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FULL PAPER

NMR and X-ray diffraction studies of the complexation of D-(−)quinic acid with tungsten(VI) and molybdenum(VI)

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By using multinuclear (^{1}H, ^{13}C, ^{17}O, ^{95}Mo, ^{183}W) magnetic resonance spectroscopy (1D and 2D), quinic acid is found to form 2 homologous complexes with both tungsten(VI) and molybdenum(VI), in aqueous solution. Two isomeric 1 : 2 (metal : ligand) complexes involving the carboxylate and the adjacent OH groups are present in the pH range 2–11. One of the W(VI) complexes with quinic acid, $WO_2(C_7H_{10}O_6)_2^{2-}$ has been isolated in the solid state and characterised by X-ray diffraction, the tungsten atom being six-coordinated in an approximate square bipyramidal geometry. This structure is identical to that proposed for the most stable complex in solution. In the presence of hydrogen peroxide and with both metals, quinic acid forms one 1 : 1 : 2 (metal : ligand : peroxide) species, also involving the carboxylate and the adjacent OH groups.

Introduction

D-(−)Quinic acid, (−)-1,3,4,5-tetrahydroxycyclohexanecarboxylic acid, occupies a prominent position among the primary metabolites originating from D-glucose and is widely found in plants.[1] It is a precursor of shikimic acid, which is involved in the biosynthesis of essential aromatic amino acids[2] and it can constitute an alternative carbon source for many microorganisms, *e.g. Aerobacter aerogenes* and *Klebsiella pneumonia*.[1] Quinic acid has also emerged in synthetic chemistry as an attractive and inexpensive starting material for the total synthesis of complex molecules and chiral reagents for asymmetric synthesis.[1]

It is known that cyclic polyols act as calcium carriers in biological systems. Such compounds can therefore be expected to be effective carriers for other metal ions, due to the formation of coordination compounds.[3] The complexation of quinic acid with some metals has been the subject of several studies. Its complexation with Cr(V),[4,5] Cr(IV),[6] V(V),[7] V(IV),[8] Zn(II), Cd(II),[9] Pt(II),[10] Cu(II)[3] and also with boron[11] has received special attention. Peroxo complexes are also important regarding their role in the oxidation of several substrates and their industrial applications[12] and a peroxo complex of quinic acid with Mo(VI) was isolated and characterised in solution by ^{13}C and ^{95}Mo NMR.[13] The coordination chemistry of quinic acid was recently reviewed.[3]

The polyhydroxy-substituted cyclohexane ring is a polyfunctional molecule that has typical characteristics of a sugar molecule and also can coordinate the metals in a variety of fashions, since it can behave as a polyhydroxy acid and as a cyclic polyol.[14] Following our previous studies on the complexes, *viz.* refs.,15,16 and oxoperoxo complexes of Mo(VI) and W(VI) with sugar derivatives,[17] we now address this important natural occurring ligand, D-quinic acid.

Experimental

Analytical grade disodium tungstate and disodium molybdate dihydrates, $Na_2MO_4·2H_2O$, hydrogen peroxide (35% in water), and tungstic and quinic acids were purchased from commercial sources and used as received.

Apparatus

The ^{13}C spectra were recorded on a Varian XL-200 instrument and the ^{1}H, ^{17}O, ^{95}Mo and ^{183}W spectra were obtained on a Varian Unity-500 NMR spectrometer. The 2D NMR spectra, DQFCOSY[18] and HETCOR[19] were recorded on a Varian Unity-500 NMR spectrometer. Elemental analyses were obtained on an EA1108-CHNS-0 Fisons Instruments. X-Ray diffraction experiments were performed on an Enraf-Nonius CAD4 four-circle diffractometer.

NMR studies in aqueous solution

Solutions of oxo complexes were prepared by adding the appropriate amounts of tungstate or molybdate and quinic acid, ranging the metal : ligand molar ratios from 4 to 0.25 : 1, total concentrations of metal and ligand from 0.10 to 1.5 M, and pH values from 2 to 12.

Solutions of peroxo complexes were prepared by adding hydrogen peroxide to metal/quinic acid solutions (pH 7, in order to avoid the decomposition of H_2O_2), the pH of each solution being then adjusted to a value between 2 and 12. A large excess of H_2O_2 was used, the molar ratios (M : H_2O_2) ranging from 1 : 2.5 to 1 : 5, to prevent the formation of oxo complexes. Molar ratios (M : L) ranged from 2 : 1 to 1 : 2, total concentrations of metal and quinic acid from 0.10 to 1.5 M, and pH values from 2 to 12.

The pH was adjusted (cautiously, to reduce the possibility of drastic local disturbances of equilibria that may be slow to disappear) by addition of DCl and NaOD; the pH* values quoted are the direct pH-meter readings (room temperature) after standardization with aqueous (H_2O) buffers.

