Coordination Chemistry Reviews
178–180 (1998) 865–902

Inorganic perchlorato complexes

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Contents

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PII S0010-8545(98)00102-7

Abstract

A summary is given of the synthesis of non-solvated inorganic perchlorato complexes and their structural characterization. The synthesis of perchlorato complexes has been extended to many elements of the periodic table by the use of efficient perchlorating reagents such as perchloric acid, $HClO_4$–Cl_2O_7 oleums and chlorine trioxide, Cl_2O_6. X-ray diffraction, EXAFS and vibrational spectroscopy show that the perchlorato ligand, $[ClO_4]$, can be strongly bonded to metals in various bonding arrangements: monodentate, bridging or chelating bidentate, simply bridging or simultaneously bridging and chelating tridentate. It is mostly an assembling ligand.

Keywords: Chlorine trioxide; Diffraction; Non-solvated; Perchlorato; Synthesis; Vibrational spectroscopy

1. Introduction

Although the perchlorate ion was discovered in 1816 [1], its coordinating ability was only demonstrated in 1961 by Hathaway and Underhill from the interpretation of the infrared spectra of copper perchlorates [2]. During the intervening 150 years or so, ClO_4^- was classified as a non-coordinating anion [3] and its very weak basicity is correlated to the very strong acidity of $HClO_4$ ($pK_a = -18$) (J. Potier, private communication). ClO_4^- was the preferred anion, and is still amply used for this purpose, for the study of the behaviour of cations in solution in the absence of any anionic interference [4]. Nevertheless, until Hathaway's work, only a few covalent perchlorates were prepared. As an example, ethyl perchlorate was first synthesized in 1862 [5]. More recently, during the 1950s, Schmeisser and Brändle, studying the reactivity of chlorine trioxide, Cl_2O_6, towards several liquid metallic chlorides, were able to prepare compounds including $[ClO_4]$ groups potentially coordinated to the metal [6]. In neither case was physical analysis used to characterize the $[ClO_4]$ arrangement. Usually, $[ClO_4]$ could only be bonded to a metal when there was no competition with stronger Lewis bases. Only if the coordination sphere of the metal is large enough to accept several bonds, can $[ClO_4]$ compete with water or organic solvents. A large number of such complexes are continuously reported [7,8], but in the majority of these compounds $[ClO_4]$ is weakly bonded to the metal. It often plays the role of a linking unit in the building of a molecular edifice.

Since the discovery of ethyl perchlorate, numerous pure organic perchlorates have been prepared and characterized [9] but, for a long time, information on pure inorganic perchlorates was surprisingly scarce and restricted to ionic salts [10,11], mainly limited by the non-reliability of the synthetic methods.

Classical preparative routes proceeding by thermal dehydration of a hydrated metal perchlorate led frequently to unexpected decomposition products (oxides, oxychlorides or chlorides) rather than anhydrous perchlorato complexes [12]. Over the past 25 years, the methods of synthesis have been considerably improved by the use of efficient perchlorating reagents, including anhydrous perchloric acid [13], $HClO_4$–Cl_2O_7 oleums [14], Cl_2O_6 [15] or chlorine perchlorate [16]. A large number of non-solvated perchlorato complexes or salts of elements over a wide range of the periodic table have been prepared and characterized by Rosolovskii and coworkers in Russia [22] as well as Christe in the US [16] and ourselves [23]. In view of the thermodynamic stability of the resulting perchlorato complexes, it appeared that $[ClO_4]$ is as strong a ligand as carbonate [17], acetate [18] or nitrate [19,20]. It can also be considered as a model for tetrahedral assembling ligands [21].

The synthetic processes are now largely controlled, but the structural data available are still limited. Only 18 structures have so far been determined either on single crystals, using X-ray powder data, or from EXAFS analysis. Vibrational spectroscopy remains the main technique used for determining the bonding mode and a local approach to a description of the molecular structure.

Although the reactivity and uses of ionic perchlorates are well developed [10], those of perchlorato complexes are still limited due to their considerable potential hazards. Some catalytic processes involving perchlorates have been nonetheless described [24] and the exploratory use of perchlorates as starting materials for the preparation of oxides, oxychlorides or chlorides as fine powders is beginning [25].

The main purpose of this paper is to briefly review the advances in synthesis, structural analysis and reactivity of inorganic perchlorato complexes and to summarize our results in this field.

2. Synthesis

Two different types of reaction can be used to synthesize perchlorato complexes:

- a dehydration of a hydrated metal perchlorate using a thermal or chemical process;
- a chemical reaction involving an efficient perchlorating reagent.

2.1. Dehydration of hydrated perchlorates

Some perchlorato complexes such as those of nickel [26], cobalt [27], zinc [28], cadmium [29] or lanthanides [30] can be prepared by warming the corresponding hydrated ionic salt in air or under vacuum. However, these results are not always strictly reproducible and decomposition sometimes leads simultaneously to by-products such as oxo or hydroxo perchlorato complexes [31]. For lanthanide complexes, phase transitions are hidden by the change from hydrated to the anhydrous form [32]. For the majority of hydrated perchlorates, the thermal method of dehydration leads to decomposition products according to the following pathway

$$\begin{array}{l} \Rightarrow MCl_n + 2nO_2 \\ M(ClO_4)_n\Delta \Rightarrow MOCl + (n-1)/2Cl_2 + (4n-1)/2O_2 \\ \Rightarrow MO_{n/2} + n/2Cl_2 + 7n/2O_2 \end{array}$$

Water may also be removed by the use of an organic solvent, e.g. alcohol, acetonitrile, DMSO, as has been reported for lanthanides [33], gallium [34] or aluminium [35]. In such cases, water in the coordination sphere of the metal is replaced by the solvent and the perchlorate remains ionic. Trying to remove the coordinated solvent by heating or under vacuum is very hazardous and may be performed only with small quantities of product and with appropriate precautions.

