DALTON
FULL PAPER

Peroxo complexes of sugar acids with oxoions of Mo^{VI} and W^{VI} as studied by NMR spectroscopy †

M. Luísa Ramos, M. Madalena Caldeira and Victor M. S. Gil *

Chemistry Department, University of Coimbra, 3000 Coimbra, Portugal

Received 1st December 1999, Accepted 15th May 2000
Published on the Web 14th June 2000

By using multinuclear ^1H, ^{13}C, ^{17}O, ^{95}Mo and ^{183}W magnetic resonance spectroscopy (1-D and 2-D), aldonic acids, alduronic acids and aldaric acids have been found respectively to form one, four and three homologous oxoperoxo complexes with Mo^{VI} and W^{VI}, in aqueous solution (pH range 2–11). Common features are the involvement of two peroxide units per metal centre and the co-ordination of the sugar acids through carboxylate and adjacent hydroxyl groups. Accordingly, 1 : 1 : 2 (metal : acid : peroxide) complexes are detected as well as 2 : 1 : 4 species in the case of the aldaric acids. The geometry around each MO^{4+} centre is approximately pentagonal bipyramidal, the M=O group occupying one of the apical positions and the two peroxo ligands being equatorial. The sugar acid is co-ordinated in one equatorial and in one apical site.

1 Introduction

The chemistry of transition metal peroxo complexes has received special attention due to their importance in a variety of industrial, pharmaceutical and biological processes. Co-ordination to a metal center activates peroxide towards the oxidation of a variety of substrates, rendering peroxometal complexes important as intermediates in biological and synthetic catalysis.[1] Peroxo complexes of molybdenum(VI) and tungsten(VI) are known to be involved in stoichiometric oxygen transfer reactions including epoxidation of alkenes and oxidation of organic and inorganic substrates,[1–10] and can be regarded as an environmentally friendly alternative to traditional oxidation reactions, representing an improvement in terms of pollution prevention.[11] These kind of compounds are also relevant in analytical chemistry, enabling the chromatographic separation of vanadate, tungstate, molybdate and chromate ions in the presence of hydrogen peroxide.[12] They have industrial applications as useful precursors of new materials,[13,14] and as bleaching accelerators.[15] In addition, molybdenum(VI) and tungsten(VI) are very efficient catalysts of bromide oxidation by hydrogen peroxide, mimicking vanadium peroxidases[16] and peroxomolybdates and peroxotungstates are potent stimulators of insulin effects in rat adipocytes.[17]

Peroxomolybdates and peroxotungstates have been known for a long time[1] and characterized in solution and in the solid state.[1,3,10,14,18] For a review on peroxo complexes of chromium, molybdenum and tungsten see ref. 1. Mixed complexes, *i.e.* peroxo metal complexes containing an additional heteroligand, have also been characterized both in aqueous solution and in the solid state. A large number of such complexes are known.[1,4,9,19–21] In all cases where the structures have been determined or inferred the metal atoms are seven-co-ordinate in a pentagonal bipyramidal geometry. The complexes are characterized by a MO^{4+} centre, the M=O group occupying one of the apical positions. For molybdate and tungstate, oxodiperoxo complexes have a large stability when compared to oxomonoperoxo species. For that reason most of the oxoperoxo complexes of molybdate and tungstate, previously characterized in the literature, have two peroxide groups co-ordinated in the equatorial plane. However, some exceptions are known. The key to stabilize oxomonoperoxo complexes is to incorporate a heteroligand that can effectively co-ordinate three sites in the pentagonal plane.[4] Bidentate ligands do not appear to be effective to do that; instead, oxodiperoxo complexes are usually formed with the heteroligand co-ordinated in one equatorial and in one apical site.[1,4,9,19–21] Vanadium(V), however, can form both mono- and di-peroxo complexes with bidentate ligands.[22]

Previously, we have carried out a systematic and comparative study of sugar acids and their complexation with metal oxoions, in aqueous solution, using multinuclear NMR spectroscopy (1-D and 2-D). Having studied some aldaric, uronic and aldonic acids and their complexation with tungstate and molybdate ions,[23–29] we now extend those studies to a new class of complexes and report on the complexation of Mo^{VI} and W^{VI} with sugar acids (Chart 1) and hydrogen peroxide.

