DALTON
FULL PAPER

Characterisation of aqueous peroxomolybdate catalysts applicable to pulp bleaching †

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The equilibrium speciation in the system $p\,H^+ + q\,MoO_4^{2-} + r\,H_2O_2 + s\,SO_4^{2-} \rightleftharpoons (H^+)_p(MoO_4^{2-})_q(H_2O_2)_r(SO_4^{2-})_s$ in 0.300 M $Na_2(SO_4)$ medium at 25 °C has been determined from potentiometric titration data in the ranges $2.0 \le pH \le 5.5$, $5.00 \le [Mo]_{tot}/mM \le 80.00$, $0 \le [H_2O_2]_{tot}/mM \le 245$ and $273.07 \le [SO_4^{2-}]_{tot}/mM \le 320.20$. Species with the following compositions were found: MoX^- (1,1,1,0), MoX (2,1,1,0), MoX_2^- (1,1,2,0), MoX_2 (2,1,2,0), MoX_2S^{2-} (2,1,2,1), $Mo_2X_4^{2-}$ (2,2,4,0), Mo_7X^{6-} (8,7,1,0), Mo_7X^{5-} (9,7,1,0), Mo_7X^{4-} (10,7,1,0) and Mo_7X^{3-} (11,7,1,0). The numbers in parentheses refer to the values of *p*, *q*, *r* and *s* in the formula above. The numbers and charges of molybdenum (Mo), peroxide (X) and sulfate (S) in each species are given in the abbreviated formula $Mo_qX_rS_s^{(2q+2s-p)-}$. The following formation constants with 3σ were obtained; $\log\beta_{1,1,1,0} = 8.53 \pm 0.03$, $\log\beta_{2,1,1,0} = 11.22 \pm 0.04$ ($pK_a = 2.69$), $\log\beta_{1,1,2,0} = 11.61 \pm 0.03$, $\log\beta_{2,1,2,0} = 13.77 (\pm 0.06)$ ($pK_a = 2.16$), $\log\beta_{2,1,2,1} = 14.50 \pm 0.06$, $\log\beta_{2,2,4,0} = 23.77 \pm 0.11$, $\log\beta_{8,7,1,0} = 56.71 \pm 0.11$, $\log\beta_{9,7,1,0} = 62.00 \pm 0.05$ ($pK_a = 5.29$), $\log\beta_{10,7,1,0} = 65.74 \pm 0.06$ ($pK_a = 3.74$), $\log\beta_{11,7,1,0} = 68.23 \pm 0.08$ ($pK_a = 2.49$). Most complexes have been verified by ^{95}Mo NMR, ^{17}O NMR, and the novel MoX_2S^{2-} complex also by FTIR spectroscopy.

Introduction

The catalytic properties of polyoxometallates (POMs) have recently found applications in the bleaching process for kraft pulp. A number of investigations have shown a highly selective delignification when adding molybdate to weakly acidic solutions in the presence of excess hydrogen peroxide.[1–3] It has also been found that the peroxomolybdates are effective in removing hexeneuronic acids from the pulp,[4] which is considered desirable for pulp bleaching. A prerequisite for a process where POMs are being used is that any environmental problem can be satisfactorily handled, including the possibility of recycling the POMs. A key for understanding the chemistry in the bleaching step is to know the speciation and behaviour of the species formed. This requires fundamental speciation studies under conditions similar to those in the bleaching step. Provided that molybdate can be recycled, peroxomolybdates can be used for obtaining a selective and efficient non-chlorine process, suitable for a closed pulp system.

Studies on peroxomolybdates have been reviewed by Connor and Ebsworth,[5] Dickman and Pope,[6] and also in *Gmelin*.[7] Most of the reviewed works include mono-, di- and, in some cases, tri- and tetra-peroxomonomolybdate complexes. Furthermore, solid peroxide-poor (H_2O_2 : Mo < 1) species have been isolated from solutions of polymolybdates mixed with small amounts of hydrogen peroxide.

Earlier studies on peroxomolybdates in solution have been carried out by various methods, such as NMR spectroscopy, conductometry and potentiometry. In conditions similar to those in this work, complexes with 2 : 1 (H_2O_2 : Mo) stoichiometry have frequently been found in solutions with excess of hydrogen peroxide,[8–17] including tetraperoxodimolybdates,[10,11,14] $H_pMo_2O_3(O_2)_4^{p-2}$, ($p = 0$–2) and diperoxomonomolybdates,[10–13] $H_pMoO_2(O_2)_2^{p-2}$, (p = 1–2). Less common in peroxide rich solutions are 3 : 1 complexes, *e.g.* $[MoO(O_2)_2(OOH)]_2^{2-}$,[14] and $MoO(O_2)_3^{2-}$,[14,15] and 4 : 1 complexes, $H_pMo(O_2)_4^{p-2}$, ($p = 0$–1).[8,14] In solutions with lower concentration of peroxide, complexes with 1 : 1 stoichiometry have been found, for example $H_2Mo_4O_9(O_2)_4$, $H_2Mo_2O_5(O_2)_2$[10] and $HMoO_3(O_2)^-$.[12,13] Formation constants for a tetraperoxodimolybdate[9] and a few peroxomonomolybdates[12,13,16,17] have been determined. Studies on peroxoheptamolybdates in solutions include diperoxoheptamolybdate,[11,15] $Mo_7O_{22}(O_2)_2^{6-}$, and hexaperoxoheptamolybdate,[11] $Mo_7O_{18}(O_2)_6^{6-}$. No formation constants were determined in these studies.

Evidence for hydrogen sulfate interaction with peroxomolybdates in solution is rare, but has been reported in strongly acidic media.[18–20] Furthermore, crystal structures of $[N(CH_3)_4]_3[H(SO_4)_2(MoO_2(O_2))_3]\cdot 3H_2O$[21] and $[(C_4H_9)_4N]_2[Mo_2O_2(O_2)_4SO_4]$[22] have been determined. Both crystals were prepared from very acidic solutions. Finally, extensive structural investigations of peroxopolymolybdates have been carried out by Stomberg *et al.*, including trimolybdates,[23,29] tetramolybdates,[24,27] pentamolybdates,[25] heptamolybdates,[26–35] octamolybdates[29,33] and decamolybdates.[34] Structural investigations of peroxomonomolybdates are less common, although diperoxo-[35] and tetraperoxo-monomolybdates[36] have been investigated.