Detailed NMR experimental conditions can be found in previous papers.[20,21]

Synthesis

The tungstate complex $K_2[WO_2(C_7H_{10}O_6)_2]·1.5H_2O$ was prepared starting from tungstic acid (750 mg, 3 mmol), potassium hydroxide (337 mg, 6 mmol) and quinic acid (1.15 g, 6 mmol). The tungstic acid was dissolved in 5 cm^3 of water with the potassium hydroxide (40 °C). After the total solubilization, quinic acid was added and the solution stirred for 30 min and

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Table 1 Crystallographic data for $K_2[WO_2(C_7H_{10}O_6)_2]\cdot1.5H_2O$

Formula	$C_{14}H_{29}K_2O_{18.5}W$
Formula weight	755.42
Size/mm	0.34 × 0.15 × 0.14
Space group	$P2_12_12$
a/Å	16.8239(13)
b/Å	17.772(2)
c/Å	8.217(4)
V/Å^3	2456.8(12)
Z	4
μ/mm^{-1}	5.125
d_{calc}/g cm^{-3}	2.042
Reflections unique	4300
Reflections observed	4016
Number of parameters	322
R, R_w	0.0267; 0.0668
GOOF	1.006
Flack parameter	−0.007(10)
$\Delta\rho_{max,\ min}$/e Å^{-3}	0.51, −0.85

the pH was adjusted to 5 (using KOH). Single crystals were obtained by slow diffusion of acetone vapour. Anal. found C, 22.41; H 3.26. Calc. for $K_2[WO_2(C_7H_{10}O_6)_2]\cdot1.5H_2O$: C, 23.95; H, 3.27%. Interference owing to metal carbide formation during combustion cannot be ruled out, affecting the experimental C-content of the crystals.

X-Ray crystallography

A prismatic transparent crystal of the tungsten complex was selected and mounted on an Enraf Nonius CAD4 four-circle diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections in the range $5.44 < \theta < 18.07°$ and refined by a least-squares method. Intensities were collected with graphite monochromated Mo-Kα radiation, using ω/θ scan techniques. 3 Reflections were measured every 3 hours as orientation and intensity controls and no significant intensity decay was observed. Lorentz-polarisation and absorption corrections based on ψ-scan measurements of $\chi = 90°$ reflections were made. The structure was solved by direct methods using the SHELXS97[22] computer program and refined by full-matrix least-squares methods on F^2 using SHELXL97.[23] The data/parameter ratio is 12.47. The chirality of the structure was determined from the refined Flack coefficient.[24] The water hydrogen atoms could not be located whilst the remaining hydrogen atoms were placed at calculated positions and refined as riding on the parent atoms using SHELXL97 defaults.

The final R_F factor was 2.7% and wR (all reflections) = 6.9%. See Table 1 for further details concerning the resolution and refinement of the crystal structure.

CCDC reference number 172995.

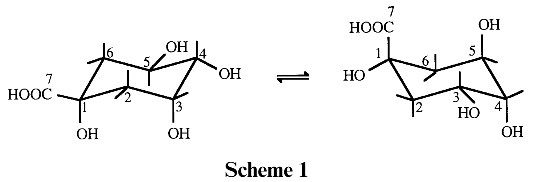
See http://www.rsc.org/suppdata/dt/b1/b109564c/ for crystallographic data in CIF or other electronic format.

Results and discussion

Structure of D-(−)quinic acid in aqueous solution

D-(−)Quinic acid has been shown to exist in DMSO solution as two chair conformers in rapid equilibrium, in an equatorial–axial ratio of 73 : 27[25] (see Scheme 1).

It was previously established by ^1H[26] and ^{13}C[27] NMR that quinic acid in aqueous solution assumes predominantly a chair conformation, the CO_2H group being equatorial. This conformation was also found in the solid state by X-ray diffraction.[28]



Scheme 1

In order to characterise the complexes formed, a proper assignment of all the proton and carbon NMR signals of the ligand is necessary, for various pH conditions. The proton and carbon chemical shifts, as well as the proton–proton coupling constants, are shown in Tables 2 and 3, for different pH values. Our results are in agreement with previous studies, except for the H-2eq and H-2ax assignments which are interchanged. In particular, the observed $J_{4,5}$, $J_{5,6ax}$ vicinal coupling constants and $J_{2eq,6eq}$ long-range coupling constant suggest the exclusive existence of the equatorial conformer. The observed long-range coupling constant $J_{2eq,6eq}$ is a result of a zig-zag H–C–C–C–H arrangement.

Complexation with W(VI) and Mo(VI)

In the presence of sodium tungstate or sodium molybdate the proton and ^{13}C spectra of aqueous solutions of D-quinic acid show new signals which are due to complexation, besides those of the free ligand when present. The observation of distinct signals for bound and free ligand is a consequence of slow ligand exchange on the NMR time-scale, which renders a speciation study more direct using this technique.

A systematic recording of spectra was performed for both W(VI)– and Mo(VI)–D-quinic acid systems, total concentrations of complexing species ranging from 2.5 to 0.10 mol dm^{-3}, metal : ligand molar ratios from 4 to 0.25 : 1, and pH values ranging from 3 to 11. Under these conditions, the spectra show two different sets of signals due to bound ligand for both systems. Signal intensity considerations led to the conclusion that these sets correspond to two different complexes. These complexes, **a** and **b**, are formed over the entire pH range covered (3–11), irrespective of the total concentrations of complexing species and of the metal : ligand molar ratios. The effect of pH* on their concentration is shown in Fig. 1 for a 0.25 mol dm^{-3} : 0.50 mol dm^{-3} W(VI)–D-quinic acid solution. The concentrations of the complexes and free ligand were estimated on the basis of the ^1H NMR signal intensities. The Mo(VI)–D-quinic acid system shows similar behaviour.