P_2O_5 has served for the dehydration of perchloric acid in the preparation of perchloryl perchlorate, Cl_2O_7 [36], to decrease the hydration level of hydrated perchlorates and for the preparation of, for example, $Zn(ClO_4)_2 \cdot H_2O$ from $Zn(ClO_4)_2 \cdot 4H_2O$ [28]. Rosolovskii used anhydrous perchloric acid to dry cobalt perchlorate [37], but this preparative method remains the exception. In spite of its potentially dehydrating power, Cl_2O_7 is weakly reactive and cannot be used as a dehydrating reagent. The most powerful dehydrating reagent appears to be chlorine trioxide, Cl_2O_6. Its use, largely developed in our work, will be discussed below.

2.2. *Perchlorating reagents*

The principle of the reaction of a perchlorating agent on a salt is to replace a labile ligand by $[ClO_4]$ in the coordination sphere of the metal. The resulting byproducts should be easily removable from the medium. Useful starting salts are chlorides, nitrates, carbonates, etc., which give, respectively, chlorine dioxide or chlorine, nitrogen oxides, CO_2, etc. The most usual perchlorating reagents are given in Table 1.

2.2.1. *Perchloric acid, $HClO_4$*

The synthesis of large quantities of anhydrous $HClO_4$ was described by Mascherpa [43]. Its thermodynamic [50], vibrational spectroscopic properties [50,52] and crystal structure at low temperature [53] were reported. Unlike HNO_3, H_2SO_4 or H_3COOH, $HClO_4$ shows no intermolecular $H–O \cdots H$ bonding [50] and is characterized by dissociation equilibria responsible for the aqueous conductivities [54]:

$$3HClO_4 = Cl_2O_7 + H_3O^+ClO_4^- \quad k_1 = 1.33 \times 10^{-4},$$

$$2(H_3O^+ClO_4^-) = HClO_4 + H_5O_2{}^+ClO_4^- \quad k_2 = 1.55 \times 10^{-3}.$$

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Table 1
Main perchlorating reagents

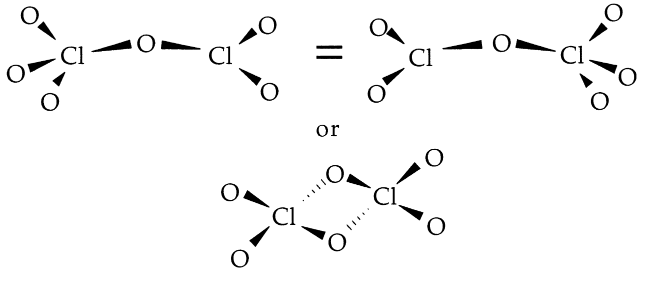
Compound	Synthesis	Aspect	mp (°C)	bp (°C)	Remarks
$AgClO_4$	Commercial product	White solid	Dec.	—	Mild perchlorating reagent used in organic chemistry or with some liquid chlorides [9,10].
$NOClO_4$	N_2O_3 or NO_2 in $HClO_4$ 72% [39]	White solid	Dec.	—	Limited to the historical synthesis of Cu $(ClO_4)_2$ [2]. Can give mixture of nitrato and perchlorato complexes. Reaction should proceed at $T>120$ °C.
$NOClO_4$	$N_2O_5+Cl_2O_7$ in CCl_4 (RT) [40] N_2O_5 or $HNO_3+Cl_2O_6$ (RT) [41] dec. $(NO_2)_mM(ClO_4)_{n+m}$ [31]	White solid	Dec.	—	Synthesis of $Cu(ClO_4)_2$ by Rosolowskii [42]. Reaction should proceed at $T>120$ °C.
$HClO_4$	1 $HClO_4$ 72% $+2H_2SO_4$ boiling at 1333 Pa [43]	Colourless liquid	−101	120.5	Highly reactive acid and mild perchlorating reagent even at low temperature, but presents and autodehydration process. Should be used in Cl_2O_7-$HClO_4$ oleum.
Cl_2O_7	$HClO_4+P_2O_5$ [36]	Colourless liquid	91.5	81	Very poor perchlorating reagant. Chlorating reagant [51]. Very unstable compound. Sometimes used in the synthesis of organic perchlorates [9].
Cl_2O_6	ClO_2+O_2/O_3 (−10 °C) [45,46]	Blood red liquid at room temp., ruby red solid at −30 °C, yellow solid at −180 °C	3.5	20 dec.	Very efficient perchlorating reagent, but the reaction temperature range is narrow. In spite of the presence of Cl(V) which can induce reduction processes, very strong oxidizer.
$ClOClO_3$	$HClO_4+ClSO_3F$ [47]	Pale yellow liquid	−117	44.5	Certainly the most efficient perchlorating agent, but very difficult to prepare, store and handle.
$FOClO_3$	$HClO_4+F_2$ [47] NF_4ClO_4 decomposition [49]	Colourless liquid	−167	−15	

2.2.2. $HClO_4$–Cl_2O_7 oleums

The above dissociation process is a significant drawback in any use of anhydrous perchloric acid in the synthesis due to formation of water. In order to displace the equilibria to the left, Rosolovskii prepared $HClO_4$–Cl_2O_7 oleums [55]. In an elegant series of experiments, this group was able to synthesize a large number of perchlorato complexes. However, Cl_2O_7 is an unpredictable chlorine oxide which can decompose spontaneously.

2.2.3. Chlorine trioxide, Cl_2O_6

Chlorine trioxide has been known since the work of Goodeve and Richardson in 1937 [45]. Its synthesis was improved by reacting an ozone/oxygen mixture with ClO_2, and its perchlorating ability discussed, around 1955, by Schmeisser [6] and confirmed in 1971 from infrared and Raman data [56]. Chlorine trioxide exists as chloryl perchlorate, $ClO_2^+ClO_4^-$, in the solid state and is in equilibrium $(Cl_2O_6)_{\text{ionic}} = (Cl_2O_6)_{\text{covalent}}$ in the liquid state. The high conductivity of Cl_2O_6 in the liquid state (0.105 S cm^{-1}) is a consequence of this equilibrium [46]. The ionic form was recently analysed by single crystal X-ray diffraction [57]. The covalent form has been identified in the solvents having low dielectric constant such as CCl_4, $CFCl_3$ or SO_2. Vibrational spectroscopy shows that terminal ClO and bridged ClOCl are simultaneously present [46]. ^{17}O and ^{35}Cl NMR spectra in SO_2 at $-40\,^{\circ}C$ suggest two types of oxygen and one type of chlorine atom (G. Schröbilgen et al., unpublished results). The most probable arrangements are:



Structural data may be compared with those of N_2O_5 which is a well known and very efficient nitrating reagent [44].