Equilibrium studies on possible peroxomolybdate species participating in the bleach process have, to our knowledge, not yet been performed. The present study was therefore performed to clarify the peroxomolybdate chemistry in a sodium sulfate medium, since Na^+ and SO_4^{2-} are the most common ions present in industrial bleach processes. The H^+–MoO_4^{2-}–H_2O_2–SO_4^{2-} system was studied in 0.300 M $Na_2(SO_4)$ medium and in the range $2.0 \le pH \le 5.5$. A limitation of $pH \le 5.5$ was necessary since the decomposition of hydrogen peroxide in peroxomolybdate solutions at higher pH values was substantial. The study is based on an earlier investigation of the H^+–MoO_4^{2-} system in the same medium, where also the pK_a value for HSO_4^- was determined.[37]

† Multicomponent Polyanions Part 59. For preceding part, see ref. 37.

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Table 1 Composition and formation constants ($\log\beta$) of species found in the $pH^+ + qMoO_4^{2-} + rH_2O_2 + sSO_4^{2-} \leftrightarrow (H^+)_p(MoO_4^{2-})_q(H_2O_2)_r(SO_4^{2-})_s$ system: $5 \le Mo \le 80$ mM, $2.0 \le pH \le 5.5$; (2,1,2,0) is "locked", the others are optimized. Error is put on Z. "X" = H_2O_2, "S" = SO_4^{2-}

(p,q,r,s)	Notation	$\log\beta \pm 3\sigma$	pK_a
(1,1,1,0)	MoX^-	8.53 ± 0.03	—
(2,1,1,0)	MoX	11.22 ± 0.04	2.69
(1,1,2,0)	MoX_2^-	11.61 ± 0.03	—
(2,1,2,0)	MoX_2	13.77 ± (0.06)	2.16
(2,1,2,1)	MoX_2S^{2-}	14.50 ± 0.06	—
(2,2,4,0)	$Mo_2X_4^{2-}$	23.77 ± 0.11	—
(8,7,1,0)	Mo_7X^{6-}	56.71 ± 0.11	—
(9,7,1,0)	Mo_7X^{5-}	62.00 ± 0.05	5.29
(10,7,1,0)	Mo_7X^{4-}	65.74 ± 0.06	3.74
(11,7,1,0)	Mo_7X^{3-}	68.23 ± 0.08	2.49

Results and discussion

The speciation model obtained is based on potentiometric data and a set of titration data at a constant Mo concentration is plotted in Fig. 1. As can be seen from the plot, the titration

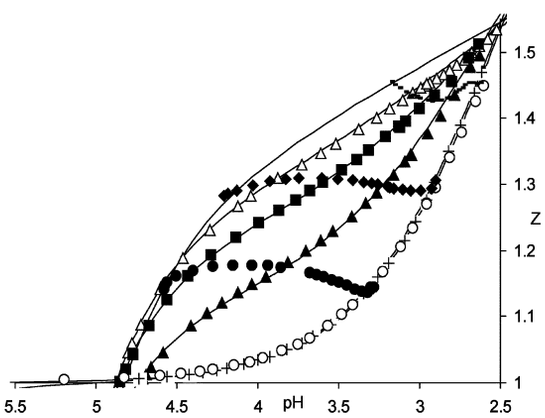

Fig. 1 Potentiometric data plotted as Z *vs.* pH for $[Mo]_{tot}$ = 20 mM and $[H_2O_2]_{tot}$ = 0–77 mM. Symbols represent experimental data points. $[H_2O_2]/[Mo]_{tot}$ = 0.25 (△), 0.5 (■), 1.0 (▲), 2.3 (+), 3.9 (○), $Z \approx 1.15$ (●), $Z \approx 1.30$ (◆), $Z \approx 1.45$ (■). The curves were calculated using the formation constants from ref. 37 and Table 1. The curve without symbols represents the model curve for a molybdate solution in the absence of peroxide, according to ref. 37.

curves coincide at H_2O_2 : Mo ≥ 2, indicating formation of strong diperoxomolybdate species and that the complex(es) present at pH 5 should bind one proton per molybdate and at pH 2.5 one and a half protons. The final model obtained is presented in Table 1. As can be seen from the distribution diagrams, Figs. 2(c) and (d), the predominant species in peroxide-rich solutions is the MoX_2^- (1,1,2,0) complex, and at low pH values MoX_2S^{2-}, a novel (2,1,2,1) sulfate complex. Fig. 2(b) shows that MoX_2^- is remarkably strong even at H_2O_2 : Mo = 1, compared to the MoX^- (1,1,1,0) complex. In peroxide-poor solutions monoperoxoheptamolybdates (p,7,1,0) predominate (*cf.* Fig. 2(a)). It should be noticed that the distribution diagrams are calculated using a constant concentration of sulfate (300 mM). This is not actually the case in our study. When the medium cation concentration is kept constant, the concentration of the sulfate medium anion will vary somewhat. However, this small variation will only have minor effects on the distribution of complexes.

Compared with the H^+–MoO_4^{2-} system,[37] the polymerisation of monomolybdates into heptamolybdates is strongly suppressed, due to formation of the strong MoX_2^- (1,1,2,0), MoX_2 (2,1,2,0) and MoX_2S^{2-} (2,1,2,1) complexes, in excess of peroxide. At H_2O_2 : Mo ≥2, peroxoheptamolybdates are extremely minor species. Furthermore, in the absence of peroxide, no dimeric anionic complexes have been found in aqueous molybdate solutions. The $Mo_2X_4^{2-}$ complex found in peroxide rich solutions is, at the moderate molybdate concentrations used in the potentiometric titrations, a minor species (*cf.* Fig. 2(c)). From the formation constants of MoX_2^- and $Mo_2X_4^{2-}$ (Table 1), the dimerisation constant, $\log K_d = \log\beta_{2,2,4,0} - 2\log\beta_{1,1,2,0}$ is 0.55.

Due to low receptivity and broad resonances, ^{95}Mo NMR spectra were recorded at high molybdate concentrations. Fig. 3 shows some spectra at pH 4 and $[Mo]_{tot}$ = 300 mM. The peroxide-rich solution (Fig. 3(a)) has a broad and nonsymmetric resonance at $\delta \sim -270$ arising from MoX_2 and Mo_2X_4 complexes. At H_2O_2 : Mo = 1 (Fig. 3(b)) two new resonances appear, from MoX ($\delta \sim -40$) and Mo_7X ($\delta \sim 40$) complexes. In a peroxide-poor solution (Fig. 3(c)) Mo_7X complexes predominate and only minor amounts of the other complexes are present. At lower pH, a new resonance appears at δ −220, as shown from the deconvoluted spectra in Fig. 4. This cannot be discerned at pH 3.08 (Fig. 4(c)) but is substantial at pH 2.16 (Fig. 4(b)) and increases further at lower pH (Fig. 4(a)). According to the speciation model, this resonance should arise from the sulfato species, MoX_2S^{2-}. This was verified by recording ^{95}Mo spectra at different sulfate concentrations and also by the fact that the resonance disappeared in a perchlorate medium. The proper assignment of resonances from MoX_2 and Mo_2X_4 species could be made by recording spectra at the same pH but with different total concentrations.

