number of ligands containing amine, carboxylate, and hydroxyl functional groups using ^{13}C NMR spectroscopy. The principal objectives of this work are to determine requirements for formation of stable oxotungsten complexes in terms of donor atoms number, type, and spatial arrangement. Structural features and kinetic effects in the complexes formed are considered with particular emphasis on those factors found important in the wider molybdenum literature: *trans* influences,[10] preferred ligand orientations[11] and formation of specific oxometallate "core" structures.[12]

EXPERIMENTAL

Samples for carbon-13 NMR were prepared by dissolution of weighed amounts of ligand and reagent grade $Na_2WO_4 \cdot 2H_2O$ (Merck) into sufficient 20% D_2O/80% H_2O to produce solutions 0.5 M in ligand and 0.5 or 1.0 M in WO_4^{2-}. After addition of 5% V/V dioxane, the pH was adjusted to 5.0 by addition of concentrated sulfuric acid or 50% W/V sodium hydroxide solution. The pH meter readings were not corrected for deuterium activity. Ligands were obtained from commercial sources except for MHEG. MHEG was synthesized by methods previously described.[8] Impurities in the NMR spectrum of a ligand were removed by recrystallization or extraction with hot ethanol.

Carbon pulse Fourier transform NMR spectra were obtained on a Varian XL-100 Spectrometer at 25.16 MHz (2.350 T). Sweep width was 5120 Hz, tip angle was 30° and sample tube diameter was 10 mm.

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Acquisition time determined the number of data points acquired: 0.800 sec (8192 points) was normally used although 1.600 sec (16384 points) was occasionally used to resolve closely spaced lines. Fourier transform data length at least twice the acquired data length was routine. Chemical shifts were measured relative to internal dioxane and reported relative to external TMS using the relation[13] $\delta_{TMS} = \delta_{dioxane} + 67.73$ ppm. Lines were assigned by comparison with similar oxomolybdenum(VI) species.[8] variation of WO_4^{2-} : ligand mole ratios and by internal consistencies among the ligands. Assignment of some of the methylene carbon resonances of HPDTA, DTPA, HEDTA and PDTA are tentative.

RESULTS

^{13}C *NMR Spectra of Oxotungsten(VI) Complexes*

Complexation is detected by the appearance of new lines or the broadening and shifting of ligand lines in the presence of tungstate. In most cases, new lines are observed and are very sharp, indicating slow exchange between free and complexed ligand. Table I gives a qualitative description of the interaction of each ligand with sodium tungstate at pH 5. Ligands are classified according to whether or not complexation occurs and to the empirical metal : ligand ratio of observed complexes. Several instances of complexes with the same empirical tungstate to ligand ratio but different actual stoichiometry or structural forms are also noted in Table II.

Chemical shifts of complexed ligands are reported in Table II. Free ligand resonances at pH 5 occur quite near their previously reported[8] values at pH 6 in most cases.

DISCUSSION

Aminopolycarboxylic Acid Complexation of Tungstate

Aminopolycarboxylic acid ligands typically form oxotungsten(VI) solution species by the reaction shown in Eq. 1:

$$WO_4^{-2} + 2H^+ + L \rightarrow WO_3L + H_2O \qquad (1)$$

pH titration studies[14,15,16] indicated this reaction is forced to completion at pH 5, the value used in this study. Reaction (1) produces a *facial* trioxotungsten moiety as proposed for WO_3(MIDA) by Kula[14] by analogy to similar oxomolybdenum compounds of known crystal structure. The WO_3 core structure is shown in Figure 1 in an EtIDA complex.

The ligands studied coordinate to WO_3 in a *facial*, tridentate manner to form stable complexes at pH 5. The mono- and bidentate ligands in Table I do not form complexes, nor does tridentate DPA(I), which complexes other metal ions as well as MIDA[17] but must do so *meridionally*. If non-oxo coordination

TABLE I
Complexation behavior of ligands studied with tungstate at pH 5.0.

Do not form complexes	*Form 1 : 1 Oxotungsten Complexes*
propyl amine	iminodiacetic acid (IDA)
acetic acid	methyl-IDA (MIDA)
β-alanine	ethyl-IDA (EtIDA)
aspartic acid (Asp)	benzyl-IDA (BzIDA)
histidine (His)	nitrilotriacetic acid (NTA)
dipicolinic acid (DPA)	hydroxyethyl-IDA (HEIDA)[a]
cyclohexanediaminetetra acetic acid (CyDTA)	*N*-methyl-*N*-hydroxyethyl glycine (MHEG)[a]
	1,2-propanediamine tetraacetic acid (PDTA)
Form 1 : 1 and 2 : 1 Oxotungsten Complexes	
ethylenediaminetetraacetic acid (EDTA)	
ethyletherdiaminetetraacetic acid (EEDTA)	
[ethylene(bisoxyethylenenitrilo)]tetraacetic acid (EGTA)	
diethylenetriaminepentaacetic acid (DTPA)	
hydroxyethylethylenediaminetriacetic acid (HEDTA)[a]	
2-hydroxy-1,3-propanediaminetetraacetic acid (HPDTA)[a]	

[a]Ligands containing hydroxyl groups can form complexes with actual stoichiometries of 2 : 2, 3 : 2, and/or 4 : 2 (see text).