The remarkable perchlorating properties of Cl_2O_6 are associated with its strongly dehydrating ability according to

$$Cl_2O_6 + H_2O \rightarrow HClO_4 + HClO_3.$$

2.3. Reactivity of perchlorating reagents towards metallic salts

In the following paragraph, we describe our preparative routes for unsolvated perchlorato complexes by the use of perchlorating reagents on metallic salts.

Caution: anhydrous perchloric acid, chlorine trioxide and perchlorato complexes are highly reactive species. The quantities of products handled should be restricted. Reactions must be carefully monitored. Any contact with organic substances must be avoided and appropriate protection should be used.

Because of the high hygroscopic nature of the reagents and products, the syntheses were performed in an all pyrex glass vacuum line (see Fig. 1) equipped with Teflon valves and Teflon protected silicon joints. A KELF grease was used on removable traps. Sampling was performed in a dry glove box filled with argon or nitrogen (<5 ppm in H_2O and O_2).

Two main steps are generally used

- the synthesis and purification of the perchlorating reagent, $HClO_4$ or Cl_2O_6 [43,46];
- the reaction of the chosen perchlorating reagent with a metallic salt [46].

2.3.1. *Synthesis of $HClO_4$ and Cl_2O_6*

Anhydrous perchloric acid is prepared according to Mascherpa [43] by dehydration, under reduced pressure (13×10^2 Pa), of 70–72% commercial $HClO_4$ in boiling 96% H_2SO_4. It is stored at 0 °C in glass ampoules that can be linked for distillation to the vacuum line.

The synthesis of Cl_2O_6 proceeds by the oxidation of ClO_2 by an O_3/O_2 mixture

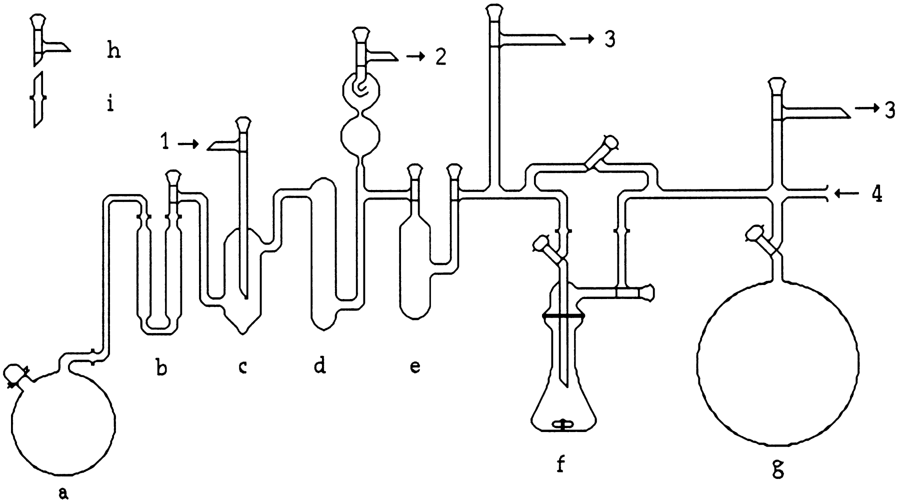


Fig. 1. Pyrex vacuum line for the synthesis of chlorine trioxide and anhydrous perchlorato complexes: (a) Synthesis of ClO_2 at 50 °C [$2KClO_3+2H_2SO_4(5N)+H_2C_2O_4\cdot2H_2O\rightarrow2ClO_2+2CO_2+4H_2O+2KHSO_4$]; (b) P_4O_{10} columns; (c) synthesis of Cl_2O_6 ($2ClO_2+2O_3\rightarrow Cl_2O_6+2O_2$) at −10 °C; (d) Cl_2O_6 trap (0 °C); (e) distilled Cl_2O_6 (−25 °C); (f) perchlorato complex synthesis; (g) 4 l bulb to collect evolved gases; (h) Rotaflo valve; (i) Rotulex joint; (1) O_3/O_2 mixture from a Siemens type ozonizer; (2) to H_2SO_4 traps and fume hood; (3) to vacuum line; (4) to IR cell (matrix type) or $HClO_4$ storage ampoule.

at −10 °C [45]. The blood red liquid is purified by trap to trap distillation under vacuum and stored at −25 °C [46].

2.3.2. Reactions

In a typical preparation, the starting material (chloride, carbonate, nitrate, hydrated perchlorate, oxide) is weighed in a reactor (Fig. 1). This reactor is evacuated and the perchlorating reagent is gradually introduced by distillation at low temperature (−180 °C). The mixture is then gently warmed to 5–15 °C until the reaction starts. The gases evolved (Cl_2, O_2, ClO_2, $HClO_4$, $HClO_3$) are collected in a 4 l round bottomed flask which is regularly pumped off. Freshly distilled $HClO_4$ must be used and the reaction time limited to 10 min. Cl_2O_6 is reacted until completely consumed. The reaction is continuously monitored by weighing and by Raman analysis. Before successive additions of perchlorating reagent, the product is ground in glove box in order to increase the surface area in contact with the reagent. The reaction is stopped when the expected weight is reached and when there is no further trace of the starting salt.

2.3.2.1. Reactions with $HClO_4$. In our laboratory, reactions using $HClO_4$ have been limited to following compounds (Table 2):

- Synthesis of $Cr(ClO_4)_3$ [58] and boron perchlorates, BCl_2ClO_4, $BCl(ClO_4)_2$ and $B(ClO_4)_3$ [59].
- Preparation of salts $A_xM(ClO_4)_{3+x}$ with $A = NH_4$, NO_2 and $M = B$ or Al [60].
- Preparation of large quantities of $Fe(ClO_4)_3$ from $ClO_2Fe_2(ClO_4)_7$ by extraction of Cl_2O_6 [24,61]. Such a reaction could not be generalized since, for example, the unknown $Ge(ClO_4)_4$ could not be prepared from $(ClO_2)_2Ge(ClO_4)_6$ [62].
- Synthesis of $Fe(ClO_4)_3 \cdot 2H_2O$ in a particularly lengthy reaction with $FeCl_3$ [24,61].

