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The coordination chemistry of periodate and tellurate ligands

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Contents

Abstract

The review describes the coordination chemistry of periodate $[IO_6H_{5-n}]^{n-}$ and tellurate $[TeO_6H_{6-n}]^{n-}$ ligands with both main group and transition metal centres. Relevant chemistry of periodic and telluric acids and their salts are reviewed, followed by discussion of the

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application of structural (single-crystal X-ray diffraction, PXRD, EXAFS) and spectroscopic (vibrational, UV-visible, multinuclear NMR) techniques to study their complexes. The known complexes of these anions with p-block metals, lanthanides and actinides, and d-block metals are systematically described, and the article concludes with an overview of the field and proposals for further studies. © 1997 Elsevier Science S.A.

Keywords: Tellurate ligands; Periodate ligands; X-ray crystallography; EXAFS; IR spectroscopy; Raman spectroscopy; UV-visible spectroscopy; NMR spectroscopy

1. Introduction

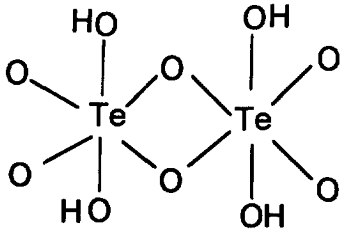
Many oxyanions including for example nitrate $[NO_3]^-$, sulfate $[SO_4]^{2-}$, and perchlorate $[ClO_4]^-$, can function as O-donor ligands towards transition metal or main group metals [1]. Although homoleptic examples are known including $[Cu(O_2NO)_2]$, and $[Cu(O_3ClO)_2]$, these are usually formed only in the absence of other ligands (including water), indicating that the binding to the metal is relatively weak. In fact the majority of complexes contain other ligands with the oxoanion weakly coordinated to one or more "free" sites on the metal centre. A consequence of the weak binding is that the oxyanion often dissociates in solution in polar solvents. The tellurate and periodate ligands which form the subject of this review differ in a number of ways from the behaviour described above. Firstly the forms present are based upon the pseudooctahedral acids $[Te(OH)_6]$ and $[IO(OH)_5]$, secondly the coordination to the metal is usually strong and remains even in aqueous solution and, thirdly the ions are able to bind to and stabilise unusually high oxidation states of the metal such as copper(III) or nickel(IV). Before describing the coordination chemistry of these two anions, it is useful to review the relevant chemistry and structures of periodic and telluric acids and their salts.

2. Telluric and periodic acids and derived ions

In contrast to the tetrahedral anions $[SO_4]^{2-}$, $[SeO_4]^{2-}$, $[ClO_4]^-$, and $[BrO_4]^-$, the heavier analogues tellurate and periodate have a more complicated chemistry due to the ability of the tellurium and the iodine to achieve 6-coordination. The free acids ortho-telluric H_6TeO_6 and ortho-periodic acid H_5IO_6 are members of the series $[Sn(OH)_6]^{2-}$, $[Sb(OH)_6]^-$, $[Te(OH)_6]$, $[IO(OH)_5]$ and $[XeO_2(OH)_4]$ based upon octahedrally coordinated central atoms in their highest oxidation states. The formulae will be written subsequently in the latter way, since this reflects the structural units present.

2.1. Telluric acid

Telluric acid, $[Te(OH)_6]$, is a white air-stable crystalline solid which exists in both monoclinic ($P2_1/n$) and cubic ($F4_132$) forms, and a third tetragonal form has been claimed [2–6]. A tetrahydrate $[Te(OH)_6]\cdot 4H_2O$ can be crystallised from aqueous solution below 10°C and is tetragonal ($I4_1/a$) [7]. All contain discrete $Te(OH)_6$ octahedra linked by H-bonding. Telluric acid forms many adducts with inorganic and organic compounds held together by hydrogen bonds, an area which has recently been reviewed [2]. On heating, $[Te(OH)_6]$ loses water to give "polymeta-telluric acid", $(H_2TeO_4)_n$, a white amorphous powder, whilst on heating in a sealed tube a viscous liquid "allotelluric acid" $(H_2TeO_4)_3 \cdot (H_2O)_4$ forms. The structure of neither form is known. One other acid has been made in crystalline form by hydrothermal synthesis, tetraoxotelluric acid $[TeO_2(OH)_2]$, which consists of sheets of corner sharing TeO_6 octahedra ($P2_1/c$) [8].



Scheme I.

All six protons in $[Te(OH)_6]$ can be removed under appropriate conditions, although in marked contrast to sulfuric or selenic acids, it is a weak acid ($K_1 \sim 2 \times 10^{-8}$, $K_2 \sim 10^{-11}$, $K_3 \sim 3 \times 10^{-15}$) [9]. Irrespecive of the stoichiometry, almost all metal tellurates contain the tellurium in an octahedral (O_6) environment. In $M^I_6[TeO_6]$ ($M^I_6 = KNa_5$, K_4Na_2, etc.) or $M^{II}_3[TeO_6]$ ($M^{II} = Ca$, Mg, Cu, etc.) there are isolated $[TeO_6]^{6-}$ anions with d(Te–O) ca. 1.91 Å [10–13]. Distorted octahedra are present in $K[TeO(OH)_5]$ [14], $[NH_4]_2[TeO_2(OH)_4]$ [15], and $Ag_2[TeO_2(OH)_4]$ [16], with d(Te–OH) ca. 0.1 Å longer than d(Te–O). The $Na_2[TeO_4]$ and $Sr[TeO_4]$ do not contain tetrahedral "sulfate-like" ions, rather TeO_6 octahedra sharing adjacent edges linked into infinite chains are present [17,18], and similar chains are found in $K[TeO_3OH]$ and $NH_4[TeO_3OH]$ [19,20]. In the $M_4[TeO_5]$ ($M = Li$ or Na) isolated edge-sharing bi-octahedra $[O_4Te(\mu\text{-}O)_2TeO_4]^{8-}$ are present [21], and there are oxo-hydroxo analogues in $Na_2K_4[Te_2O_8(OH)_2] \cdot 14H_2O$, $K_4[Te_2O_6(OH)_4] \cdot xH_2O$ [22,23]. Notably in the latter the OH groups are *cis* to the TeO_2Te bridge (Scheme I).However in $Cs_2K_2[TeO_5]$ isolated trigonal bipyramidal anions are present [24], and in $Rb_6[Te_2O_9]$ both discrete tbp TeO_5 and tetrahedral TeO_4 groups were found [25]. These latter salts were made by heating mixtures of the appropriate oxides in sealed tubes, but thus far all tellurates obtained from aqueous media, appear to contain TeO_6 units.

2.2. Periodic acid

A short review on periodic acid and metal periodates was published in 1967 [26]. *Ortho*-periodic acid (sometimes called *para*-periodic acid), $[IO(OH)_5]$ is a white crystalline solid (monoclinic $P2_1/n$) with octahedrally coordinated iodine d(I–O) = 1.78 Å and d(I–OH) = 1.89 Å, the molecules being linked into a 3D network by

H-bonding [27]. On heating in air it loses water to form $H_7I_3O_{14}$, and on heating in vacuum water loss gives *meta*-periodic acid HIO_4, $[IO_3(OH)]$. Various other periodic acids were reported in the older literature, but none appear to have been confirmed by more recent work. Solid $[IO(OH)_5]$ is protonated by concentrated $HClO_4$, H_2SO_4 or H_2SeO_4 to $[I(OH)_6]^+$ (cf. $[Te(OH)_6]$), obtained as solid salts in $[I(OH)_6][HSO_4]$ and $[I(OH)_6]_2[SO_4]$ [28,29]. More pertinent to the present review are the various equilibria observed in aqueous solutions of $[IO(OH)_5]$ involving deprotonation, dehydration and dimerization:

$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad K = 5.1 \times 10^{-4}$

$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \quad K = 4.9 \times 10^{-9}$

$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \quad K = 2.5 \times 10^{-12}$

$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O \quad K = 29$

$2H_4IO_6^{2-} \rightleftharpoons H_2I_2O_{10}^{4-} + 2H_2O \quad K \text{ ca. } 800$

The old literature on periodate salts is very confused and structures deduced from analytical data alone are clearly unreliable. Siebert [29,30] used vibrational spectroscopy to distinguish salts containing the tetrahedral $[IO_4]^-$ anion from octahedral $[IO_6H_{5-n}]^{n-}$ salts. It is also possible to identify the tetrahedral and octahedral forms in aqueous solution by ^{127}I-NMR spectroscopy [31], although the very broad lines ($W_{1/2} = 1000$–$20\,000$ Hz) resulting from the fast quadrupolar relaxation of the iodine nucleus, preclude distinguishing the monomeric and dimeric forms containing octahedrally coordinated iodine.

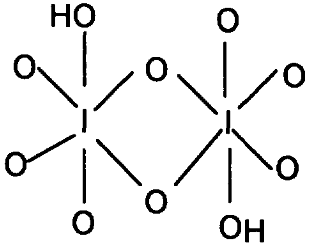
The regular tetrahedral $[IO_4]^-$ ion (d(I–O) = 1.78 Å) is present in the alkali-metal and ammonium salts [32,33], whilst the $M_3[IO_5]$ (M = K, Rb or Cs) contain square-pyramidal $[IO_5]^{3-}$ ions [34]. Structurally characterised examples containing discrete pseudo-octahedral IO_6 groups include: $K_4Li[IO_6]$ [35], $K_2Na[IO_4(OH)_2] \cdot 4H_2O$ (*cis* OH groups) [36], $Na_2[IO_3(OH)_3]$ [37], $Na(H_3O)[IO_3(OH)_3]$ [38], $[Mg(H_2O)_6][IO_3(OH)_3]$ [39], $[NH_4]_2[IO_3(OH)_3]$ [40], $Li[IO_2(OH)_4] \cdot H_2O$ [41]. Typically d(I–O) is ca. 1.81-1.85 Å and d(I–OH) ca. 0.1 Å longer. Dimeric anions based upon edge-sharing octahedra are also known including $K_4[O_3(OH)I(\mu\text{-}O)_2I(OH)O_3] \cdot 8H_2O$ (Scheme II)[42] and face sharing bioctahedra are found in $K_4[O_3I(\mu\text{-}O)_3IO_3]$ (Scheme III)[43].

3. Physical measurements

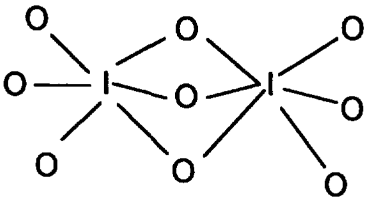
Systematic coverage of the properties of the complexes is in Section 4, but here some general points about the application of various techniques to the study of these complexes are discussed.

3.1. X-ray crystallography

For molecular complexes obtainable as crystals, single-crystal X-ray diffraction is the most reliable method of establishing their constitution, whilst for crystalline



Scheme II.



Scheme III.

materials produced only as powders, X-ray powder diffraction (PXRD) may, if the pattern can be indexed, identify the space group and establish the basic structure.

The study [44,45] of $M^I[SnIO_6]$ (M = Na-Cs, NH_4) illustrates the use and limitations of PXRD. The space group was identified as $P6_322$, and the structure consists of hexagonal close packed double layers of oxide ions, with Sn and I in octahedral holes ordered within the layers, and with the alkali metal between the layers. Ordering of the layer stacking along the *c*-axis occurs with alternating I and Sn, which is also found in the lead analogues, but not in the $M[GeIO_6]$ compounds which belong to the space group P312 with the *c*-axis halved. The PXRD patterns for the $M[SnIO_6]$ compounds (Fig. 1) show the increase in the *c* cell dimension with the size of M, where reflections with $l>0$ shift systematically with changes in $r(M^+)$. Rietveld refinement of the data leads to atom positions, although the positions of the weakly diffracting oxygen may not be obtained with high precision. EXAFS spectroscopy (Section 3.2) combined with PXRD overcomes this problem. A program for simultaneously refining PXRD and EXAFS data has been applied to $Rb[GeIO_6]$ as a test compound [46].

Single-crystal X-ray diffraction is necessary to establish the more complicated structures of the molecular periodates and tellurates. The first problem is that of obtaining good quality single crystals. Often the complexes are soluble only in water and stable over a limited pH range, which limits the conditions under which crystal growth can be attempted. It has been observed that often mixed counter cations are more successful in producing crystals than species containing a single cation, e.g., $Rb_2Na_4[OsO_2\{TeO_4(OH)_2\}_2]\cdot 16H_2O$ or $Na_5K[RuO_2\{IO_5(OH)\}_2]\cdot 8H_2O$ [47,48]. Indeed examples of crystals grown from strongly alkaline solutions in glass vessels sometimes contain Na^+ in addition to the cation originally present, e.g.,

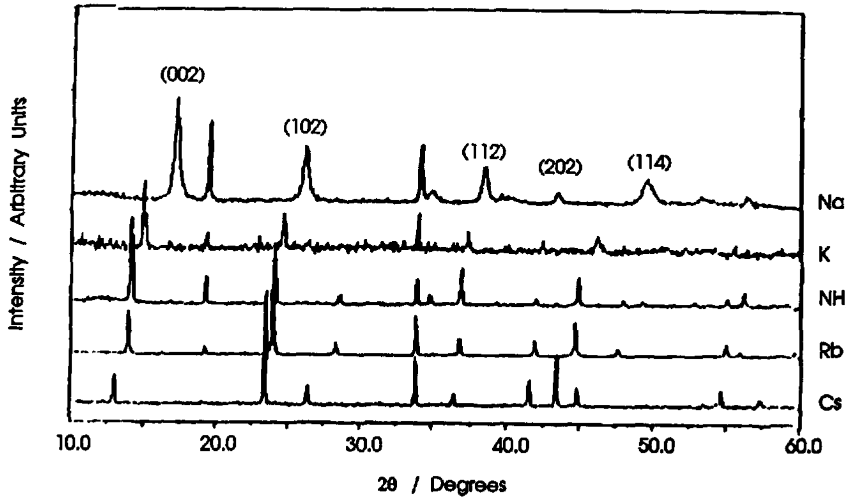


Fig. 1. PXRD patterns of M[$SnIO_6$] from Ref. [45].

$K_4Na_2[Pt(OH)_2\{IO_5(OH)\}_2]\cdot 10H_2O$ [49], again a reflection of the stringent packing requirements that need to be met.

The periodato or tellurato ligands in the molecular periodate or tellurate complexes are usually protonated to some degree (based upon charge balance arguments supported by vibrational spectroscopic data — see below) and the crystals are often heavily hydrated. The very weakly diffracting hydrogen atoms are rarely observed convincingly in the electron density maps, and thus discrimination of I(Te)=O and I(Te)–OH groups has usually been made on the basis of the longer (typically ca. 0.1 Å) I(Te)–OH bonds. The presence of hydrogen-bonded networks involving the anions and the water of hydration also complicates the interpretations [47–50]. In a number of cases, particularly in some of the heteropolyanion clusters, the hydrogen atom positions have not been identified.

3.2. Extended X-ray absorption fine structure (EXAFS)

EXAFS spectroscopic studies provide information about the local environment of the primary absorber atom, specifically the distances to surrounding atoms out to ca. 5 Å, the coordination numbers in the various shells, and information about the identity of the back-scattering atoms [51]. Since the various parameters are correlated to some degree, and there are limitations about the number of independent variables that can be extracted from the data, it is desirable to have good model compounds, or to be able to fix some of the variables during the data processing. A good model compound may be a related complex for which the X-ray single-crystal structure is known, and then EXAFS data on this can be used to check the data collection, data quality and obtain reliable estimates of some of the variables used to fit EXAFS data on compounds whose structures are not known. Alternatively

PXRD data or spectroscopic data may give information about the identities of the atom(s) and the coordination numbers in the various shells surrounding the primary absorber, and in the EXAFS data treatment these can be fixed.

