Base Hydrolysis of Aqueous Chromium(III) Solutions: On the Existence of $[Cr(OH)_4]^-$, and Speculation regarding a New Chromium Polyoxocation

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The base hydrolysis of chromium(III) aqueous solutions was investigated in an attempt to determine whether a $[CrO_4Cr_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ polyoxocation (*i.e.* Cr_{13}) analogous to the tridecameric aluminium and gallium ions (Al_{13} and Ga_{13}) is formed. Clay mineral intercalation studies showed that a species formed during base hydrolysis of aqueous solutions of Cr^{3+} has approximately the same height, relative to the phyllosilicate sheets, as that of the Ga_{13} polyoxocations. Gel permeation chromatography of the hydrolysed solution revealed that a chromium species was eluted at exactly the same volume as were the other tridecameric ions, under analogous conditions. These results indicate that a chromium ion similar in size to that of the known $[GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ does form during base hydrolysis. Quantitative pillaring studies also suggested that the chromium species has a similar charge. Infrared studies of sulfate salts formed from the chromium-containing cations present in the hydrolysed solutions indicated that no tetrahedrally co-ordinated chromium was present; this implies that the chromium species cannot be analogous to the Al_{13} and Ga_{13} polyoxocations as they both contain a central tetrahedrally co-ordinated metal atom. Since this tetrahedral central atom in the tridecamers has been postulated to arise because of the existence of $[M(OH)_4]^{x-}$ ions in solution at high pH, its apparent absence in the case of chromium led to an investigation of whether or not $[Cr(OH)_4]^-$ ions, the formation of which has generally been assumed, really exist. Through ultraviolet–visible and near-infrared spectroscopic studies, as well as the analysis of titration curves, it is concluded that no $[Cr(OH)_4]^-$ ions are formed upon hydrolysis of solutions of Cr^{3+} to $OH^-:Cr^{3+}$ mole ratios of $\geqslant 4:1$. For these reasons it is speculated that the large species present in hydrolysed chromium solutions may be $[Cr_{12}(OH)_{28}(H_2O)_{12}]^{8+}$ ions in which the central tetrahedral position is vacant.

The $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ polyoxocation which forms upon base hydrolysis of aqueous solutions of Al^{3+} consists of a central tetrahedrally co-ordinated aluminium surrounded by twelve edge-linked octahedrally co-ordinated aluminiums.[1] The net structure is that of the Baker–Figgis ε isomer[2] of the Keggin structure[3,4] (the α isomer). This Al_{13} species can be viewed as being a sub-unit of the spinel crystal structure.[5,6] Aluminium is considered to be a 'parent' of the $M^{II}Al_2O_4$ spinel minerals,[7–9] and itself forms a γ-Al_2O_3 oxide that has a tetragonally distorted spinel type of structure.[10] Such behaviour is also known for other spinel parents, Ga^{3+}, Fe^{3+} and Cr^{3+}, which form the spinel oxides γ-Ga_2O_3,[11] γ-Fe_2O_3[12] and γ-Cr_2O_3.[13] A mechanism which has been suggested for the formation of the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ion implies that the formation of $[Al(H_2O)_6]^{3+}$ ions at low pH and of $[Al(OH)_4]^-$ ions at high pH is critical.[14,15] While the validity of this mechanism has not been proven, and indeed evidence exists that under some circumstances the tridecamer can form by another mechanism,[16] the existence of both octahedral and tetrahedral species may give some indication as to whether a tridecameric unit with a central tetrahedrally co-ordinated metal ion surrounded by octahedrally co-ordinated ions could be expected. Interestingly, $[Ga(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ ions form in the respective solutions at low pH, and $[Ga(OH)_4]^-$, $[Fe(OH)_4]^-$ and $[Cr(OH)_4]^-$ are also believed to form at high pH.[17] Studies of the hydrolysis of gallium(III) salt solutions were successful in determining that a gallium polyoxocation of analogous structure to that of $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ was formed upon the hydrolysis of gallium(III) salt solutions.[6,18,19] In addition, evidence has also been found which supports the view that an $[FeO_4Fe_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ion may be formed upon base hydrolysis of iron(III) salt solutions.[6] This leads to the question of whether or not a similar species can be formed in the chromium(III) system.