The above data indicate that $HClO_4$: (i) should be considered as a mild perchlorating reagent, used instead of Cl_2O_6 when the oxidiative power of the latter is too high towards some elements such as Cr or B; (ii) is a good solvent for $AClO_4$ salts ($A = NH_4$, NO_2 or alkali metals) [42].

2.3.2.2. Reactions with Cl_2O_6. In many cases, anhydrous perchloric acid did not give the desired perchlorato complex, and for a majority of preparations, Cl_2O_6 was a more efficient perchlorating reagent. Products prepared by the use of chlorine trioxide are given in Tables 3 and 4.

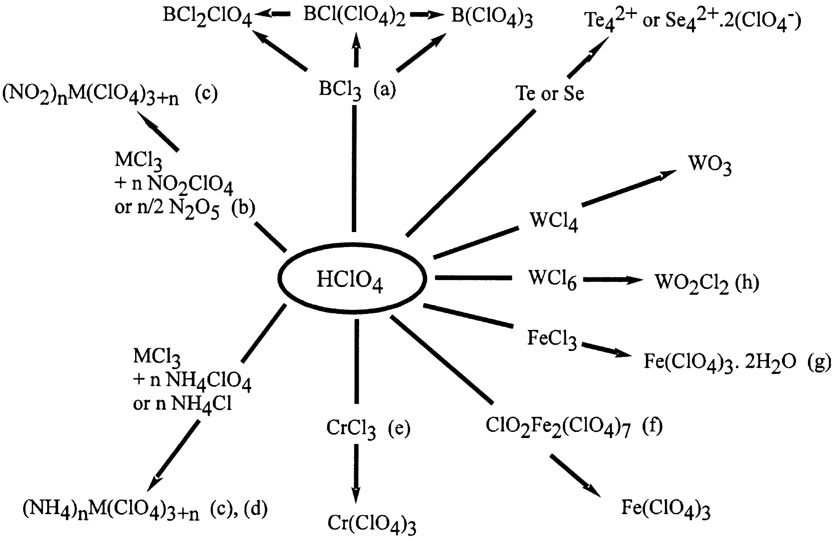
With anhydrous metallic chlorides, the principal reaction occurring can be written as follows:

$$MCl_n + (n+1)Cl_2O_6 \rightarrow ClO_2M(ClO_4)_{n+1} + nClO_2 + n/2Cl_2.$$

With hydrated chlorides a two steps pathway is followed:

- synthesis of a hydrated perchlorate, $M(ClO_4)_n \cdot mH_2O$;
- dehydration of the hydrated perchlorate by elimination of $HClO_3$ and $HClO_4$.

Table 2
Synthesis of perchlorato complexes by the use of $HClO_4$



(a) $HClO_4$ was added stoichiometrically to BCl_3 to obtain the expected composition, BCl_2ClO_4 and $BCl(ClO_4)_2$ are liquid, stable at room temperature and below −78 °C, respectively; the latter decomposes to give $B(ClO_4)_3$ and BCl_2ClO_4 on increasing the temperature. $B(ClO_4)_3$ is a white solid stable at $T<0$ °C; (b) NO_2ClO_4 and N_2O_5 were prepared according to literature methods [41,42]; (c) $n=1$ with M=B and $n=1$–3 with M=Al; (d) a double salt $NH_4Al(ClO_4)_4 \cdot (HClO_4)_{0.5}$ was isolated; (e) "hygroscopic form" prepared by dehydration of $CrCl_3 \cdot nH_2O$ with $SOCl_2$; (f) prepared from $FeCl_3$ and Cl_2O_6 (see Table 3); $Fe(ClO_4)_3$ is quantitatively obtained after repeated washing; (g) long time reaction with $FeCl_3$, this reaction is an illustration of self dehydration of anhydrous $HClO_4$ leading to hydrated perchlorate (see Section 2.2.1); (h) an intermediate unstable perchlorate $WO_xCl_y(ClO_4)_z$ was detected.

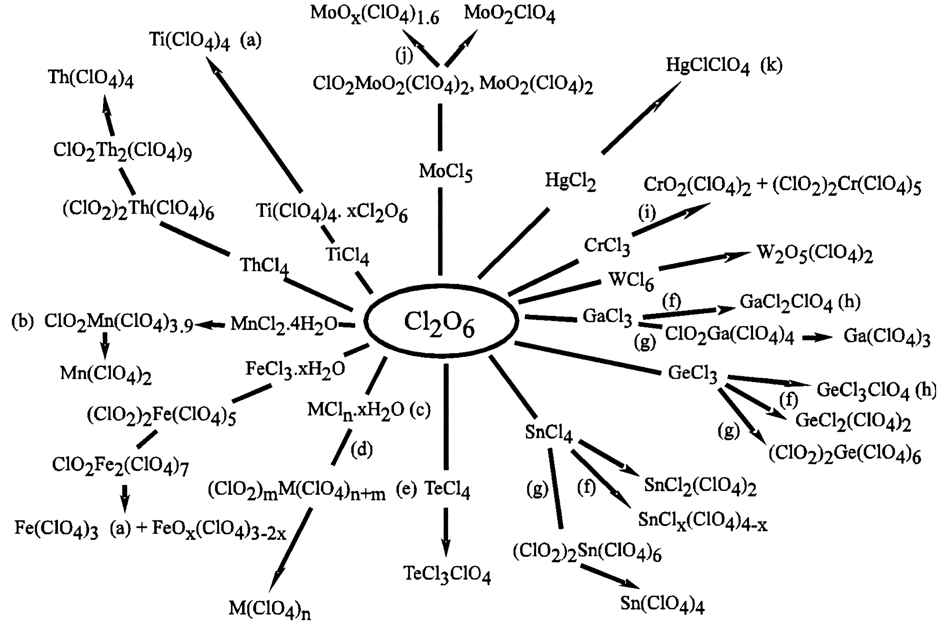
The chloryl salt, $ClO_2M(ClO_4)_{n+1}$, generally decomposes on heating to give the corresponding $M(ClO_4)_n$.