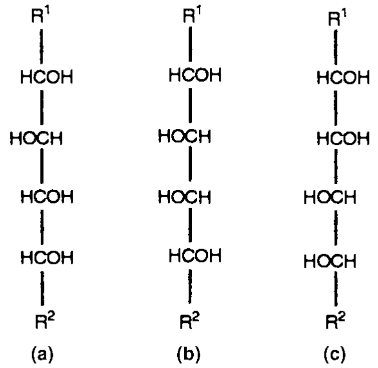

Chart 1 Fischer projections of sugar acids (a) gluco configuration ($R^1 = CO_2H$, $R^2 = CH_2OH$, D-gluconic acid; $R^1 = CHO$, $R^2 = CO_2H$, open chain of D-glucuronic acid; $R^1 = CO_2H$, $R^2 = CO_2H$, D-glucaric acid; (b) galacto configuration ($R^1 = CO_2H$, $R^2 = CH_2OH$, D-galactonic acid; $R^1 = CHO$, $R^2 = CO_2H$, open chain of D-galacturonic acid; $R^1 = CO_2H$, $R^2 = CO_2H$, galactaric acid; (c) manno configuration ($R^1 = CO_2H$, $R^2 = CH_2OH$, L-mannonic acid).

2 Experimental

Analytical grade disodium tungstate and disodium molybdate dihydrates $Na_2MO_4{\cdot}2H_2O$ and commercially available hydrogen peroxide (35% in water) and sugar acids were used. The

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† Electronic supplementary information (ESI) available: multinuclear NMR data. See http://www.rsc.org/suppdata/dt/b0/b003620j/

DOI: 10.1039/b003620j

hydrogen peroxide was added to metal/sugar acid solutions (pH 7) in order to avoid the decomposition of H_2O_2. The pH was then 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 buffers. 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 sugar acid from 0.10 to 1.5 M, and pH values from 2 to 11.

The ^{13}C NMR spectra were obtained on a Varian XL-200 instrument and the ^{1}H, ^{17}O, ^{95}Mo and ^{183}W spectra on a Varian Unity-500 NMR spectrometer. The detailed conditions can be found in previous papers.[23–29] The 2-D NMR spectra, DQF (double quantum filtered) COSY[30] and HETCOR (heteronuclear correlation),[31] were recorded on a Varian Unity-500 NMR spectrometer.

3 Results and discussion

We have carried out the studies of the complexation of sugar acids with Mo^{VI} and W^{VI}, in the presence of a large excess of hydrogen peroxide, in a parallel manner, owing to the expected similarities. Depending on pH, concentration and molar ratios, mixtures of sodium tungstate or sodium molybdate, sugar acids and H_2O_2 in aqueous solution show ^{1}H and ^{13}C NMR signals ascribed to the peroxo complexes, in addition to those of "free" ligand eventually present. The observation of distinct signals for bound and "free" ligand is a consequence of slow ligand exchange on the NMR timescale. The systems appear considerably simpler than the oxo systems studied previously.

The way 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. The ^{95}Mo, ^{183}W and ^{17}O chemical shifts help to elucidate the nature of the metal centre in the complexes. It is noted that although the quadrupolar molybdenum nucleus gives rise to broad signals, the spin 1/2 tungsten-183 nucleus gives sharp signals. As a result, in some favourable cases the vicinal tungsten–proton coupling constants can also help to establish some structural details, in addition to the vicinal proton–proton coupling constants which reflect the conformation of the bound ligand.