The hydrolytic behaviour of $[Cr(H_2O)_6]^{3+}$ solutions has been studied in some detail at $OH^-:Cr^{3+}$ mole ratios of 1.0:1 and below; dimers, trimers and tetramers form under such conditions, and their structures have been investigated.[20] The species which form between $OH^-:Cr^{3+}$ ratios of 1 and 2.5:1 are much less well understood. Between hydrolysis ratios of 2.5 and 3:1 a gel phase is formed, and at a ratio of 3:1 the hydroxide $Cr(OH)_3 \cdot 3H_2O$ precipitates. Above a hydrolysis ratio of $OH^-:Cr^{3+} = 4:1$ the hydroxide species can dissolve completely (whether or not this occurs depends on the solution concentration and temperature) and is said to result in $[Cr(OH)_4]^-$ ions in solution.[17] Clay mineral pillaring studies have shown that a polyoxocation species slightly larger than the aluminium tridecamer is indeed formed upon hydrolysis. The only interpretation which has been put forth for this result, however, is that there may have been intercalation of the chromium trimer in such a manner that it is oriented on end in the phyllosilicate basal space.[21]

Very few cases are known of structures in which chromium is believed to exist in tetrahedral co-ordination, the primarily quoted one being the α-$[CrO_4W_{12}O_{36}]^{5-}$ heteropoly oxometalate which has been reported to have the true Keggin structure, with chromium said to be in the central tetrahedral position.[4] This strong tendency exhibited by chromium to prefer octahedral co-ordination implies that it would not be likely to form a $[CrO_4Cr_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ species. In contrast, however, chromium hydroxide dissolves in alkaline solutions, supposedly forming tetrahedral $[Cr(OH)_4]^-$ ions,[17] suggesting that the opposite might be true. As previously discussed, this may be an important indication of the ability of the metals to form $[MO_4M_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ions.

To examine the question of whether or not a Cr_{13} polyoxocation could be formed, studies of the base hydrolysis of aqueous solutions of Cr^{3+} were undertaken.

Experimental

The aqueous solutions of Cr^{3+} were prepared by dissolving $CrCl_3 \cdot 6H_2O$ (Fisher) and $Cr(ClO_4)_3 \cdot xH_2O$ (Aesar, 99.9%) salts in deionized/distilled water, to form 0.2 mol dm^{-3} solutions. Samples of these solutions were diluted with water to *ca.* 0.05 mol dm^{-3}, and then base hydrolysed through the addition of *ca.* 0.2 mol dm^{-3} NaOH, to varying $OH^-:Cr^{3+}$ ratios ($OH^-:Cr^{3+}$ referring to the number of moles of OH^- added per mole of Cr^{3+} ions), with vigorous stirring. These turbid solutions were heated at 70 °C until they became clear, and then cooled in ice.

Ultraviolet–visible spectra were recorded for the hydrolysed chromium solutions. Spectra were run from 900 to 200 nm (11 100–50 000 cm^{-1}) on a Cary 219 spectrometer. The concentrations employed were those which were found to produce acceptable absorbances (0.5–2.0 absorbance units). The samples were contained in 1.0 cm pathlength quartz cells.

Gel permeation chromatography (GPC) was carried out on a hydrolysed chromium solution having an $OH^-:Cr^{3+}$ ratio of *ca.* 2.25:1. To ensure good separation of the various species present, a column (length 74 cm, void volume 48 cm^3) consisting of Sephadex G-25 followed by G-10 was used as the stationary phase. The eluent was deionized/distilled water. Injection volumes of 5 cm^3 were used, and samples were taken every 2 cm^3, starting at 48 cm^3. These samples were analysed using an ARL 35000C ICP/AES spectrometer at a wavelength of 2677.16 nm for chromium.

Near-infrared spectra were obtained with a Nicolet 8000 FTIR spectrometer. An SiO_2 beamsplitter and a liquid-nitrogen-cooled indium antimonide detector were employed; the spectral region available with this combination was from about 12 000 to 2500 cm^{-1}. These spectra were run at a resolution of 16 cm^{-1}. Samples were contained in quartz cells and a special sample holder was built to ensure that no stray light passed around the sample cell.