Due to the existence of generally labile chloride ions in hydrated metal chlorides, reactions are easier than with anhydrous salts where chlorine is often a part of a compact lattice. As an example, the synthesis of $Ni(ClO_4)_2$ starting from anhydrous $NiCl_2$ needed 12 successive additions of Cl_2O_6 while, for an equivalent quantity of Ni, only two additions were needed with nickel chloride hexahydrate [31]. Note that the "reaction rate" can be improved using "hygroscopic" anhydrous chlorides prepared by dehydration with $SOCl_2$ [63]. This can be explained in terms of residual water molecules introducing defects in the lattice and by the fact that the particle size generally decreases during the dehydration process.

It can be seen from Table 3 that the above described reactions are not general:

- Oxo-perchlorato complexes of group 6 elements and of rhodium could be prepared. In this case, besides its perchlorating behaviour, Cl_2O_6 acts simultaneously as an oxidant.

Table 3
Reactivity of Cl_2O_6 towards metallic chlorides



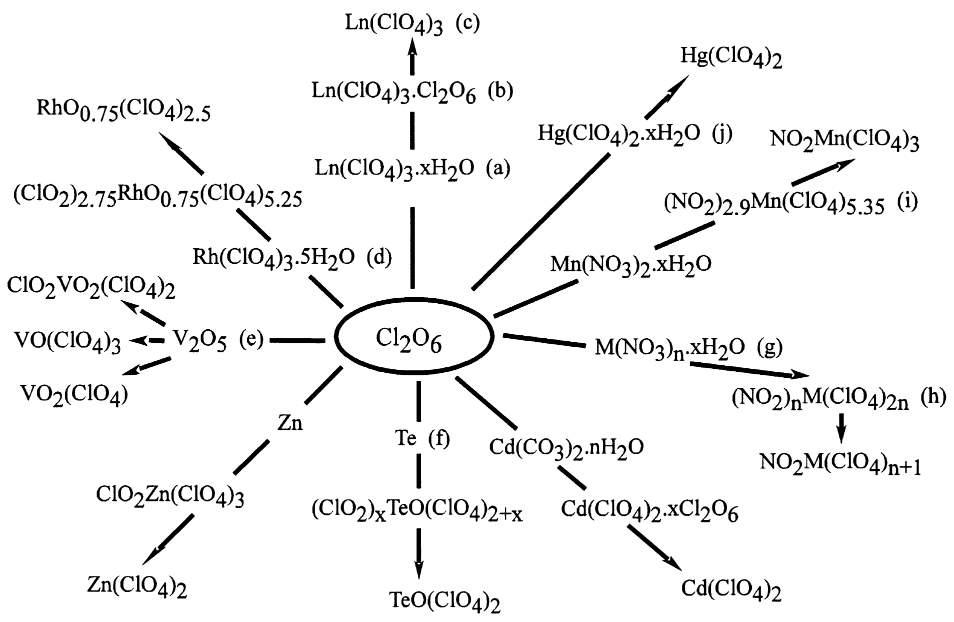
Metallic chlorides are generally available and used without purification. Perchlorato complexes given in this table [see (h) for exception] are solids which decompose into an oxo-perchlorate, oxide or oxychloride before melting.

(a) Sublime at $T \leq 60$ °C; for iron, the yield is less than 10%; (b) mixed valence Mn (II)/(III) compound; (c) M = Co, Ni, Cu, Cd, In, Tl, Sc, La, Pr and Er; n is the oxidation state of M; (d) $0 < x < 6$; quickest reaction times when $x > 0$; (e) definite chloryl salt with $m = 1$ for M = Co, Ni, Cu, In, Tl and Er; with $m =$ 0.33 for La; mixture of Cl_2O_6 and $M(ClO_4)_n$ complex for M = Cd, Pr and Sc ($m = 0.25$); the decomposition of the chloryl salt into the corresponding $M(ClO_4)_n$ occurs at $T > 70$ °C for Tl complexes, Tl_2O_3 starts to be formed at $T \geq 95$ °C; the synthesis of cadmium perchlorate from chloride is arduous; (f) insufficient Cl_2O_6; (g) excess Cl_2O_6; (h) liquid perchlorate at room temperature; (i) $CrCl_3$ "hygroscopic" form; the red liquid $CrO_2(ClO_4)_2$ is separated from the solid $(ClO_2)_2Cr(ClO_4)_5$ under vacuum; (j) mixed valence Mo(V)/(VI) compound; (k) the reaction is very difficult and $HgClClO_4$ is generally mixed with $HgCl_2$ which is easily removed by sublimination.

- Partial substitutions of chlorides with $GeCl_4$, $SnCl_4$, $TeCl_4$, $HgCl_2$ and $GaCl_3$ were observed. They were explained by electronic and/or structural considerations [64]. $GeCl_4$ and $SnCl_4$ are liquid at room temperature, with individual tetrahedral units. $TeCl_4$ may be written as $TeCl_3^+Cl^-$ where the chloride ion can easily be displaced by ClO_4^-.