M^{VI}/aldonic acids/H_2O_2

Aldonic acids complex with Mo^{VI} and W^{VI} forming a large number of species.[27–29] However, when an excess of hydrogen peroxide is added to the solutions the systems become much simpler. In particular, only one set of ^{1}H and only one set of ^{13}C NMR signals of bound ligand were detected for solutions of molybdate or tungstate, aldonic acids (D-gluconic, D-galactonic and L-mannonic) and hydrogen peroxide over the entire pH range covered (2–11). As an example, Fig. 1 shows a ^{1}H NMR spectrum for a D_2O solution of Mo^{VI}/D-gluconic acid/H_2O_2. This indicates the formation of only one complex (named peroxo complex **a** for comparison with the other systems). The effect of pH* on its concentration is shown in Fig. 2, for a 0.50:0.50:1.25 mol dm^{-3} Mo^{VI}/D-gluconic acid/H_2O_2 solution. The approximate concentrations of the complex and "free" ligand are based on ^{13}C signal intensities, excluding the carboxylate due to its longer relaxation time. The other aldonic systems show a similar behaviour both with molybdate and tungstate.

The high frequency ^{13}C NMR shifts observed for the carboxylic and the adjacent carbinol carbon nuclei upon complexation ($\Delta\delta$ 4 ≈ 5 and 9 ≈ 11, respectively) are characteristic of the involvement of these groups in complexation.[27–29,32–34] Accordingly, only proton H-2 undergoes a significant chemical shift, which is to high frequency ($\Delta\delta$ 0.8 ≈ 0.9). The ^{95}Mo and ^{183}W spectra show only one signal, broad and sharp respectively. The chemical shifts observed (δ −237 to −238 and −586 to −587, relative to external reference Na_2MO_4, for M = Mo and W, respectively) are characteristic of diperoxo complexes possessing a MO^{4+} center.[1,3,10,14] The metal nuclei are more shielded in peroxo complexes when compared to the octahedral oxo complexes containing the same ligands.[27–29] In particular, those are in agreement with the ^{95}Mo shifts previously found by Dengel *et al.* for mononuclear diperoxo complexes of molybdate with oxalic, glycolic, malic and citric acids.[35] The ^{183}W signals fall in the region of oxodiperoxotungstates in water.[10,13] The oxygen shifts detected (δ 841–842 and δ ≈658, relative to external reference D_2O, for molybdate and tungstate, respectively) are typical of terminal M=O groups of MO^{4+} centers,[1,36,37] no signals due to M–O–M bridges being present.[38–42] Severe broadening of the peroxide ^{17}O resonances due to nuclear quadrupolar relaxation precluded any detection of the $M(O_2)$ ^{17}O signals.[36,43]

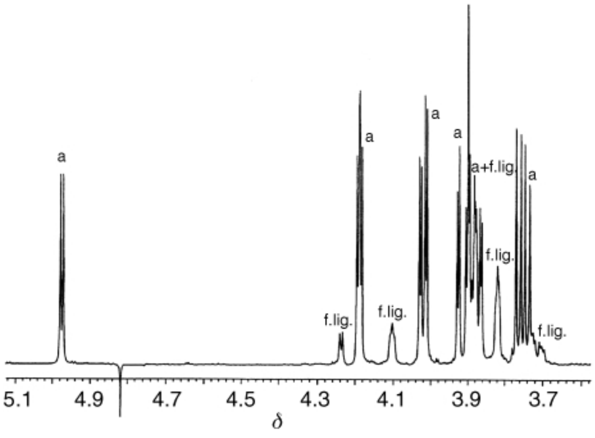


Fig. 1 ^{1}H NMR spectrum (499.843 MHz) of a D_2O 0.050:0.050:0.125 mol dm^{-3} solution of Mo^{VI}/D-gluconic acid/H_2O_2, pH* 4.0, 298 K, with suppression of the residual OH signal (δ 4.82).