Precipitated salts of the hydrolysed chromium solutions were prepared by adding sulfate, selenate, phosphate or arsenate counter ion solutions which had been adjusted to the pH of the hydrolysed chromium solutions. This was done until counter ion:Cr mole ratios of 0.5 to 3.0:1 had been reached. The resulting suspensions were left for several days (or longer), and the precipitates were collected by centrifugation, washed several times with distilled water and dried in air.

Fourier-transform infrared (FTIR) spectra of CsI pellets of the chromium sulfate and selenate salts were run on a Mattson Galaxy 4030 spectrometer at a resolution of 2 cm^{-1}.

To examine the d_{001} spacings of pillar interlayered clay minerals prepared using hydrolysed chromium solutions as the intercalant, oriented thin films were prepared on glass slides as previously described for the gallium and aluminium systems.[19] Powder X-ray diffraction patterns (utilizing graphite-monochromated Cu-Kα radiation) of the slides were run from 4 to 22° in 2θ employing a step width of 0.02° in 2θ and a step scan time of 4 s.

Results and Discussion

Pillaring Studies.—Pillaring studies of hydrolysed chromium(III) solutions have revealed a wide range of behaviours, depending on the conditions of hydrolysis, the temperatures at which the solutions were aged, and the time of aging.[21–26] For this reason, the hydrolyses of the chromium(III) solutions were carried out to $OH^-:Cr^{3+}$ ratios of *ca.* 2.25:1 in a very similar manner to that which produced tridecamers for aluminium, gallium and iron solutions.[6,18,19,27] In the case of chromium (unlike gallium and iron), the polyoxocations did not appear to decompose rapidly, and high-temperature aging was required to clarify the colloidal suspensions which were initially formed upon hydrolysis. As soon as the solutions had cleared they were cooled in an ice-bath. Clay mineral pillaring studies of the hydrolysed chromium(III) solutions were carried out in a similar manner to those of hydrolysed solutions of Ga and Al.[28] The d_{001} XRD peaks obtained for the chromium pillar interlayered clay minerals were often broad, and their positions varied, but on those occasions when sharp d_{001} peaks were observed the *d* spacings tended to be between 19.1 and 19.4 Å (Fig. 1), which is virtually the same as that seen for the Ga_{13}-montmorillonite intercalates.[28] As the ionic radii of Ga^{3+} and Cr^{3+} are virtually the same, this shows that while the hydrolysed chromium solutions frequently contain a variety of species, under some conditions they form a unit which has the same effective height in its orientation between the phyllosilicate sheets as would be expected for a chromium-containing tridecameric polyoxocation.

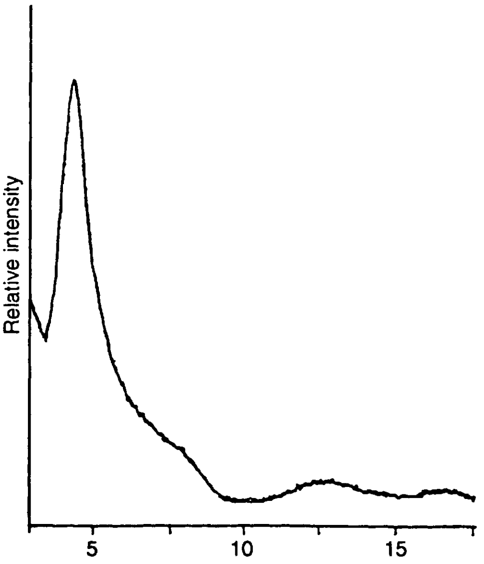


Fig. 1 Powder XRD pattern for a chromium pillar interlayered clay mineral (montmorillonite)

A study of the d_{001} spacings achieved as a function of solution loading showed that the maximum *d* spacing was reached at a loading of *ca.* 8 milliequivalents of Cr^{3+} per gram of montmorillonite.[25] This is about the same as was found for the quantitative pillaring studies undertaken utilizing hydrolysed aqueous solutions of Al and Ga.[18] In the case of the Ga_{13} solutions, this was done to give an indication of the relative amounts of the ions present, where it was assumed that the gallium species had an equal charge to that of the $Al_{13}{}^{7+}$ ions. In the case of chromium, if we assume that equal amounts of the ions are present (*e.g.* same percentage of $Ga_{13}{}^{7+}$ and $Cr_x{}^{z+}$), then the data suggest similar charges for the chromium polyoxocations and the Ga_{13} and Al_{13} ions.