TABLE II
^{13}C NMR shifts of tungsten complexes.

Ligand	W: Ligand Ratio	Isomer	Assignments[a] C′	G′	α′	β′	Others					
IDA	1 : 1		181.84	57.74								
MIDA	1 : 1		179.82	67.01	51.92							
EtIDA	1 : 1		180.35	63.42	59.23	9.94						
							o	*m*	*p*			
BzIDA	1 : 1		179.76	63.74	67.34	134.01	132.41	130.55	130.25			
HEIDA	1 : 1	I	180.08	64.22	64.85	59.0[b]						
	2 : 2	II	179.2[b]	63.23	62.50	69.36						
NTA	1 : 1		179.45	65.58								
							NCH_2	CH_2O^-				
MHEG	2 : 2	I	180.38	65.83	48.59		64.94	69.13				
	2 : 2	II	180.14	65.91	48.82		64.76	68.96				
							o′	o°	β°	α°	G°	C°
EDTA	1 : 1		179.06	63.38	57.20					51.86	58.81	171.34
	2 : 1		179.49	63.56	57.82							
EEDTA	1 : 1		180.24	64.32	62.91	68.42			65.88	56.22	58.78	171.51
	2 : 1		180.16	64.32	62.98	68.25						
EGTA	1 : 1		180.15	64.31	62.60	68.08	70.80	71.02	65.88	55.99	58.65	171.45
	2 : 1		180.15	64.31	62.60	68.08	70.80					
			C′	G′	CH_2	CH_3	CH°	G_m°	C_m°			
PDTA	1 : 1	I	179.12[c]	65.56[c]	58.52	15.45	N.A.[g]	55.56	171.36			
			179.00[c]	64.53[c]								
			C_m'	G_m'	CH	CH_3	CH_2°	G°	C°			
	1 : 1	II	179.49[c]	63.41[c]	60.53	15.58	N.A.[g]	58.73	171.64[c]			
			179.39[c]	63.34[c]					171.56[c]			
			C′	G′	α′	β′	β°	α°	G°	C°	G_b°	C_b°
DTPA	1 : 1		179.69	63.74	53.29	51.44	50.17	59.61	57.33	172.55	57.6[b]	177.14
	2 : 1		179.22	63.65	57.56	51.44					57.7[b]	172.41
							α_h°	G_h°	C_h°	NCH_2	CH_2OH	
HEDTA[e]	1 :1		179.06	63.53	51.18		56.82	57.79	171.26	57.91	57.05	
							α_h'	G_h'	C_h'	NCH_2	CH_2O^-	
	4 : 2	I	179.98[d]	63.73[d]	55.16		57.94	61.27	179.61	61.79	69.17[b]	
			179.78[d]	63.53[d]								
							α_h'	G_h'	C_h'	NCH_2	CH_2O^-	
	4 : 2	II	179.85[d]	63.38[d]	55.16		57.94	61.00	179.54	61.79	69.17[b]	
			179.66[d]	63.23[d]								
							α°	G°	C°			
HPDTA[f]	2 : 2		179.32[b,c,d]	65.35[b,c,d]	61.43	74.60[b]	59.52	58.60	171.44			
			178.43[b,c,d]	64.10[b,c,d]								
	4 : 2		180.74[c,f]	67.09[c,f]	63.37	77.32						
			179.90[c,f]	65.35[c,f]								

[a]Primed symbols indicate signals from carbons in coordinated sites. Superscript ° indicates signals from uncoordinated sites. Carbons labelled:

IDA $(^-O_2CCH_2)_2NH$ (CG)

MIDA $(^-O_2CCH_2)_2NCH_3$ (CG, α)

EtIDA $(^-O_2CCH_2)_2NCH_2CH_3$ (CG, α, β)

BzIDA $(^-O_2CCH_2)_2NCH_2$  (CG, α, β)

HEIDA $(^-O_2CCH_2)_2NCH_2CH_2OH$ (CG, α, β)

NTA $(^-O_2CCH_2)_3N$ (CG)

MHEG $^-O_2CCH_2N(CH_3)CH_2CH_2OH$ (CG, α)

EDTA $(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)_2$ (CG, α)

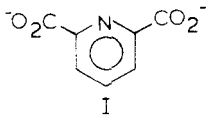
EEDTA $(^-O_2CCH_2)_2NCH_2CH_2OCH_2CH_2N(CH_2CO_2^-)$ (CG, α, β)

EGTA $(^-O_2CCH_2)_2NCH_2CH_2OCH_2CH_2OCH_2CH_2N(CH_2CO_2^-)_2$ (CG, α, β, O)

TABLE II (*Continued*)

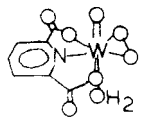
PDTA	$(^{-}O_2CCH_2)NCH_2CH(CH_3)N(CH_2CO_2^{-})_2$					
	CG	α	α_m	M	G_m	C_m
DTPA	$(^{-}O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^{-})CH_2CH_2N(CH_2CO_2^{-})_2$					
	CG	α	β	G_b	C_b	
HEDTA	$(^{-}O_2CCH_2)NCH_2CH_2N(CH_2CO_2^{-})CH_2CH_2OH$					
	CG	α	α_h	G_h	C_h	
HPDTA	$(^{-}O_2CCH_2)_2NCH_2CH(OH)CH_2N(CH_2CO_2^{-})_2$					
	CG	α	β	α	G	C

[b]broad.
[c]pairs of lines produced by asymmetry in the ligand.
[d]pairs of lines produced by asymmetry of the $W_2O'_5$ complex.
[e]see Figure 4 for further details.
[f]see Figure 5 for further details; 2 : 2 and 4 : 2 carboxyl lines overlap.
[g]not assigned.