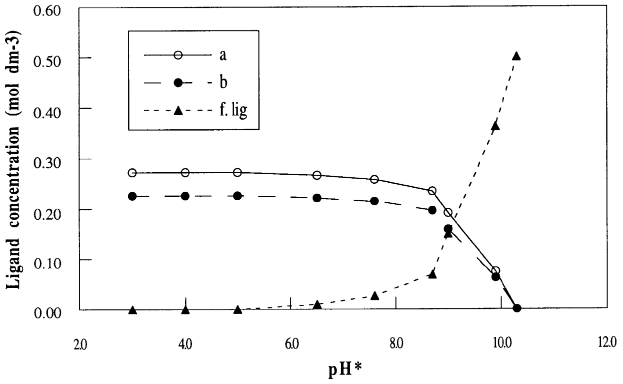


Fig. 1 Concentration of the ligand as a function of pH*, obtained by ^1H NMR for a 0.25 mol dm^{-3} : 0.50 mol dm^{-3} solution in D_2O of sodium tungstate(VI) and D-quinic acid, temperature 298 K.

The ^1H and ^{13}C assignments were done with the aid of homonuclear and heteronuclear correlation experiments (COSY and HETCOR, respectively). Tables 4 and 5 show the proton and carbon NMR parameters.

The way in which the ligand is bonded to the metals can be established from the proton and carbon chemical shifts, relative to the free ligand at the same pH. For both tungstate and molybdate systems, the high frequency ^{13}C shifts observed for the carboxylic and the adjacent carbinol carbon nuclei upon complexation ($\Delta\delta$ 5 and 10–12, respectively) are characteristic

Table 2 ^{1}H NMR parameters[a] for quinic acid in D_2O solution (0.20 mol dm^{-3}), 298 K

	H-2eq	H-2ax	H-3	H-4	H-5	H-6ax	H-6eq	$J_{2eq,3}$	$J_{2ax,3}$	$\lvert J_{2eq,2ax}\rvert$	$J_{3,4}$	$J_{4,5}$	$J_{5,6ax}$	$J_{5,6eq}$	$\lvert J_{6ax,6eq}\rvert$	$J_{2eq,6eq}$[b]
pH* = 3.1																
δ	2.10	2.17	4.23	3.62	4.10	1.98	2.21	3.1	3.4	15.1	3.3	9.4	10.9	4.7	13.5	2.7
pH* = 5.0																
δ	2.02	2.11	4.20	3.60	4.07	1.93	2.12	3.1	3.3	15.0	3.2	9.3	10.9	4.7	13.5	2.7
pH* = 7.0																
δ	2.02	2.11	4.20	3.60	4.07	1.93	2.12	3.1	3.3	15.0	3.2	9.3	10.9	4.7	13.5	2.7

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_H 1.3) as internal reference; J values in Hz. [b] ^4J due to a zig-zag H–C–C–C–H arrangement.

Table 3 ^{13}C NMR chemical shifts[a] for quinic acid in D_2O solution (0.20 mol dm^{-3}), 298 K

	C-1	C-2	C-3	C-4	C-5	C-6	C-7
pH* = 3.0							
δ	77.54	38.45	71.65	76.45	68.06	41.86	180.32
pH* = 5.0							
δ	78.53	38.93	71.98	76.78	68.54	42.25	182.86
pH* = 6.9							
δ	78.57	38.96	71.99	76.79	68.57	42.26	182.94

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference.

of involvement of these groups in complexation;[15–17,20,21,29–36] the other carbon shifts are much smaller. This is also supported by the small ^{1}H shifts observed upon complexation.

The ^{183}W, ^{95}Mo, and ^{17}O chemical shifts help to elucidate the nature of the metal centre in the complexes. The respective parameters are shown in Tables 6, 7 and 8, respectively. The ^{183}W spectra show two sharp signals, at δ −4.0 and 0.80 ppm, the more intense one lying at lower frequency. Their relative intensities exactly match the relative concentrations of **a** and **b** in solution. The chemical shift values can be compared with those found for pairs of isomeric 1 : 2 (metal : ligand) tungstate complexes with α-hydroxyacids possessing a MO_2^{2+} centre, the carbon atom that bears the hydroxy group being a tertiary one.[35] The ^{95}Mo spectrum is a broad signal that can be analysed as two close signals (δ 70 and 73 ppm) as expected for the two complexes, regarding the observed relationship between δ^{183}W/δ^{95}Mo for homologous species.[17] Accordingly, the ^{17}O NMR spectra show signals (δ 637 and 827 ppm, relative to external reference D_2O, for tungstate and molybdate, respectively), due to terminal M=O bonds but no signals for M–O–M bridges are detected.[15,16,20,21,30–32,37–41] Also consistent with the proposed 1 : 2 (metal : ligand) stoichiometry is the fact that (a) solutions having metal : ligand molar ratios larger than 0.5 : 1 have ^{183}W, ^{95}Mo and ^{17}O spectra showing free metal and ^{1}H and ^{13}C spectra with no signals for free ligand and (b) solutions having metal : ligand molar ratios smaller than 0.5 : 1 have ^{183}W, ^{95}Mo and ^{17}O spectra showing no signals for free metal and ^{1}H and ^{13}C spectra with an appropriate amount of free ligand. All these findings point to **a** and **b** being the diastereomers **1** and **2**.