After deconvolution the chemical shift values shown in Fig. 5 were obtained. The downfield change with decreasing pH for the MoX_2 and Mo_2X_4 complexes is due to protonation of MoX_2^- and $Mo_2X_4^{2-}$ into MoX_2 and $Mo_2X_4^-$, beginning at pH around 3.5. The resonance at $\delta \sim -220$, which shows no pH dependence, originates from the MoX_2S complex. Integration of some spectra in the pH range studied by potentiometry (2–5.5) showed that the ^{95}Mo NMR data are in accordance with the speciation model given in Table 1.

For the ^{17}O NMR measurements, enrichment to 3% of single (Mo–O), bridged (Mo–O–Mo) and terminal (Mo=O) oxygens was obtained by addition of $H_2{}^{17}O$. Hydrogen peroxide and sulfate oxygens do not exchange with water and will therefore be scarcely visible. Some experiments were also performed with $H_2{}^{17}O_2$. Unfortunately, the chemical shifts for different peroxo-groups were not distinguishable. In the present study we have focused on the terminal oxygen behaviour in peroxide-rich solutions.

At 298 K, a typical ^{17}O NMR spectrum of such a solution reveals a broad unresolved resonance at $\delta \sim 840$, arising from the MoX_2 and Mo_2X_4 complexes. Due to slower exchange it splits into two separate resonances when the temperature is decreased from 298 to 278 K. To be able to make reliable assignments and obtain accurate chemical shift data for evaluation of the protonation behaviour, it was necessary to work at a lower temperature (278 K) than used in the potentiometric study. The ^{17}O chemical shift values obtained are plotted in Fig. 6 and the shift behaviour is strikingly similar to that of the ^{95}Mo shifts (*cf.* Fig. 5). The protonation of MoX_2^- (δ 834) and $Mo_2X_4^{2-}$ (δ 833) to give MoX_2 (δ 874) and $Mo_2X_4^-$ (δ 871) indicates pK_a values close to 2 for the protonated complexes. However, with decreasing pH the area of the MoX_2 resonance increases considerably compared to the Mo_2X_4 resonance, indicating that the protonated monomer is "stronger" than the protonated dimer. The resonance at δ 873, which shows no pH dependence and increases with decreasing pH, originates from the MoX_2S complex.

The ^{17}O and ^{95}Mo NMR data are in good agreement and give strong support to the speciation model obtained from potentiometric data. Furthermore, interesting structural information was obtained by comparing the ^{17}O and ^{95}Mo NMR integrals. All species having two peroxo-groups bound to molybdenum seem to have the same number of terminal oxygens (most probably one) per molybdenum atom.

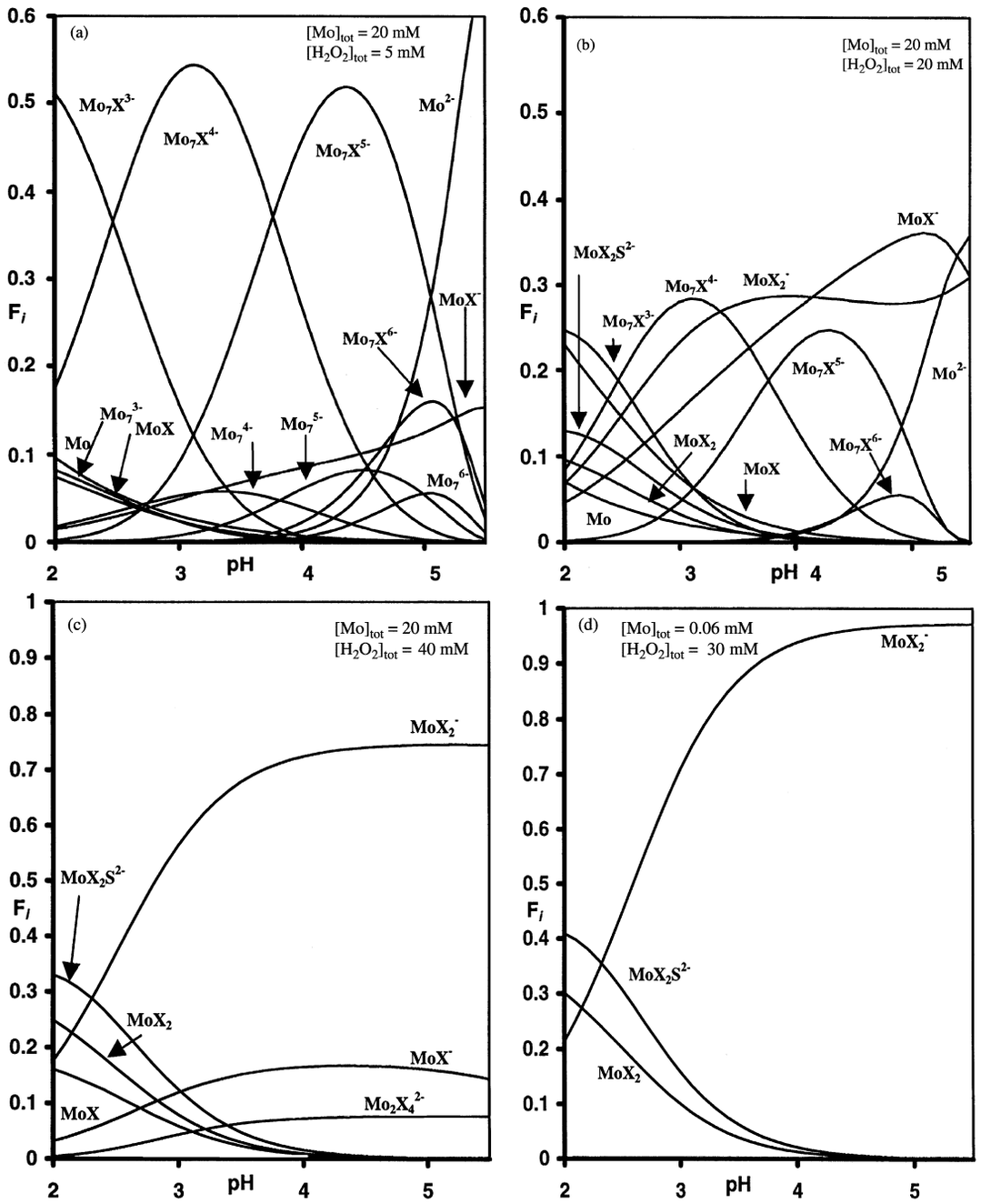

Fig. 2 (a)–(d) Distribution diagrams plotted as F_i *vs.* pH. F_i is defined as the ratio between [Mo] in a species and $[Mo]_{tot}$ in solution. Species with $F_i \leq 0.03$ have been excluded. In (d) similar concentrations of molybdate and peroxide to those in the bleach process have been used.