Other considerations of the reactivity of chlorine trioxide and the characteristics of the resulting compounds can be developed on the basis of the hard–soft–acid–base (HSAB) concept introduced by Pearson [66–69,177]. ClO_4^- is a hard base and will interact more easily with hard acids such as Al^{3+}, Ga^{3+}, Fe^{3+}, Ln^{3+} etc. than with

Table 4
Reactivity of Cl_2O_6 towards metals, oxides, nitrates, carbonates and hydrated perchlorates



(a) With Ln = Y, La to Nd and Sm to Lu; prepared from corresponding oxides in boiling commercial perchloric acid (72%); (b) definite chloryl salt for La and Er [see Table 3(c) and (e)], Cl_2O_6 is generally lost at room temperature, only $Pr(ClO_4)_3 \cdot Cl_2O_6$ could be analysed; (c) two crystallographically different forms of $Ln(ClO_4)_3$ complexes were characterized, a "low temperature" form from La to Ho and a "high temperature" form for Lu; depending on the temperature Er, Tm and Yb exist with either structures; (d) prepared from $RhCl_3 \cdot 3H_2O$ in boiling commercial perchloric acid (72%); no reaction of $RhCl_3 \cdot 3H_2O$ with Cl_2O_6; (e) the reaction was complex and the products difficult to isolate as pure compounds [32]; (f) unlike tellurium, selenium gives spontaneously SeO_2 with Cl_2O_6; (g) M = Co, Ni, Cu, Zn, Cd, Hg, Pr, Th with $x \leq 3$; for higher water content, NO_3 decomposes and a mixed nitryl-chloryl salt was obtained; (h) generally, $(NO_2)_nM(ClO_4)_{2n}$ salt is a $NO_2M(ClO_4)_{n+1} \cdot (n-1)NO_2ClO_4$ mixture; definite nitryl salts were characterized only with M = Cu and Hg; note that $NO_2Hg(ClO_4)_3$ could not be isolated from $(NO_2)_2Hg(ClO_4)_4$ since an intermediate compound exploded; (i) mixed valence Mn(II)/(III) salt; (j) hydrated perchlorate prepared from HgO in boiling commercial perchloric acid (72%) no chloryl salt could be isolated.

boundary acids, Ni^{2+}, Cu^{2+}, Zn^{2+} etc. or soft acids like Pd^{2+}, Cd^{2+}, Hg^{2+} etc. Indeed, as an example, the synthesis of perchlorato complexes of elements of group 12 is difficult and, with mercury, $HgClClO_4$ is obtained rather than $Hg(ClO_4)_2$. In the periodic table, the acidity hardness decreases down a column, so, for example, the synthesis of perchlorato complexes in column 12 are more difficult from Zn to Hg. The O^{2-} ion is among the hardest bases and, with very hard acids such as Si^{4+} or Ge^{4+}, can compete with ClO_4^-. SiO_2 is obtained at once [62] while unstable germanium complexes easily decompose into GeO_2. In the same way, with increase in the acidity hardness with the oxidation state of the metal, oxo-perchlorato complexes are systematically prepared with Mo(V or VI), V(V), Cr(VI) and W(VI) rather than simple perchlorates. Direct reactions with oxides, as described in Table 4, are difficult using Cl_2O_6 and drastic conditions had to be developed to partially replace oxygen by $[ClO_4]$ in V_2O_5 [31]. In the lanthanide series, the starting oxide is boiled in concentrated perchloric acid to initiate the reaction. Although the basicity of H_2O is higher than that of ClO_4^-, its hardness (Table 5) is equivalent to that of Cl^- and the substitution of H_2O by $[ClO_4]$ consequently seems easy. However, reactions can be driven by other forces and, particularly, structural effects. During reactions with nitrates, NO_3^- is not eliminated as with chlorides, carbonates or water, but transformed into NO_2^+. This transformation is observed in strong acidic media [70] or with strong oxidative acceptors such as ClO_2^+.

The general reaction can be written as follows:

$$M(NO_3)_n + 2n(ClO_2ClO_4) \rightarrow nNO_2ClO_4 + M(ClO_4)_n + 2nClO_2 + n/2O_2.$$

Definite $NO_2M(ClO_4)_{n+1}$ salts are often prepared, although $(NO_2)_2M(ClO_4)_{n+2}$ were synthesized with copper and mercury. In general mixed salts, $NO_2M(ClO_4)_{n+1} \cdot mNO_2ClO_4$ are obtained. With hydrated nitrates, water elimination, $[NO_3]$ to $[ClO_4]$ replacement, and NO_3^- to NO_2^+ transformation occur simultaneously [31]. If the hydration level is high, up to $5H_2O$ per metal, NO_3^- is partially transformed into nitrogen dioxide and a chloryl nitryl salt is obtained [31].

A survey of the perchlorato complexes and salts prepared by our group, and those of Rosolovskii and Christe is given in Table 6.

3. Structural analysis

3.1. From crystallographic data

Although coordination of the perchlorato group was unambiguously demonstrated by Hathaway by infrared spectroscopy in 1961, a description of various modes of coordination was developed only in the 1970s from single crystal analysis of $ML_n(ClO_4)_m$ complexes. L is an organic base and/or water and two main kinds of $[ClO_4]$ arrangements, monodentate and bidentate, were described [7]. However, owing to the presence of the organic base, the bond distances of the metal to perchlorate oxygen are longer than expected from the effective ionic radii listed by Shannon and Prewitt [160], and are characteristic of a weak coordination bond strength of ligands with the metal.

The first crystal structure determination of a pure inorganic perchlorato complex was that of $Sn_3O_2(ClO_4)_4Cl_4$ in 1980 [143]. Since then, 18 crystal structures of such complexes have been solved

- by X-ray diffraction on single crystals: $Sb_2Cl_6(O)(OH)ClO_4$ [146], $Ti(ClO_4)_4$ [65], $Zr(ClO_4)_4$ [89], $Hf(ClO_4)_4$ [93], $(ClO_2)_2Sn(ClO_4)_6$ [144], $Rb_4Bi_2(ClO_4)_{10}$ [149], $Cu(ClO_4)_2$ [112], $Nd_2(OH)_3(ClO_4)_3$. $5H_2O$ [80], $Pr_2(OH)_3H_2O(ClO_4)_3$ [80], $Yb(ClO_4)_3$. H_2O [158], $HClO_4$ [53] and Cl_2O_7 [53];