Table 4 ^{1}H NMR parameters[a] for W(VI) + quinic acid, Mo(VI) + quinic acid, W(VI) + quinic acid + H_2O_2 and Mo(VI) + quinic acid + H_2O_2, 298 K

	H-2eq	H-2ax	H-3	H-4	H-5	H-6ax	H-6eq	$J_{2eq,3}$	$J_{2ax,3}$	$\lvert J_{2eq,2ax}\rvert$	$J_{3,4}$	$J_{4,5}$	$J_{5,6ax}$	$J_{5,6eq}$	$\lvert J_{6ax,6eq}\rvert$	$J_{2eq,6eq}$[b]
W(VI) + quinic acid																
Complex **a**[c] (pH* 3.0)																
δ	2.27	2.08	4.23	3.61	4.05	1.75	2.37	2.9	3.3	15.0	3.4	9.8	11.8	4.7	12.9	2.9
$\Delta\delta$	0.17	−0.09	0.0	−0.01	−0.05	−0.23	0.16									
Complex **b**[c] (pH* 3.0)																
δ	2.30	2.02	4.23	3.62	4.12	1.82	2.40	3.1	3.2	14.9	3.4	9.8	11.6	4.7	13.0	2.9
$\Delta\delta$	0.20	−0.15	0.0	0.0	0.02	−0.16	0.19									
Mo(VI) + quinic acid																
Complex **a**[d] (pH* 3.0)																
δ	2.28	2.07	4.18	3.58	4.01	1.75	2.39	2.9	3.1	14.8	3.1	9.1	12.3	4.5	12.4	2.8
$\Delta\delta$	0.18	−0.10	−0.05	−0.04	−0.09	−0.23	0.18									
Complex **b**[d] (pH* 3.0)																
δ	2.30	1.99	4.19	3.59	4.10	1.84	2.39	2.8	3.0	14.7	3.1	9.0	12.3	4.4	12.3	2.8
$\Delta\delta$	0.20	−0.18	−0.04	−0.03	0.0	−0.14	0.18									
W(VI) + quinic acid + H_2O_2																
Complex **a**[e] (pH* 5.0)																
δ	2.19	2.08	4.20	3.63	4.19	1.85	2.26	2.8	2.6	14.5	2.8	9.5	12.5	4.9	12.5	2.8
$\Delta\delta$	0.17	−0.03	0.0	0.03	0.12	−0.08	0.14									
Mo(VI) + quinic acid + H_2O_2																
Complex **a**[f] (pH* 5.0)																
δ	2.28	2.11	4.23	3.66	4.30	1.93	2.34	2.8	2.7	14.5	2.8	9.6	12.1	4.9	12.2	2.8
$\Delta\delta$	0.26	0.0	0.03	0.06	0.23	0.0	0.22									

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_H 1.3) as internal reference; J values in Hz. [b] ^4J due to a zig-zag H–C–C–C–H arrangement. [c] 0.25 : 0.50 mol dm^{-3} W(VI)–quinic acid solution. [d] 0.25 : 0.50 mol dm^{-3} Mo(VI)–quinic acid solution. [e] 0.50 : 0.50 : 2.5 mol dm^{-3} W(VI)–quinic acid–H_2O_2 solution. [f] 0.50 : 0.50 : 2.5 mol dm^{-3} Mo(VI)–quinic acid–H_2O_2 solution.

Table 5 ^{13}C NMR chemical shifts[a] for W(VI) + quinic acid, Mo(VI) + quinic acid, W(VI) + quinic acid + H_2O_2 and Mo(VI) + quinic acid + H_2O_2, 298 K

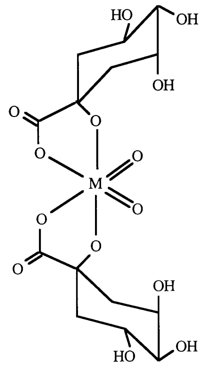
	C-1	C-2	C-3	C-4	C-5	C-6	C-7
W(VI) + quinic acid							
Complex **a**[b] (pH* 5.0)							
δ	89.89	38.41	72.02	76.94	68.04	41.11	187.45
$\Delta\delta$	11.36	−0.52	0.04	0.16	−0.50	−1.14	4.59
Complex **b**[b]							
δ	90.10	37.93	72.14	76.84	68.14	42.05	187.45
$\Delta\delta$	11.57	−1.00	0.16	0.06	−0.40	−0.20	4.59
Mo(VI) + quinic acid							
Complex **a**[c] (pH* 5.0)							
δ	90.41	38.28	72.06	76.84	68.22	40.37	186.43
$\Delta\delta$	11.88	−0.65	0.08	0.06	−0.32	−1.88	3.57
Complex **b**[c]							
δ	90.57	37.04	72.21	76.70	68.29	41.98	186.35
$\Delta\delta$	12.04	−1.89	0.23	−0.08	−0.25	−0.27	3.49
W(VI) + quinic acid + H_2O_2							
Complex **a**[d] (pH* 5.0)							
δ	89.09	39.94	72.56	77.02	68.49	43.81	187.47
$\Delta\delta$	10.56	1.01	0.58	0.24	−0.05	1.56	4.61
Mo(VI) + quinic acid + H_2O_2							
Complex **a**[e] (pH* 5.0)							
δ	89.16	39.90	72.80	77.13	68.88	43.81	186.37
$\Delta\delta$	10.63	0.97	0.82	0.35	0.34	1.56	3.51

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference. [b] 0.25 : 0.50 mol dm^{-3} W(VI)–quinic acid solution. [c] 0.25 : 0.50 mol dm^{-3} Mo(VI)–quinic acid solution. [d] 0.50 : 0.50 : 2.5 mol dm^{-3} W(VI)–quinic acid–H_2O_2 solution. [e] 0.50 : 0.50 : 2.5 mol dm^{-3} Mo(VI)–quinic acid–H_2O_2 solution.