Peroxomolybdosulfate complexes

(a) Potentiometric data. In contrast to the MoX_2S^{2-} (2,1,2,1) complex found in the present study, peroxomolybdosulfate complexes reported earlier have been found only under very acidic conditions.[18–20] Thus, the crystals presented by Hashimoto *et al.*[21] (corresponding to a (7,3,3,2) complex) were prepared under such conditions. The crystalline compound presented by Salles *et al.*[22] (corresponding to a (4,2,4,1) complex) was prepared under less acidic conditions, but neither a (4,2,4,1) nor a (7,3,3,2) complex proved to be relevant in our study. However, protonation of the (2,1,2,1) complex is likely to occur, although it was not possible to verify a (3,1,2,1) complex by potentiometry in the pH range used in this study.

(b) ^{17}O and ^{95}Mo NMR data. The absence of a chemical shift change vs. pH for the resonances at δ_O 873 (Fig. 6) and δ_{Mo} indicates that the complex either does not protonate or that the protonation occurs at a far distant sulfate oxygen and so does not affect the chemical shifts. The fact that the MoX_2S^{2-} complex starts to form at relatively low pH, indicates that the presence of hydrogen sulfate (1,0,0,1) or the MoX_2 (2,1,2,0) complex might be of importance for the formation of the complex. According to the equilibrium reaction (1,1,2,0) + (1,0,0,1) $\rightleftharpoons$ (2,1,2,1) or (2,1,2,0) + (0,0,0,1) $\rightleftharpoons$ (2,1,2,1).

(c) FTIR spectroscopic data. When a ligand of high symmetry, such as SO_4^{2-} (T_d), coordinates to a metal, its symmetry is lowered and changes in the IR-spectrum will occur. Of the nine fundamental vibrational modes in free SO_4^{2-}, only two are infrared-active, *i.e.* ν_3 at ~1104 cm^{-1} (F_2) and ν_4 at ~613 cm^{-1} (F_2).[38] When the symmetry is lowered the degenerate vibrations will split and Raman active modes will appear in the infrared spectrum ($\nu_1 + \nu_2$). In a 20 mM MoO_4^{2-}, 80 mM H_2O_2 solution in 0.300 M $Na_2(SO_4)$ medium, ν_3 is split into three strong bands (1166, 1108 and 1042 cm^{-1}) which indicates a symmetry lower

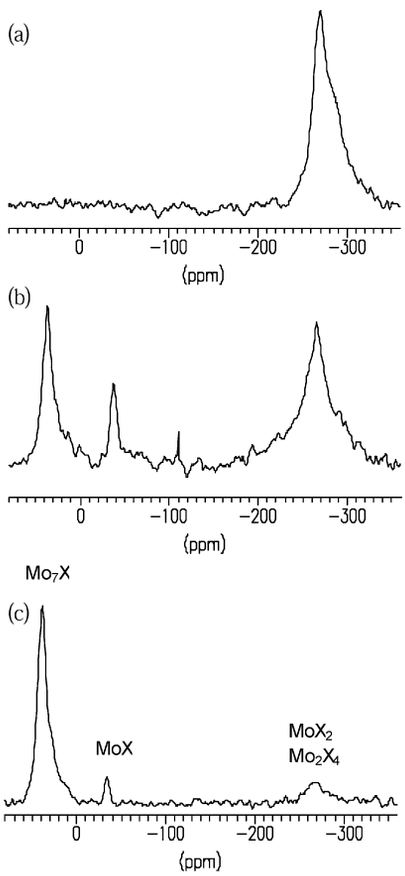

Fig. 3 ^{95}Mo NMR spectra of three solutions at around pH 4 and $[Mo]_{tot}$ = 300 mM, with H_2O_2/Mo = 3 (a), 1 (b) and 0.5 (c), respectively.

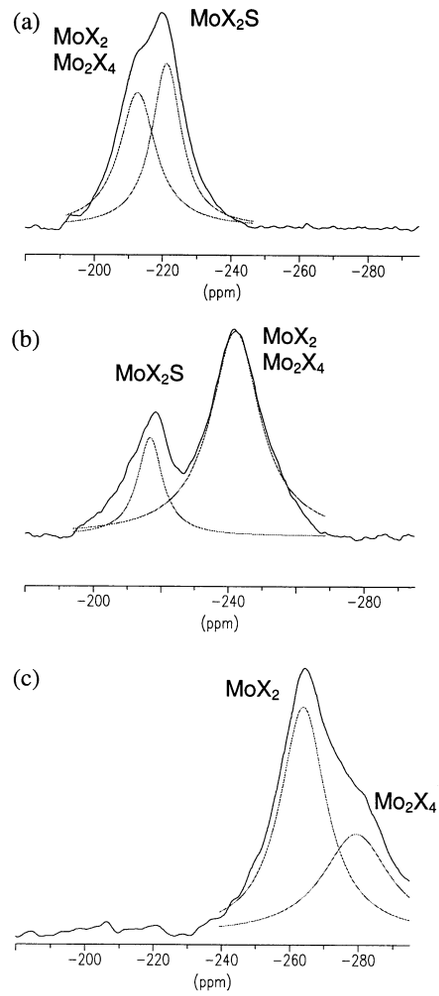

Fig. 4 ^{95}Mo NMR deconvoluted spectra at varying pH and with H_2O_2/Mo ≥ 2: (a) pH 1.39, $[Mo]_{tot}/[H_2O_2]_{tot}$ = 240/724 mM; (b) pH 2.16, 300/900 mM, (c) pH 3.08, 300/600 mM.

than C_{3v} (Fig. 7). This shows that sulfate interacts with the peroxomolybdate complexes. However, no further attempt has been made to elucidate the coordination mode of sulfate.

As can be seen in Figs. 2(c) and (d), the concentration of the MoX_2S^{2-} (2,1,2,1) complex is decreasing with increasing pH. This is illustrated by the decrease in intensities for the ν_3 bands from pH 2.08 to 3.74 in Fig. 8. The medium band at 908 cm^{-1} shows a similar pH dependence as the ν_3 bands and are tentatively attributed to $\nu_1(SO_4)$, while the strong bands at ~ 870 cm^{-1} are attributed to the ν_1(O–O) mode of the peroxo groups. Finally, ν(M=O) appears at 976 cm^{-1}.