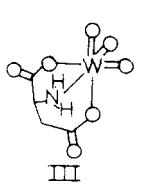
I

sites are occupied by water or hydroxide ion, the WO_3 moiety can proceed to form isopolytungstate oligomers, or at higher pH, revert to WO_4^{-2}. Kinetic instability of two coordinate ligands formed by displacement of a third dentate by hydroxide ion has been proposed[18] from studies of the reverse of reaction (1). Thermodynamic stability of the WO_3 moiety in the tridentate complexes apparently comes from the small *trans* influence of carboxylate and amine ligands,[10] which allows formation of three tungsten–oxygen double bonds. So little charge transfer occurs that WO_3 does not convert to a *cis* WO_2 form to which DPA could coordinate as it does in the less sterically hindered $WO(O_2)DPA(H_2O)$ peroxo complex(II).[19]

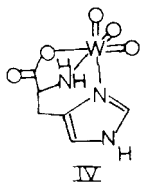


II

Aspartic acid and histidine fail to complex tungstate, even though these ligands can form facially tridentate complexes, III and IV. Two of the chelate rings formed by each ligand would be six- and seven-membered and therefore less stable than the five-membered rings formed by MIDA. Earlier pH titration studies of these ligands also gave no evidence for complexation.[15] Thus, the free energy balance between WO_3L and oxotungsten forms is relatively fine and only favored chelate rings result in complexes.



III



IV

IDA, MIDA, EtIDA, and BzIDA

Strong, inert complexes are produced with these ligands as exemplified by the sharp lined spectrum of WO_3EtIDA^{2-} shown in Figure 1. Complexation is seen to produce downfield shifts, caused by the displacement of protons from the amine sites. Protonation shifts in amine[13] and aminoacid[20] spectra are generally upfield, and the net effect of complexation to the less acidic WO_3 moiety is usually a downfield shift. IDA, EtIDA and BzIDA form similar complexes as shown in Table II.

NTA

$WO_3(NTA)^{-3}$ has been found[9] to be of the same structure as the $WO_3(MIDA)^{-2}$ complex; however, rapid exchange takes place between the free, pendant $CH_2CO_2^{-}$ group and the two bound ones to yield the single, averaged lines for each type of carbon reported in Table II. Because similar IDA derivative complexes show no sign of lability in their carbon spectra, an associative mechanism is suggested in Scheme 1:

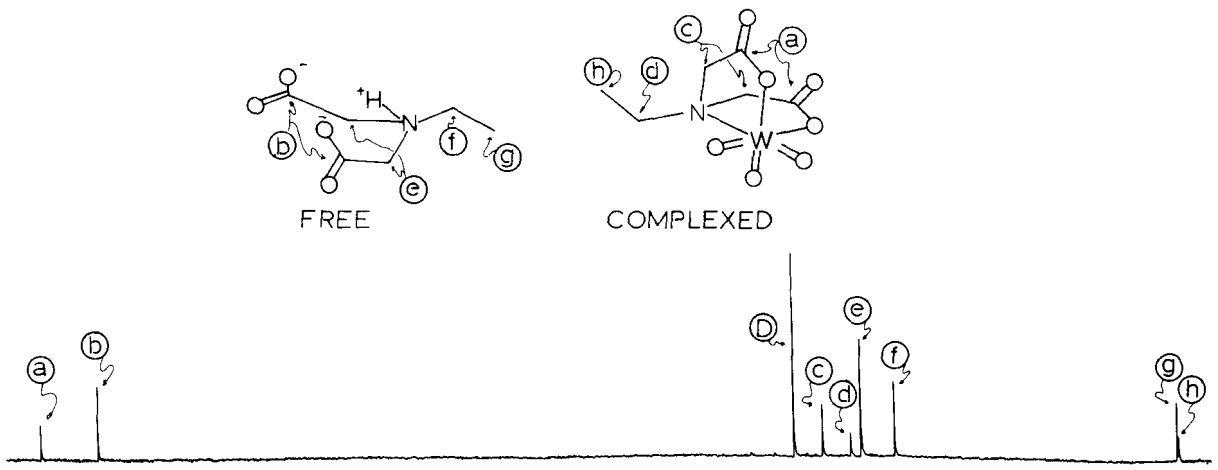
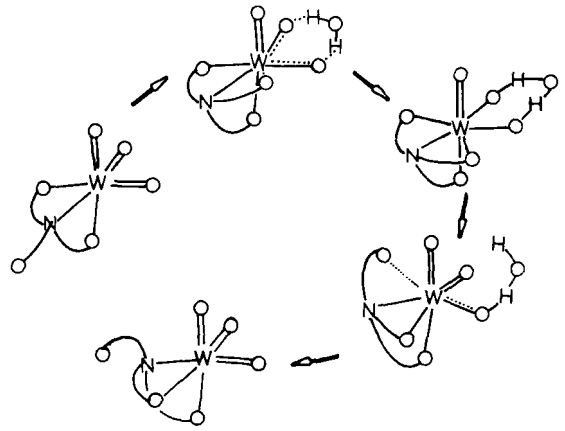