Table 6 ^{183}W NMR chemical shifts[a] for W(VI) + quinic acid and W(VI) + quinic acid + H_2O_2, 298 K

	$\delta^{183}W$	$^3J_{W-H}$
W(VI) + quinic acid		
Complex **a**[b] (pH* 5.0)	−4.0	—[c]
Complex **b**[b] (pH* 5.0)	0.8	—[c]
W(VI) + quinic acid + H_2O_2		
Complex **a**[d] (pH* 5.0)	−611.9	—[c]

[a] δ Values relative to external reference Na_2WO_4, pH* = 9.5, *J* values in Hz. [b] 0.25 : 0.50 mol dm^{-3} W(VI)–quinic acid solution. [c] Not resolved. [d] 0.50 : 0.50 : 2.5 mol dm^{-3} W(VI)–quinic acid–H_2O_2 solution.



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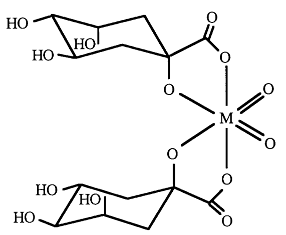

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Table 7 ^{95}Mo NMR chemical shifts[a] for Mo(VI) + quinic acid and Mo(VI) + quinic acid + H_2O_2, 298 K

	^{95}Mo	$\Delta\nu_{1/2}$
Mo(VI) + quinic acid		
Complex **a**[b] (pH* 5.0)	70	308
Complex **b**[b] (pH* 5.0)	73	280
Mo(VI) + quinic acid + H_2O_2		
Complex **a**[c] (pH* 5.0)	−253	849

[a] δ Values relative to external reference Na_2MoO_4, pH* = 9.0; $\Delta\nu_{1/2}$ in Hz. [b] 0.25 : 0.50 mol dm^{-3} Mo(VI)–quinic acid solution. [c] 0.50 : 0.50 : 2.5 mol dm^{-3} Mo(VI)–quinic acid–H_2O_2 solution.

Table 8 ^{17}O NMR chemical shifts[a] for W(VI) + quinic acid, Mo(VI) + quinic acid, W(VI) + quinic acid + H_2O_2 and Mo(VI) + quinic acid + H_2O_2, 298 K

	$-\mathrm{M}={}^{17}\mathrm{O}$	$-\mathrm{M}-{}^{17}\mathrm{O}-\mathrm{M}-$
W(VI) + quinic acid Complexes **a** + **b**[b] (pH* 5.0)	637	—
Mo(VI) + quinic acid Complexes **a** + **b**[c] (pH* 5.0)	827	—
W(VI) + quinic acid + H_2O_2 Complex **a**[d] (pH* 5.0)	655	—
Mo(VI) + quinic acid + H_2O_2 Complex **a**[e] (pH* 5.0)	838	—

[a] δ Values relative to external reference D_2O. [b] 0.25 : 0.50 mol dm^{-3} W(VI)–quinic acid solution. [c] 0.25 : 0.50 mol dm^{-3} Mo(VI)–quinic acid solution. [d] 0.50 : 0.50 : 2.5 mol dm^{-3} W(VI)–quinic acid–H_2O_2 solution. [e] 0.50 : 0.50 : 2.5 mol dm^{-3} Mo(VI)–quinic acid–H_2O_2 solution.

The two ligand molecules are magnetically equivalent, complex **a** being slightly more stable than **b** mainly for steric reasons involving the non-complexed rings. These geometries are also consistent with only small changes of the proton coupling constants upon complexation.

The NMR evidence points to the sole formation of the homo-complexes but this cannot be considered as completely unambiguous as coincident chemical shifts cannot be totally excluded.

Crystal structure

The tungsten(VI) complex $K_2[WO_2(C_7H_{10}O_6)_2]\cdot 1.5H_2O$ crystallises in an orthorhombic unit cell in the non-centrosymmetric space group $P2_12_12$, exhibiting a three-dimensional infinite polymeric structure. The tungsten atom is bound to two oxygen atoms O1 and O2, with bond distances 1.743(5) Å for both atoms, as usual for the tungstate ion. Two quinic acid molecules coordinate each tungstate ion. The coordinated oxygen atoms come from the carboxyl group [bond distances 2.174(5) and 2.182(5) Å for O71A–W1 and O71B–W1] and from the hydroxy group on C1 [bond distances 1.925(5) and 1.938(4) Å for O1B and O1A, respectively]. The tungsten atom is 6-coordinate in an approximate square bipyramidal geometry, with an O1–W1–O2 angle of 104.0(2)°. The two potassium atoms are spread over three positions: K1 occupies a general position with a refined occupation factor 1.0; K2 also occupies a general position but with an occupation factor of 0.5; K3 occupies a special position of symmetry 2b. Potassium and tungsten atoms are bridged by oxygen atoms (see Fig. 2) forming short K2–K1–W1–K3–W1′–K1′–K2′ chains further interlinked by the quinic acid ligands.