Peroxomonomolybdate complexes

The predominance of diperoxomonomolybdate complexes MoX_2^- and MoX_2 in peroxide rich solutions has been reported by several authors,[9–13,17] while the monoperoxomonomolybdate complexes have been proposed to exist only in small amounts in such solutions.[12] Indeed, potentiometric measurements at 20 mM $[Mo]_{tot}$ shows that monoperoxo complexes are minor in the peroxide-rich solutions used in this study (Fig. 2(c)). Their presence decreases further if $[Mo]_{tot}$ is increasing, due to the formation of the dimeric complexes (p,2,4,0). In ^{95}Mo NMR solutions at 300 mM $[Mo]_{tot}$ and 900 mM H_2O_2 the monoperoxomonomolybdate complexes cannot be detected at all (Fig. 3(a)). Of the studies where stability constants have been presented, only one was performed in the presence of sulfate.[12] Here, the corresponding logβ formation constants, 8.0 and 13.4 for MoX^- and MoX_2^- respectively, are not in particularly good agreement with those found in this study. Triperoxo-[14,15] and tetraperoxo-monomolybdate[8,14] complexes have been proposed to exist under conditions similar to those in this study, but neither (p,1,3,0) nor (p,1,4,0) species seem to be relevant in explaining our experimental data. Under industrial conditions, with molybdate concentrations below one millimolar, high peroxide to molybdate ratio and pH ≤ 5 the predominant species

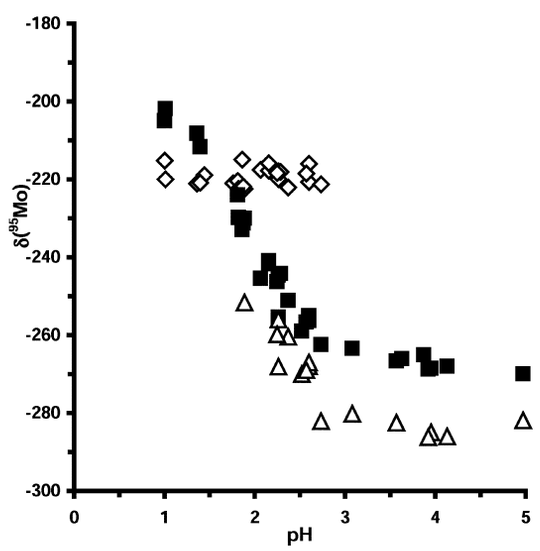

Fig. 5 ^{95}Mo NMR chemical shifts as a function of pH from solutions with H_2O_2/Mo ≥ 2. Mo_2X_4 (△), MoX_2 (■), MoX_2S (◇).

are likely to be MoX_2^- (1,1,2,0), and MoX_2 (2,1,2,0) or MoX_2S^{2-} (2,1,2,1) at low pH (Fig. 2(d)). The predominance of the (p,1,2,0) over the (p,1,1,0) complexes (Fig. 2(b)–(d)) has also been found in the peroxovanadate system.[39]

It should be mentioned that co-variation of (1,1,2,0) and (2,1,2,0) together with the other complexes included in the model, results in a model with higher 3σ-values for all complexes, although (1,1,2,0) and (2,1,2,0) are necessary in

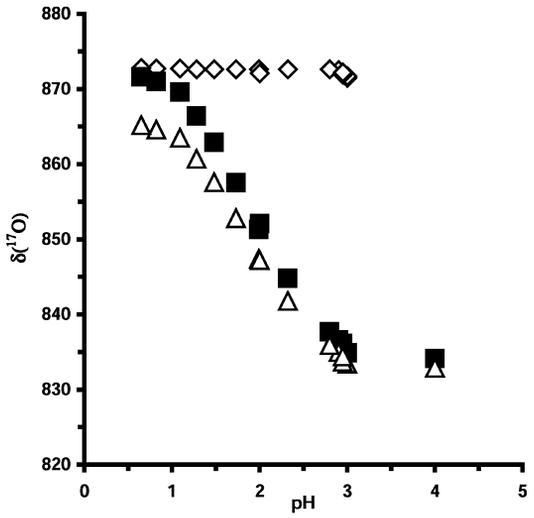

Fig. 6 ^{17}O NMR chemical shifts of terminal oxygens as a function of pH from solutions with $H_2O_2/Mo \geq 2$. Mo_2X_4 (△), MoX_2 (■), MoX_2S (◇).

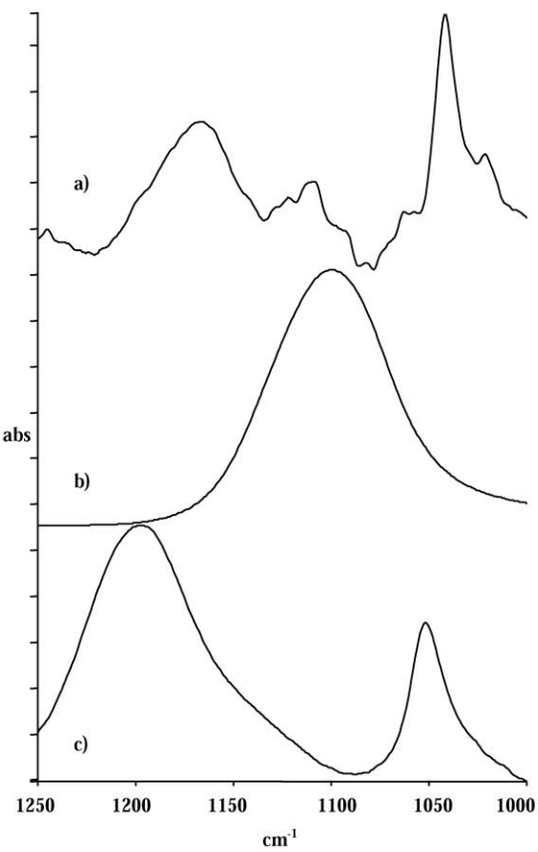

Fig. 7 FTIR spectra illustrating: (a) the splitting of ν_3 into three strong bands (1166, 1108 and 1042 cm^{-1}) in a 20.0 mM MoO_4^{2-}, 80.0 mM H_2O_2 solution at pH 2.91 (ν_3 bands arising from free SO_4^{2-} and HSO_4^- have been subtracted); (b) the ν_3 band (~1104 cm^{-1}) in free SO_4^{2-}, pH 6; (c) the splitting of ν_3 into two strong bands (~1196 and ~1050 cm^{-1}) in HSO_4^- (pH 1).

explaining the experimental data. Therefore, in the final calculation (1,1,2,0) is varied while (2,1,2,0) is locked. In a similar calculation, (2,1,2,0) is varied while (1,1,2,0) is locked. The resulting 3σ-value for (2,1,2,0) is given in parentheses in Table 1.