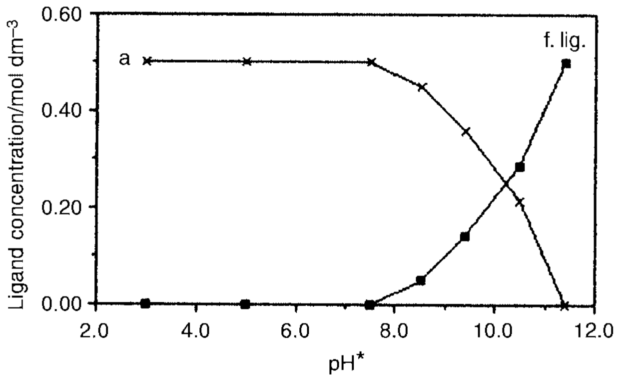


Fig. 2 Concentration of the ligand as a function of pH*, obtained by ^{13}C NMR for a 0.50:0.50:1.25 mol dm^{-3} aqueous solution (50% D_2O) of sodium molybdate(VI), D-gluconic acid and hydrogen peroxide, 294 K.

The above data are consistent with the formation of a mononuclear diperoxo complex. The existence of equal contents of metal and ligand (aldonic acid) is confirmed by the fact that, for example, 0.50:0.50:2.5 mol dm^{-3} Mo^{VI}/D-aldonic acid/H_2O_2 solutions, at pH* 5.0, have ^{13}C, ^{17}O and ^{95}Mo NMR spectra with no signals for "free" ligand or for free metal, whereas 0.25:0.50:2.5 mol dm^{-3} solutions have about 50% of "free" ligand and no signal for free metal, and 0.50:0.25:2.5 mol dm^{-3} Mo^{VI}/D-aldonic acid/H_2O_2 solutions have about 50% of free metal. Free metal is in the peroxomolybdate forms $[MoO_2(O_2)_2]^{2-}$ and $[Mo_2O_3(O_2)_4]^{2-}$ 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 bound ligand. If two ligand molecules were co-ordinated in a bidentate fashion to a seven-

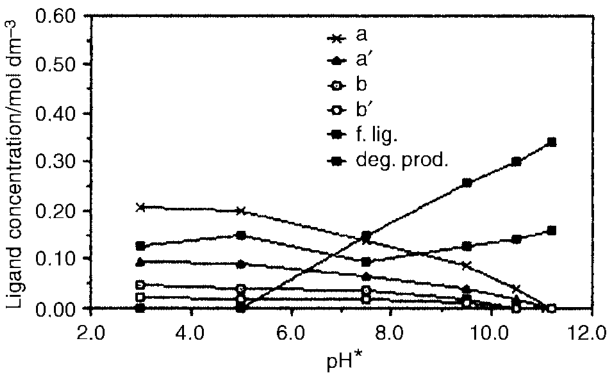
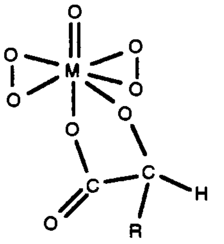


Fig. 3 Concentration of the ligand as a function of pH*, obtained by ^{13}C NMR for a 0.50 : 0.50 : 1.25 mol dm^{-3} aqueous solution (50% D_2O) of sodium molybdate(VI), D-galacturonic acid and hydrogen peroxide, 294 K.

co-ordinated metal atom possessing a pentagonal bipyramidal geometry, two ^1H and ^{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 molybdate with glycolic[35] and citric acids,[44] we can propose structure **1** [R = $(CHOH)_3CH_2OH$]. The metal(VI) centre is co-ordinated by seven oxygen atoms in essentially a pentagonal bipyramidal arrangement. One of the apical positions is occupied by the M=O oxo group and the two bound η^2-peroxo ligands occupy equatorial positions. The two remaining positions are occupied by the α-hydroxycarboxylic moiety of the aldonic acid. Owing to the *trans* influence of the apical oxo ligand, the axial M–O distance is expected to be longer than the equatorial M–O distance. The hydroxyl group is assumed to occupy an equatorial position so as to form a strong bond, whereas the carboxylic group occupies the remaining apical position, as previously proposed in the case for the 1 : 2 oxo complexes of Mo^{VI} and W^{VI} with aldonic acids.[27–29]