Multi-edge EXAFS studies using the iodine or tellurium K-edges (the I or Te L_{III}-edges are of little use due to the short data sets resulting from the proximity of the corresponding L_{II}-edges) and the metal K- (for 3d or 4d metals) or L_{III}-edges (5d metals) have been reported for a number of systems and exemplify the approach and the information obtained. For the layered periodates $M[PbIO_6]$ [44,45,52], examples of the background subtracted iodine K-edge and lead L_{III}-edge data are shown in Fig. 2 along with the corresponding Fourier transforms. From the PXRD data it was possible to fix the coordination numbers of the lead as six oxygens for shell one, and three iodines as shell two, whilst for the iodine data shell one contains six oxygens and shell two three lead atoms. Note also that the multi-edge EXAFS approach allows some checking of the internuclear distances since *d*(I...Pb) is the second shell distance in both sets of data. More remote shells were not a significant feature of the EXAFS in this case, but in the germanium K-edge data of $K[GeIO_6]$ a further feature at ca. 5 Å corresponded to the *d*(Ge...Ge) distance and this was in excellent agreement with the *a* cell parameter obtained from PXRD. For crystalline complexes that cannot be obtained as single crystals the PXRD-EXAFS approach is the best currently available to obtain structural information, and for

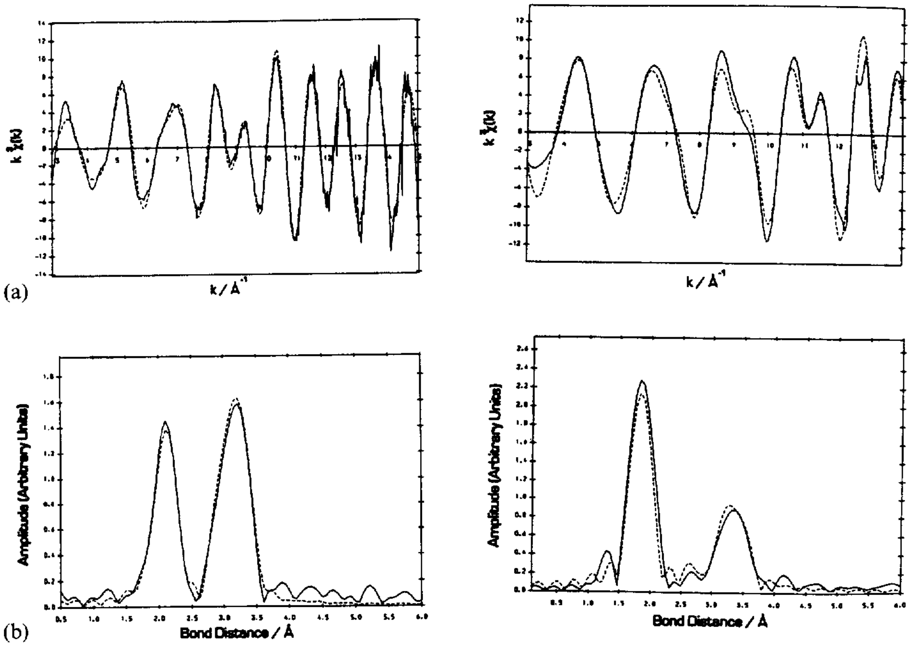


Fig. 2. Examples of lead L_{III} and iodine K-edge EXAFS spectra of $K[PbIO_6]$. (a) Background subtracted EXAFS and (b) the corresponding Fourier Transforms. Full line, experimental data; broken line, theoretical fit. From Ref. [45].

amorphous materials and poorly crystalline ones lacking sufficient long-range order to produce an adequate powder pattern, EXAFS is the only way to obtain some bond length information.

The multi-edge EXAFS approach has also been applied to variety of molecular periodate and tellurate complexes [47]. Taking as our example, the $[OsO_2\{TeO_4(OH)_2\}_2]^{6-}$ anion known from the X-ray single-crystal study to contain a pseudooctahedral osmium centre with two *trans* osmyl groups $d(Os{=}O) = 1.750(5)$ Å and four oxygens from two chelating $TeO_4(OH)_2$ groups $d(Os{-}O) = 2.014(1)$ Å with the non-bonded $d(Os...Te) = 3.115(2)$ Å. The osmium L_{III} edge EXAFS data refined straighforwardly to fit three shells $d(Os{=}O) = 1.75$ Å[1], $d(Os{-}O) = 2.02$ Å and $d(Os...Te) = 3.10$ Å, clearly in excellent agreement. However the fitting of the Te K-edge data was more problematic, and illustrates a general problem in these compounds which arises from the fact that the six oxygens fitted as shell one have different $d(Te{-}O)$ distances (from the X-ray data), two short 1.8474(5), 1.840(5) Å (Te=O), and four longer 1.978(5), 1.991(5), 1.968(5), 1.984(5) Å (Te–OH and Te–O(Os)). The EXAFS technique is unable to resolve small bond length differences and usually they are grouped into one at an average distance. Moreover the data treatment assumes a Gaussian distribution of distances, and if the actual distances have a markedly non-Gaussian spread, then the EXAFS determined (average) bond length and the average from X-ray single-cystal work may be significantly different. In this case the EXAFS data fitted to one shell (6 × O) gave $d(Te{-}O) = 1.94$ Å, whilst a two shell fit (2 × O, 4 × O) gave $d(Te{-}O) = 1.86$, 1.97 Å respectively, and a statistical treatment showed the two shell fit to be permissible in this case. The non-bonded $d(Te...Os)$ was insensitive to the treatment adopted for the Te–O shells and refined to 3.11 Å. However for the corresponding periodate $[OsO_2\{IO_5(OH)\}_2]^{6-}$ the iodine K-edge data had to be fitted to a single shell of six oxygen atoms, attempts to split this shell into shorter I=O and longer I–OH and I–O(Os) failed. The best treatment of the data has to be decided on a compound by compound basis and is discussed in more detail in [47]. Structural information from multi-edge EXAFS studies lacks the fine detail that single-crystal X-ray work can provide, but is very useful when crystals are not available. EXAFS can also be used to study complexes in solution; for example the ^{195}Pt-NMR chemical shift of $[Pt(OH)_2\{IO_5(OH)\}_2]^{6-}$ varies with the pH of the solution, but a Pt L_{III}-edge EXAFS study revealed the same basic structural unit in both solid and solution, and hence it was inferred that the NMR shifts reflect different degrees of protonation, rather than a gross structural change [49].

3.3. IR and Raman spectroscopy

The IR and Raman spectra of various periodate anions were discussed by Siebert [29,30] and the spectra of a variety of molecular periodate complexes have recently been reported by Griffith et al. [53]. Fig. 3 shows the vibrational spectra of

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[1] The systematic errors in EXAFS determined bond lengths for well-defined shells are usually quoted as ca. ±0.02 Å.

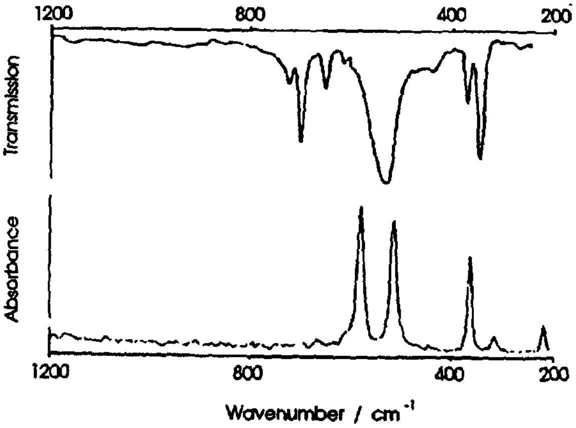

Fig. 3. IR and Raman spectra of K[NiIO$_6$] from Ref. [52] by permission of the Royal Society of Chemistry.

K[NiIO$_6$] typical of a layered periodate [52]. The completely deprotonated periodate groups show no strong vibrations greater than ca. 750 cm^{-1}, with ν(IO) modes in the range ca. 750–600 cm^{-1} and lower frequency vibrations due to ν(NiO) and δ(OIO). Attempts to produce more detailed assignments based upon the site symmetry of the iodine or a full factor group analysis have been unsuccessful [44,54] The vibrations are only very slightly influenced by changes in the alkali-metal present. The heavier alkali metal metaperiodates M[IO$_4$] are poorly soluble in water and often contaminate periodato-complexes made at low pH. The presence of the tetrahedral $[IO_4]^-$ ion is easily recognised [30] by a strong feature ca. 850 cm^{-1} (ν^3) since the octahedral $[IO_6H_{5-n}]^{n-}$ groups absorb <800 cm^{-1}.

Vibrational spectra typical of a hydrated periodate, in this case $Na_5[Ag\{IO_5(OH)\}_2]\cdot 12H_2O$ [53], are shown in Fig. 4. The very strong and broad IR features near 3500 and 1640 cm^{-1} are the ν(OH) and δ(HOH) of the lattice water and obscure the ν(OH) of the $[IO_5(OH)]^{5-}$ group. However a medium intensity feature near 1100 cm^{-1} which shifts to ca. 850–900 cm^{-1} on deuteration[2] is assignable as δ(IOH) and is the best fingerprint for protonation of the periodato-groups. Vibrational spectra have also been reported for the Anderson type heteropolyanions $[IM_6O_{24}]^{5-}$ (M=W or Mo) and $[Fe_4I_3O_{24}H_{15-n}]M'_n$ (M'=Na, K, etc.) [53,55]. Despite partial deuteration of the latter compounds, attempts to identify the δ(IOH) modes were unsuccessful.

The vibrational spectra of tellurate ligands have been less studied, but conform closely to those of the periodate analogues. For example in $Na_7K[Mn\{TeO_4(OH)_2\}_2]\cdot 3H_2O$ the major features in the IR spectrum and their assignments are (cm^{-1}): 3300 ν(OH); 1660 δ(HOH); 1153 δ(TeOH); 690, 563

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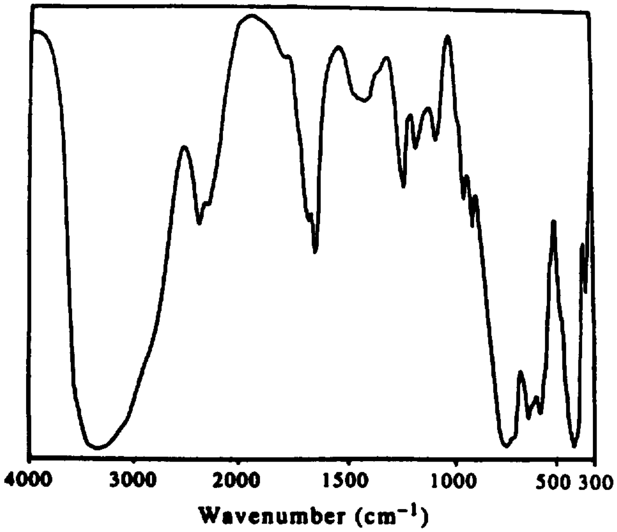
[2] In our experience full deuteration of these salts is almost impossible to achieve, but partial deuteration by dissolution or suspension of the complex in D_2O followed by pumping to dryness in vacuum, is adequate to allow identification of this vibration.



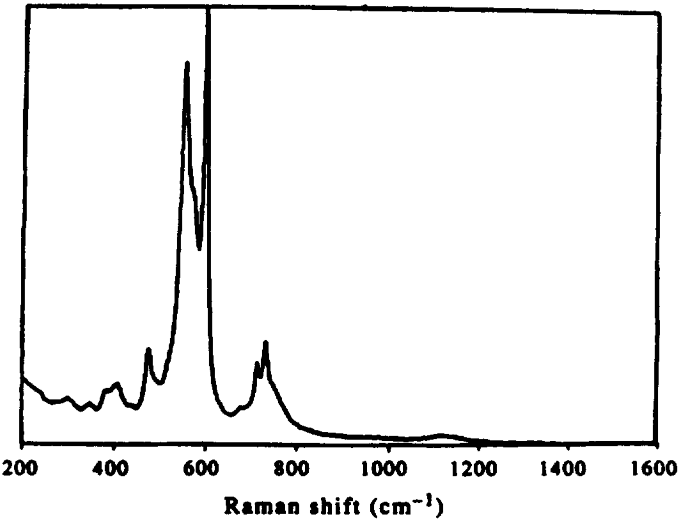


Fig. 4. IR and Raman spectra of $Na_5[Ag\{IO_5(OH)\}_2]\cdot 12H_2O$ from Ref. [53] by permission of Pergamon Press.

ν(TeO); 486, 348 ν(MnO) + ν(TeO). Raman features were observed at 737, 682, 621, 590, 513, and 380 cm^{-1} [45,56].

3.4. UV-visible spectroscopy

Interest in the electronic spectra of periodato- or tellurato-complexes arises mainly from the fact that in some cases they provide examples of the spectra of unusually high oxidation states of the metal ions. The presence of transitions in the UV region at ca. 220 nm (45 450 cm^{-1}) in the $[IO_6H_{5-n}]^{n-}$ ions and at ca. 210 nm (47 600 cm^{-1}) in $[TeO_6H_{6-n}]^{n-}$ should be noted [57,58].

3.5. *Multinuclear NMR spectroscopy*

Tellurium-125 (I = 1/2, 6.99%, 31.55 MHz, $D_p = 2.21 \times 10^{-3}$, $D_c = 12.5$) is a relatively straightforward nucleus to observe and has a large chemical shift range ca. 4000 ppm. Telluric acid in water has $\delta = 713$ (relative to Me_2Te at $\delta = 0$) and coordination of tellurate ions to a metal centre results in moderate high frequency shifts in the resonance, e.g., in $[M\{TeO_4(OH)_2\}_2]^{5-}$ M = Cu $\delta = 774.5$, M = Ag $\delta = 774$, M = Au $\delta = 753$ [59]. The resonance in the silver complex was a broad doublet due to coupling to $^{107/109}Ag$ of ca. 75 Hz. The $\delta(^{125}Te)$-NMR spectrum of the dimeric anion in $Na_8K_2H_4[Pd_2Te_4O_{24}H_2]$ showed two resonances in a 1:1 ratio at 804 and 852 ppm, consistent with the crystal structure which revealed two terminal tellurate groups and two bridging tellurates; however in the initial reaction mixture only a single resonance at 801 ppm was found suggesting a monomer was the formed first (cf. $[Pt(OH)_2\{TeO_5(OH)\}_2]^{8-}$) [60]. In contrast the ^{125}Te-NMR spectra of solutions of $K_6Na_2[Pt(OH)_2\{TeO_5(OH)\}_2]$ showed three resonances (Fig. 5) each with ^{195}Pt satellites (^{195}Pt, $I = 1/2$, 33%) which vary in intensity with the pH of the solution and are thought to due to different degrees of protonation of the same basic anion. Three resonances were also observed in the ^{195}Pt-NMR spectra which can be correlated with those in the tellurium spectra via the ^2J coupling constants [60].

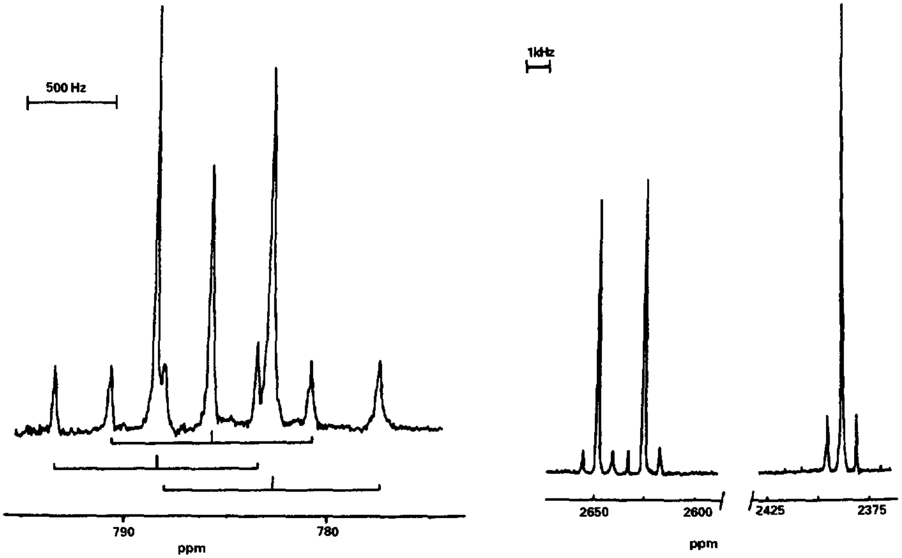


Fig. 5. The $^{125}Te\{^1H\}$-NMR spectrum (left) and $^{195}Pt\{^1H\}$-NMR spectrum (right) of $K_6Na_2[Pt(OH)_2\{TeO_5(OH)\}_2] \cdot 12H_2O$ in water from Ref. [60] by permission of the American Chemical Society.

In contrast to the $I=1/2$ ^{125}Te nucleus, ^{127}I is quadrupolar (^{127}I, $I=5/2$, 100%, 20.1 MHz, $D_p=9.34\times10^{-2}$, D_c 5.3×10^2, $Q=-0.79\times10^{-28}$ m^2) and the large quadrupole moment results in very broad (often unobservably broad) lines unless the iodine is situated in an environment of cubic symmetry, effectively either a regular tetrahedral or octahedral one. In coordinated periodates, the iodine is in a distorted octahedral environment, and although a resonance can usually be observed it may be 20–30 kHz broad. Since ^{127}I is relatively a very receptive nucleus, the appearance of a resonance at ca. 2800–3100 ppm (relative to $I^-=0$) is good evidence for an $[IO_6H_{5-n}]^{n-}$ group (the chemical shift scale is at least 4000 ppm based on the few known values), but correspondingly the broad lines do not allow identification of different environments or indicate whether more than one complex is present [31]. A typical spectrum that of $[OsO_2\{IO_5(OH)\}_2]^{6-}$ is shown in Fig. 6.

4. Periodate and tellurate complexes

Complexes of both ions have been reported for many of the metallic elements, and Fig. 7 gives an indication of the distribution of reported complexes across the periodic table. Generally the tellurate complexes are less numerous and less thoroughly characterised than the periodates. Even for the periodates, examination of Fig. 7 shows little hard knowledge about the early d-block metals and some surprising gaps among later groups.

The first reports of materials subsequently identified as periodate or tellurate complexes were made over 100 years ago, and scattered reports of such compounds appeared in the next 50 years [9,26]. The structures and even the correct formulations of many of these compounds have only been established in the last 30 years. In some cases it is impossible to identify species reported in early papers, particularly those obtained in an impure form or only in solution due to the lack of reported data. This review will concentrate upon recent work, and references to the older literature will only be made in the case of compounds for which no recent reports were found.