Gel Permeation Chromatography.—When base-hydrolysed solutions of Cr^{3+} ($OH^-:Cr^{3+}$ = 2.25:1) were run through the chromatography column several bands became apparent, confirming that species of distinctly different sizes were present. Substantial amounts of the chromium appeared at the void volume (48 cm^3), showing that some species too large to be slowed by the column were formed. One species, however, was eluted after exactly the same volume of eluent as was required for both the Al_{13} and $GaAl_{12}$ tridecameric polyoxocations (60 cm^3), indicating that the hydrolysed chromium solution contains a species of very similar size.

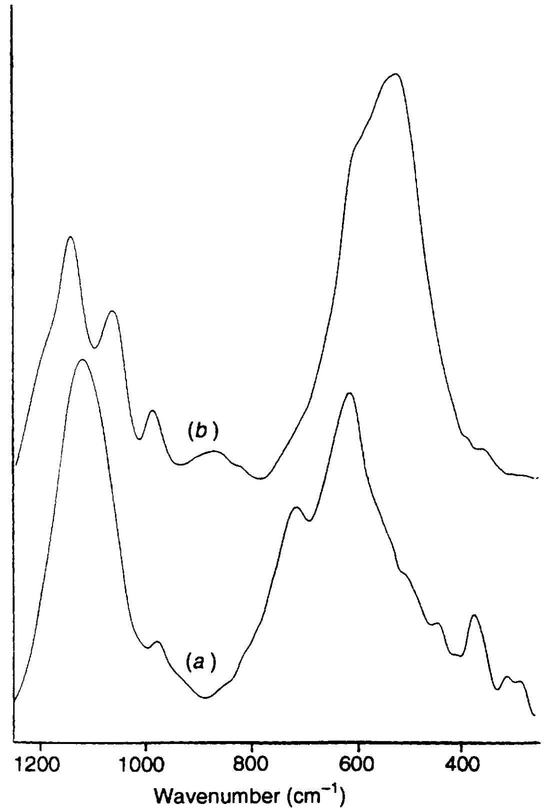


Fig. 2 Infrared spectra (CsI pellets) of sulfate salts prepared from (*a*) hydrolysed aluminium(III) solutions and (*b*) hydrolysed chromium(III) solutions (OH^- : Cr^{3+} = 2.25 : 1)

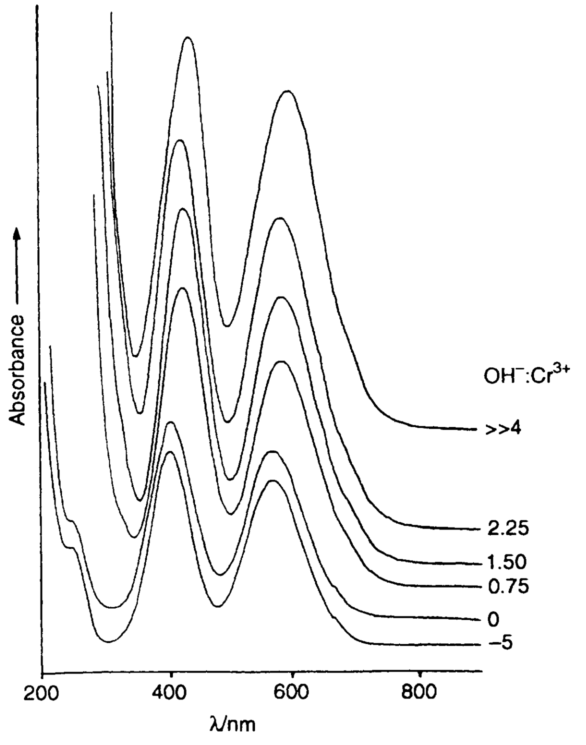


Fig. 3 Ultraviolet–visible spectra of hydrolysed chromium(III) solutions as a function of extent of hydrolysis (H_3O^+ : Cr^{3+} = 5 for spectrum in which OH^- : Cr^{3+} is denoted as –5)