Peroxodimolybdate complexes

Hardly any species with nuclearity between monomolybdate and heptamolybdate have been reported to exist in aqueous solution. However, in the presence of peroxide, a dimeric complex, $Mo_2X_4^{2-}$ (2,2,4,0), has been found in a number of studies,[14,15,40] and has also been crystallised.[41] In a study by Campbell *et al.*,[15] this complex was suggested to be the principal species at excess of peroxide in the pH range 2.5–5, in solutions containing 0.1–1 M MoO_4^{2-}. At the highest molybdate concentration used in the present potentiometric study (80 mM), the dimer is found to be a minor species compared to the monomeric complexes. However, at the high molybdate concentrations used in the ^{95}Mo and ^{17}O NMR measurements, the dimer is an important species (Fig. 4). Finally, the protonation of the dimer (3,2,4,0) indicated from the ^{95}Mo and ^{17}O NMR shift curves (Figs. 5 and 6) could not be confirmed from the potentiometric data, due to the moderate concentration of molybdate used in the titrations.

Peroxoheptamolybdate complexes

Crystal structure determinations of peroxoheptamolybdates prepared from peroxide-poor solutions,[26–32] as well as speciation studies of such solutions,[11] suggest the predominance of diperoxoheptamolybdate (p,7,2,0) complexes. In addition, Csányi[11] proposed hexaperoxoheptamolybdates (p,7,6,0) in solution. The best explanation of our potentiometric data was obtained when including a series of (p,7,1,0) complexes. Even though (p,7,2,0) complexes cannot be ruled out, they cannot explain our experimental data, neither together with (p,7,1,0) complexes nor by replacing them. Moreover, integration of ^{95}Mo spectra (such as those shown in Fig. 3(b) and (c)) strongly supported (p,7,1,0) complexes. However, in an ongoing ^{17}O NMR study at high molybdate concentration ($Mo_{tot} \geq 300$ mM) in sodium perchlorate medium, both (p,7,1,0) and (p,7,2,0) complexes were found. It thus seems that the speciation of peroxoheptamolybdates is strongly dependent on the ionic medium.

Decomposition of hydrogen peroxide

At pH ≥ 5.5, most of the peroxomolybdate solutions slowly lose their colour as the concentration of peroxide decreases. The solutions also show decreasing pH-values with time, due to decomposition of peroxomolybdates into molybdates. From manganometric titrations of 20 mM molybdate, 80 mM peroxide solutions kept in the dark at 25 °C, it was found that after six days less than 60% of the peroxide remained in a solution with a starting pH of 5.60. At pH 2.65, the solution contained almost 90% of its original peroxide concentration.

According to Nardello *et al.*[14] decomposition of peroxide should occur through a redox reaction between two peroxo bridges bound to the same molybdenum atom, which will remain in its +VI oxidation state. The complexes involved in the catalysis are said to be $(Mo(O_2)_4^{2-})$[8] or $(MoO(O_2)_3^{2-})$.[14] Due to unstable solutions, we have not been able to perform any equilibrium studies on these complexes.

It should be noticed that the formation of peroxomonomolybdates from a sodium monomolybdate solution consumes protons. This is especially the case for the strong (1,1,2,0) and (2,1,2,0) complexes. In molybdate solutions with poor buffer capacity the increase in pH, when adding peroxide, is of the order of several units, resulting in a fast decomposition of the hydrogen peroxide. Adding a small amount of peroxide to a heptamolybdate solution will result in the formation of peroxoheptamolybdate complexes. This formation will not lead to any noticeable consumption of protons because of the similarities in strength and uptake of protons between the heptamolybdates and peroxoheptamolybdates. In addition, a polymolybdate solution generally has a higher buffer capacity than a monomolybdate solution.