This review seeks to provide coverage of molecular metal periodato- and tellurato-

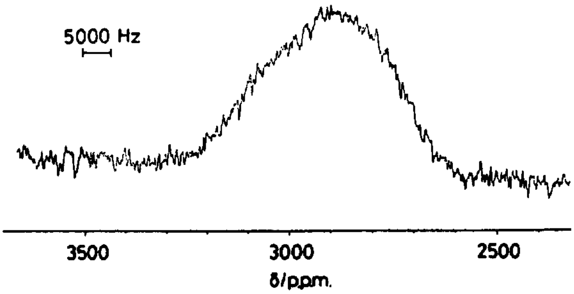
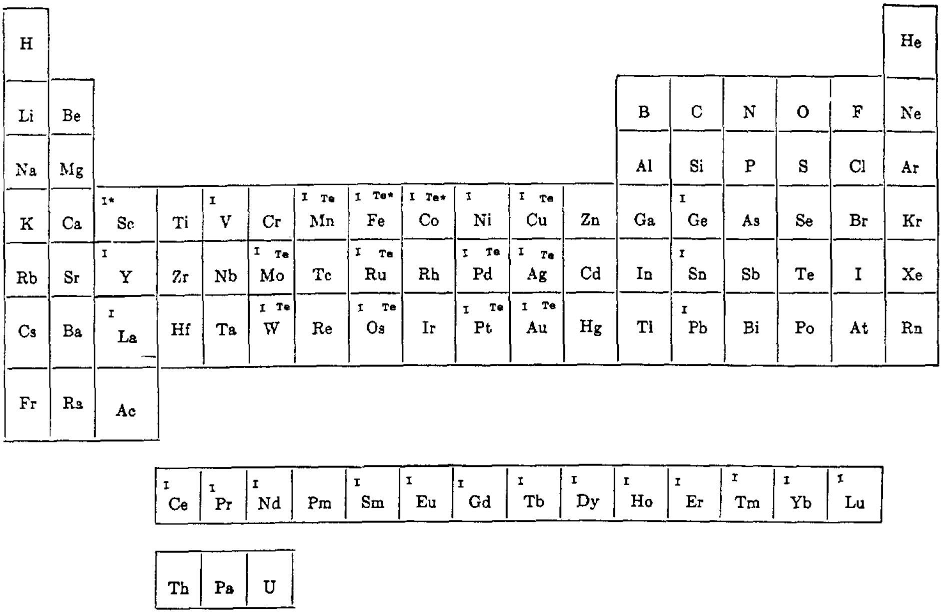


Fig. 6. The ^{127}I-NMR spectrum of $[OsO_2\{IO_5(OH)\}_2]^{6-}$ in water from Ref. [31] by permission of the Royal Society of Chemistry.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	I* Sc	Ti	I V	Cr	I Te Mn	I Te* Fe	I Te* Co	I Ni	I Te Cu	Zn	Ga	I Ge	As	Se	Br	Kr
Rb	Sr	I Y	Zr	Nb	I Te Mo	Tc	I Te Ru	Rh	I Te Pd	I Te Ag	Cd	In	I Sn	Sb	Te	I	Xe
Cs	Ba	I La	Hf	Ta	I Te W	Re	I Te Os	Ir	I Te Pt	I Te Au	Hg	Tl	I Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

I Ce	I Pr	I Nd	Pm	I Sm	I Eu	I Gd	I Tb	I Dy	I Ho	I Er	I Tm	I Yb	I Lu

Th	Pa	U

Fig. 7. Distribution of periodate and tellurate complexes in the periodic table. Key: I or Te – at least one thoroughly characterised periodate or tellurate complex; I* or Te* – complexes exist but are incompletely characterised (usually lacking structural data); where neither symbol appears no complexes have been reported, or claims contain little data.

complexes. It also includes species like the layered periodates $M[M'IO_6]$ (M = alkali metal, M′ = Mn, Ni, Sn etc) which can be made by solution methods, and which can be described either as polymeric units based upon $M'O_6$ and IO_6 octahedra sharing edges, or as close packed oxide layers with M′ and I in the octahedral holes. Tellurate analogues do not seem to be formed in solution, but species such as $Li_2[TiTeO_6]$ or $K_2[GeTeO_6]$ made by heating together the constituent oxides have been intensively studied. These have structures based upon TeO_6 and MO_6 octahedra sharing edges and are thus structurally related to the periodates. These tellurates are usually viewed as mixed metal oxides rather than complexes and have (somewhat arbitrarily) been excluded.

4.1. Complexes of the P-block metals

Little is known about group 13 compounds. An aluminium periodate with a 3:1 I:Al ratio formulated $Al(IO_4)_3 \cdot 12H_2O$ probably contains $[Al(H_2O)_6]^{3+}$ ions [61]. Two gallium(III) periodates formulated $Li_7[Ga(IO_6)_2] \cdot 4H_2O$ and $[Ga_5(IO_6)_3] \cdot H_2O$ have been reported [62,63] but the structures are unknown. Poorly characterised tellurates of Al, Ga and In are precipitated from aqueous solutions of KOH, $[Te(OH)_6]$ and the appropriate MCl_3 (M = Al, Ga or In) [64].

Group 14 periodates are much better characterised. Frydrych reported [65–67] alkali-metal germanium, tin and lead periodates of formula M[M'IO$_6$] (M = NH$_4$, K, Rb, Cs; M' = Ge, Sn, Pb) formed by reaction of MNO$_3$ and [IO(OH)$_5$] with GeCl$_4$, SnCl$_4$ or [Pb(O$_2$CMe)$_4$] in aqueous acetic acid. Subsequently Na[GeIO$_6$] and Na[SnIO$_6$] were obtained [54,68], but attempts to prepare Na[PbIO$_6$], lithium analogues or to incorporate silicon, were unsuccessful [44,68]. The germanium and tin compounds are white, the lead yellow powders, insoluble in water and unaffected by cold dilute acids or bases. The structures established by PXRD are based upon double layers of hexagonally close packed oxide ions with M' and I occupying octahedral holes within the layers and alkali metals between the layers (Fig. 1, Fig. 8). Alternatively the structure can be described in terms of M'O$_6$ and IO$_6$ octahedra sharing edges to form a two-dimensional sheet with the M ions between these sheets. The germanium compounds belong to the space group P312 with identical atoms above each other along the *c*-axis (Section 3.1), whereas in the Sn or Pb compounds the space group is P6$_3$22 with stacking alternating I and M' above each other [44,65–68]. More precise combined PXRD and multi-edge EXAFS (Fig. 2) studies have confirmed the structures [44,52]. As expected from the structures the M'–O and I–O distances are almost independent of M and are *d*(Ge–O) = 1.89 Å, *d*(Sn–O) = 2.05 Å, *d*(Pb–O) = 2.15 Å and *d*(I–O) = 1.87 Å. The IR and Raman spectra [45,54,68] are typical of layered periodates (Section 3.3) and confirm the absence of constitutional water or protonation of the periodate groups. Attempts to prepare analogous tellurates M$_2$[M'TeO$_6$] or MH[M'TeO$_6$] from aqueous solutions have been unsuccessful [45], although for example M$_2$[GeTeO$_6$] with a pyrochlore structure have been made from the constituent oxides at high temperatures [69].

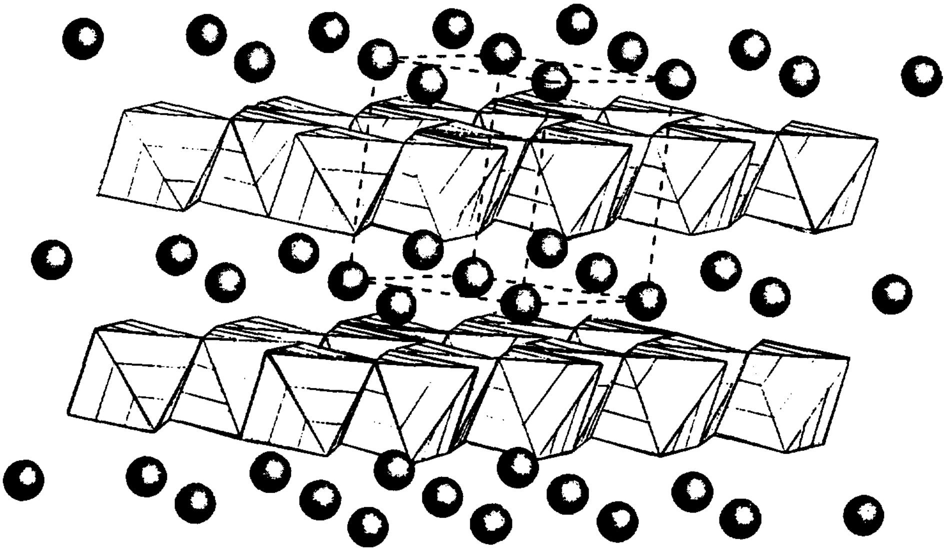


Fig. 8. The structure of M[GeIO$_6$] from Ref. [45].

4.2. Complexes of the lanthanides and actinides

The reaction of scandium, yttrium and lanthanide (except Ce) salts with periodate ions in aqueous solution produce compounds with a metal:periodate ratio of 1:1 obtained as hydrates and variously formulated as $LnH_2IO_6 \cdot nH_2O$ or $LnIO_5 \cdot 4H_2O$ [70–78]. Vibrational spectroscopy and subsequently X-ray crystallography showed that the compounds of the elements Pr–Lu and Y were isostructural $[Ln(H_2O)_3IO_4(OH)_2]$ and contain linked $IO_4(OH)_2$ octahedra and distorted bi-capped trigonal prismatic LnO_8 groups (Fig. 9) [75–78]. The IR spectrum of the lanthanum complex differs in detail from those of the other lanthanides and it may have a different structure [74]. Scandium compounds with Sc:I ratios of 1:2 and 2:3 have also been reported [70].

Cerium(III) salts react with periodates to give impure cerium(IV) periodate, contaminated with cerium(III) iodate [79]. Pure $[CeHIO_6] \cdot 4H_2O$ is obtained as a deep yellow solid by precipitation of aqueous cerium(IV) solutions with periodate ions, or oxidation of Ce(III) salts and $[IO(OH)_5]$ in water with ozone [62,79–82]. The solid is insoluble in water, diamagnetic as expected for Ce(IV) and has a very weak IR band at ca. 1050 cm^{-1} which disappears on deuteration ((δ)IOH). The complex dissolves in concentrated aqueous MOH (M = K, Rb or Cs) to form pale yellow solutions from which alcohol precipitates $M[CeIO_6] \cdot 2H_2O$. Neither LiOH or NaOH dissolve $[CeHIO_6] \cdot 4H_2O$ but NaOH reacts with the latter in suspension to form $Na[CeIO_6] \cdot 3H_2O$. The solid alkali-metal salts have a broad UV-visible band at ca. 330 nm assigned as $IO_6 \rightarrow Ce(4f)$ charge transfer and lack the δ(IOH)

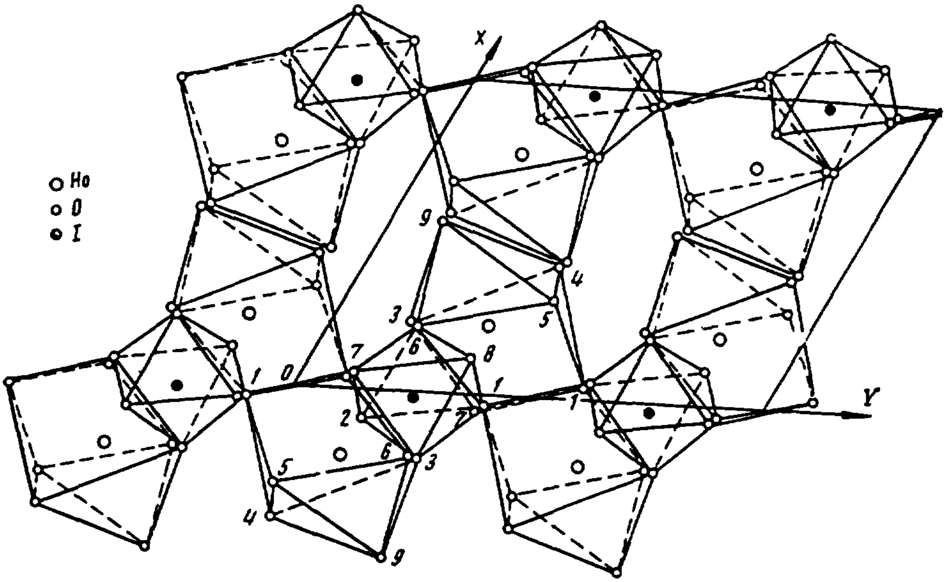


Fig. 9. The structure of $[Ln(H_2O)_3IO_4(OH)_2]$ (Ln = Pr–Lu) compounds from Ref. [75] by permission of the Royal Society of Chemistry.

vibration of the parent complex. PXRD studies showed the complexes are amorphous, but the iodine K-edge EXAFS revealed a first shell of six oxygens at 1.87 Å typical of an IO_6 group and two ceriums in shell two [82]. The Ce L_{III}-edge data was of limited value due to the short data sets, but placed an oxygen shell at ca. 2.28 Å although the coordination number could not be determined, the data fit being insensitive to varying the occupancy of the shell between six and eight oxygens. The structure of the $M[CeIO_6]\cdot nH_2O$ thus seems to differ from that of the layered periodates (Section 3.1), possibly the Ce(IV) ion is too large to fit in the octahedral holes, and adopts the more usual 8-coordination.

Attempts to prepare praseodymium(IV) analogues by ozonisation of praseodymium(III) nitrate mixed with periodate ions in concentrated alkali gave deep yellow materials of variable composition which decomposed to green Pr(III) on drying [45]. Ozonisation of aqueous terbium(III) nitrate solution containing KIO_4 and KOH is reported to give red-brown Tb(IV) solutions from which the appropriate alkali-metal nitrate precipitates $Li[TbIO_6]\cdot 16H_2O$, $Na[TbIO_6]\cdot 7H_2O$ and $K[TbIO_6]\cdot 8H_2O$ [83]. The colour and the magnetic measurements μ ca. 8 B.M. seem to confirm Tb(IV), but the constitution is unclear. The large amounts of water are particularly surprising in comparison with the Ce(IV) salts, and since Tb(IV) is not stable in water in the absence of coordinating anions at least part of the terbium coordination sphere must be periodate groups.

A material with the unlikely formula $[Ce(NO_3)_3]_3[H_2IO_6]$ (no evidence was given to support the constitution implied) has been used as a powerful oxidant towards a variety of organic substrates [84].

Little is known about actinide periodates — compounds claimed with little supporting data include: a white thorium periodate, apparently $ThIO_6\cdot 5H_2O$ precipitated from acidified thorium nitrate solution on heating with sodium periodate [80]; a yellow uranyl periodate $Li_{16}[UO_2I_6O_{50}]\cdot 8H_2O$ [62], and there are some solution studies of the UO_2^{2+}–IO_4^- system [85].

4.3. *Complexes of the group 4 and 5 metals*

Nothing seems to be known about Ti, Zr or Hf periodate complexes, apart from an old report of white materials with ratios Ti:I of 7:2 and Zr:I 3:2 [80].

A yellow periodatovanadate(V), $Na_6[H_2V_2I_2O_{16}]\cdot 10H_2O$ has been obtained and structurally characterised independently by two groups [86,87]. It is formed from reaction of periodic acid with $Na_3VO_4\cdot xH_2O$ or V_2O_5 in $NaHCO_3$. The structure (Fig. 10) consists of edge sharing $IO_5(OH)$ octahedra and VO_5 square pyramids, dimerised via vertex sharing. There are two terminal V=O groups, V–O(7) = 1.620(3) and V–O(8) 1.679(3) Å, three V–OI bridges V–O(1) 1.999(3), V–O(4) 2.093(3) and V–O(5) 1.901(3) Å. One of the bridging oxygens O(4′) may weakly interact with the second vanadium at 2.533(3) Å. The $\nu(V{=}O)$ bands occur in the Raman spectrum at 940 and 835 cm^{-1} [86]. The compound is poorly soluble in water and the ^{51}V-NMR spectra of such solutions show several pH dependent resonances at $\delta = -400$ to -600 typical of polyvanadates indicating it breaks up in solution; however the MAS-^{51}V-NMR spectrum of the powdered solid shows a single sharp resonance

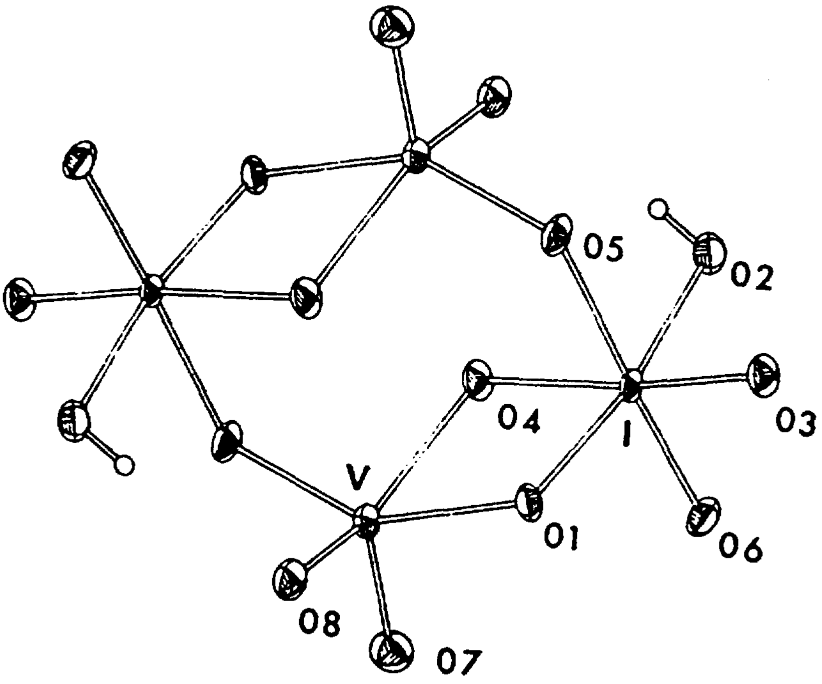


Fig. 10. The structure of $Na_6[H_2V_2I_2O_{16}] \cdot 10H_2O$ from Ref. [86] by permission of Zeitschrift für Naturforschung.

at −83 ppm [88]. Thermogravimetric studies of the decomposition of this complex show water lost in three stages and finally decomposition to $Na_3[VO_4]$ [89]. Periodatovanadates with a 2:1 V:I ratio precipitated as very poorly soluble yellow solids from reactions of V_2O_5 or $M_3[VO_4]$ ($M = Na$, K, NH_4) and H_5IO_6 in aqueous acid solution were reported in 1923 [90]. Re-examination [88] of these compounds has shown that the sodium salt obtained from weakly acid solution is $Na_6[H_2V_2I_2O_{16}] \cdot 10H_2O$, but at lower pH or with the larger K or NH_4 counter ions, species with a 2:1 ratio are formed. Preliminary PXRD studies show poor crystallinity, but it is possible that a heteropolyanion based upon a $V_4I_2O_{19}$ unit may be present.