Table 1 Ultraviolet–visible spectroscopy results for hydrolysed chromium perchlorate solutions

Sample OH : Cr ratio	λ_1/nm	λ_2/nm	ε_1/dm^3 mol^{-1} cm^{-1}	ε_2/dm^3 mol^{-1} cm^{-1}
–5*	575	405	10.8	12.6
0	573	404	10.5	15.1
1	582	420	13.5	17.2
1.75	585	422	15.7	20.1
2.25	588	422	17.1	19.4
⩾4	588	422	20.2	22.2

* H_3O^+ : Cr^{3+} = 5 : 1

Infrared Spectra.—Sulfate (and selenate) salts of the chromium species present in the fraction which eluted from the GPC column at 60 cm^3 were precipitated and dried. The infrared spectrum of a CsI pellet of the sulfate salt is shown in Fig. 2. This reveals only one strong band between 800 and 300 cm^{-1}; this band is at *ca.* 530 cm^{-1}, in an appropriate position [by comparison to the gallium and iron(III) salts][6] to indicate octahedrally co-ordinated chromium atoms [*e.g.* (Cr–OH)$_{O_h}$]. [The shoulder just above 600 cm^{-1} which can be seen on the band at 530 cm^{-1} is absent for the selenate salts, indicating that it is the $\nu_4(SO_4)$ band.] No evidence was seen of any band which could be construed to indicate tetrahedrally co-ordinated chromium, regardless of the length of time the solutions were allowed to age, the temperature they were held at, or the hydrolysis ratios to which they were taken. This suggests very strongly that while a chromium species similar in size to that of the aluminium and gallium tridecameric polyoxocations does form, it does not contain a central tetrahedrally co-ordinated chromium atom.

Ultraviolet–Visible and Near-infrared Spectra of Hydrolysed Chromium Solutions.—It has been accepted to some degree in the chemical literature that a $[Cr(OH)_4]^-$ ion exists.[29–31] Therefore it is puzzling that the large cation (similar in size to that of the Al_{13} ion) which forms during the base hydrolysis of chromium solutions does not appear to have a central tetrahedrally co-ordinated chromium atom. It was decided to investigate the evidence for the existence of the tetrahydroxochromate ion. The belief in the formation of a $[Cr(OH)_4]^-$ ion upon the hydrolysis of chromium(III) solutions to OH^- : Cr^{3+} mole ratios of ⩾4 : 1 apparently relates back to work done by Ficke and Windhausen[32] in 1924 in which their titration results were interpreted under the assumption that the $[Cr(OH)_4]^-$ ion was present. No subsequent studies appear to have been carried out to prove (or disprove) this. The characterization of analogous $[M(OH)_4]^{z-}$ ions in solutions of Al^{III}, Ga^{III}, Zn^{II} and Fe^{III}[17,33–36] seems to have reinforced the hypothesis that a $[Cr(OH)_4]^-$ ion exists.

When ultraviolet–visible spectra were run of aqueous chromium(III) perchlorate solutions that had been base hydrolysed to varying OH^- : Cr^{3+} ratios, gradual shifts of the bands with increasing degrees of hydrolysis were observed, as well as slight increases in absorption coefficients (Fig. 3, Table 1). In the case of the solutions having OH^- : Cr^{3+} ⩾ 4 : 1 (and in which the hydroxide phase formed at OH^- : Cr^{3+} = 3 : 1 had completely dissolved), however, the absorption coefficients were only of the order of 22 dm^3 mol^{-1} cm^{-1}, which would be somewhat low for a tetrahedrally co-ordinated species. Nothing was seen from these spectra to suggest that any such species could be present. In particular, it is noteworthy that no significant differences were seen between the spectra of the solutions having OH^- : Cr^{3+} mole ratios of 2.25 and ⩾4 : 1.