Experimental

Chemicals and analyses

The molybdate stock solutions, sulfuric acid solutions, sodium

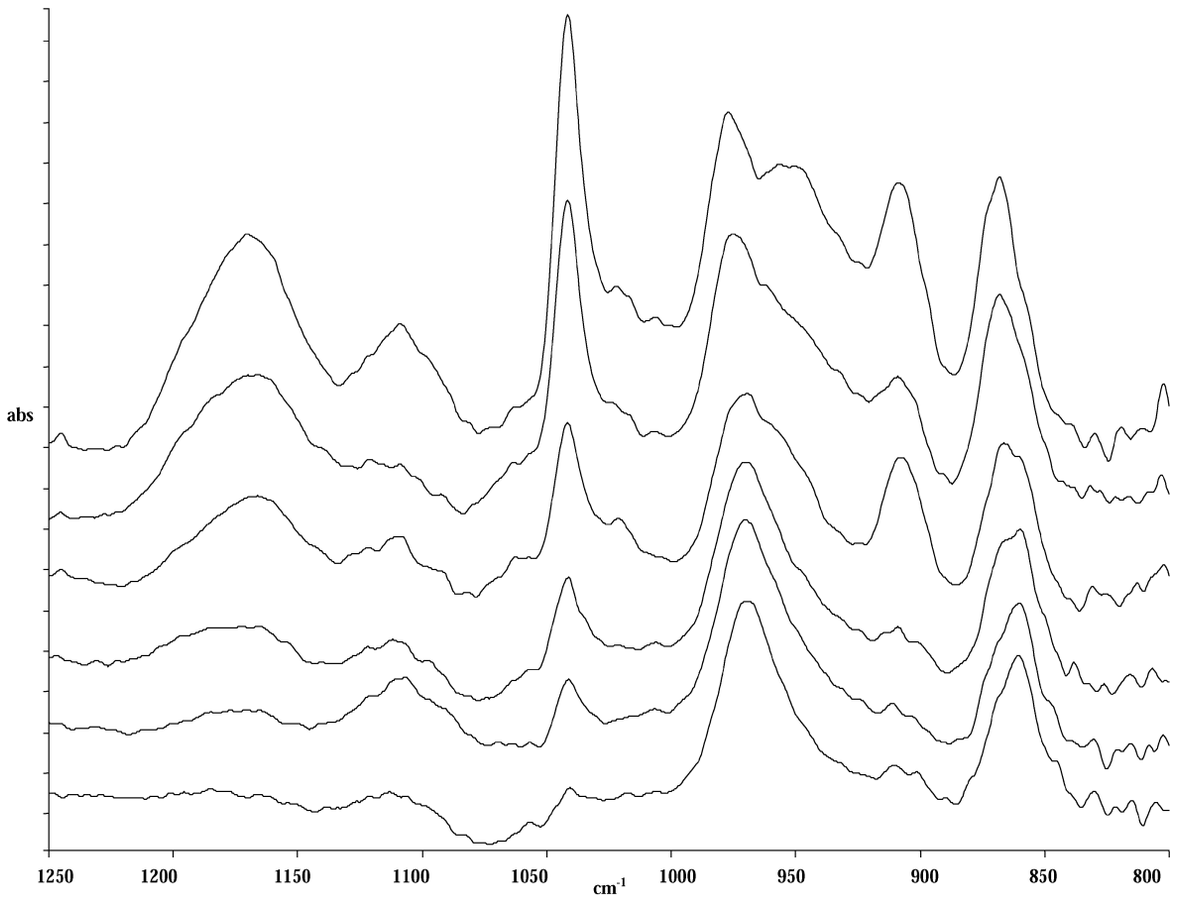

Fig. 8 FTIR spectra of 20.0 mM MoO_4^{2-}, 80.0 mM H_2O_2 solutions, illustrating the decrease in intensities for the ν_3 bands (1166, 1108 and 1042 cm^{-1}) and the ν_1 band at 908 cm^{-1} with increasing pH. From top to bottom; pH 2.08, 2.53, 2.91, 3.20, 3.38 and 3.74.

hydroxide solutions and the disodium sulfate were prepared according to ref. 37. Hydrogen peroxide stock solutions were prepared from 30% (9.7 M) hydrogen peroxide (E. Merck *p.a.*), standardised against potassium permanganate, and stored in black plastic bottles at ~4 °C. Potassium permanganate solutions, prepared from ampoules to give 20 mM solutions, were standardised against disodium oxalate solutions, and stored in dark glass bottles. The oxalate solutions were prepared from $Na_2C_2O_4$ (E. Merck *p.a.*), dried for ~1.5 h at ~200 °C. In all preparation of solutions boiled and distilled (Milli-Q plus 185) water was used. All solutions were protected from CO_2(g) by the use of argon gas.

To avoid decomposition of peroxide in the solutions during preparation and titration, certain procedures had to be followed. Since the decomposition of peroxide in the titration solutions increased rapidly above pH 5.5, the sulfuric acid was always added prior to the addition of hydrogen peroxide during the preparation of each solution. The solutions were then allowed to equilibrate for about 20 min before starting the titration. Furthermore, black glass equipment was used in the preparation and titration of all solutions.

Potentiometric measurements

The EMF measurements were carried out as a series of potentiometric titrations in 0.300 M $Na_2(SO_4)$ medium at 25 °C (± 0.05 °C, thermostatted oil-bath) with an automated, computer controlled potentiometric titrator. Generally, equilibrium was reached within 15 min. Each titration curve consists of two separate titrations, one beginning at the lower pH value, the other at the higher pH value. The endpoints of the two titrations should coincide. Together, these two titrations explain the complete titration curve for the given concentrations (for further information, see ref. 37).

Data treatment

The studied equilibria are written with the components H^+, MoO_4^{2-}, H_2O_2, SO_4^{2-} according to reaction (1).

$$p\,H^+ + q\,MoO_4^{2-} + r\,H_2O_2 + s\,SO_4^{2-} \rightleftharpoons (H^+)_p(MoO_4^{2-})_q(H_2O_2)_r(SO_4^{2-})_s \quad (1)$$

The formation constants are denoted $\beta_{p,q,r,s}$ and the complexes are given in the notation (p,q,r,s). The total concentration of each component is given by eqns. (2)–(5).

$$H = h + \Sigma\Sigma\Sigma\Sigma p\beta_{p,q,r,s}h^p b^q c^r d^s \quad (2)$$

$$B = b + \Sigma\Sigma\Sigma\Sigma q\beta_{p,q,r,s}h^p b^q c^r d^s \quad (3)$$

$$C = c + \Sigma\Sigma\Sigma\Sigma r\beta_{p,q,r,s}h^p b^q c^r d^s \quad (4)$$

$$D = d + \Sigma\Sigma\Sigma\Sigma s\beta_{p,q,r,s}h^p b^q c^r d^s \quad (5)$$

H is the total concentration of H^+ (over the zero level of H_2O, MoO_4^{2-}, H_2O_2 and SO_4^{2-}), B is the total concentration of molybdate, C of hydrogen peroxide, and D of sulfate. h, b, c and d are the corresponding free concentrations.

In the least squares computer program LAKE,[42] formation constants for arbitrary but systematically chosen complexes $(H^+)_p(MoO_4^{2-})_q(H_2O_2)_r(SO_4^{2-})_s$ are varied, so that the sum of error squares, $U = \Sigma(H_{calc} - H_{exp})^2/B$ is minimized. H_{calc} is the calculated H for one specific titration point when using a certain speciation model in LAKE, while H_{exp} is the analytically determined H in that point. The set of complexes giving the lowest U-value forms the model, which best explains the

experimental data. Since all errors were placed on eqn. (2), *i.e.* H^+, the concentrations of the other components are assumed to be correct.

Modelling and construction of distribution diagrams were performed using the computer program SOLGASWATER.[43]

Potentiometric data

The pK_a value for HSO_4^- and the formation constants for the complexes in the $H^+ - MoO_4^{2-}$ system have been reported earlier.[37] The formation constants for the *p*,*q*,*r*,*s* complexes were determined from 50 titrations (705 points) within the range $2.0 \le pH \le 5.5$, $5.00 \le B/mM \le 80.00$, $0 \le C/mM \le 245$, and $273.07 \le D/mM \le 320.20$. The titration curves ($Z$ *vs.* $-\log[H^+]$) for B = 20.00 mM are illustrated in Fig. 1. Z is the average uptake of protons per molybdate ion, defined by $Z = (H - h - [HSO_4^-])/B$.

In order to check the reliability of the titrations some of them were performed as "constant" Z titrations. Here, instead of keeping C constant with varying Z values during the titration, C is varied, $0.00 \le C/mM \le 77.00$, while Z is kept approximately constant. "Constant" Z titrations were performed for $Z \approx 1.15$, 1.30 and 1.45.

FTIR spectroscopic measurements

The IR spectra were collected with a Perkin-Elmer Spectrum 2000 FTIR spectrometer, equipped with a deuterated triglycine sulfate (DTGS) detector. All sample solutions were analysed with the attenuated total reflection (ATR) technique. The spectra were recorded with a horizontal ATR accessory and a diamond crystal as the reflection element (Perkin-Elmer). The angle of incidence for this setup is approximately 45°. A small volume of each sample solution was applied directly onto the diamond crystal and sealed with a lid. For each sample 32 scans were collected. Spectra of water and a 0.300 M Na_2SO_4 solution were used for subtraction. The purpose of these measurements was to evaluate possible sulfate interaction with the peroxomolybdate complexes. Therefore, only peaks arising from this interaction were evaluated. All calculations and plotting were accomplished with Spectrum 2000 for Windows, Perkin–Elmer.