Vanadium has been incorporated into molybdo- and tungsto-tellurates (Section 4.4). Little is known about niobium or tantalum complexes. There is an old report of compounds formulated $NbIO_6 \cdot 4.5H_2O$ and $TaIO_6 \cdot 1.5H_2O$ [91] which are presumably heteropolyanions of some form, and a brief report of a telluroniobate $K_8H_2[TeNb_{12}O_{38}] \cdot 13H_2O$, the formulation of the latter being based upon analysis and the determination of the unit cell parameters [92]. A detailed study is clearly necessary to fully characterise this material.

4.4. *Complexes of the group 6 metals*

The reaction of chromium(III) salts with periodate in either acid or basic solution results in oxidation to chromate, $[CrO_4]^{2-}$ with no evidence for periodato-complexes of intermediate oxidation states [45]. The long known compounds M[$CrIO_6$] (M = NH_4, K, etc.) prepared from $M_2[Cr_2O_7]$ and M[IO_3] in acid solution, which could from the formula be Cr(IV) complexes of an *ortho*-periodate, are in fact Cr(VI)–I(V) compounds. The X-ray structure of the potassium salt shows a tetrahedral CrO_4 group vertex linked to a trigonal iodate(V) IO_3 unit [93]. A brown powder formulated as [Cr(*o*-phenanthroline)$_2IO_6$] has been described [94]. The formulation as a Cr(V) complex is based upon the paramagnetism (1.94 B.M.), ESR and UV-visible spectra and analytical data.

In contrast to the dearth of chromium complexes, heteropolyanions of molybdenum and tungsten incorporating iodine or tellurium have been studied in considerable detail.

The reactions of [IO(OH)$_5$] with hydrated MoO_3 or WO_3 or the corresponding $[MO_4]^{2-}$ ions, result in a variety of complexes depending upon the reaction conditions, especially the pH [95,96]. At high pH, the isostructural complexes $K_6[Mo_2I_2O_{16}]\cdot 10H_2O$ and $K_6[W_2I_2O_{16}]\cdot 10H_2O$ are obtained [97], which probably contain identical anions to the materials variously formulated $K_3H_2[IO_5MoO_4]\cdot 4H_2O$, $Na(NH_4)_2H_2[IO_5MO_4]\cdot xH_2O$ (M = Mo or W) in the early literature [95,98]. The structure of the molybdenum complex (Fig. 11) reveals edge-sharing octahedra, with a structure related to that of the vanadium complex (Fig. 10), except that in the molybdenum complex the metal is clearly 6-coordinate

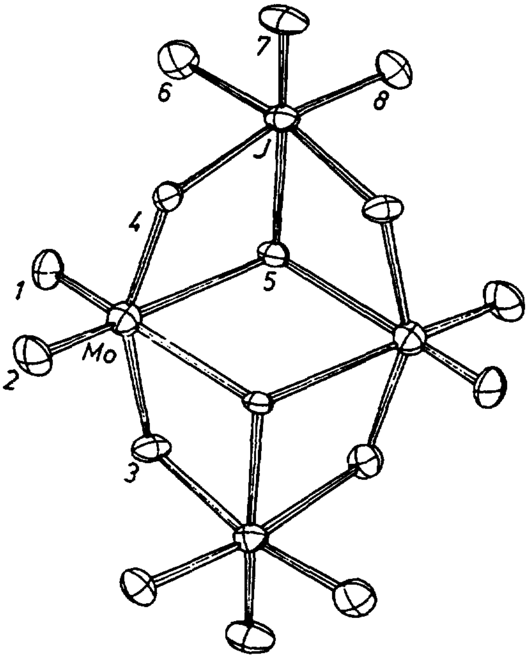


Fig. 11. The structure of $K_6[Mo_2I_2O_{16}]\cdot 10H_2O$ from Ref. [97] by permission of Zeitschrift für Anorganische und Allgemeine Chemie.

and the periodate groups are not protonated. The terminal I–O bonds average 1.816(4) and the bridging ones 1.986(4) Å, whilst the terminal *d*(Mo–O) are 1.717(5) and 1.725(4) Å, and the bridging Mo–O range from 1.922(4) to 2.274(4) Å. In aqueous solution the complexes partially hydrolyse to $[MO_4]^{2-}$ and $[IO_4]^-$ ions.

The hexamolybdo- and hexatungsto-periodate complexes $[IM_6O_{24}]^{5-}$ (M = Mo or W) were prepared in the 1890s by combination of $[IO(OH)_5]$ and MoO_3 or WO_3 in aqueous solution at low pH [95,98,99]. Recent descriptions of the synthesis of the K^+ and hexadecylpyridinium$^+$ salts are in Ref. [50]. The structure [100] of the anion in $K_5[IMo_6O_{24}] \cdot 5H_2O$ is that originally proposed by Anderson [101], and is similar to that in Fig. 12, consisting of a central IO_6 octahedron edge linked to six MoO_6 octahedra, the anion having approximate D_{3d} symmetry. The vibrational [53], ^{95}Mo-NMR ($\delta = -11$) [102] and ^{17}O-NMR [103] spectra have been reported.

Hexamolybdo- and hexatungsto-tellurate anions $[TeM_6O_{24}]^{6-}$ are readily obtained by reaction of telluric acid with the appropriate hydrated MO_3 or metal molybdate or tungstate in aqueous solution. The equilibria present in such solutions have been investigated as a function of pH [104,105].

Alkylammonium salts $[R_{4-n}H_nN]_6[TeMo_6O_{24}]$ have also been prepared from methanol solution [106]. The structure of $K_6[TeMo_6O_{24}] \cdot 7H_2O$ was the first example of an Anderson type heteropolyanion determined [107,108] and contains a nearly planar hexagon of MoO_6 groups surrounding a central TeO_6 unit. The structure of $Na_6[TeW_6O_{24}] \cdot 22H_2O$ (Fig. 12) is very similar [109]. Evans [107,108] also reported the structures of $(NH_4)_6[TeMo_6O_{24}] \cdot 7H_2O$ and $(NH_4)_6[TeMo_6O_{24}] \cdot$

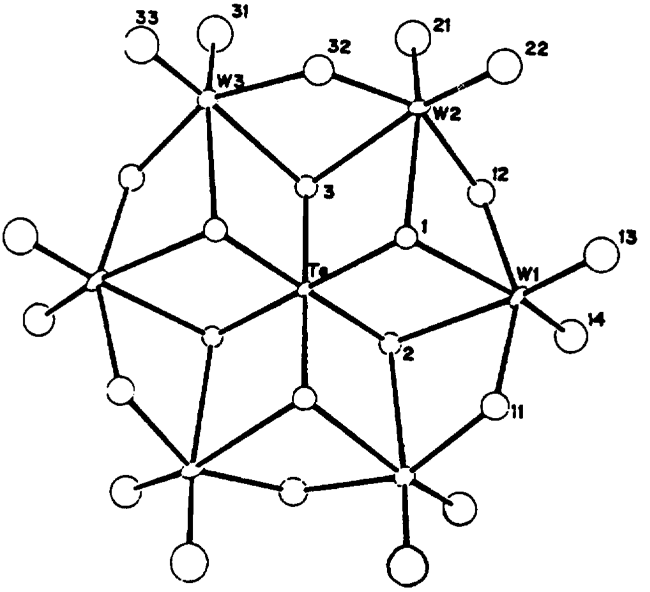


Fig. 12. The structure of an Anderson type heteropolyanion, the $[TeW_6O_{24}]^{6-}$ anion from Ref. [109] by permission of Acta Crystallographica.

$Te(OH)_6 \cdot 7H_2O$. The latter contains octahedral $Te(OH)_6$ molecules hydrogen bonded to the neighbouring anions. The structures of several other salts have been reported by Robl and Frost in a study of the hydrogen bonding networks viz: $Li_6[TeMo_6O_{24}] \cdot 18H_2O$ and $Li_6[TeMo_6O_{24}] \cdot Te(OH)_6.18H_2O$ (Fig. 13) [110]; $Na_6[TeMo_6O_{24}] \cdot 22H_2O$ [111]; $Na_4(NH_4)_2[TeMo_6O_{24}] \cdot 16H_2O$ [112]; $Rb_6[TeMo_6O_{24}] \cdot 10H_2O$ and $Rb_6[TeMo_6O_{24}] \cdot Te(OH)_6.10H_2O$ [113]; $Cs_6[TeMo_6O_{24}] \cdot 2Te(OH)_6 \cdot 4H_2O$ [114]. Complexes with other transition metal cations have been reported including $M_3[TeMo_6O_{24}] \cdot nH_2O$, $(NH_4)_{2x}M_{3-x}[TeMo_6O_{24}] \cdot nH_2O$ (M = Zn, Ni, Mn etc.) [115,116], and $M'_2[TeMo_6O_{24}] \cdot nH_2O$ (M′ = Nd or Eu) [117]. Spectroscopic data on the hexamolybdotellurate compounds include single-crystal IR and Raman spectra [118], ^{95}Mo ($\delta = +10$) [102] and ^{17}O-NMR [103] data.

Crystals of $(NH_4)_{12}[Te_6Mo_{12}O_{60}] \cdot 8H_2O$ separate on cooling a hot aqueous solution of $[Te(OH)_6]$ and MoO_3 in a 1:1.8 molar ratio, which need to be separated quickly to prevent conversion into hexamolybdotellurate anions [119]. The structure (Fig. 14) is composed of a ring of six corner-sharing TeO_6 octahedra, each octahedron bonded to two distorted face-sharing MoO_6 octahedra via common corners and edges. An octamolybdotellurate anion is present in $(^nBu_4N)_4[TeMo_8O_{29}(OH_2)]$ (Fig. 15), formed by reaction of $[Te(OH)_6]$ with $[^nBu_4N]_4[\alpha\text{-}Mo_8O_{26}]$ in MeCN [120]. Unusually, one of the molybdenum atoms (Mo(7)) is 5-coordinate and the unique water molecule oxygen is O(30).

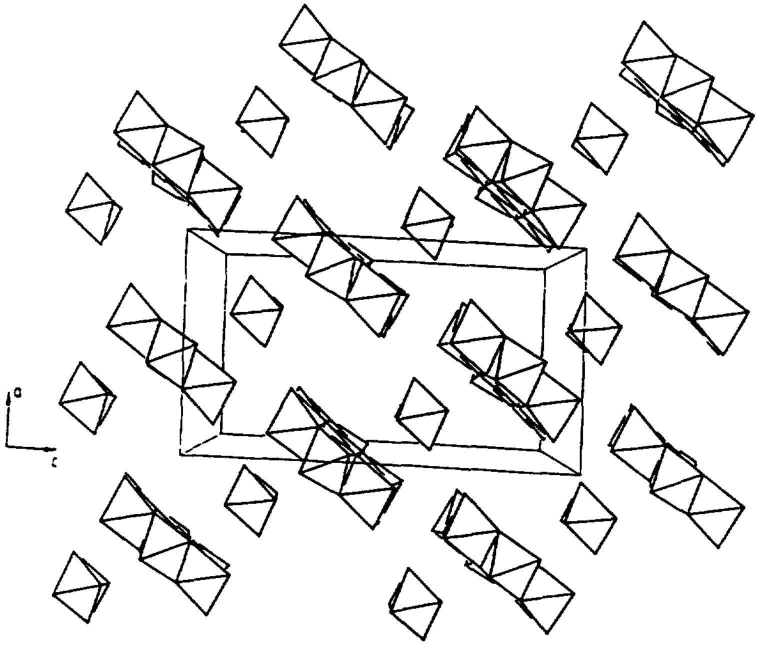


Fig. 13. The unit cell of $Li_6[TeMo_6O_{24}] \cdot Te(OH)_6 \cdot 18H_2O$ showing the $Te(OH)_6$ molecules and the anions only, from Ref. [110] by permission of Zeitschrift für Anorganische und Allgemeine Chemie.

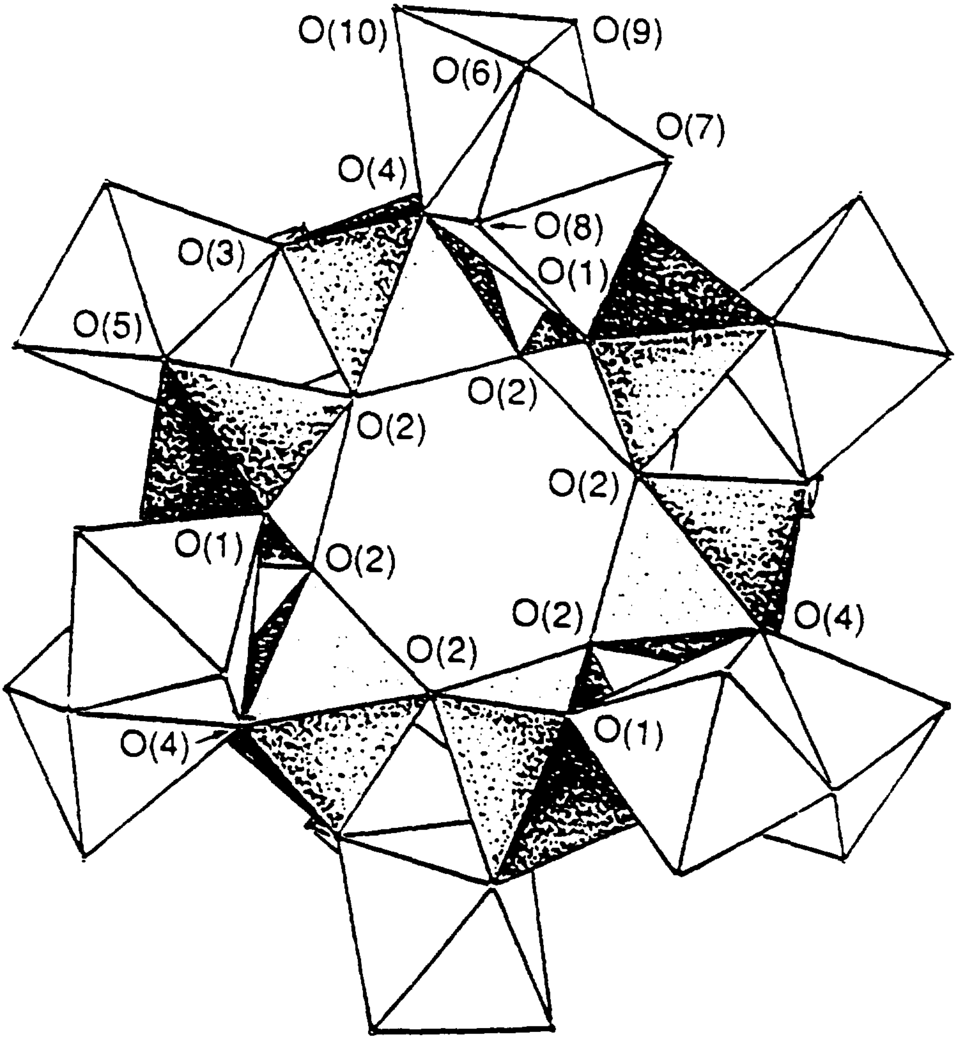


Fig. 14. The structure of the $[Te_6Mo_{12}O_{60}]^{12-}$ anion. The shaded octahedra are TeO_6 units. From Ref. [119] by permission of the Royal Society of Chemistry.

A brief report of $Na_2[TeW_{12}O_{40}]\cdot 24H_2O$ has been published [121], although structural confirmation is lacking. Mixed transition metal anions $M_6[TeWMo_5O_{24}]\cdot nH_2O$ (M=Na, K, NH_4) [122], $M_7[TeVMo_5O_{24}]\cdot nH_2O$ [123] and $M_7[TeVW_5O_{24}]\cdot nH_2O$ [124] have been reported. Characterisation is based upon analysis, determination of the unit cell parameters and molecular weights, and all are assumed to be based upon $[TeM_6O_{24}]$ type anions. Multinuclear NMR spectroscopy (^{51}V, ^{95}Mo, ^{183}W and ^{17}O) on these compounds would be a useful way on confirming their identity and structure.