It has been stated that chromium appears to exist in a tetrahedral environment in the α-$[CrO_4W_{12}O_{26}]^{5-}$ ion.[37] This conclusion was based on the appearance of a weak band at 8300 cm^{-1} in the near-infrared region for aqueous solutions of tungstochromic acid. This band was assigned to the (Cr–O)$_{T_d}$ ${}^4T_2 \longleftarrow {}^4T_1(F)$ transition, since calculations reported in that work assumed that the lowest-energy band would be due to the

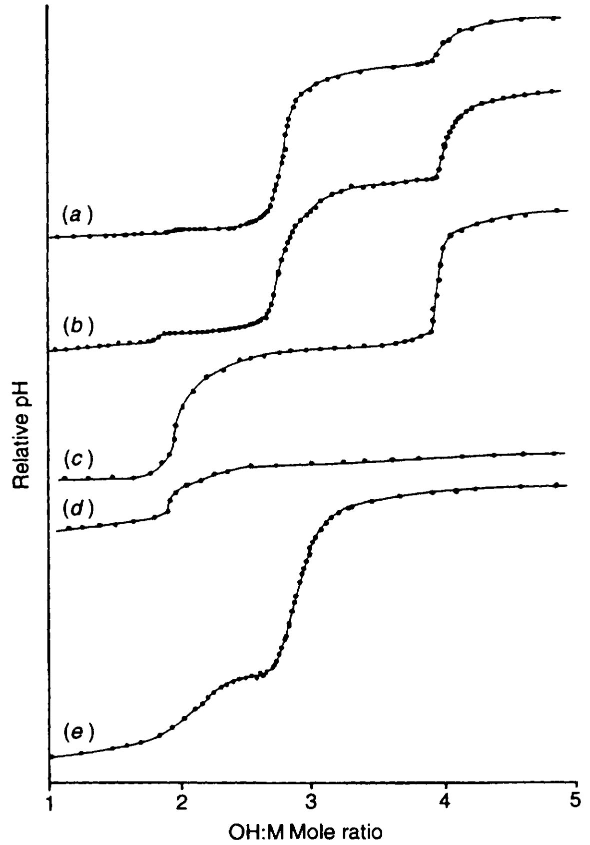


Fig. 4 Back-titration curves for hydrolysed solutions of Al^{III} (*a*), Ga^{III} (*b*), Zn^{II} (*c*), Mg^{II} (*d*) and Cr^{III} (*e*)

tetrahedral chromium and would fall at (4/9) × 10*Dq* for the $[Cr(H_2O)_6]^{3+}$ ion (10*Dq* being 17 400 cm^{-1}), and therefore at about 7700 cm^{-1}. Near-infrared spectra of the solutions used in our work were obtained to see if any evidence for tetrahedral chromium could be found. Chromium solutions which had a hydrolysis ratio of well above 4:1 revealed a sharp band in this region (*ca.* 8625 cm^{-1}), as well as a somewhat weaker one at *ca.* 7385 cm^{-1}. However, after comparing spectra at various hydrolysis ratios, and spectra of NaOH solutions containing no chromium, it was found that these two bands had nothing to do with the presence of chromium, but rather were a function of the solution pH and thus represented some aspect of the H_3O^+/OH^- character of the bulk aqueous solutions. (Indeed, this may have been a complicating factor in the studies used to determine the co-ordination number of the chromium in the difficult-to-prepare $[CrW_{12}O_{40}]^{5-}$ ion.) We were therefore unable to find any UV/VIS or infrared evidence to confirm that a $[Cr(OH)_4]^-$ species forms in aqueous solution under these conditions.