FIGURE 1 ^{13}C NMR spectrum of 0.5 M Na_2WO_4 and saturated (<0.5 M) EtIDA at pH 5. Line labelled D is the internal reference dioxane. Other lines correspond to free and coordinated EtIDA as shown.



EDTA, EEDTA, and EGTA

Each of these diamine ligands consists of two IDA moieties linked together, each of which can form a WO_3L complex. Coordination at a given IDA site produces deprotonation shifts at that site. The remaining IDA site can experience enhanced protonation shifts because the uncharged WO_3 group has less effect on the free end of the molecule than the charged proton it displaced. The similar MoO_3 $EDTA^{4-}$ complex was found[6] to be 20 times more basic than $(H^+)EDTA^{3-}$. The *bis* WO_3 complex is deprotonated at both ends. The diametric shifts with each complexation clearly separate the carbon NMR signals of the various forms of the EDTA complex, as shown in Figure 2. The 5- and 8-atom separation between the IDA-type sites of EEDTA and EGTA respectively eventually result in no resolution of bound sites in 2 : 1 complexes from 1 : 1 complexes or free sites in 1 : 1 complexes from free ligand as reported in Table II. The second pK_a values for these latter two ligands are much higher[17] than that of EDTA and both IDA sites are fully protonated at pH 5.

DTPA

The connecting linkage between IDA sites in DTPA contains a glycine-like site which like other bidentate sites does not complex tungstate. Table II reports large protonation shifts for signals of carbons near the center nitrogen with each tungstate coordination. Large deprotonation shifts are seen for the carbon resonances in the IDA sites with each complexation, showing that the end nitrogens are more protonated at pH 5 than the more basic central nitrogen. These results confirm earlier ^{13}C [21] and ^1H [22] NMR investigations of protonation of the free ligand which found the end nitrogens to be more protonated than the center one at intermediate pH values.

PDTA and CyDTA

The presence of the methyl group on the diamine linkage of PDTA creates an asymmetric center and also differentiates the two IDA sites. Two carboxylate lines are seen with complexation to a given IDA site because the methyl group renders each glycinate ($-CH_2CO_2^-$) arm anisochronous, as seen in Figure 3. Rapid inversion and rotation about the nitrogen–carbon bond interchange the positions of the glycinate

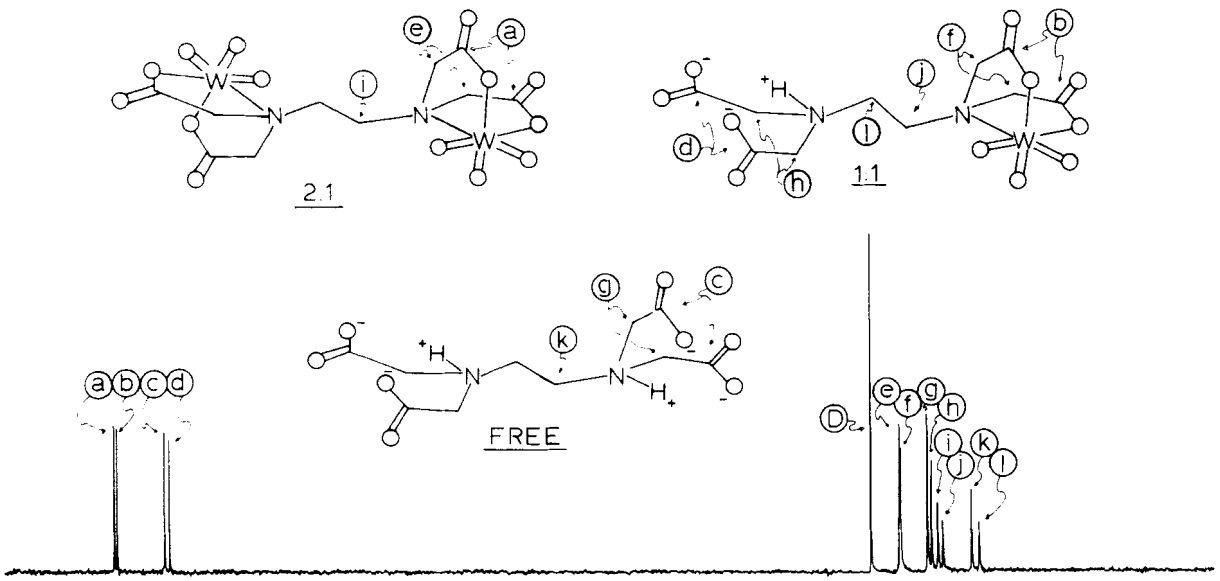
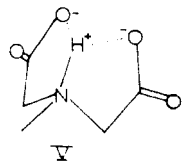