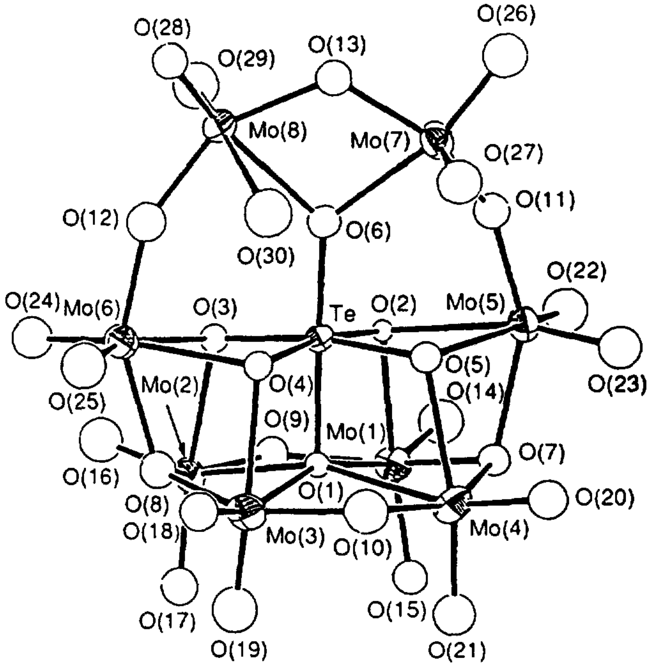


Fig. 15. The structure of the $[TeMo_8O_{29}(OH_2)]^{4-}$ anion, from Ref. [120] by permission of the Royal Society of Chemistry.

4.5. *Complexes of the group 7 metals*

Periodate and tellurate complexes appear to be known only for manganese in this group, but the periodates in particular have been studied in some detail.

The reaction of $M[IO_4]$ (M = Na-Cs) with $[Mn(H_2O)_6]^{2+}$ in warm aqueous acid solutions precipitated dark red-brown $M[MnIO_6] \cdot nH_2O$ compounds [125,126] containing Mn(IV). These were erroneously formulated as Mn(III) $M_2Mn_2I_2O_{11} \cdot nH_2O$ in older literature [127]. The complexes are insoluble in water, although seem to slowly decompose in boiling water. PXRD studies revealed relatively poor crystallinity, but identified the space group as P312 and hence they have structures analogous to that of $M[GeIO_6]$ (Section 3.1 and Section 4.1) [128] and this was subsequently confirmed by Mn and I K-edge EXAFS studies which placed *d*(Mn–O) ca. 1.89 Å and *d*(I–O) ca. 1.86 Å [52,126]. The water content appears rather variable and presumably is simply trapped in the lattice, since dehydration does not change the PXRD pattern. The magnetic moments of ca. 4 B.M. and the UV-visible spectra confirm the manganese(IV) formulation [125,126]. In contrast, hypochlorite oxidation of $[Mn(H_2O)_6]^{2+}$ and $Na_2[H_3IO_6]$ in aqueous alkaline solution produces deep red crystalline complexes $M_7H_4[Mn(IO_6)_3] \cdot nH_2O$ (M = Na or K) [126,129,130]. The single-crystal X-ray structure of the sodium salt revealed an octahedral manganese(IV) centre coordinated to two $IO_5(OH)$ and one $IO_4(OH)_2$

group (Fig. 16), and hence the formulation is $Na_7[Mn\{IO_5(OH)\}_2\{IO_4(OH)_2\}] \cdot 18H_2O$ [126,131]. Spectroscopic data confirm the Mn(IV) formulation and the protonation of the periodate groups. In solution the complexes slowly decompose to permanganate with some periodate reduced to iodate. Lister [129,130] obtained a solution of the free acid "$H_{11}[Mn(IO_6)_3]$" by passing the sodium salt through an ion-exchange resin, and obtained estimates for the various pK_a values.

Attempts to make tellurate equivalents of $M[MnIO_6]$ have been unsuccessful [56], but Lister prepared complexes formulated as $K_6H_8[Mn(TeO_6)_3] \cdot 5H_2O$ and $Na_7H_7[Mn(TeO_6)_3] \cdot 5H_2O$ by hypochlorite oxidation of $[Mn(H_2O)_6]^{2+}$ and $[Te(OH)_6]$ in alkaline solution [130,132]. The anion is less stable than the periodate and dissociates tellurate ions in solution, making isolation of pure complexes difficult. A recent re-investigation [56] of these salts isolated a pure sample of $Na_7K[Mn\{TeO_4(OH)_2\}_3] \cdot 3H_2O$ by peroxodisulfate oxidation. The instability in solution prevented growth of crystals for an X-ray study, but the UV-visible spectrum is consistent with an $Mn^{IV}O_6$ centre and the Mn and Te K-edge EXAFS data provided bond lengths of $d(Mn–O) = 1.90$ Å and $d(Te–O) = 1.94$ Å. The vibrational spectrum contains a band at $1145\ cm^{-1}$ assigned at $\delta(TeOH)$ and the structure is likely to be that shown in Scheme IV.

4.6. Complexes of the group 8 metals

A 1:1 Fe(III):IO_6 complex was reported in solution [133] although the evidence is not strong. However addition of lithium ions to a solution containing KOH, KIO_4 and $[Fe(H_2O)_6]^{3+}$ precipitated $LiK[FeIO_6]$, which has been proposed as a method for the gravimetric determination of lithium [134]. Other than a brief account of its IR spectrum which is similar to those of $K[MnIO_6]$ or $K[NiIO_6]$ and

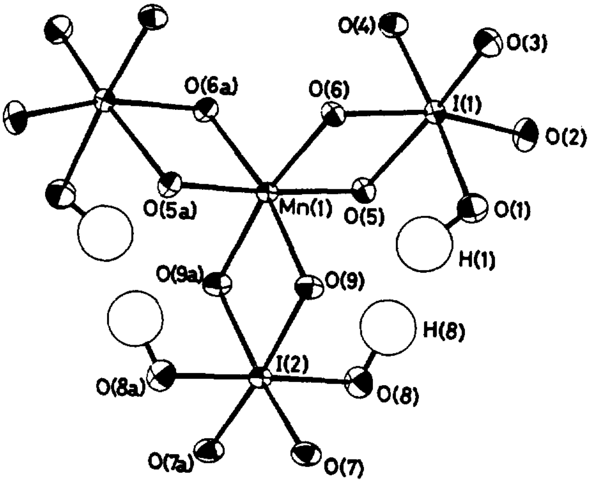
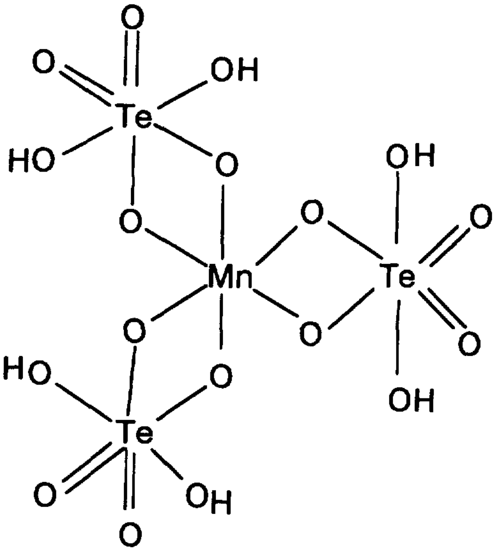


Fig. 16. The anion in $Na_7[Mn\{IO_5(OH)\}_2\{IO_4(OH)_2\}] \cdot 18H_2O$ from Ref. [126] by permission of the American Chemical Society.



Scheme IV.

confirms the absence of IOH groups [29], nothing seems to be known about this material.

The insoluble yellow-brown powder precipitated from hot aqueous acid solutions of $NaIO_4$ and $[Fe(H_2O)_6](NO_3)_3$ has the composition $[Fe_4I_3O_{24}H_{15}]$ and was suggested to be the acid form of an Anderson type heteropolyanion [135]. The magnetic moment of 4.3 B.M. per Fe was interpreted as non-magentically dilute Fe(III) rather than Fe(IV). Addition of the reaction mixture containing $[Fe_4I_3O_{24}H_{15}]$ to concentrated aqueous NaOH produced a green insoluble material formulated as $Na_5[Fe(H_2IO_6)_2(OH)_2]$ [135,136]. Freshly prepared $[Fe_4I_3O_{24}H_{15}]$ dissolves in concentrated aqueous KOH, RbOH or CsOH to give deep brown solutions, from which acetone or ethanol precipitate $M_4[Fe_4I_3O_{24}H_{11}]$, whilst stirring a suspension of $[Fe_4I_3O_{24}H_{15}]$ with aqueous NaOH or LiOH gave $Na_5[Fe_4I_3O_{24}H_{10}]$ and $Li_6[Fe_4I_3O_{24}H_9]$, respectively [55]. A single-crystal X-ray study of $K_6Na_2[Fe_4I_3O_{24}H_7] \cdot 14H_2O$ confirmed an Anderson type polyanion with a central FeO_6 unit edge-linked to IO_6 and FeO_6 units (Fig. 17), although unfortunately in the crystal studied the peripheral octahedra were disordered [55]. Iron and iodine K-edge EXAFS studies confirmed the presence of a similar structural unit in the parent acid form and in the other complexes. Room temperature ^{57}Fe-Moessbauer spectra of these compounds could be satisfactorily fitted to two iron sites, both high spin Fe(III) from the isomer shifts, whilst at 4.2 K the Moessbauer spectra showed two sextet components indicating magnetic ordering at the low temperature. The magnetic moments of 5.3 B.M. for the alkali metal salts, indicate the materials are not magnetically dilute. Attempts to oxidise these compounds to Fe(IV) with peroxodisulfate or ozone were unsuccessful [55]. The production of brown $Na_5[Fe_4I_3O_{24}H_{10}]$ by reaction of *isolated* $[Fe_4I_3O_{24}H_{15}]$ with aqueous NaOH con-

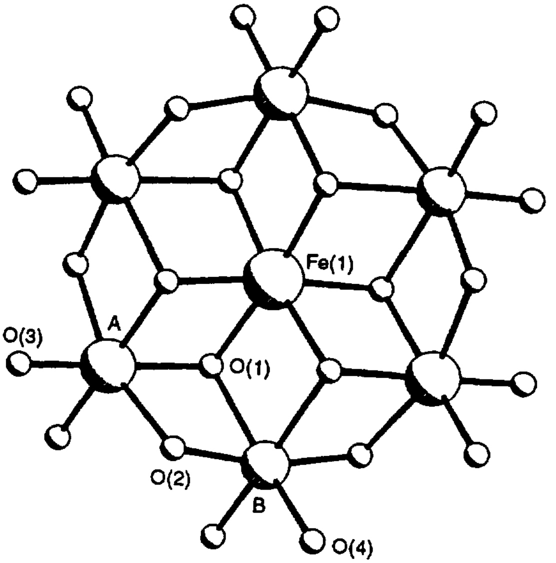


Fig. 17. The (disordered) Anderson type anion in $K_6Na_2[Fe_4I_3O_{24}H_7] \cdot 14H_2O$ from Ref. [55] by permission of the Royal Society of Chemistry. Atoms A and B are alternatively Fe and I.

trasts with the green $Na_5[Fe(H_2IO_6)_2(OH)_2]$ made by adding NaOH to the *reaction mixture* used to make $[Fe_4I_3O_{24}H_{15}]$. A re-examination of the reaction [55] concluded that the green material was not homogeneous, but the species present in the mixture remain unclear.

Two telluroferrate(III) anions have been reported [137]. Yellow $Li_7[Fe\{TeO_4(OH)_2\}_2(OH)_2] \cdot 3H_2O$ precipitates from reaction of $[Te(OH)_6]$ and iron(III) nitrate in weakly alkaline solution followed by addition of Li_2SO_4. Brown $Li_6[Fe_4Te_3O_{24}H_{12}] \cdot 2H_2O$ is formed similarly in a more strongly basic solution. The magnetic moment of the former is normal for high spin Fe(III) 5.92 B.M., but the latter is not magnetically dilute (3.4 B.M.) [137].

The reaction of $[RuO_4]^-$ or $[RuO_4]^{2-}$ with $NaIO_4$ in aqueous NaOH solution was reported [138] to give the red–brown Ru(VI) complex $Na_6[Ru(OH)_2(IO_6)_2] \cdot nH_2O$. Re-examination [48] showed the complex was a ruthenyl (RuO_2^{2+}) derivative $Na_6[RuO_2\{IO_5(OH)\}_2] \cdot 18H_2O$. An X-ray study of the $NaK_5[RuO_2\{IO_5(OH)\}_2] \cdot 8H_2O$ (note again crystals are produced only with mixed cations) revealed the structure shown in Fig. 18, with $d(Ru{=}O) = 1.732(8)$ Å and $d(Ru–OI) = 2.008(8)$, 2.016(8) Å, whilst O(6), O(4) and O(5) are I=O bonds 1.795(9)–1.833(10) Å, O(7) at 1.990(9) Å is I–OH [48]. The yellow osmium analogue $Na_6[OsO_2\{IO_5(OH)\}_2] \cdot 18H_2O$ made from $K_2[OsO_2(OH)_4]$, $NaIO_4$ and NaOH [31,50], is isomorphous with the ruthenium complex [50] and Os and I edge EXAFS studies confirm a very similar structure [47]. Spectroscopic data on these two anions include IR and Raman [31,48,50,53], ^{17}O- and ^{127}I-NMR (Fig. 6) [31], and UV-visible [31,48,50] data. The corresponding tellurate complexes

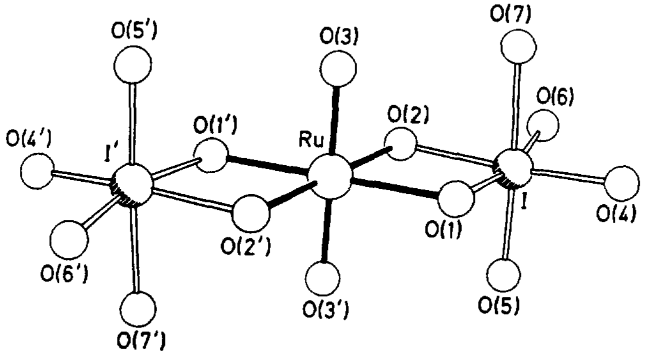


Fig. 18. Structure of the anion in $NaK_5[RuO_2\{IO_5(OH)\}_2]\cdot 8H_2O$ from Ref. [48] by permission of the Royal Society of Chemistry.

yellow $M_6[RuO_2\{TeO_4(OH)_2\}_2]\cdot nH_2O$ (M = Na or K) and fawn $Na_6[OsO_2\{TeO_4(OH)_2\}_2]\cdot 8H_2O$ are made from $[RuO_4]^{2-}$ or $[OsO_2(OH)_4]^{2-}$, and $[Te(OH)_6]$ in alkaline solution, and have similar structures on the basis of vibrational and NMR spectra [31,48,53]. The structures were finally confirmed by a single-crystal X-ray study [47] of $Rb_2Na_4[OsO_2\{TeO_4(OH)_2\}_2]\cdot 16H_2O$ (Fig. 19) with d(Os–O(1)) = 1.750(5) Å, d(Os–OTe) = 2.015(5), 2.013(5) Å, with Te–O(4) and Te–O(7) the Te=O links 1.847(5), 1.840(5) Å, and Te–O(6) and Te–O(3) the Te–OH at 1.991(5), 1.984(5) Å. The $[RuO_2\{TeO_4(OH)_2\}_2]^{6-}$ ion behaves as a 2-electron oxidant towards activated alcohols, but the both the ruthenium and osmium periodate complexes are 6-electron oxidants converting primary alcohols to aldehydes and carboxylic acids, and secondary alcohols to ketones [48,50]. Catalytic oxidation of alcohols, aldehydes and primary alkyl halides by $K[IO_4]$ in the presence of the ruthenium and osmium periodate complexes has also been observed [50].

Orange-yellow crystals of $[RuO_2(2,2'\text{-bipy})\{IO_3(OH)_3\}]\cdot 1.5H_2O$ were produced by reaction of $[RuO_4]^-$, $Na[IO_4]$ and 2,2'-bipyridyl in aqueous acetone, and is the first example of a coordinated $[IO_3(OH)_3]^{2-}$ ligand [139]. The structure is shown in Fig. 20, the significant (averaged) bond lengths from two independent molecules

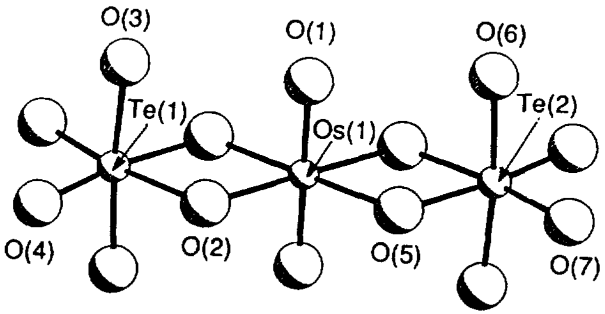


Fig. 19. Structure of the anion in $Rb_2Na_4[OsO_2\{TeO_4(OH)_2\}_2]\cdot 16H_2O$ from Ref. [47] by permission of the Royal Society of Chemistry.