Titration Curves for the Hydrolysis of Chromium(III) *Solutions.*—The forward- and back-titration curves of metal-ion solutions exhibit plateaus which can be an indication of the different species present at varying $OH^-:M^{n+}$ mole ratios. The titration curves of aqueous solutions of Al and Ga clearly show two plateaus at high hydrolysis ratios. The first appears at a ratio of 3:1, when the hydroxide or hydroxide oxide phases are formed, and the second at a ratio of 4:1, above which these phases dissolve yielding $[M(OH)_4]^-$ ions in solution [Fig. 4(*a*) and 4(*b*)]. In addition, very small plateaus occur at hydrolysis ratios of about 2:1, which are in the appropriate region for polyoxocation formation.[18] The plateaus are visible for either forward- or back-titrated solutions. Similarly, for zinc(II) solutions, plateaus are visible at $OH^-:Zn^{2+}$ = 2:1, which corresponds to the precipitation of $Zn(OH)_2$ and $OH^-:Zn^{2+}$ = 4:1, at which point $[Zn(OH)_4]^{2-}$ forms [Fig. 4(*c*)]. For magnesium, however, it is known that no $[Mg(OH)_4]^{2-}$ ion is formed.[17] In accordance with this, only one plateau is seen for these solutions, at $OH^-:Mg^{2+}$ = 2:1, and this corresponds to the precipitation of $Mg(OH)_2$ [Fig. 4(*d*)]. It is interesting that in the case of chromium only two plateaus are observed, one at an $OH^-:Cr^{3+}$ ratio of about 2.1:1, the second at 3.0:1 [Fig. 4(*e*)]. The first of these must be related to the polyoxocation formation; the second is due to the precipitation of $Cr(OH)_3 \cdot 3H_2O$. No plateau is observed at a hydrolysis ratio of 4:1, however, even for the back-titration curves of clear solutions having $OH^-:Cr^{3+}$ ratios $\geqslant$4:1 and which become cloudy when the $OH^-:Cr^{3+}$ ratios fall to between 3 and 4:1. This marked difference between the hydrolytic behaviour of chromium at very high pH, and of Ga, Al and Zn under analogous conditions, indicates that different species must be present at very high hydrolysis ratios (Table 2).

All of these results strongly support the view that no $[Cr(OH)_4]^-$ ion is formed upon hydrolysis of chromium(III) solutions. It is more likely that the solution species present at very high $OH^-:Cr^{3+}$ ratios is an octahedrally co-ordinated $[Cr(OH)_6]^{3-}$ ion, or a derivative thereof (*e.g.* polyoxoanions). This point has been previously questioned, with suggestions having been made that the species present at high pH could be colloidally dispersed chromium(III) oxides.[38,39]

Conclusion

The strong similarities in the hydrolytic behaviours of Al^{3+} and Cr^{3+} suggested that it might be possible to synthesise a $[CrO_4Cr_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ polyoxocation through the base hydrolysis of aqueous solutions of Cr^{3+}. Clay mineral pillaring and gel permeation chromatography studies showed indeed a large ionic species was formed which was similar in both size and charge to the $[GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ polyoxocation, which supported this view. Infrared spectroscopic studies, however, suggest very strongly that there is no tetrahedrally co-ordinated chromium present in the polyoxocations formed. This result is consistent with infrared and UV/VIS spectroscopic studies of chromium solutions carried out at very high pH, and with the shape of titration curves for chromium solutions; these studies concluded that there is no tetrahedral $[Cr(OH)_4]^-$ species formed in solutions hydrolysed to $OH^-:Cr^{3+}$ ratios of $\geqslant$4:1.

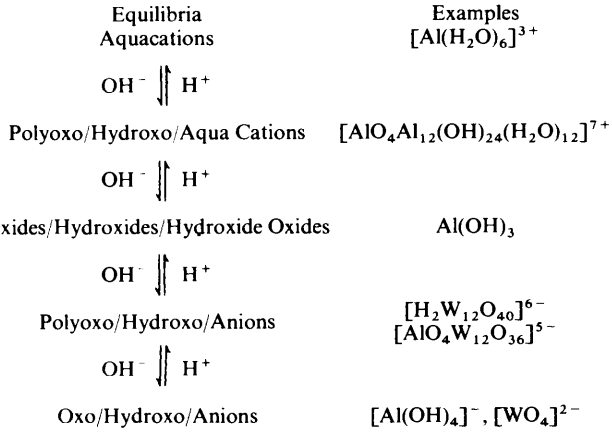
The results which have been put forth so far for the chromium system are in accord with the interpretations made by Bornholdt *et al.*[40] from extended X-ray absorption fine structure (EXAFS) studies of hydrolysed chromium solutions ($OH^-:Cr^{3+} \approx$ 2.2:1), which also revealed only the presence of octahedrally co-ordinated chromium. The bond lengths determined in their work were similar to those known to exist in the $[Cr_2(OH)_2(H_2O)_8]^{4+}$ dimer, and from this it was concluded that the polyoxocations involved edge-linked octahedra.