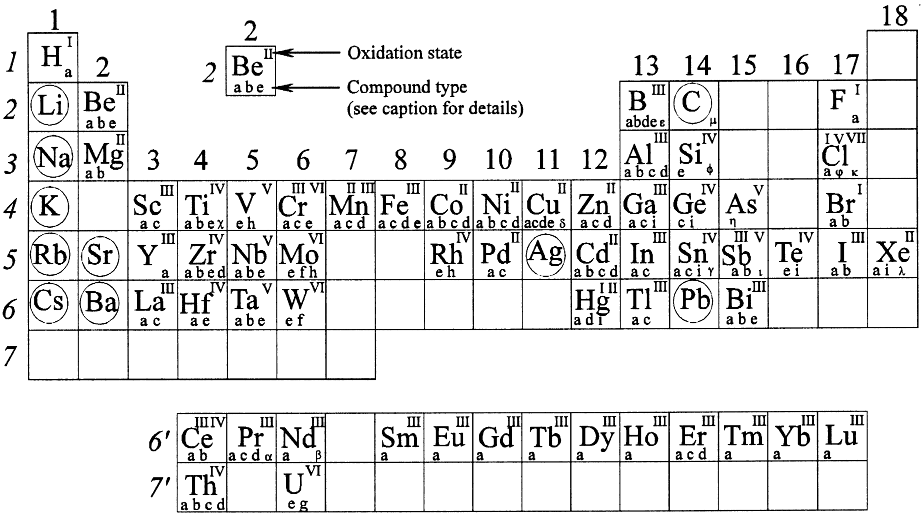
Table 5
Classification of ClO_4^- towards some anions, groups and molecules

From electronic data:	NH_3[a]	CH_3CN[a]	O^{2-}[a]	H_2O[b]	NO_3^-[b]	Me_2SO[b]	$S_2O_7^{2-}$[c]	SO_3F^-[d]	Cl^-[a]	ClO_4^-[e]	Br^-[a]		
Dq (cm^{-1})	1080	1070	860	850	801	773	757	734	720	690	680		
										←Increasing basicity			
From electronegativity data[f]:	$CF_3SO_3^-$	ClO_4^-	SO_4^{2-}	PO_4^{2-}	NO_3^-	CO_3^-	OH^-	I^-	Br^-	Cl^-	H_2O	O^{2-}	F^-
χ	1.87	2.96	3.21	3.25	4.38	5.05	8.86	9.15	9.40	9.47	9.53	15.27	17.36
	Increasing hardness→												

[a]Ref. [169]; [b]Ref. [20]; [c]Ref. [170]; [d]Ref. [171]; [e]Ref. [24]; [f]Mulliken-Jaffé scale.

From the basicity scale, $[ClO_4]$ is easily replaced in the coordination sphere by stronger bases like $[H_2O]$, [O], $[CH_3CN]$, etc. Experiments show that efficient perchlorating reagents can replace anions or groups or react with them up to an electronegativity value of 10. Reactions are performed with chlorides, carbonates, hydroxides or nitrates. Other salts are avoided. Bromides lead to unstable side oxides and iodides to iodine perchlorates. Fluorides, due to their hardness cannot be replaced. Phosphates and sulphates polymerize [106]. However, triflates $[SO_3CF_3]$ are easily replaced by $[ClO_4]$ [63].

Table 6
State of the art in the knowledge of inorganic perchlorato complexes



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H$^{\mathrm{I}}$ a																	
2	○ Li	Be$^{\mathrm{II}}$ abe											B$^{\mathrm{III}}$ abdeε	○ C μ			F$^{\mathrm{I}}$ a	
3	○ Na	Mg$^{\mathrm{II}}$ ab											Al$^{\mathrm{III}}$ abcd	Si$^{\mathrm{IV}}$ e ϕ			Cl$^{\mathrm{I\ V\ VII}}$ aφ κ	
4	○ K		Sc$^{\mathrm{III}}$ ac	Ti$^{\mathrm{IV}}$ abeχ	V$^{\mathrm{V}}$ eh	Cr$^{\mathrm{III\ VI}}$ ace	Mn$^{\mathrm{II\ III}}$ acd	Fe$^{\mathrm{III}}$ acde	Co$^{\mathrm{II}}$ abcd	Ni$^{\mathrm{II}}$ abcd	Cu$^{\mathrm{II}}$ acde δ	Zn$^{\mathrm{II}}$ acd	Ga$^{\mathrm{III}}$ aci	Ge$^{\mathrm{IV}}$ ci	As$^{\mathrm{V}}$ η		Br$^{\mathrm{I}}$ ab	
5	○ Rb	○ Sr	Y$^{\mathrm{III}}$ a	Zr$^{\mathrm{IV}}$ abed	Nb$^{\mathrm{V}}$ abe	Mo$^{\mathrm{VI}}$ efh			Rh$^{\mathrm{IV}}$ eh	Pd$^{\mathrm{II}}$ ac	○ Ag	Cd$^{\mathrm{II}}$ abcd	In$^{\mathrm{III}}$ ac	Sn$^{\mathrm{IV}}$ aciγ	Sb$^{\mathrm{III\ V}}$ ab ι	Te$^{\mathrm{IV}}$ ei	I$^{\mathrm{III}}$ ab	Xe$^{\mathrm{II}}$ ai λ
6	○ Cs	○ Ba	La$^{\mathrm{III}}$ ac	Hf$^{\mathrm{IV}}$ ae	Ta$^{\mathrm{V}}$ abe	W$^{\mathrm{VI}}$ ef						Hg$^{\mathrm{I\ II}}$ adi	Tl$^{\mathrm{III}}$ ac	○ Pb	Bi$^{\mathrm{III}}$ abe			
7																		

6′	Ce$^{\mathrm{III\ IV}}$ ab	Pr$^{\mathrm{III}}$ acdα	Nd$^{\mathrm{III}}$ a β		Sm$^{\mathrm{III}}$ a	Eu$^{\mathrm{III}}$ a	Gd$^{\mathrm{III}}$ a	Tb$^{\mathrm{III}}$ a	Dy$^{\mathrm{III}}$ a	Ho$^{\mathrm{III}}$ a	Er$^{\mathrm{III}}$ acd	Tm$^{\mathrm{III}}$ a	Yb$^{\mathrm{III}}$ a	Lu$^{\mathrm{III}}$ a
7′	Th$^{\mathrm{IV}}$ abcd		U$^{\mathrm{VI}}$ eg											