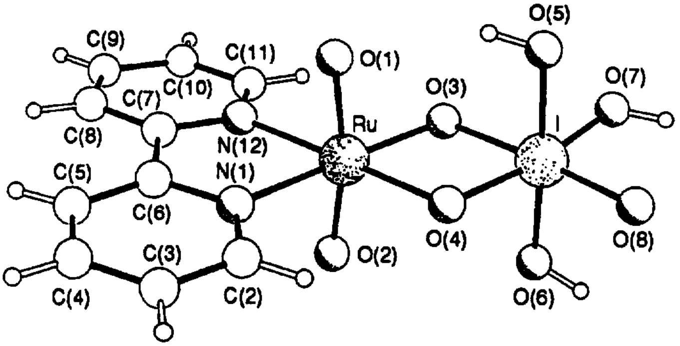


Fig. 20. The structure of $[RuO_2(2,2'\text{-bipy})\{IO_3(OH)_3\}]\cdot 1\cdot 5H_2O$ from [139] by permission of the Royal Society of Chemistry.

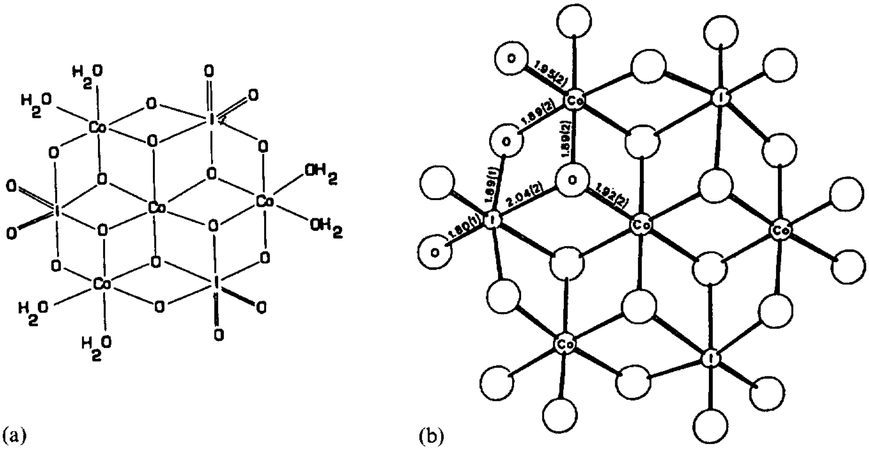


Fig. 21. Schematic of (a) and the structure of (b) the anion in $[Li(H_2O)_4]_2H[Co_4I_3O_{24}H_{12}]\cdot 3H_2O$ from Ref. [146] by permission of the American Chemical Society.

being $d(Ru{=}O) = 1.727$, $d(I{=}O)$ I–O(8) = 1.796, $d(I\text{–}OH) = 1.90$ Å. The complex is a stereospecific alkene epoxidation catalyst using $Na[IO_4]$ as co-oxidant, and a stoichiometric 6-electron oxidant.

4.7. Complexes of the group 9 metals

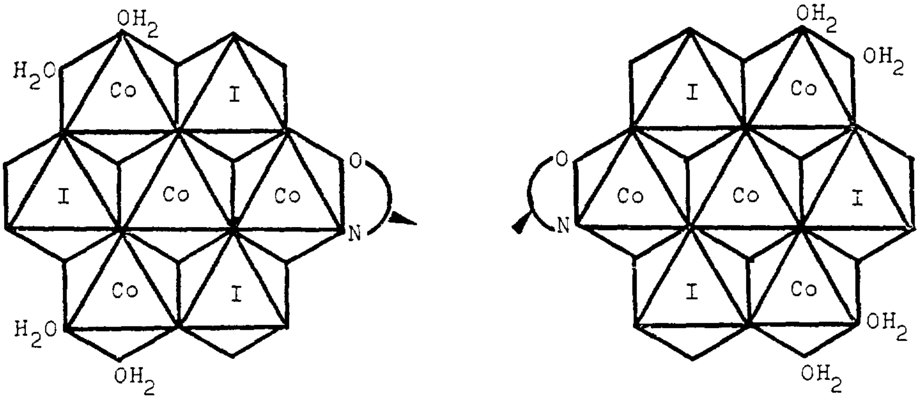
Nothing seems to be known about complexes of rhodium or iridium, but there are a large number of reports of both cobalt(III) periodates and tellurates, although X-ray structural characterisation of the latter compounds are not available.

Cobalt(III) periodates with Co:I ratios of 1:1, 1:2 and 4:3 have been reported. A 1:1 species is reported to exist in solution [133], and a solid green 1:1 complex has been reported in an impure form as its sodium salt made by reaction of $NaIO_4$,

$[Co(H_2O)_6]^{2+}$ and $Na_2S_2O_8$ in boiling dilute acid solution [140]. There seem to be no recent reports of this species and its existence must be regarded are uncertain. Alkaline hypochlorite oxidation of solutions containing $[Co(H_2O)_6]^{2+}$ and an alkali metal periodate, followed by purification were reported to lead to deep green 1:2 complexes formulated [141] $Na_5H_2[Co(IO_6)_2]\cdot10H_2O$ and $K_4H_3[Co(IO_6)_2]\cdot3H_2O$, and impure Ba^{2+} and La^{3+} salts were obtained by metathesis. These materials have been re-examined on a number of occasions [55,62,130,142,143], but the nature is still unclear. In acid solution conversion into the 4:3 complex (below) with liberation of some periodate and also $[Co(H_2O)_6]^{2+}$ occurs and the IR spectra show the presence of δ(IOH) modes and hence the periodate groups are protonated to some degree. However the materials are usually weakly paramagnetic presumably due to the presence of some Co(II), although whether as a constituent or impurity is not clear. Moreover the ^{59}Co-NMR spectrum of the sodium salt revealed two resonances very similar to those of the 4:3 complex, and attempts to model the Co and I EXAFS data were unsuccesful. This system illustrates the difficulties of satisfactorily identifying complexes of this type in the absence of a single-crystal X-ray structure. In summary it seems that materials with an analytical composition close to a Co:I ratio of 1:2 can be obtained, and that these decompose in solution as a function of pH to the 4:3 complex, liberating periodate and Co(II). The most studied complex $Na_5[Co\{IO_5(OH)\}_2(OH)_2]\cdot nH_2O$ as originally formulated, either is rarely obtained pure (perhaps due to its easy conversion into the 4:3 species) or perhaps it is an alkali-metal cobalt(II) complex of a larger periodato-cobalt(III) anion.

In contrast to the uncertainties surrounding the other cobalt periodates, the 4:3 complex is thoroughly characterised. It is usually obtained by acidifying the $Na_5[Co\{IO_5(OH)\}_2(OH)_2]\cdot nH_2O$ with $HClO_4$ or HNO_3, but [140,142] can be made directly from $Na[IO_4]$ and $Na_3[Co(CO_3)_3]\cdot3H_2O$ in perchloric acid solution [144]. Both the free acid $[Co_4I_3O_{24}H_{15}]\cdot nH_2O$ and salts with various alkali-metal, alkaline earth and Ag^+ cations are known [140,142,144,145], all are dark green solids and in contrast to the iron(III) analogues are easily soluble in water. Titrimetric studies show that three hydrogens are easily replaced with virtually identical pK_a values [146]. Single-crystal X-ray structures of $[Li(H_2O)_4]_2H[Co_4I_3O_{24}H_{12}]\cdot3H_2O$ [146,147], $NaH_2[Co_4I_3O_{24}H_{12}]\cdot11H_2O$ [148] reveal the anion to be of the Anderson type with a central CoO_6 octahedron surrounded by alternating IO_6 and CoO_6 octahedra sharing edges. The structure of the lithium salt (Fig. 21) reveals a distorted octahedron about the central cobalt d(Co–O) (av) = 1.92 Å, the periodate groups are not protonated d(I=O) (av) = 1.80 Å and the peripheral cobalts carry two water molecules d(Co–OH$_2$) (av) = 1.95 Å [147]. The site of the acid proton was not certainly identified, and it was suggested to be associated with one of the lattice waters. In the sodium salt, two different anions were identified, $[Co_4I_3O_{16}(OH)_2(H_2O)_6]^-$ and $[Co_4I_3O_{18}(OH_2)_6]^{3-}$, presumably a result of the very similar magnitude of the three pK_a values [148]. In keeping with the structure of the anion, the ^{59}Co-NMR spectrum reveals two cobalt resonances [31]. The reaction of the acid form of the complex with liquid ammonia, neat ethylenediamine (en), aqueous glycine (gly) or L-alanine (L-ala), replaced the aquo groups on the cobalt with other ligands affording $H_3[Co_4I_3O_{18}(NH_3)_6]\cdot9.5H_2O$,

$H_3[Co_4I_3O_{18}(en)_3]\cdot 5H_2O$, $[NH_4]_7H[Co_4I_3O_{18}(OH_2)_4(gly)]_2\cdot 14H_2O$, and $[NH_4]_2H_2[Co_4I_3O_{18}(OH_2)_4(L\text{-}ala)]\cdot 9H_2O$, respectively [149]. The L-alanine complex was separated into two diastereoisomers (Scheme V)by column chromatography; UV and CD spectra were reported for these complexes.



Scheme V.

A bis(tellurate) of cobalt(III), $K_3H_6[Co(TeO_6)_2]\cdot 2H_2O$ possibly $K_3[Co\{TeO_3(OH)_3\}_2(OH_2)_2]$, was obtained [132] by reaction of $[Te(OH)_6]$, $[Co(H_2O)_6]^{2+}$ and KOCl in dilute alkali, as a green powder. Acidification appears to give a species with a Co:Te ratio of 4:3, but no details are available on the latter species. In strongly alkaline solutions a dark green tris(tellurate) $K_3[Co\{TeO_2(OH)_4\}_3]\cdot 2H_2O$ is obtained, although this is paramagnetic indicating cobalt(II) impurties [150]. The similarities with the cobalt(III) periodate systems seem strong, but an X-ray crystal structure of one or more of these compounds is badly needed to provide certain identification of the anion(s) present. A number of substituted tellurates have been described [151,152]. For example, $[Te(OH)_6]$ and *cis*-$[Co(en)_2Cl_2]Cl$ react in aqueous alkali to form $[Co\{TeO_2(OH)_4\}(en)_2]Cl$ and $[Co(en)_2\{Te_2O_6(OH)_4\}Co(en)_2]^{2+}$ separated by chromatography, and a third type $[\{Co(en)_2\}_2\{Te_2O_{10}\}\{Co(en)_2\}_2]^{4+}$ is obtained by varying the conditions. Analogues of some of these with 1,2-propanediamine and *trans*-1,2-cyclohexanediamine have also been obtained [151]. Related penta- and hexanuclear species have been described [152]. All are believed to be based upon $CoO_{6-n}N_n$ and TeO_6 octahedra linked via edge sharing, and in some cases diastereoisomers have been separated chromatographically, or prepared directly from chiral starting materials. The proposed structures were based upon analysis, UV-visible and circular dichroism spectra.

4.8. *Complexes of the group 10 metals*

Peroxodisulfate oxidation of a mixture of $[Ni(H_2O)_6]^{2+}$ and alkali metal periodate in hot weakly acidic aqueous solutions produced reddish-black powders $M[NiIO_6]\cdot nH_2O$ (M=Na or K) [153]. More recently the NH_4, Rb and Cs analogues have been prepared, but attempts to make Li or NR_4 salts failed [45,52].

Ozone oxidation at ambient temperatures of a similar mixture can be used in place of the peroxodisulfate [52]. Although usually formulated as containing small amounts of water, thoroughly dried samples show little evidence for water in their IR spectra, and if some samples do contain water it is presumably adventitiously trapped in the lattice rather than constitutional [52]. PXRD studies established the compounds to belong to the space group P312 [128,154,155], and recent Rietveld refinements coupled with nickel and iodine K-edge EXAFS data has confirmed these structures and places $d(\text{Ni–O}) = 1.87$ Å and $d(\text{I–O}) = 1.86$ Å [45,52]. The vibrational spectra (Fig. 3) [52] are very similar to those of other layered periodates and confirm that the IO_6 groups are not protonated. The diffuse reflectance spectra of freshly prepared samples contain a broad feature at 18 500 cm^{-1} assigned to the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of a low-spin d^6 ion in an approximately O_h environment. Whilst the formulation of these complexes as containing nickel(IV) is indicated by the above data, and is supported by measurements of the energy of the nickel K-absorption edge [156], the weak paramagnetism and the presence of ESR signals shows the situation to be more complicated. Typically the complexes have magnetic moments ca. 1 B.M. at room temperature [52,153,157] whilst for a low-spin d^6 ion any contributions from temperature-independent paramagnetism should be not more than 0.5 B.M. The freshly prepared $M[NiIO_6]$ ($M = Cs$, Rb or NH_4) are ESR silent, but develop ESR resonances with age, whilst the Na and K salts even when freshly prepared have weak ESR resonances typical of a low-spin d^7 ion and hence Ni(III) impurities [52,158]. In pressed discs the samples exhibit weak electrical conductance typical of poor semi-conductors. It thus appears that like many high valent nickel oxo-species, these samples contain some Ni(III) and possibly Ni(II) as well as Ni(IV) centres. Thermal decomposition of $K[NiIO_6]$ occurs on gentle heating and was claimed [158] to result in a green complex containing Ni(II) and the unusual state I(VI). However a re-examination of the products by PXRD and IR spectroscopy identified KIO_3 and KIO_4 among the products, along with nickel(II) [52]. The complexes also decompose in boiling water. On standing at room temperature, the dark red-black powders become duller in appearance over several months but otherwise appear visually unchanged. However the diffuse reflectance spectra show that the lowest energy absorption has changed from ca. 18 500 cm^{-1} in the freshly prepared complexes to 17 000–15 500 cm^{-1}, although PXRD and EXAFS studies reveal no significant change in the basic lattice. The IR spectra of old samples also show a new band at ca. 850 cm^{-1} typical of $[IO_4]^-$ [45,52]. It seems that on standing the complexes slowly decompose probably to mixed valence materials retaining the same basic structure, the lower energy UV-visible absorption being due to an intervalence charge transfer band.

Peroxodisulfate oxidation of mixtures of nickel(II) salts and periodates in aqueous alkali forms brown bis(periodato)nickelate(IV) complexes [50,136,137]. The anion present has not been structurally characterised but the complex appears from the analysis and the vibrational spectrum to be $Na_6[Ni\{IO_5(OH)\}_2(OH)_2] \cdot H_2O$ analogous to the palladium and platinum complexes. A $[Co(en)_3]_2[Ni\{IO_5(OH)\}_2(OH)_2]$ salt has also been obtained [50]. A complex formulated as $Li_2[NiI_6O_{24}] \cdot 6H_2O$ has been described [62] but is incompletely characterised. Despite at least one report in the older literature of a nickel(III) periodate complex [159] none have been observed in recent work. The complex $Na_6[Ni\{IO_5(OH)\}_2(OH)_2]\cdot H_2O$ functions as a 6e oxidant towards primary alcohols corresponding to the reduction of the periodate to iodate and Ni(IV) to Ni(II). There are a number of studies on the kinetics of oxidation of alcohols, amines and aldehydes by $K[NiIO_6]$ dissolved in aqueous KOH/KIO_4 [160–164]. The major problem here is that the nature of the active nickel(IV) species is far from clear. It is usually formulated at $[Ni(H_nIO_6)_2(OH)_2]^{8-2n}$ and characterised by a UV-visible band at 410 nm assigned as metal to ligand charge transfer $(Ni(t_{2g})\rightarrow$periodate). The assignment is clearly in error since for a high valent d^6 ion with π donor periodate (or oxide) ligands the charge transfer will be $\pi(IO_6)\rightarrow Ni(e_g)$.

Attempts to prepare tellurate complexes of nickel(IV) have been unsuccessful. Attempts to oxidise mixtures of nickel(II) and telluric acid in alkaline solution with hypochlorite usually fail to increase the nickel oxidation state [165]. The report [165] of a black material formed using a large excess of hypochlorite possibly an impure nickel(III) complex, could not be reproduced [45], and the black colour may be due to a higher oxide of nickel.

Palladium(IV) and platinum(IV) periodates are obtained by boiling strongly alkaline aqueous solutions of $[M'Cl_6]^{2-}$ (M′=Pd or Pt) with periodate ions [49,50,166]. Although originally suggested to be $[M'(IO_6)_2]^{6-}$ ions with tridentate IO_6 groups face sharing with the $M'O_6$ groups [166], re-examination has shown the platinum compounds to contain $[Pt(OH)_2\{IO_5(OH)\}_2]^{6-}$ [49]. Pale yellow crystals of $K_4Na_2[Pt(OH)_2\{IO_5(OH)\}_2]\cdot 10H_2O$ contain the anion shown in Fig. 22 [49]. The vibrational spectra are consistent with this formulation [49,50,53]. The $^{195}Pt\{^1H\}$-NMR spectra are pH dependent; on dissolving the complex in water the main feature has $\delta=+2620$ (relative to $[PtCl_6]^{2-}$, $\delta=0$) and minor features at +2400, +2655 and +2730, which on acidification are reversibly converted into the species with $\delta=+2400$ (pH=2). Concentration of any of these solutions resulted in recovery of the original complex. A Pt L_{III}-edge EXAFS study of the solution containing only the species with $\delta=+2400$ showed it to contain a very similar

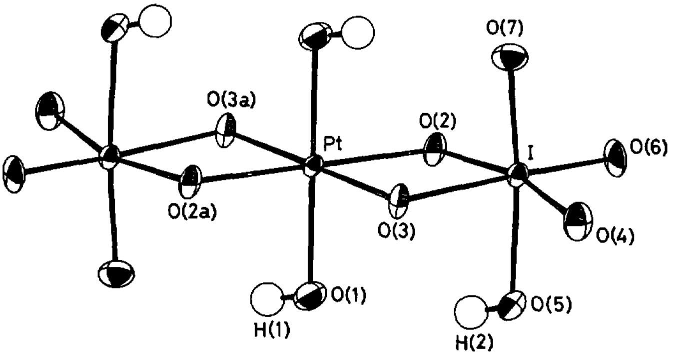


Fig. 22. The structure of the anion in $K_4Na_2[Pt(OH)_2\{IO_5(OH)\}_2]\cdot 10H_2O$ from Ref. [49] by permission of Gordon and Breach.

species to that in Fig. 22, and thus the different resonances were attributed to anions with different degrees of protonation [45]. The orange palladium(IV) complexes $M_6[Pd(OH)_2\{IO_5(OH)\}_2]\cdot nH_2O$ (M = Na or K) have not been obtained as crystals suitable for an X-ray study, but have very similar vibrational spectra to the platinum(IV) complexes and reasonably have been assumed to contain a similar anion [45,50,53]. However the $K_6[M'(OH)_2\{IO_5(OH)\}_2]\cdot nH_2O$ are not isomorphous by PXRD [45] and palladium and iodine K-edge EXAFS data [47] indicate that the Pd(IV) complex may well be a dimer $[Pd_2I_4O_{24}H_2]^{10-}$ similar to the palladium(IV) tellurate (below). Discriminating these two structures by EXAFS is a challenging problem and needs confirmation by a full X-ray study. Attempts to prepare platinum(II) periodate complexes failed [166], but yellow-brown $Na_6[Pd\{IO_5(OH)\}_2]\cdot 11H_2O$ is formed by stirring $Na_2[PdCl_4]$ in aqueous NaOH with periodic acid [50]. Unlike the complexes of Pd(IV) or Pt(IV) which are 6-electron oxidants towards alcohols, the Pd(II) complex is a 4-electron oxidant via the periodate groups alone (I(VII)→I(V)) [50].