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M^{VI}/alduronic acids/H_2O_2

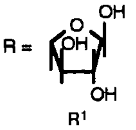
Alduronic acids exist in aqueous solution as an equilibrium between the pyranosic and the furanosic anomers. In a previous study we have studied the structure of D-galacturonic and D-glucuronic acids in aqueous solution and their complexation with molybate and tungstate.[26] When an excess of hydrogen peroxide is added to solutions containing oxo complexes of alduronic acids with molybdate or tungstate four individual sets of signals for bound ligand were detected, besides the "free" ligand pyranosic forms, in the whole pH range covered (2–10). Signal intensity considerations enabled the conclusion that these sets correspond to four different complexes (**a**, **a**′, **b** and **b**′). Species **a** and **a**′ are the dominant species.

The effect of pH* on the concentrations of peroxo complexes **a**, **a**′, **b** and **b**′ is shown in Fig. 3, for a 1 : 1 : 2.5 Mo^{VI} : D-galacturonic acid : H_2O_2 molar ratio. Since the ^1H NMR signals of **b** and **b**′ are too broad, the approximate concentrations of the complexes and "free" ligand are based on the intensities of the ^{13}C signals in the anomeric region. Signals due to degradation products are detected, especially at high pH*, the major degradation product being formic acid. The other alduronic systems show a similar behaviour.

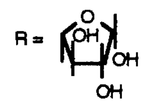
Regarding major species **a** and **a**′, comparison of ^1H and ^{13}C NMR chemical shifts with the corresponding values for the "free" ligand (namely for the positions 2, 3, and 4 in the rings) shows that the bound ligand molecules are the α- and β-furanose forms, the β anomer being responsible for the signals of larger intensity (species **a**). The pronounced high frequency shifts for the nuclei of positions 6 and 5 ($\Delta\delta$ 4–5.5 for C-6 and 10–12.5 for C-5; 0.7–0.9 for H-5) provide evidence for complexation involving the carboxylic group and the adjacent carbinol group. Furanosic forms which are the less stable forms of the acid in aqueous solution are, however, preferred in complexation. This finding agrees with our previous study on oxo complexes of molybdate and tungstate with uronic acids,[26] and confirmed by Hlaïbi *et al.* for oxo complexes of tungstate with D-galacturonic acid.[34] The total assignment of the minor species (**b** and **b**′) was not possible. They are only detected in more concentrated solutions and show very broad ^1H signals. It was, however, possible to assign the carboxylic and the anomeric ^{13}C NMR signals. High ^{13}C frequency shifts for the carboxylic group and the anomeric carbon nucleus are recorded, upon complexation, which suggests the involvement of the carboxylic group and probably the ring oxygen atom of the pyranosic forms in complexation.

^{17}O, ^{95}Mo and ^{183}W NMR parameters for all four species **a**, **a**′, **b** and **b**′ are similar to those found for the peroxo complexes with aldonic acids.

A study of signal intensities as a function of concentration as was done for aldonic acids points to 1 : 1 : 2 (metal: ligand- :peroxide) complexation at least for the major species **a** and **a**′.



R¹



R²

The proposed structures for these complexes are as shown in **1**, with R = R¹ or R² respectively.