FIGURE 2 ^{13}C NMR spectrum of 1.0 M Na_2WO_4 and 0.5 M EDTA at pH 5 and the species present in solution. Line labelled D is dioxane internal reference. Other lines as shown.

arms relative to the methyl so that single, averaged lines are produced for uncomplexed sites in the molecule. The low temperature spectrum in Figure 3 on the other hand shows that this exchange process can be slowed sufficiently to permit observation of small chemical shift differences for the uncomplexed arms of one of the 1 : 1 chelates and also for one end of the free PDTA ligand itself. The uncomplexed ends of these molecules are strongly protonated at pH 5. "Proton chelates"[23,24] are formed by the acetate arms and the nitrogen center, (V). Similar structures are found in crystal structures of $H_2(EDTA)^{2-}$.[25,26] The chelate structure causes the rate of nitrogen inversion to be slowed appreciably.



V

The carboxylate resonances of the more populous WO_3PDTA isomer show a greater separation than the resonances of the other isomer. The site favored for complexation is therefore the one most differentiated by the methyl group. The X-ray crystal structure of $(MoO_3)_2EDTA^{4-}$ shows that the IDA sites of that molecule lie *trans* to each other across the diamine linkage in the solid state.[25] Because this is the conformation with the least steric interferences between the glycinate arms at each end of the molecule, it is probably the major conformer in solution. Kula also surmises a *trans* arrangement for the *bis* $(MoO_3)_2$-EDTA complex from proton NMR of the solution species.[6] Models of the PDTA tungstate complexes show that the *trans* orientation of the IDA sites causes the IDA site further removed from the methyl group through bonds to be actually closer through space, as shown in Figure 3. The more favored complex is therefore the one formed by the less hindered site bonded to CH_2.

The *bis* $(WO_3)_2PDTA^{4-}$ complex does not form, apparently due to steric hindrance from the methyl group. It is therefore not surprising that the greater steric constraints placed by the cyclohexane linkage of *trans*-CyDTA results in no observable complexation. Models show that WO_3 cannot be fit to a given, equatorial IDA site because of the steric requirements of the other, *gauche* site. The rotation of an IDA site to an accessible axial position apparently does not occur.

Complexes with a W_2O_5 Core. MHEG and HEDTA

Facially tridentate coordination of MHEG or the corresponding hydroxy-ethyl end of HEDTA requires use of the hydroxyethyl arm. However, the more basic ether oxygens in diglycolic acid, EEDTA and EGTA do not coordinate to tungstate. Two forms of 1 : 1 tungstate : MHEG complexes are found, as reported in Table II. The hypothetical WO_3MHEG^{-1} complex

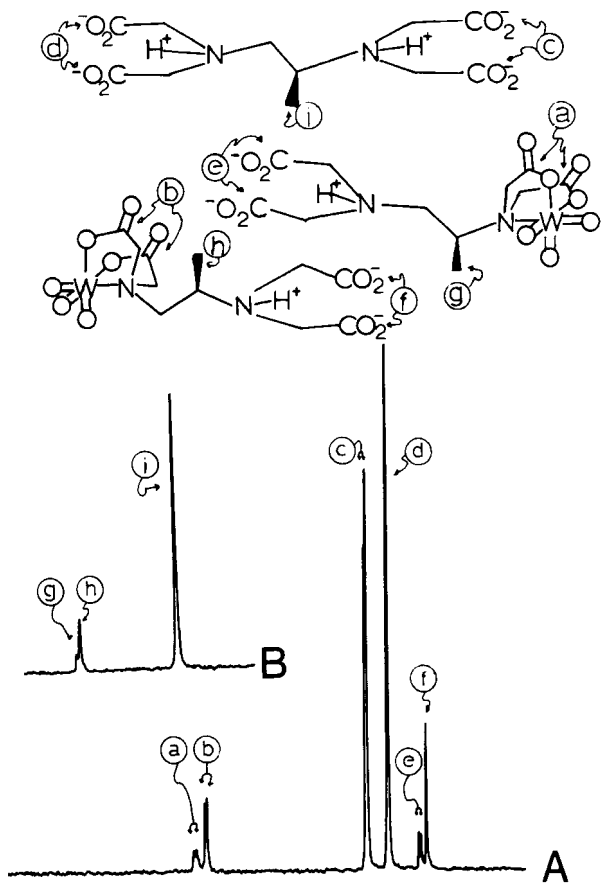
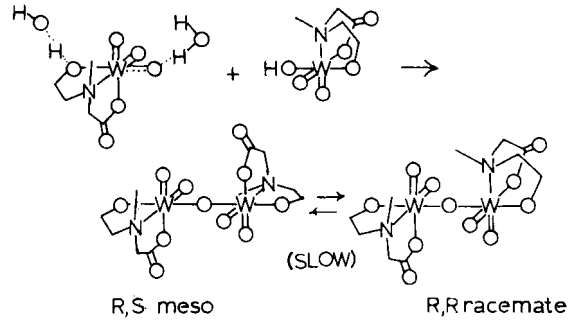