The quinic acid ligands are deprotonated both in the carboxyl and hydroxy group on C1 and adopt chair conformations. The 6-membered ring C1A–C2A–C3A–C4A–C5A–C6A has an average ring bond distance of 1.522(4) Å and an

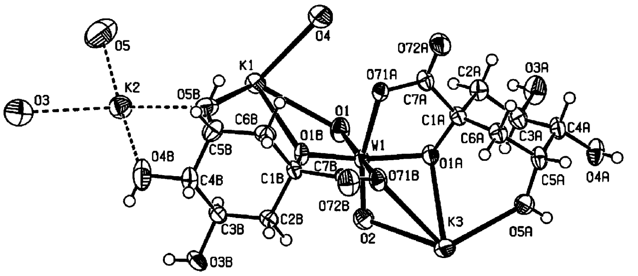


Fig. 2 X-Ray structure of potassium bis-quinato tungstate hydrate. Disordered water molecules are omitted for clarity.

average torsion angle of 54.3(3)°. The Cremer and Pople parameters[42] are $Q = 0.558(7)$ Å, $\theta = 171.1(7)°$, $\phi = 328(5)°$.

The 6-membered ring C1B–C2B–C3B–C4B–C5B–C6B has an average ring bond distance of 1.524(4) Å and an average torsion angle of 53.3(3)°. The Cremer and Pople parameters are $Q = 0.541(7)$ Å, $\theta = 175.3(7)°$, $\phi = 293(9)°$.

In both rings the hydroxy group on C1 adopts an axial position related to the Cremer and Pople plane, as does the hydroxy group on C5, while the other hydroxy and carboxyl groups adopt an equatorial position.

The absolute structure was determined from X-ray analysis using the significant anomalous dispersion of tungsten at the Mo-Kα wavelength and confirmed the chirality of D-quinic acid (C3 and C5 are *R* chiral centers).

Complexation with W(VI) and Mo(VI) in the presence of hydrogen peroxide

When an excess of hydrogen peroxide is added to mixtures of sodium tungstate or sodium molybdate with D-quinic acid, in aqueous solution, the systems become simpler, showing only one set of ^{1}H and ^{13}C signals due to complexed forms, besides those of the free ligand. This indicates the formation of only one complex (namely peroxo complex **a**). The effect of pH* on its concentration is shown in Fig. 3, for a 0.50 mol dm^{-3} : 0.50 mol dm^{-3} : 1.25 mol dm^{-3} W(VI)/D-quinic/H_2O_2 solution. The concentrations of the complex and "free" ligand were estimated on the basis of the ^{13}C NMR signal intensities. Signals due to degradation products are also detected, especially at high pH.

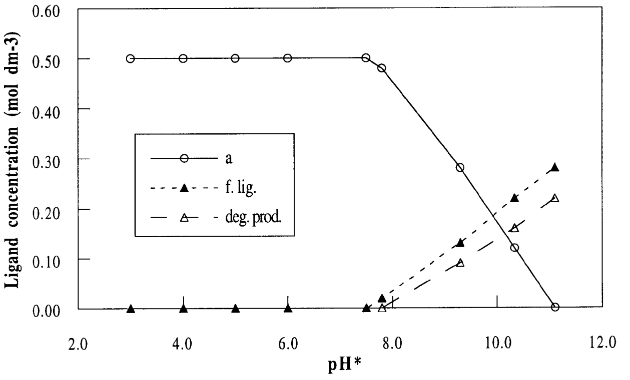
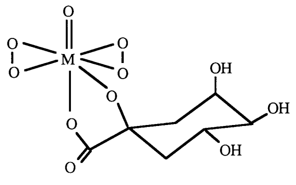


Fig. 3 Concentration of the ligand as a function of pH*, obtained by ^{13}C NMR for a 0.50 mol dm^{-3} : 0.50 mol dm^{-3} : 1.25 mol dm^{-3} aqueous solution (50% D_2O) of sodium tungstate(VI), D-quinic acid and H_2O_2, temperature 298 K.

The high frequency ^{13}C NMR shifts observed for the carboxylic and the adjacent carbon nuclei ($\Delta\delta$ 4–5 and 11 ppm) (Table 5) suggest that quinic acid is involved with both metal centres by the carboxylate and the adjacent OH group.[15–17,20,21,29–36] The ^{183}W and ^{95}Mo NMR chemical shifts observed (δ −612 and −253 ppm, relative to external reference Na_2MO_4, for M=W and Mo, respectively) (Tables 6 and 7) can be compared with those found for oxoperoxo complexes of W(VI) and Mo(VI) with sugar acids, previously studied.[17] In particular, the ^{95}Mo NMR chemical shift also reproduces the value of ref. 13 for the peroxo complex of molybdate with quinic acid and are in agreement with those found for mononuclear diperoxo complexes of molybdate with oxalic, glycolic, malic and citric acids.[13] The ^{183}W signals also fall in the region of oxodiperoxo tungstates in water.[43,44] The oxygen shifts detected (δ 655 and 838 ppm, relative to external reference D_2O, for tungstate and molybdate, respectively) (Table 8) are typical of terminal M=O bonds of Mo^{4+} centers,[17,45–47] no signals due to M–O–M bridges being present.[15,16,20,21,30–32,37–41] Severe broadening of the peroxide ^{17}O resonances due to nuclear quadrupolar relaxation precluded any detection of the $M(O_2)$ ^{17}O signals.[46,48]