M^{VI}/aldaric acids/H_2O_2

When an excess of hydrogen peroxide is added to solutions containing oxo complexes of Mo^{VI} and W^{VI} with D-glucaric acid three individual sets of signals for the bound ligand in the $^1H/^{13}C$ NMR spectra are detected in the pH range 2–11. Two of them (**a** and **a**′) have about the same intensity. The third one (**b**) is largely dominant in solutions having higher metal content. Signal intensity measurements for various concentration conditions are compatible with either three or two peroxo complexes, one of them containing two non-equivalent molecules of ligand. This ambiguity is removed by the results of metal/galactaric acid/H_2O_2 solutions, where due to the higher symmetry of galactaric acid only two spectra of the bound ligand are recorded. We can then deduce the existence of three complexes (**a**, **a**′, **b**) with D-glucaric acid, **a** and **a**′ being the same for galactaric acid.

The way in which the concentrations of the various species vary with pH* for both molybdate/D-glucaric acid/H_2O_2 and molybdate/galactaric acid/H_2O_2 systems (Figs. 4 and 5, respectively) strongly support this proposal; a direct comparison of Fig. 4(b) with 5(b) shows that the concentration of species **a** formed with galactaric acid is about the same as that of the concentration of species **a** plus the concentration of species **a**′ formed with D-glucaric acid.

For both systems, the ^{95}Mo NMR spectra show only one broad signal (δ −237 and −240 for galactaric and D-glucaric

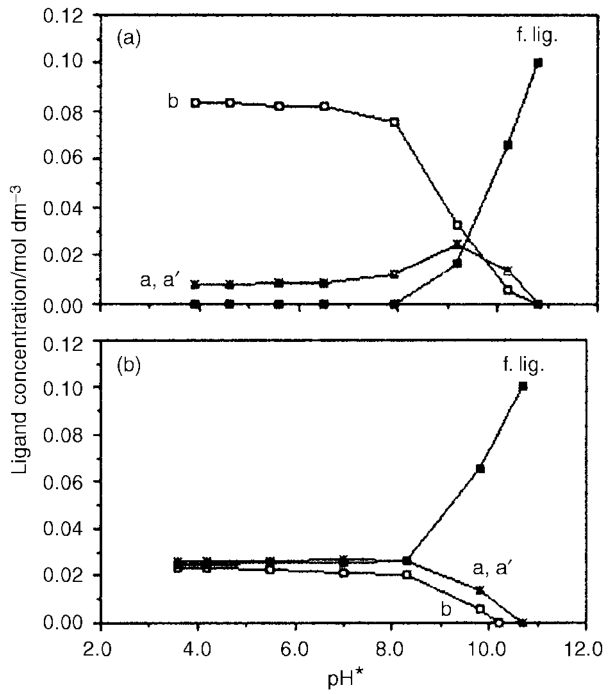


Fig. 4 Concentration of the ligand as a function of pH*, obtained by ^{1}H NMR for (a) a 0.20 : 0.10 : 0.50 mol dm^{-3} solution in D_2O of sodium molybdate(VI), D-glucaric acid and hydrogen peroxide, 298 K and (b) a 0.10 : 0.10 : 0.50 mol dm^{-3} solution in D_2O of sodium molybdate(VI), D-glucaric acid and hydrogen peroxide, 298 K.