Since it appears that a $[CrO_4Cr_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ion has not been synthesised by the procedures employed, the question remains as to what is the structure of the chromium species which has approximately the same height as that of the Ga_{13} ion, elutes through a GPC column at the same eluent volume as do the Al_{13} ion and $GaAl_{12}$ ions, and appears to have a similar charge to those of these polyoxocations. One possibility is suggested by comparison of the present synthetic procedures with those used to make the heteropoly oxometalates. The method of formation of the Al_{13} ion through the base hydrolysis of acidic aluminium salt solutions is very similar to the manner in which the heteropoly oxometalates having the Keggin structure are synthesised (Scheme 1). In the latter case, acid is added to the alkaline solutions which contain the ions of interest, which are generally in tetrahedral co-ordination. For example, for $[AlO_4W_{12}O_{36}]^{5-}$ the starting solution would

Table 2 Observed *vs.* expected titration plateau positions for hydrolytic species of Al^{III}, Ga^{III}, Zn^{II}, Mg^{II} and Cr^{III}

	Al^{III}	Ga^{III}	Zn^{II}	Mg^{II}	Cr^{III}
Species			$Zn(OH)_2$	$Mg(OH)_2$	
t.h.r.			2.0	2.0	
o.p.p.			2.0	2.0	
Species	*a*	*a*			*b*
t.h.r.	2.46	2.46			2.33
o.p.p.	≈2.0	≈2.0			≈2.1
Species	$Al(OH)_3$	$GaO(OH){\cdot}H_2O$			$Cr(OH)_3{\cdot}3H_2O$
t.h.r.	3.0	3.0			3.0
o.p.p.	≈3.0	≈3.0			≈3.0
Species	$[Al(OH)_4]^-$	$[Ga(OH)_4]^-$	$[Zn(OH)_4]^{2-}$		$[Cr(OH)_4]^-$
t.h.r.	4.0	4.0	4.0		4.0
o.p.p.	4.0	4.0	4.0		None

t.h.r. = Theoretical hydrolysis ratio, o.p.p. = observed plateau position. [a] $[MO_4M_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ tridecamer. [b] Proposed $[Cr_{12}(OH)_{28}(H_2O)_{12}]^{8+}$ dodecamer.



Scheme 1

contain $[Al(OH)_4]^-$ and $[WO_4]^{2-}$ ions in a 1 : 12 mole ratio. Upon the addition of acid the tungstate ions become octahedrally co-ordinated and come to surround a central tetrahedral aluminium. As is true for the Al_{13} polyoxocation, the mechanism of formation of the heteropoly oxometalates has not been established.[4] The fact that complexes such as the α-$[H_2W_{12}O_{40}]^{6-}$ ion, which is missing the central tetrahedral heteroatom,[4] can form may mean that a central tetrahedral species is also not necessary for the ε-isomer polyoxocations (using the Baker–Figgis notation[2]). This could mean that an analogous situation exists for chromium, with a $[Cr_{12}(OH)_{28}(H_2O)_{12}]^{8+}$ ion being formed. Such an ion would be more likely to have an ε than an α isomeric structure, as there would not be the problem of high metal charge leading to a preference for apical linkages. It may also mean that it might be possible to form isostructural compounds in which other ions such as Zn^{II} or Ga^{III} substitute into the central tetrahedral position (*i.e.* $ZnCr_{12}$ and $GaCr_{12}$).

Further studies of chromium salts precipitated using varying counter ions may be able to confirm or disprove whether this postulated dodecameric structure is correct.

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