Tellurate complexes of Pd(IV) and Pt(IV) can be obtained by boiling $[M'Cl_6]^{2-}$ (M' = Pd or Pt) with $[Te(OH)_6]$ in concentrated alkali or in the case of palladium by hypochlorite or peroxodisulfate oxidation of $[PdCl_2]$ in the presence of alkali and $[Te(OH)_6]$ [60,165,166]. The X-ray structure of $K_6Na_4[Pt(OH)_2\{TeO_5(OH)\}_2]\cdot 12H_2O$ reveals (Fig. 23) a very similar anion to that in the periodate analogue, with Te–O(3) the TeOH group $d(\text{Te–O}) = 2.076(11)$ Å and Te–O(4) and Te–O(5) are Te=O groups, 1.872(11), 1.867(7) Å respectively [60]. The $^{195}Pt\{^1H\}$- and $^{125}Te\{^1H\}$-NMR spectra (Fig. 5) reveal three main species in solution which interconvert by varying the pH of the solutions, and are believed to reflect different degrees of protonation of the tellurate groups with slow proton exchange. Pt L_{III}-edge EXAFS studies of the solution forms suggest no major change in the platinum environment [60].

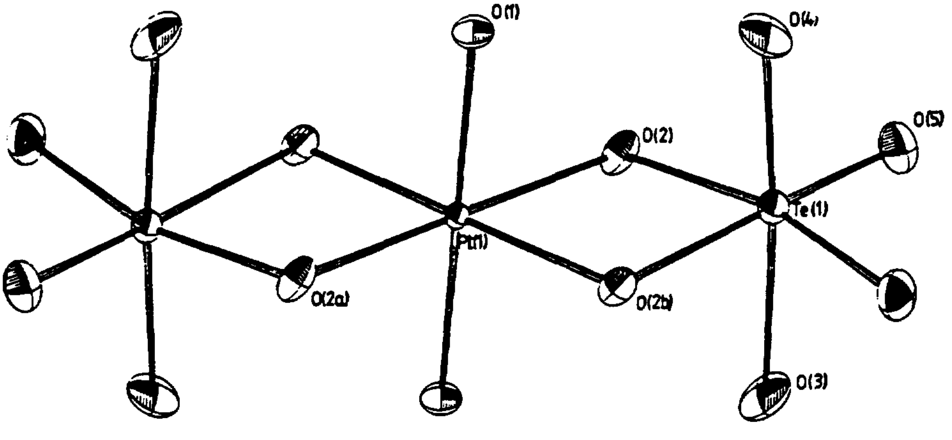


Fig. 23. The structure of the anion in $K_6Na_4[Pt(OH)_2\{TeO_5(OH)\}_2]\cdot 12H_2O$ from Ref. [60] by permission of the American Chemical Society.

The palladium system is more complex in that the solution formed by reacting $[PdCl_6]^{2-}$ and $[Te(OH)_6]$ in a 1:2 molar ratio in aqueous NaOH contained only a single $^{125}Te\{^1H\}$-NMR resonance at 801 ppm, and palladium K-edge EXAFS data on this solution suggested a $[Pd(OH)_2(TeO_6H_n)_2]^{10-n}$ ion similar to that in Fig. 23. However on concentration of the solution deep orange crystals of the dimer $Na_8K_2H_4[Pd_2Te_4O_{24}H_2] \cdot 20H_2O$ (Fig. 24) separated, which on dissolution in cold water has a $^{125}Te\{^1H\}$-NMR spectrum containing two singlets in a 1:1 ratio ($\delta =$ 804, 856) showing the structure is maintained in solution. On adding weak acids (including $[Te(OH)_6]$) to solutions of the dimer, new ^{125}Te-NMR resonances appear indicating different degrees of protonation, whilst on boiling these solutions reversion to monomer species with $\delta = 801$, 795 is observed. In the X-ray structure of the dimer [60] in Fig. 24 examination of the bond lengths suggests O(1,2,3,11 and 12) belong to Te=O groups (1.810(8)–1.829(8) Å) and O(4) at 1.988(8) Å is a Te–OH group, which leaves four protons required for charge balance unaccounted for. The bond lengths involving bridging oxygen atoms offer no clear evidence for the sites of protonation, although presumably the four doubly bridging oxygens are the more likely sites than the triply bridging ones.

4.9. Complexes of the group 11 metals

Copper(III) and silver(III) compounds containing periodate and tellurate groups were reported many years ago [167,168], and were among the first examples reported to contain these rare oxidation states. Malaprade [169] and Malatesta [170] subsequently obtained pure samples and recognised that they were coordination complexes, and these materials are among the most thoroughly studied periodate and tellurate compounds.

Hydrothermal reaction of CuO, $[Te(OH)_6]$ and KOH at 230°C produced green crystals of the copper(II) complex $K_2[Cu\{TeO_4(OH)_2\}] \cdot H_2O$ which has an infinite

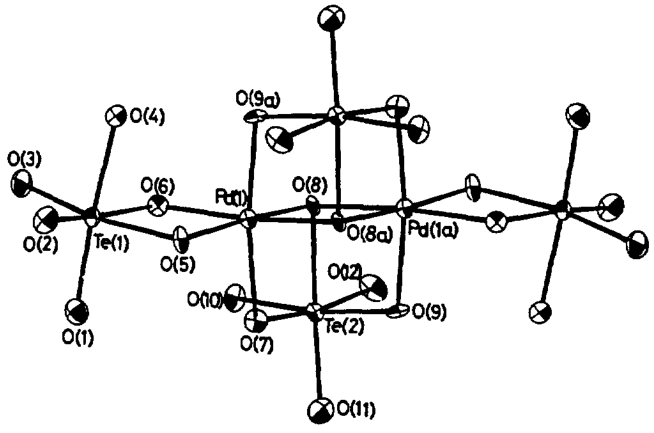


Fig. 24. The structure of the anion in $Na_8K_2H_4[Pd_2Te_4O_{24}H_2] \cdot 20H_2O$ from Ref. [60] by permission of the American Chemical Society.

chain anion composed of square planar CuO_4 groups which share *trans* edges with $TeO_4(OH)_2$ octahedra d(Cu–O) = 1.950 Å [171]. In $[Cu_2\{IO_5(OH)\}]\cdot 2H_2O$ square CuO_4 units corner share with $IO_5(OH)$ octahedra and one water molecule completes a square pyramidal arrangement about the copper [172]. There is also a blue $Na_6[Cu\{IO_5(OH)\}_2]\cdot 13H_2O$ which probably contains copper(II) in a tetragonal octahedral environment [173,174].

The brown copper(III) periodate complexes are usually prepared by oxidation of a copper(II) salt and a periodate in alkaline solution with hypochlorite or peroxodisufate, although periodate itself will slowly perform the oxidation. Ozone has also been used as the oxidant. Alternatively a copper anode may be dissolved electrolytically in a strongly alkaline solution of periodate [170,175–181]. The formulations were somewhat confused in the older reports and often written as $M_7[Cu(IO_6)_2]\cdot nH_2O$ (M = K or Na) [170,175,177], although more recent studies have arrived at the formulations $M_5[Cu\{IO_5(OH)\}_2]\cdot nH_2O$ and the basis for this is discussed in detail in [176]. It should be noted that, in some of the older work, specific analyses for the alkali metals were not carried out, rather after removal of the Cu and I, the residues were fumed to dryness with concentrated sulfuric acid and weighed as alkali metal sulfate, which could lead to error. The vibrational spectra [53,176] confirm protonation of the periodate groups, whilst the diamagnetism points to a square planar Cu(III) environment. A low precision X-ray study [182] of "$Na_3KH_3[Cu(IO_6)_2]\cdot 14H_2O$" established a planar copper centre coordinated to two IO_6 octahedra, and placed a water molecule 2.9 Å from the copper producing a square pyramidal geometry, and this has been often quoted in textbooks. An accurate single-crystal X-ray study of $KNa_4[Cu\{IO_5(OH)\}_2]\cdot 12H_2O$ [183] revealed square planar CuO_4 units edge sharing with $IO_5(OH)$ groups d(Cu–O) = 1.84(2) Å, with the nearest water molecule to the copper at 2.71(1) Å too long for a significant interaction. A further structure [184] of a material formulated (on the basis of the X-ray study alone) as $K_4H_4[Cu(IO_6)_2](O_2)\cdot 6H_2O$ arrived at a similar copper geometry and d(Cu–O) value, and examination of the values show that one of the terminal I–O distances at 1.97 Å is clearly an IOH group. The O_2 unit is claimed to be a superoxide group, but the reported d(O–O) (1.22 Å) is far too short, and the identity of this "group" must be regarded with some scepticism.

Deep yellow silver(III) periodate complexes are made by peroxodisulfate oxidation of $AgNO_3$ in alkaline periodate solution, dissolution of AgO or anodic dissolution of a silver electrode in alkaline periodate [170,176,178,185–187]. The kinetics of the reaction between $[Ag(OH)_4]^-$ and periodate (and tellurate) have been investigated [187]. The formulation of the products as $M_5[Ag\{IO_5(OH)\}_2]\cdot nH_2O$ (M = Na or K) follows from similar studies to those described previously for the copper analogues [53,176,187] and the structure of $K_5[Ag\{IO_5(OH)\}_2]\cdot 8H_2O$ [188] confirms the nature of the anion present (Fig. 25), with d(Ag–O) = 1.98 Å (av) and with the IOH groups perpendicular to the $O_2IO_2AgO_2IO_2$ plane (O(3) and O(12)). Gold(III) periodates have been less studied than the lighter analogues, but are easily made from $H[AuCl_4]$ and $[IO_4]^-$ in alkaline solution [50,180,188] The structure of $KNa_4[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 15H_2O$ (Fig. 26) shows the expected planar arrangement about the gold, and also the slightly folded nature of the anion [50].

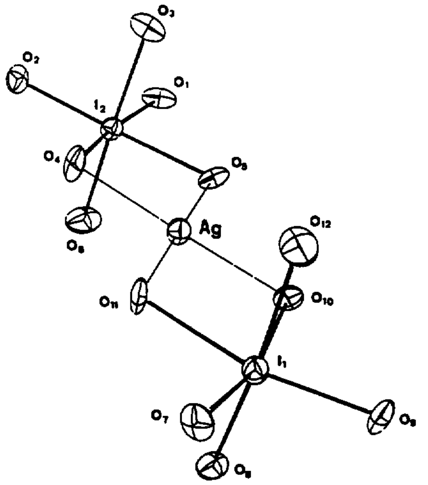


Fig. 25. The structure of the anion in $K_5[Ag\{IO_5(OH)\}_2] \cdot 8H_2O$ from Ref. [188] by permission of Academic Press Inc.

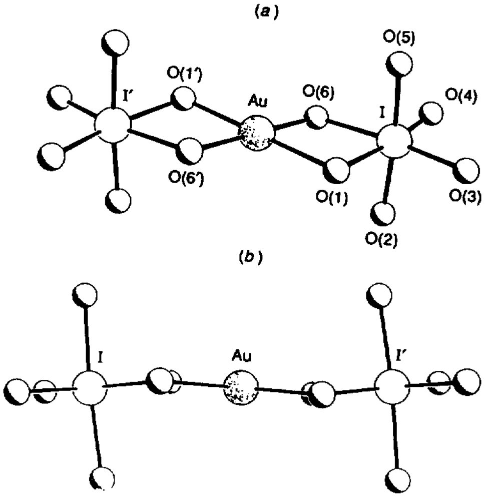


Fig. 26. The structure of the anion in $KNa_4[Au\{IO_5(OH)\}_2] \cdot KOH \cdot 15H_2O$ from Ref. [50] by permission of the Royal Society of Chemistry. Both perspective and side-on views are shown.

The pure solid Cu, Ag and Au periodates are stable at room temperature for months, and alkaline solutions decompose only slowly, although decomposition is immediate at low pH. This stability has allowed detailed study of their spectroscopic properties including: vibrational [53,176,189,190], PES- [174], ^{127}I- and ^{109}Ag-NMR [31], and EXAFS data [47]. The UV-visible spectra have been recorded on several occasions [58,159,191–194], although there are some disagreements in detail, mostly about whether d–d transitions can be identified. Fig. 27 shows the

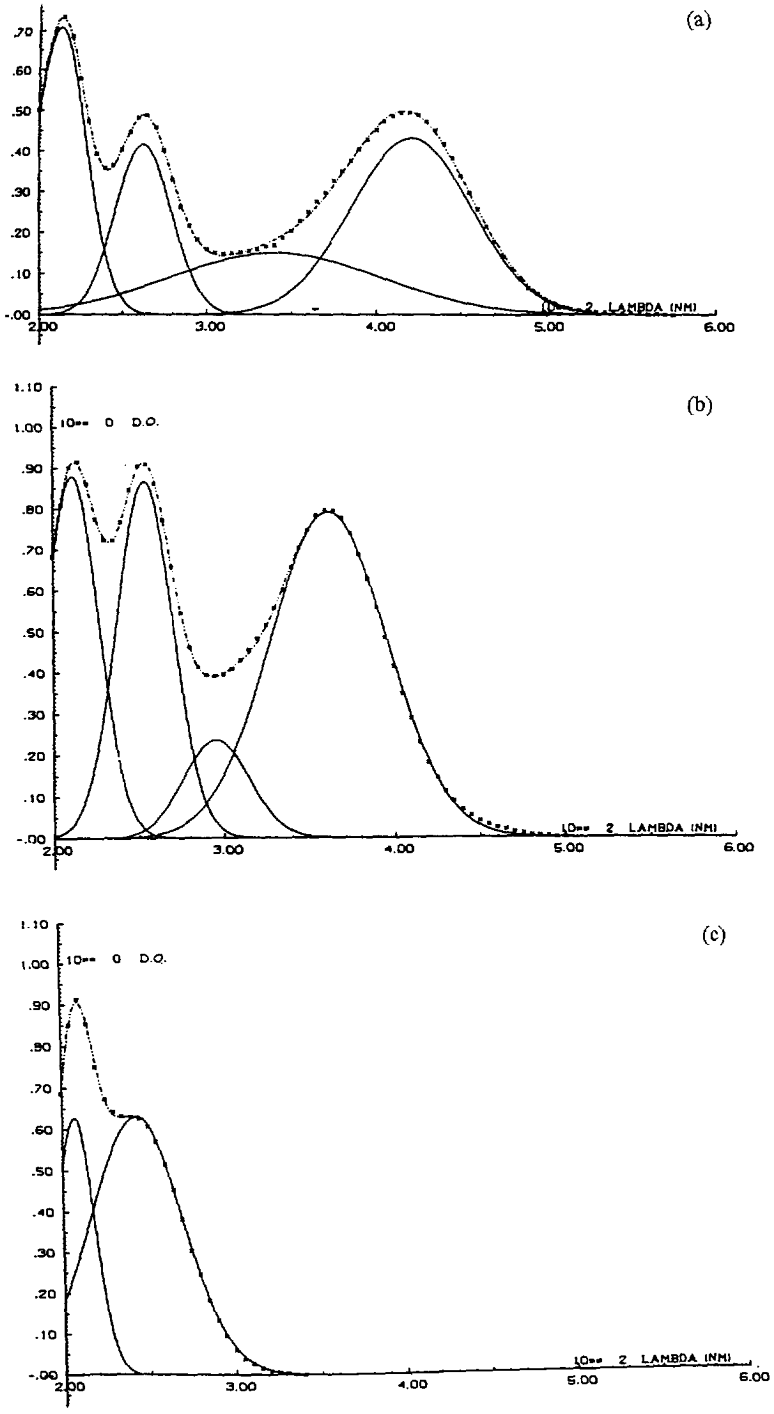


Fig. 27. UV-visible spectra and Gaussian analysis fits of the anions of (a) $[Cu\{IO_5(OH)\}_2]^{5-}$, (b) $[Ag\{IO_5(OH)\}_2]^{5-}$ and (c) $[Au\{IO_5(OH)\}_2]^{5-}$ modified from Ref. [176].