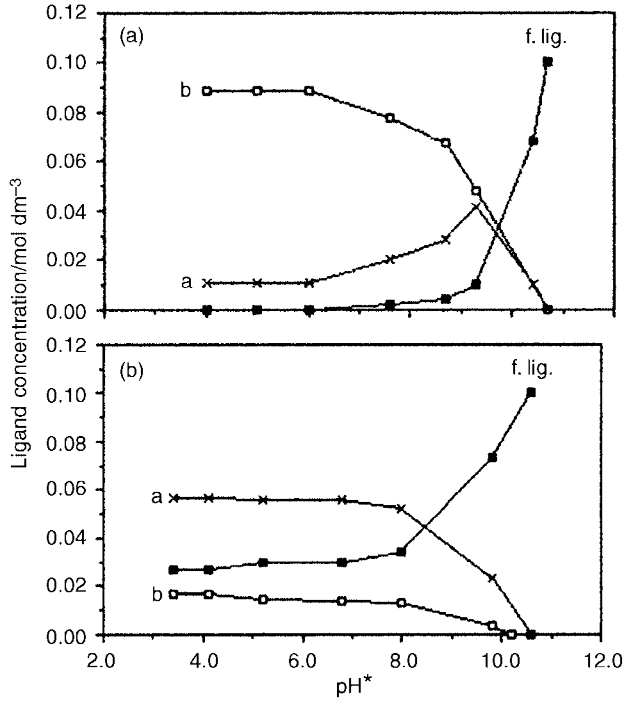
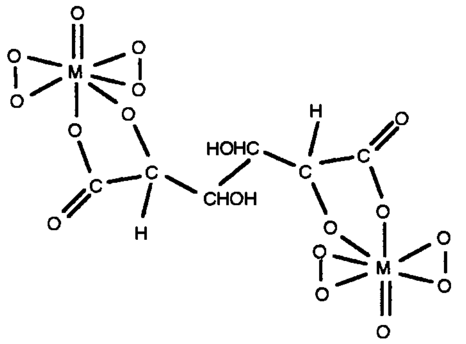


Fig. 5 Concentration of the ligand as a function of pH*, obtained by ^{1}H NMR for (a) a 0.20 : 0.10 : 0.50 mol dm^{-3} solution in D_2O of sodium molybdate(VI), galactaric acid and hydrogen peroxide, 298 K and (b) a 0.10 : 0.10 : 0.50 mol dm^{-3} solution in D_2O of sodium molybdate(VI), galactaric acid and hydrogen peroxide, 298 K.

acids, respectively). However, the ^{183}W NMR spectra show two pairs of signals (δ −585.9, −588.3 and −586.9, −590.6) in the case of D-glucaric acid and two sharp peaks (δ −586.9, −587.3) in the case of galactaric acid. One pair of signals (δ −586.9, −590.6) with D-glucaric acid and one of the signals (δ −587.3) with galactaric acid are more intense for solutions with higher ligand content, corresponding to species **a** and **a′** (with D-glucaric acid) and **a** (with galactaric acid). For solutions with higher metal content those signals decrease and the other signals become more intense, corresponding to species **b**. These values observed for ^{95}Mo and ^{183}W chemical shifts are characteristic of diperoxo complexes possessing a MO^{4+} center[1,3,10,13,14,35] and the oxygen shifts detected are similar to those found for the peroxo complexes with aldonic and alduronic acids.

As far as complexes **a** and **a′** are concerned, the high frequency shifts observed upon complexation for C-1, C-2 and H-2, and C-6, C-5 and H-5, respectively, suggest the involvement of CO_2H-1 and OH-2 in **a** and of CO_2H-6 and OH-5 in **a′**. These two patterns of complexation lead to only one complex, **a**, with galactaric acid. For species **a** and **a′** we propose a structure similar to that of **1** [R = $(CHOH)_3CO_2H$]. The stoichiometry of these species is 1 : 1 : 2 (metal : ligand : peroxo), as was found in the previous systems.

Concerning complex **b**, we note the shifts to high frequencies of both carboxylic groups and the adjacent carbinol carbon nuclei, upon complexation, characteristic of the involvement of all these groups in complexation. The other carbon shifts are much smaller. Accordingly, only protons H-2 and H-5 undergo a significant chemical shift, which is to high frequency. In addition, the observation of two ^{183}W signals of equal intensity in the case of D-glucaric acid point to **b** as being a dinuclear 2 : 1 : 4 (metal : ligand : peroxo) species (**2**). Owing to symmetry, only one ^{183}W NMR signal is observed in the case of galactaric acid. The ligand molecule is tetradentate and bridges the two metal centers. The geometry around each MO^{4+} center is approximately pentagonal bipyramidal, the M=O group occupying one of the apical positions and the two peroxo ligands being equatorial. The remaining apical and equatorial positions are occupied by the two donor groups of the ligand, the carboxylic and the adjacent OH group, respectively, as discussed before. A similar structure was found by X-ray diffraction for the species $[Mo_2O_2(O_2)_4(C_4H_2O_6)]^{4-}$ formed with molybdate, tartaric acid and hydrogen peroxide,[45] this structure being maintained in aqueous solution as is revealed by spectroscopic data.[45]