NMR measurements

^{95}Mo NMR spectra were recorded at 32.59 MHz on a Bruker AMX 500 MHz spectrometer at 25 ± 1 °C. Field-frequency stabilisation was achieved by placing the 8 mm sample tube into a 10 mm tube containing D_2O. All chemical shifts are reported relative to the external reference 1 M MoO_4^{2-}, assigned to 0 ppm. Typically, spectral widths of 307 ppm (10 kHz) were used, and data for the FID were accumulated in 16k blocks. Linear back prediction and exponential line-broadening (50 Hz) was applied before Fourier transformation. Spectra were integrated after baseline correction. The deconvolution subroutine of the software program 1D WINNMR was used to obtain more precise integral values.

^{17}O NMR spectra were recorded at 67.8 MHz at 298 and 278 K on a Bruker DRX 500 MHz spectrometer. Typically, pulse width = 10 μs (approx. 40°), pulse repetition time = 0.1 s, spectral widths of 1200 ppm (81.4 kHz) were used, and data for the FID were accumulated in 8k blocks. Spectra were integrated after baseline correction. The deconvolution subroutine of the software program, 1D WINNMR was used. Enrichment of the samples to 3% was done by addition of $H_2{}^{17}O$ (12 atom% ^{17}O, Cambridge Isotope Laboratories) to the samples. The peroxide sites were not involved in the ^{17}O isotope enrichment, being inert for oxygen exchange.

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References

1 R. Agnemo, 9th ISWPC, Montréal, Canada, 1997, D2–1. ISBN 1–896742–14–9.
2 V. Kubelka, R. C. Francis and C. W. Dence, *J. Pulp Pap. Sci.*, 1992, **18**, J108.
3 J. Jakara, A. Paren, J. Patola and T. Viitanen, *Paperi Puu*, 1994, **76**, 559.
4 E. Bergnor-Gidnert and P. Tomani, *Proceedings of the 1998 International Pulp Bleaching Conference*, 1998, **1**, 185.
5 J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 279.
6 M. H. Dickman and M. T. Pope, *Chem. Rev.*, 1994, **94**, 569.
7 *Gmelin Handbook of Inorganic Chemistry, Mo Suppl.*, Springer Verlag, Berlin, 1989, vol. 3b.
8 A. J. Dedman, T. J. Lewis and D. H. Richards, *J. Chem. Soc.*, 1963, 2456.
9 I. I. Alekseeva and K. B. Yatsimirskii, *Russ. J. Inorg. Chem.*, 1969, **14**, 221.
10 E. Richardson, *J. Less-Common Met.*, 1960, **2**, 360.
11 L. J. Csányi, *Transition Met. Chem.*, 1989, **14**, 298.
12 L. J. Csányi, I. Horváth and Z. Galbács, *Transition Met. Chem.*, 1989, **14**, 90.
13 S. U. Kreingol'd and A. N. Vasnev, *Russ. J. Inorg. Chem.*, 1980, **25**, 1355.
14 V. Nardello, J. Marko, G. Vermeersch and J. M. Aubry, *Inorg. Chem.*, 1995, **34**, 4950.
15 N. J. Campbell, A. C. Dengel, C. J. Edwards and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1989, 1203.
16 L. J. Csányi, *Acta Chim. Acad. Sci. Hung.*, 1958, **14**, 79.
17 J. M. Aubry and B. Cazin, *Inorg. Chem.*, 1988, **27**, 2013.
18 F. Chauveau, P. Souchay and G. Tridot, *Bull. Soc. Chim. Fr.*, 1955, 1519.
19 F. C. Palilla, N. Adler and C. F. Hiskey, *Anal. Chem.*, 1953, **25**, 926.
20 Y. Schaeppi and W. D. Treadwell, *Helv. Chim. Acta*, 1948, **31**, 577.
21 M. Hashimoto, H. Ichida and Y. Sasaki, *J. Coord. Chem.*, 1996, **37**, 349.
22 L. Salles, F. Robert, V. Semmer, Y. Jeannin and J.-M. Brégeault, *Bull. Soc. Chim. Fr.*, 1996, **133**, 319.
23 R. Stomberg and S. J. Olson, *Alloys Compd.*, 1996, **237**, 39.
24 S. Olson and R. Stomberg, *Z. Kristallogr.*, 1996, **211**, 895.
25 I. Persdotter, L. Trysberg and R. Stomberg, *Acta Chem. Scand. Ser. A*, 1986, **40**, 1.
26 R. Stomberg and L. Trysberg, *Acta Chem. Scand.*, 1969, **23**, 314.
27 R. Stomberg, L. Trysberg and I. Larking, *Acta Chem. Scand.*, 1970, **24**, 2678.
28 I. Larking and R. Stomberg, *Acta Chem. Scand.*, 1972, **26**, 3708.
29 L. Trysberg and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1981, **35**, 823.
30 I. Persdotter, L. Trysberg and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1986, **A40**, 335.
31 R. Stomberg and S. Olsson, *Z. Kristallogr.*, 1997, **212**, 311.
32 R. Stomberg, *Acta Chem. Scand.*, 1968, **22**, 2024.
33 R. Stomberg and S. Olsson, *Z. Kristallogr.*, 1997, **212**, 699.
34 I. Persdotter, L. Trysberg and R. Stomberg, *Acta. Chem. Scand., Ser. A*, 1986, **40**, 83.
35 C. B. Shoemaker, D. P. Shoemaker and L. W. McAfee, *Acta Crystallogr., Sect. C*, 1985, **41**, 347.
36 R. Stomberg, *Acta. Chem. Scand.*, 1969, **23**, 2755.
37 Part 58. F. Taube, I. Andersson and L. Pettersson, *Polyoxometalates: From Topology to Industrial Applications*, ed. M. T. Pope and A. Müller, Kluwer Academic Publishers, 2001, pp. 161–174.
38 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, USA, 4th edn., 1986.
39 I. Andersson, S. Angus-Dunne, O. Howarth and L. Pettersson, *J. Inorg. Biochem.*, 2000, **80**, 51.
40 P. Souchay, *Bull. Soc. Chim. Fr.*, 1949, 122.
41 R. Stomberg, *Acta. Chem. Scand.*, 1968, **22**, 1076.
42 N. Ingri, I. Andersson, L. Pettersson, A. Yagasaki, L. Andersson and K. Holmström, *Acta Chem. Scand.*, 1996, **50**, 717.
43 G. Eriksson, *Anal. Chim. Acta*, 1979, **112**, 375.