The above data are consistent with the formation of a mononuclear diperoxo complex. The existence of equal contents of metal and ligand (quinic acid) is confirmed by the fact that, for example, 0.50 : 0.50 : 2.5 mol dm^{-3} W(VI)/D-quinic acid/H_2O_2 solutions, at pH* 5.0, have ^{13}C, ^{17}O and ^{183}W NMR spectra with no signals for free ligand or for free metal, whereas, 0.25 : 0.0.50 : 2.5 mol dm^{-3} solutions have about 50% free ligand and no signal for free metal, and 0.50 : 0.25 : 2.5 mol dm^{-3} W(VI)/D-quinic acid/H_2O_2 solutions have about 50% free metal. Free metal is in the peroxotungstate forms $[WO_2(O_2)_2]^{2-}$ and $[W_2O_3(O_2)_4]^{2-}$[42,43] due to the large excess of hydrogen peroxide present in solution. Also consistent with the 1 : 1 metal : ligand stoichiometry is the detection of only one ^{1}H set and only one ^{13}C set of signals for the bound ligand. If two ligand molecules were coordinated in a bidentate fashion to a 7-coordinated metal atom possessing a pentagonal bipyramidal geometry, two ^{1}H and two ^{13}C sets of signals of equal intensities would appear for the bound ligand.

All these findings point to a 1 : 1 : 2 (metal : ligand : peroxide) stoichiometry for the complex. Guided by the structures found by X-ray diffraction for the oxodiperoxo complexes of molybate with glycolic[13] and citric acids[49] we can propose structure **3**.



3

This structure was also previously proposed for the peroxo complex of molybdenum, $K_2[MoO(O_2)_2(quin)]\cdot 2H_2O$[13] by comparison with the X-ray determined structure of the related glycolate complex.

In such a structure, seven oxygen atoms coordinate the metal in essentially a pentagonal bipyramidal arrangement. The M=O oxo group occupies one of the apical positions and the two bound η^2-peroxo ligands occupy equatorial positions. The remaining positions are occupied by the α-hydroxycarboxylic moiety of the quinic acid. The hydroxy group is assumed to occupy an equatorial position around the metal atom so as to form a strong bond, whereas the carboxylic group occupies the remaining apical position, as previously proposed in the case for the oxoperoxo complexes of Mo(VI) and W(VI) with sugar acids.[17]

Conclusion

The system addressed in this paper can be regarded as an extension of the previous systematic studies on the complexation of metal oxo ions, namely tungstate and molybdate, with the main sugar acids, aldaric,[20,21,29] alduronic,[15] and aldonic[16,30–32] acids, also in the presence of hydrogen peroxide.[17]

Irrespective of pH, 1 : 2 (metal : ligand) complexation occurs, the ligand behaving as an α-hydroxycarboxylic acid (O-1 and

O-7 as binding sites) and two diastereoisomers were detected in solution. One of the complexes with W(VI) was isolated and characterised in the solid state by X-ray diffraction. This structure is similar to that proposed for the most stable 1 : 2 (metal : ligand) tungstate and molybdate oxo complexes of α-hydroxyacids having a MO_2^{2+} centre, as established on the basis of NMR and steric considerations.

In the presence of hydrogen peroxide, only one complex is detected. Common features to both Mo and W peroxo complexes are the involvement of two peroxide units per metal centre and the coordination of the ligand through O-1 and O-7.

It is known that ionized organic OH functions are relatively hard bases, which may displace the carboxylate groups from the first coordination sphere of the metal ion. Thus, at high pH values, polyhydroxycarboxylic acids can coordinate exclusively through ionized OH functions, without COO^- coordination.[50] This we have found to occur in previous studies of oxo complexes of sugar acids involving $M_2O_5^{2+}$ metal centres,[15,16,20,21,30–32] but not in the present study where MO_2^{2+} and MO^{4+} centres are present. Over the pH range used, coordination is established through the carboxylate and adjacent hydroxy groups. Accordingly, two 1 : 2 (metal : acid) oxo complexes and one 1 : 1 : 2 (metal : acid : peroxide) oxoperoxo complex are detected.

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References

1 A. Barco, S. Benetti, C. De Risi, P. Marchetti, G. P. Pollini and V. Zanirato, *Tetrahedron : Asymmetry*, 1997, **8**, 3515 and references therein.

2 C. Alves, M. T. Barros, C. D. Maycock and M. R. Ventura, *Tetrahedron*, 1999, **55**, 8443 and references therein.

3 S. E. Castillo-Blum and N. Barba-Behrens, *Coord. Chem. Rev.*, 2000, **196**, 3 and references therein.

4 R. Codd, A. Levina, L. Zhang, T. W. Hambley and P. A. Lay, *Inorg. Chem.*, 2000, **39**, 990.

5 R. Codd and P. A. Lay, *J. Am. Chem. Soc.*, 1999, **121**, 7864.

6 R. Codd, P. A. Lay and A. Levina, *Inorg. Chem.*, 1997, **36**, 5440.

7 R. Codd, T. W. Hambley and P. A. Lay, *Inorg. Chem.*, 1995, **34**, 877.

8 Y. Allegretti, E. G. Ferrer, A. C. González Baró and P. A. M. Williams, *Polyhedron*, 2000, **19**, 2613.

9 Y. Inomata, T. Haneda and F. S. Howell, *J. Inorg. Biochem.*, 1999, **76**, 13.

10 G. Hata, Y. Kitano, T. Kaneko, H. Kaway and M. Mutoh, *Chem. Pharm. Bull.*, 1992, **40**, 1604.

11 A. Flores-Parra and R. Contreras, *Coord. Chem. Rev.*, 2000, **196**, 85.

12 Y. Ogata and Y. Sawaki, in *Organic synthesis by oxidation with metal compounds*, ed. W. J. Mijs and C. R. H. I. de Jonge, Plenum Press, New York and London, 1986, ch. 16.