FIGURE 3 Carboxyl region (A) and methyl region (B) of ^{13}C NMR spectrum of 1 M Na_2WO_4 and 0.5 M PDTA at pH 5 and the species present in solution. Spectrum obtained at 0°C.

would be enantiomeric, but would not produce two sets of NMR lines. Oxomolybdenum complexes with similar ligands are found to contain Mo_2O_5 oxo bridged structures.[8,12] A similar W_2O_5 core is shown in Scheme 2:

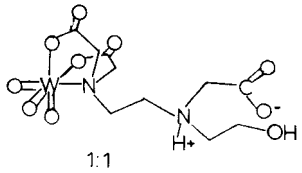


These products are formed by tautomeric conversion of the hydroxyl to a stronger alkoxy ligand, and condensation of two W OH groups. The dimer bridges only through the oxo *trans* to the alkoxy dentate because the larger *trans* influence of alkoxy[8,10] weakens that oxo bond more than the influence of carboxylate or amine dentates weaken the bond to the oxo *trans* to themselves. Thus only two stereochemical forms exist as shown in Scheme 2. The two sets of signals reported for the tungstate MHEG complexes in Table II are assigned to these stereoisomers.

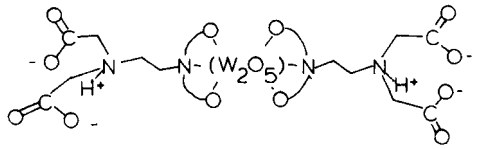
The condensation reaction also occurs in the HEDTA-tungstate system. The reaction may be written as

$$2(2WO_4^{=} + HEDTA^{3-} + 4H^+) \longrightarrow [WO_3HEDTA(W_2O_5)HEDTA\ WO_3]^{6-} + 5H_2O \quad (2)$$

Potentiometric pH titration finds the four-proton stoichiometry required by eq. 2. Consecutive coordination of tungstate by HEDTA results in many different molecules. Complexation of one tungstate by the IDA-like end of HEDTA produces a simple, 1 : 1 complex like that of EDTA.



Complex formation at the hydroxyl bearing end produces 2 : 2 dimers like the two forms of the MHEG complex.



Further complexation by either the 1 : 1 or 2 : 2 complexes results in 3 : 2 dimeric complexes. The two kinds of 3 : 2 complexes are made different by the arrangements of the ligands about the W_2O_5 core structure. Coordination to all available positions of HEDTA produces two 4 : 2 tungstate : HEDTA species which are also different from one another. Figure 4 shows that the apparent superabundance of lines in the carboxyl regions of spectra obtained in solutions of differing tungstate : HEDTA mole ratio can be explained by these 1 : 1, 2 : 2, 3 : 2 and 4 : 2 species.

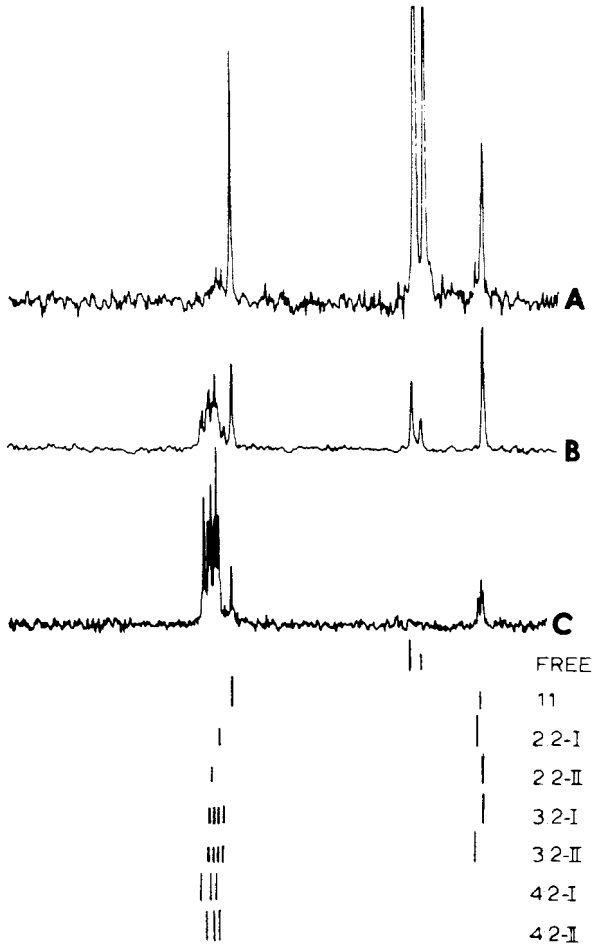
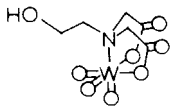


FIGURE 4 Carboxyl regions of ^{13}C spectra of (A) 0.25 : 1, (B) 0.5 : 1, and (C) 2 : 1 mole ratios for Na_2WO_4 to HEDTA. HEDTA is 0.5 M in all cases. Stick spectra correspond to the species discussed in the text, and are labelled by the tungsten to ligand stoichiometry of each species (e.g., 2 tungstates and 2 HEDTA molecules form the 2 : 2 dimeric species discussed in the text) and the isomeric form of the complex. Placement of stick spectra lines corresponds to the observed lines. The 3 : 2 lines are tentative. The size of the stick lines is proportional to the number of carbons contributing to the line in each species.