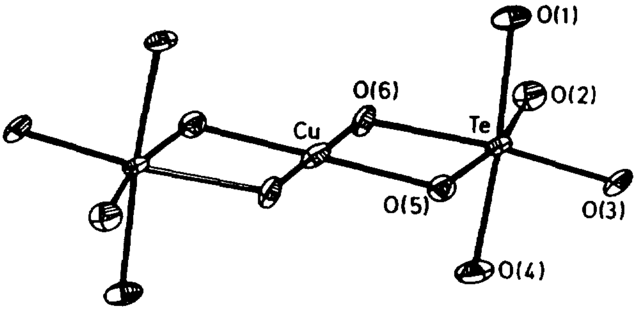


Fig. 28. The anion in $Na_5[Cu\{TeO_4(OH)_2\}_2] \cdot 16H_2O$ from Ref. [59] by permission of the Royal Society of Chemistry.

changes with metal and the results of a Gaussian analysis; the highest energy band is an internal transition of the periodate group, but the other two bands in the Cu and Ag compounds are assignable as ligand (σ and π) to metal ($d_{x^2-y^2}$) charge transfer, the gold shows only the lower energy CT band, and there was no evidence for d–d bands [58]. Other workers using different Gaussian fits believe that d–d bands can be resolved under the low energy tails of the first charge transfer band.

Tellurato-complexes of Cu(III), Ag(III) and Au(III) have been obtained by similar routes to the periodate analogues replacing periodate with tellurate ions [59,170,174–177,179,187,189]. After similar doubts about the correct formulations in early work, the complexes isolated were shown to be of the type $M_5[M'\{TeO_4(OH)_2\}_2] \cdot nH_2O$ (M = Na or K; M′ = Cu, Ag or Au) [59,176,187]. Only the copper complex has been characterised by a single-crystal X-ray [59] which revealed the anion shown in Fig. 28. The Te–O bond lengths establish that O(1) and O(4) are TeOH groups d(Te–O) = 1.996(4) and 1.968(4) Å and O(2) and O(3) Te=O (1.849(4) and 1.856(4) Å). Also notable is the fact that the $d(Cu^{III}–O)$ bond length is almost 0.1 Å shorter than that in the Cu(II) analogue described earlier in this section. Spectroscopic data on the tellurate complexes include: vibrational [59,176,189], PES [174], and EXAFS [47] data. The ^{125}Te-NMR spectra show high frequency shifts from $[Te(OH)_6]$ $\delta = +713$ to $+774.5$ (Cu), $+774$ (Ag) and $+753$ (Au), whilst the ^{109}Ag-NMR spectrum of the $[Ag\{TeO_4(OH)_2\}_2]^{5-}$ had $\delta = +2798$ (relative to $Ag^+_{(aq)}$), the very large shift presumably reflecting the high silver oxidation state [59]. Reported UV-visible spectra again show some disagreement in detail [58,59,189], but the main features are L to M charge transfer and occur at similar energies to those in the periodates.

Oxidation of organic substrates by group 11 periodato- or tellurato-complexes have also been studied [50,195–200]. Oxidised substrates include primary and secondary alcohols, amines and aldehydes. Towards primary alcohols the copper periodate complex is a 1-electron oxidant, the silver and gold compounds 2-electron oxidants, indicating that the metal but not the periodate is involved. However towards an activated primary halide (4-methoxybenzyl chloride) the unexpected result was that the metal and one periodate group (reduced to iodate) were the active oxidants.

5. Summary and conclusions

In this final section some general observations about periodate and tellurate ligands are made. Consideration of the data in Section 4 reveals that periodate complexes are more widespread than tellurate complexes, and where both are known the periodates appear more robust than the analogous tellurates. There is little similarity to complexes of oxoanions containing lighter group 16 or 17 elements (Cl, Br, S or Se) since none of these form octahedral oxoanions, and the effects of the different coordination numbers on the ligand properties are developed further below. Similar complexes based upon antimonate $[Sb(OH)_6]^-$ or stannate $[Sn(OH)_6]^{2-}$ ions are unknown, the few reported attempts to prepare them having failed [45,56,175]. It seems likely that the protons in these anions are too weakly acidic to be removed even in strongly basic aqueous media. The same problem would not apply to perxenate since $[XeO_6]^{4-}$ ions are known. The synthesis of perxenates is a hazardous undertaking and the complexes if formed may be explosively unstable; nonetheless the possibility that transition metal complexes could be obtained is intriguing.

Periodate and tellurate ligands seem to favour one oxidation state of each metal, often a surprisingly high one among the latter transition metals, for example Ru(VI), Pd(IV), Cu(III) or Ag(III). Only for the pairs Cu(II)–Cu(III) and Pd(II)–Pd(IV) are characterised complexes with coordinated periodate groups in two different oxidation states known. Further work is required to understand why both ligands stabilise manganese(IV) but apparently not manganese(III) [126], or why layered periodates can be easily prepared containing Mn(IV) or Ni(IV) but apparently not Fe(IV) [55]. Comparison with other σ and π donor ligands such as oxide or fluoride would lead one to expect that periodate complexes of several oxidation states of manganese, iron or nickel would be obtainable depending on the reaction conditions. Although periodate is a strong oxidant, tellurate is only weakly oxidising and thus their ability to stabilise high oxidation states results from the nature of the bonding discussed below, rather than from their oxidising power. Indeed, even in the case of the periodate complexes, the syntheses usually utilise peroxodisulfate, hypochlorite or ozone as oxidant rather that the periodate itself.

A small number of structural types dominate the coordination chemistry. The layered periodates $M'MIO_6$ all contain small tetravalent metals (M) and alkali-metal (not Li) or ammonium ions (M′). Lithium is presumably too small to stabilise the lattice and larger M(IV) ions such as cerium(IV) too large to fit in the octahedral holes. Incorporation of trivalent M ions such as Fe(III), Co(III) would be feasible on size grounds, but would require either an equivalent number of H^+ or M′ ions for charge balance. Again ion size is likely to be a key factor and in an $M'_2M^{III}IO_6$ compound with the same basic structure, there may not be space to fit in a second large M′ ion. However the report that $KLiFe0_6$ is formed by specific incorporation of lithium from a mixture of alkali-metals [134] is interesting. The $r(Li^+)$ of 0.74 Å is similar to that of $r(M^{IV})$ and possibly the lithium is incorporated into the empty octahedral holes within the close-packed oxide layers of the $M'MIO_6$ structure. This compound requires reinvestigation and particularly structural characterisation, but could be the first member of a series of compounds $M'LiM^{III}IO_6$, where M^{III} could be Fe, Co, Mn, Ni, etc., and M′ Na–Cs).

In the molecular anions, the common coordination mode of the periodate and tellurate groups is as bidentates with the $I(Te)O_6$ octahedron sharing an edge with the central metal. Monodentate binding through a single vertex is rare, although it occurs in the $[H_2V_2I_2O_{16}]^{6-}$ ions (Figure 10) where the IO_6 unit edge shares with one vanadium and then vertex shares with the second. Edge-sharing is also present in larger structures such as the Anderson type polyanions (Figure 12, Figure 17 and Figure 21) and in the tellurate dimer $[Pd_2Te_4O_{24}H_2]^{14-}$ (Figure 24). Face-sharing does not seem to be favoured, presumably it leads to a close approach M...I(Te) and destabilising repulsions (note however that the $[I_2O_9]^{4-}$ (III) is a confacial bi-octahedron). It is notable that in the edge-sharing structures, the $M(\mu\text{-}O)_2I(Te)$ units are distorted with the O–M–O and O–I(Te)–O angles substantially less than 90° which is consistent with M...I(Te) repulsions. The interplay of factors such as central atom radius and overall anionic charge in determining the structures of iso- and heteropolyanions have been well discussed by Pope [201], and such factors will be relevant in the present complexes, particularly in determining which metal ions can form Anderson type anions. The initially surprising absence of any periodate complexes of chromium, may be due to the ease with which chromium forms Cr^{6+}, which prefers tetrahedral over octahedral sites, and is thus similar to the well-known absence of iso- or heteropolychromates built from CrO_6 groups contrasting with the extensive chemistry based upon MoO_6 or WO_6 groups.

The difficulty of identifying the extent and the site(s) of protonation of the periodate and tellurate groups in the complexes has been stressed several times in this article, and indeed in a few cases including the Pt(IV) complexes there is direct NMR evidence for the existence of anions with different degrees of protonation in solution as a function of pH [49,60]. For the Anderson anion of cobalt in the material of composition $NaH_2[Co_4I_3O_{24}H_{12}]\cdot 11H_2O$, two different anions have been structurally characterised $[Co_4I_3O_{18}(H_2O)_6]^{3-}$ and $[Co_4I_3O_{18}(H_2O)_4(OH)_2]^-$ [148]. This is not unreasonable given the similar first three pK_a values reported for this ion [146]. In spite of this ability to vary the degree of protonation of the periodate or tellurate groups at least to some degree and in some complexes, a survey of the well characterised compounds (Section 4) reveals that some types are much more common than others. For periodate groups in the bis or tris-(periodato) metallate anions, the $[IO_5(OH)]^{4-}$ appears the commonest [31,48–50,86,126,188], with $[IO_4(OH)_2]^{3-}$ [126] and $[IO_3(OH)_3^{2-}$ [139] much rarer. In the layered periodates $M'MIO_6$, in $[M_2I_2O_{16}]^{6-}$ (M = Mo or W) and in the Anderson heteropolyanions $[IM_6O_{24}]^{5-}$ the IO_6 groups are fully deprotonated [52,53,97,100]. Similarly in the tellurate complexes, $[TeO_4(OH)_2]^{4-}$ is common [31,48,59,176], $[TeO_6]^{6-}$ is present in $[TeM_6O_{24}]^{6-}$ [108–114,118], whilst $[TeO_5(OH)]^{5-}$ seems rare [60] and coordinated $[TeO_3(OH)_3]^{3-}$ as yet unknown.Although no detailed theoretical treatment of the ligand properties of periodate or tellurate groups has been undertaken, the major features which make these anions strongly binding ligands and allow them to stabilise high oxidation states of many transition metals, are relatively clear. The very different ligand properties of periodate and tellurate compared to those of lighter anions such as $[SeO_4]^{2-}$ or $[BrO_4]^-$, is due to the fact that the central iodine or tellurium have lower electronegativities and are coordinated to six rather than four oxygens. This results in much less electron drift from oxygen to the central non-metal, and thus more electron density remains available on the oxygens for donation to a metal centre. The periodate or tellurate group functions as a strong σ and π donor via these oxygens, which is usually supplemented by the chelate effect. Thus their ability to stabilise high valent metal centres derives from similar bonding to oxide ligands although the σ and π donation to the metal competes with similar donation towards the I or Te centres. Indeed our description of the complexes as "metal centres coordinated by periodate or tellurate ligands" derives from the way they are synthesised — a description in terms of metal and iodine or tellurium centres bonded to oxide or a combination of oxide/hydroxide ligands would be an acceptable alternative. As ligands, periodate and tellurate are more analogous to $[MoO_6]^{6-}$ or $[WO_6]^{6-}$ groups in heteropolyanions than to perchlorate or sulfate. This analogy is supported by the fact that for example Mn(IV) or Ni(IV) centres are found in O_6 environments in anions such as $[NiMo_9O_{32}]^{6-}$ [202] or $[MnNb_{12}O_{38}]^{12-}$ [203]. Analysis of the UV-visible spectra of $[Mn\{IO_5(OH)\}_2\{IO_4(OH)_2\}]^{7-}$ and $[Mn\{TeO_4(OH)_2\}_3]^{8-}$ [56,126] identify the periodate and the tellurate groups as weak field ligands, slightly below F^- in the spectrochemical series. The ligand field splittings are very similar to those found in Mn(IV) complexes with molybdate or niobate ligands reinforcing the analogy drawn above. In conclusion, it should be noted that further variety in the ligands should be achievable by replacing O or OH groups in the periodate or tellurate group by fluorine, leading to ligands derived from, for example, $[TeF_4(OH)_2]$ or $[IF_4O(OH)]$. A substantial amount of work has been reported with pentafluoroorthotellurate (teflate) $[F_5TeO]^-$, which bonds only through oxygen to both high and low valent metals either as a monodentate or bridging bidentate [204,205], but very little is known about the ligand properties of less highly fluorinated analogues.

6. Future work

It is apparent from Figure 7 and Section 4 that despite the considerable progress in the investigation of the ligand properties of periodate and tellurate groups, particularly in the last 20 years, much scope for further work remains. This work falls into two main categories, synthesis and study of new complexes and detailed reinvestigation of presently incompletely characterised compounds.

Areas where little or nothing is known include the groups 4 and 5 metals. The oxophillic M^{4+} (M = Ti, Zr or Hf) should form tris or perhaps tetrakis complexes with tellurate or periodate with 6- or 8-coordinate metal centres. In group 5, only the $[V_2H_2I_2O_{16}]^{6-}$ ion is well characterised, although periodates with a V:I ratio of

2:1 were prepared in early work, but need detailed characterisation, and similarly I/Te–Nb/Ta heteropolyanions are highly likely to form. Among later groups the absence of rhodium and especially iridium complexes is notable. Both tellurate and periodate should afford complexes of the M(III) ions and, more interestingly, iridium(IV) and possibly iridium(V) and rhodium(IV) should be obtainable in water soluble anions.

Complexes reported but incompletely characterised include the tellurates of iron(III) and cobalt(III) for which both mononuclear and Anderson type polyanions may exist and for which X-ray structures are badly needed. Despite several studies, the constitution of the "bis(periodate)" complexes of cobalt(III) and iron(III) also remain unclear, and again structural characterisation will be required.

Although characterisation of complexes of simple oxygen donor anions may appear straightforward in comparison with compounds in many areas of modern coordination chemistry, the descriptive chemistry in Section 4 shows this is not so. In fact, thorough characterisation requires a combination of many spectroscopic and structural techniques. For the periodate and tellurate compounds, single crystal X-ray studies, usually regarded by the chemist as the definitive characterisation method for crystalline solids, may not provide a full understanding of the constitution. The problem as stated before lies in the location of the hydrogen atoms. In only a very limited number of cases where the crystal and data quality were particularly high, have the hydrogen atoms been directly observed in the difference maps. In the majority of cases the protonation of the oxygen atoms in the periodate or tellurate ligands is inferred from examination of the d(I–O) or d(Te–O) bond lengths (Section 3.1) and their presence (although not the number or positioning of the IOH or TeOH groups) confirmed by vibrational spectroscopy. In poor quality crystals errors may arise due to unrecognised positional disorder between I=O/I–OH groups, and since different degrees of protonation of at least some anions appear possible, anions with different charges may be present. For example, in early studies some copper(III) periodate complexes were formulated $M_7[Cu(IO_6)_2]\cdot nH_2O$, although most recent studies have concluded $IO_5(OH)$ groups are present (Section 4.9). It is worth remembering that distinction of, for example, $M_5[Cu\{IO_5(OH)\}_2]\cdot 2MOH\cdot nH_2O$ and $M_7[Cu(IO_6)_2]\cdot(n+2)H_2O$ by X-ray crystallography alone is not straightforward, and may be impossible if the crystal quality (and hence the resulting data quality) is not high. Further complications arise from the large amounts of lattice water, and the alkali-metal:anion ratio in the crystal studied may not be integral, charge balance being maintained by some H_3O^+ (e.g., Ref. [59]). Unexpected ions may be present, for example, the adventitious incorporation of Na^+ due to corrosion of the glass vessel [49].

With the power of modern spectroscopic techniques, it has become common in many areas of coordination chemistry to provide conventional analyses for only some of the elements present (if organic ligands are present, typically C, H, N, and possibly halide), the analytical data serving to support the constitution derived spectroscopically or structurally and as proof of adequate purity. For the compounds which are the subject of this review analytical data must be as complete as possible.

Certainly analyses for the transition metal, I/Te and alkali-metals are essential, whilst water content can be estimated by TGA (although some oxygen loss due to decomposition may accompany water loss, this usually does not cause problems in practice). Estimating alkali-metal content "by difference" or by weight as M_2SO_4 after removing other elements and fuming down the residue with sulfuric acid, as sometimes done, is inadequate and may account for some of the discrepancies in the literature. Identification of the elements present by energy dispersive X-ray analysis is also very desirable, and will detect adventitious sodium, or $[SO_4]^{2-}$ or Cl^- impurities left by use of peroxodisulfate or hypochlorite as oxidants.

The amine or amino-acid substituted derivatives of cobalt(III) periodate and tellurate anions (Section 4.7) and the recently reported $[RuO_2(2,2'\text{-bipy})\{IO_3(OH)_3\}]\cdot 1.5H_2O$ [139] show that N or O donor ligands may be incorporated fairly easily, and with appropriate choice of the co-ligand may facilitate transfer of the periodate/tellurate chemistry into non-aqueous solvents. Apart from some examples of the use of alkylammonium or $[Co(en)_3]^{3+}$ cations by Griffith and co-workers [48,50], the cations used to isolate periodate or tellurate complexes are mostly limited to alkali metals or NH_4^+. Use of tetraalkylammonium, tetraphenylphosphonium or alkali-metal-cryptates as cations may promote solubility of the complexes in polar organics and potentially offers an unexplored route to crystals for X-ray structural studies.

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Note added in proof

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