13 A. C. Dengel, W. P. Griffith, R. D. Powell and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1987, 991.

14 S. J. Angyal, *Adv. Carbohydr. Chem. Biochem.*, 1989, **47**, 1.

15 M. L. Ramos, M. M. Caldeira and V. M. S. Gil, *Carbohydr. Res.*, 1996, **286**, 1.

16 M. L. Ramos, M. M. Caldeira and V. M. S. Gil, *Carbohydr. Res.*, 2000, **329**, 387.

17 M. L. Ramos, M. M. Caldeira and V. M. S. Gil, *J. Chem. Soc., Dalton Trans.*, 2000, 2099.

18 U. Piantini, O. W. Sørensen and R. R. Ernst, *J. Am. Chem. Soc.*, 1982, **104**, 6800.

19 A. D. Bax and G. A. Morris, *J. Magn. Reson.*, 1981, **42**, 51; A. D. Bax, *J. Magn. Reson.*, 1983, **53**, 517; J. A. Wilde and P. H. Bolton, *J. Magn. Reson.*, 1984, **59**, 343.

20 M. L. Ramos, M. M. Caldeira, V. M. S. Gil, H. van Bekkum and J. A. Peters, *Polyhedron*, 1994, **13**, 1825.

21 M. L. Ramos, M. M. Caldeira, V. M. S. Gil, H. van Bekkum and J. A. Peters, *J. Coord. Chem.*, 1994, **33**, 319.

22 G. M. Sheldrick, SHELXS, A computer program for the determination of crystal structures, University of Göttingen, Germany, 1997.

23 G. M. Sheldrick, SHELXL, A computer program for the determination of crystal structures, University of Göttingen, Germany, 1997.

24 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

25 A. Flores-Parra, D. M. Gutiérrez-Avella and R. Contreras, *Magn. Reson. Chem.*, 1989, **27**, 544.

26 J. Corse, R. E. Lundin, E. Sondheimer and A. C. Waiss, Jr., *Phytochemistry*, 1966, **5**, 767.

27 C. J. Kelley, R. C. Harruff and M. Carmack, *J. Org. Chem.*, 1976, **60**, 3600.

28 C. Abell, F. H. Allen, T. D. H. Bugg, M. J. Doyle and P. R. Raithby, *Acta Crystallogr., Sect. C*, 1988, **44**, 1287.

29 M. L. Ramos, M. M. Caldeira and V. M. S. Gil, *Inorg. Chim. Acta*, 1991, **180**, 219.

30 M. L. Ramos, M. M. Caldeira and V. M. S. Gil, *Carbohydr. Res.*, 1997, **297**, 191.

31 M. L. Ramos, M. M. Caldeira and V. M. S. Gil, *Carbohydr. Res.*, 1997, **299**, 209.

32 M. L. Ramos, M. M. Caldeira and V. M. S. Gil, *Carbohydr. Res.*, 1997, **304**, 97.

33 V. M. S. Gil, *Pure Appl. Chem.*, 1989, **61**, 841.

34 J.-E. Berg, S. Brandänge, L. Lindblom and P.-E. Werner, *Acta Chem. Scand. Ser. A*, 1977, **31**, 325.

35 M. Hlaïbi, S. Chapelle, M. Benaïssa and J.-F. Verchère, *Inorg. Chem.*, 1995, **34**, 4434.

36 M. Hlaïbi, M. Benaïssa, S. Chapelle and J.-F. Verchère, *Carbohydr. Lett.*, 1996, **2**, 9.

37 R. I. Maksimovskaya and K. G. Burtseva, *Polyhedron*, 1985, **4**, 1559.

38 J. J. Hastings and O. W. Howarth, *J. Chem. Soc., Dalton Trans.*, 1992, 209.

39 M. Filowitz, W. G. Klemperer, L. Messerle and W. Shum, *J. Am. Chem. Soc.*, 1976, **98**, 2345.

40 M. Filowitz, R. K. Ho, W. G. Klemperer and W. Shum, *Inorg. Chem.*, 1979, **18**, 93.

41 K. F. Miller and R. A. D. Wenthworth, *Inorg. Chem.*, 1979, **18**, 984.

42 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.

43 V. Nardello, J. Marko, G. Vermeersch and J. M. Aubry, *Inorg. Chem.*, 1998, **37**, 5418.

44 H. Nakajima, T. Kudo and M. Mizuno, *Chem. Lett.*, 1997, 693.

45 M. H. Dickman and M. T. Pope, *Chem. Rev.*, 1994, **94**, 569.

46 M. Postel, C. Brevard, H. Arzoumanian and J. G. Riess, *J. Am. Chem. Soc.*, 1983, **105**, 4922.

47 V. Conte, F. Di Furia, G. Modena and O. Bortolini, *J. Org. Chem.*, 1988, **53**, 4581.

48 M. S. Reynolds and A. Butler, *Inorg. Chem.*, 1996, **35**, 2378.

49 J. Flanagan, W. P. Griffith, A. C. Skapski and R. W. Wiggins, *Inorg. Chim. Acta*, 1985, **96**, L-23.

50 M. van Duin, J. A. Peters, A. P. G. Kieboom and H. van Bekkum, *Recl. Trav. Chim. Pays-Bas*, 1989, **108**, 57.