The relative abundance of the two isomers of the 4 : 2 HEDTA dimers are much different from the *almost* equal abundance of the two forms of 2 : 2 MHEG : tungstate complex. The steric requirements of the trailing group of HEDTA complex, $-CH_2-CH_2N(CH_2CO_2)_2\ WO_3$, is much greater than the trailing methyl group of MHEG; models show that the steric interaction between the ligands is greater for the *racemic* form, so the more intense lines (I in Table II) are assigned to the *meso* molecule.

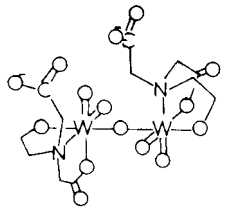
HEIDA and HPDTA

HEIDA is potentially quadridentate, like NTA. Unlike the single species found for WO_3NTA^{3-}, two complexes are formed between tungstate and HEIDA. One (type I in Table II) is the usual WO_3L form with a pendant, uncoordinated hydroxyethyl arm (VI).



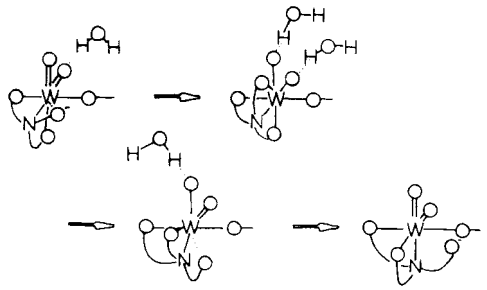
VI

The other form (VII) is coordinated through the hydroxyl, whose proton is lost in the process, resulting in the W_2O_5 core structure found in the alkoxy bonded MHEG and HEDTA species.



VII

Just as in WO_3NTA^{3-}, rapid exchange takes place between the bound and free glycinate arms, yielding a single merged NMR signal for the two. This exchange also interconverts the two isomers of the dimer and only one, averaged signal results for the two forms. Scheme 3 shows this in more detail. Throughout the



exchange of carboxylate dentates the alkoxyl group remains firmly coordinated *trans* to the bridging oxo. The small upfield shift of the signal for the rapidly exchanging carboxylates of (VII) relative to the line for the fixed carboxylates of VI is in keeping with the approximately 2 ppm upfield shift difference between free and bound carboxylates of WO_3NTA^{3-}.

The HPDTA ligand is structurally similar to HEIDA and forms 1 : 1 and 2 : 2 complexes directly

analogous to those of HEIDA. The substitution on the hydroxyl-bearing carbon makes it an asymmetric center, which causes the glycinate arms in both forms of complex to be anisochronous. Fast exchange of the bound and free glycinate arms in the alkoxy bound form does not interchange their orientation relative to the asymmetry. Thus a prediction of two sets of two lines, one set for each form, can be made for the carboxylate region of the spectrum. Figure 5 shows that relatively broad lines occur, but the general form is as predicted. Exchange between bound and unbound alkoxy groups is sufficiently slow that one of the WO_3 moieties of the *bis* complex resides in a typically IDA chelate environment, as shown by the sharp pair of carboxylate lines for the 4 : 2 complex.

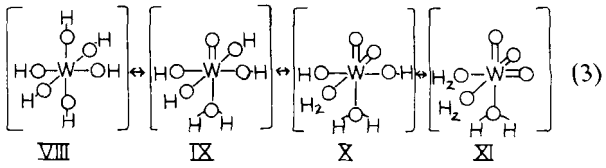
Long Term Stability of Oxotungsten Complexes with Aminopolycarboxylic Acids at pH 5

Many of the complexes reported here may be metastable under the high concentrations and low pH employed. Examinations of sealed samples used in this study revealed that large, colorless, clear hexagonal crystals were formed in 80% of them over a period of many months. White powders were also often present. The crystals contained no ligand molecules when redissolved at high pH. The white powders were virtually all free ligands. It has been observed that equilibration in isopolytungstates can take many days and the very hard tungsten (VI) ion could be expected to be more stabilized by hard oxo ligands in the solid state than the relatively softer amine and carboxylate dentates of the ligands used in this study. While the conclusions regarding solution behavior described by this study are not affected by this observation, there is an equilibrium established between a solid oxotungsten species and the dissolved forms which is not treated.