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4 Conclusion

Following our previous systematic and comparative study of sugar acids and their complexation with tungstate and molybdate oxoions, in aqueous solution, using multinuclear NMR spectroscopy (1-D and 2-D),[23–29] we have now extended those studies to a new class of complexes, the oxoperoxo complexes of Mo^{VI} and W^{VI} with sugar acids. These systems turn out to be much simpler as far as the number of species present in aqueous solution is concerned. Thus, aldonic acids, alduronic acids and aldaric acids are found to form, respectively, one, four and three homologous oxoperoxo complexes with Mo^{VI} and W^{VI}. Common features are the involvement of two peroxide units per metal centre and the co-ordination of the sugar acids through carboxylate and adjacent hydroxyl groups. It is known that ionized organic OH functions are relatively hard bases, which may displace the carboxylate groups from the

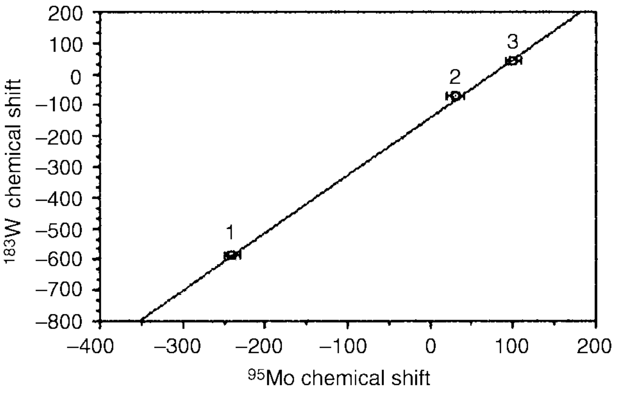

Fig. 6 Correlation of ^{183}W with ^{95}Mo shifts observed for homologous complexes of (1) MO^{4+} (this work), (2) $M_2O_5^{2+}$ and (3) MO_2^{2+} (from refs. 23–29).

first co-ordination sphere of the metal ion. Thus, at high pH values, polyhydroxycarboxylic acids can co-ordinate exclusively through ionized OH functions, without COO^- co-ordination.[46] This we have found to occur in previous studies of oxo complexes of sugar acids involving $M_2O_5^{2+}$ metal centres,[23–29] but not in the present study where MO^{4+} centres are present. In all the pH range the co-ordination is established through the carboxylate and adjacent hydroxyl groups. Accordingly, 1 : 1 : 2 (metal : acid : peroxide) complexes are detected as well as 2 : 1 : 4 species in the case of aldaric acids.

In this study new data were obtained for ^{95}Mo and ^{183}W chemical shifts associated with M=O centres. These results together with those previously found for the oxo complexes with sugar acids enable a correlation study of ^{183}W and ^{95}Mo shifts observed for homologous complexes, as was carried out by other authors for other complexes of W^{VI} and Mo^{VI}.[47,48] The previously found linear correlation that parallels the ratio of nuclear charges is nicely sustained by our data plotted in Fig. 6: $\delta_W = 1.8\delta_{Mo} - 137.3$. We recall that these metal shifts are mainly due to changes in the paramagnetic contribution to the metal shielding. Work is in progress in order fully to understand the above relationship.

Acknowledgements

This work has been supported by "Fundação para a Ciência e Tecnologia", of the Portuguese Ministry of Science and Technology (Project PRAXIS QUI-63/96). The authors are grateful to the referees for their comments.

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