CONCLUSIONS

Complexation of tungstate occurs when the coordinating groups of the ligand stabilize a discrete oxotungsten core structure. The complexation reaction written in Eq. (1) can be examined as a reaction between the ligand and the hypothetical products of the diprotonation of tungstate written in Eq. (3):

$$WO_4^{2-} + 2H^+ + 2H_2O \longrightarrow$$



(3)

VIII IX X XI

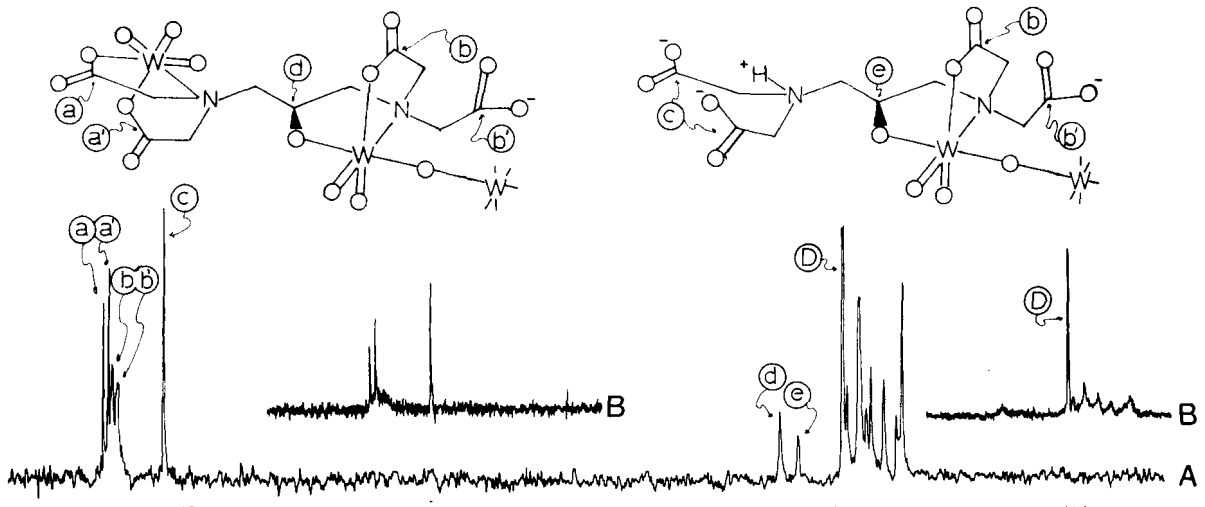
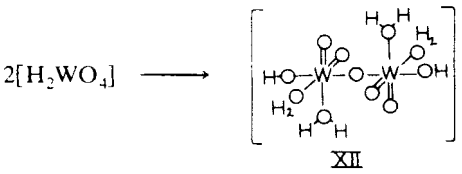


FIGURE 5 ^{13}C NMR spectrum of 1 M Na_2WO_4 and 0.5 M HPDTA at pH 5. (A) ambient temperature; (B) at 0°C. Line labelled D is dioxane reference. Drawings include only part of the W_2O_5 core structure for clarity. Assignments for lines labelled b and b′ may actually be reversed. Fast exchange between the b complexed and b′ uncomplexed form and the b′ complexed and b uncomplexed form is indicated by the disappearance of both resonances into broad signals at 0°C. See text.

The expansion of the tungsten coordination shell from four to six is predicted from the behavior of molybdate.[28] The actual product of Eq. (3) is difficult to ascertain experimentally because the diprotonated forms polymerize through condensation when appreciable ($>10^{-4}$ M at pH 5) concentrations exist. Two of the diprotonated tungstates of Eq. (3) might form a dimeric species like XII *en route* to polymer formation:



XII

The most stable polymeric form however is the α-Keggin species produced by Eq. (4).[1]

$$12WO_4^{2-} + 18H^+ \longrightarrow W_{12}O_{39}^{6-} + 9H_2O \quad (4)$$

The steric arrangement of oxo, hydroxyl, and water ligands in the hypothetical species VIII–XII are dictated by their *trans* influences. Strongly *trans* influencing ligands are found *trans* to weakly influencing ones when steric conditions permit. A ranking of *trans* influencing ability of ligands in the chemically similar Mo(VI) system has been made by the observed lengthening of bonds *trans* to each ligating group found in crystal structures. The ranking found,

$$N^{3-} > RN^{2-} \sim O^{2-} > RO^- \sim (\eta_2)\mu\text{–}O^{2-} \text{ (linear)} > RS^- > (\eta_2)\mu\text{–}O^{2-} \text{ (bent)} > R_3N \sim RCO_2^- > R_2S > \text{acac} > H_2O \geq ROH > R_2O$$

should be roughly the same for tungsten, particularly for ligands with a given coordinating atom.

Stable complexes in aqueous solution result when ligands coordinate to one of the forms VIII–XII with ligating groups in place of the water or hydroxyl ligands of that form. The *facially* tridentate ligands of this study form complexes similar to XI and XII with slightly stronger amine and carboxylate ligands in the place of water and alkoxy ligands in the place of hydroxyl. The $W_{12}O_{39}^{6-}$ polymer itself consists of tungstate environments similar to IX where (μ_2) bridging oxo ligands take the place of hydroxyl and an (μ_4) bridging oxo ligand takes the place of water. Although bidentate ligands with strong ligating groups, such as catechol, are able to stabilize X by forming *bis* ligand complexes, the bidentate ligands of this study cannot do so with relatively weak amine and carboxylate ligating groups. Because the low pH and high tungstate concentrations of this study place all complexation reactions in competition with polymerization, mono- and bidentate coordination and even tridentate coordination in certain cases (i.e., aspartate and histidine) do not provide sufficient stability to overcome the polymerization reaction.

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