Compound type: a, $M(ClO_4)_n$ with n = oxidation state of the element; b, $A_mM(ClO_4)_{n+m}$ (A = akali metal or R_4N^+ [R = H or C_nH_{2n+1}]; c, $(ClO_2)_mM(ClO_4)_{m+n}$ ($m \leq 1$, except for Cr, Fe and Th where $m = 2$ was reached); d, $(NO_2)_mM(ClO_4)_{n+m}$ ($m \leq n$); e, $MO_x(ClO_4)_{n-2x}$ ($0.25 < x < 2$); f, $A_mMO_x(ClO_4)_{n-2x+m}$ (A = alkali metal); g, $(NO_2)_mMO_x(ClO_4)_{n-2x+m}$; h, $(ClO_2)_mMO_x(ClO_4)_{n-2x+m}$; i, $MCl_m(ClO_4)_{n-m}$; α, $Pr_2(OH)_3H_2O(ClO_4)_3$; β, $Nd_2(OH)_3(ClO_4)_3 \cdot 5H_2O$; χ, $Ti_6O_4Cl_x(ClO_4)_{16-x}$; δ, $Cu(OH)ClO_4$, $Cu_2O(ClO_4)_2$; ϵ, $R_4N^+BCl_3(F_3)ClO_4^-$; ϕ, Ph_3SiClO_4, γ, $Cl_3SnClO_4^-$, $Sn_3O_2Cl_4(ClO_4)_4$; η, $ClO_2AsF_5ClO_4$; ι, $Sb_8Cl_{24}O_5(ClO_4)_6$, $Sb_2Cl_6O(OH)ClO_4$; φ, liquid Cl_2O_6; κ, Cl_2O_7, λ, $FXeClO_4$; μ, CF_3ClO_4, $RFClO_4$ $C(N_3)_3ClO_4$; ○, ionic.

References: H: [44,53,54]; Be: [73,74]; Mg: [75]; Sc: [77]; Y: [77]; La: [77]; Ce: [78–80]; Pr: [81,82] (α); Nd: [77,83] (β); Sm: [33,77]; Eu: [33,77]; Gd: [77]; Tb: (J.L. Pascal and F. Favier, unpublished results); Dy: [77]; Ho: [33,77]; Er: [33,77]; Tm: [33,77]; Yb: [85,162]; Lu: [33]; Th: (J.L. Pascal and F. Favier, unpublished results); U: [86,87]; Ti: [17,64,67,88,90] (χ), [91] Zr: [92–94]; Hf: [95,96,179]; V: [7,32]; Nb: [97]; Ta: [98]; Cr: [17,60,99,100]; Mo: [47,101]; W: [102,103]; Mn: [32,104]; Fe: [63,100,105,106]; Co: [24,32,38,107–110]; Rh: [111]; Ni: [24,27,32,110,112]; Pd: [113]; Cu: [2,24,32,43,114,115]; Zn: [32,116,117]; Cd: [64,118–120]; Hg: [64,118,121]; B: [39,61,122–127] (ϵ); Al: [62,122,125,130– 137]; Ga: [47,138–140]; In: [140,141]; Tl: [141]; Si: [7,144,145] (ϕ); Ge: [64,163]; Sn: [64,100,146–148] (γ); As: (R.J. Gillespie et al., unpublished results) (η); Sb: [150] (τ), [151]; Bi: [152,153]; Te: [63]; F: [49,154]; Cl: (G. Schröbilgen et al., unpublished results) [46–48] (φ), [57,154–157] (κ); Br: [48,158,159]; I: [160]; Xe: [161] (λ); C: [180] (μ).

- by powder X-ray diffraction and Rietveld analysis: $Yb(ClO_4)_3$ (low and high temperature forms) [82], $Tm(ClO_4)_3$ (high temperature form) [32], $Eu(ClO_4)_3$ [32], $Lu(ClO_4)_3$ [32];
- by a combination of EXAFS and X-ray powder diffraction analysis: $Ni(ClO_4)_2$ [107], $Co(ClO_4)_2$ [107].

The structures of Cd, Mn and Zn complexes are related to those of Ni and $Co(ClO_4)_2$. $Ln(ClO_4)_3$ complexes (Ln = Y, La to Er) are isostructural with

$Eu(ClO_4)_3$ or the low temperature form of $Yb(ClO_4)_3$. Preliminary structural data were also obtained for Ga and $In(ClO_4)_3$ from EXAFS results [137].

In comparison with the success in synthesizing the more than 200 perchlorato complexes known today, structural information is sadly lacking. Due to the strong oxidative properties and very weak basicity of $[ClO_4]$, no suitable solvent has yet been found for the preparation and the crystallization of anhydrous perchlorates. They are generally obtained as microcrystalline powders rather than as single crystals.

Six different coordination modes of the $[ClO_4]$ group have been found among the structures resolved: monodentate, bridging bidentate, chelating bidentate, symmetrical or pseudo-symmetrical bridging tridentate, simultaneously bridging and chelating tridentate and bridging bidentate pseudo-tridentate.

As observed for other oxyanion ligands, interatomic distances and bond angles within the $[ClO_4]$ group change upon coordination. The Cl–O bond length involved in coordination, Cl–O_b (with O_b = bridging oxygen), is expected to increase while that in terminal Cl–O (Cl–O_t) should decreases with respect to the isolated ion. The electron distribution induced by coordination increases with the number of bonds to the metal and, therefore, the Cl–O_b bond length progressively shortens in monodentate to tridentate arrangements. Whatever the bonding mode, angular distortions minimize the Cl–O repulsions. Note that in perchlorato complexes, the length of metal to oxygen bonds are related to the effective ionic radius of the metal in the corresponding surroundings.

3.1.1. *Monodentate $[ClO_4]$*

Typical examples of monodentate $[ClO_4]$ groups are found in $HClO_4$ and Cl_2O_7 [53]. Bridging oxygens have long Cl–O_b distances, respectively, 1.619 and 1.723 Å, while the three terminal Cl–O_t bonds are short ($\approx$1.410 Å). The angular distortions are consistent with the bond length distribution: the pyramidal ClO_{3t} opens ($\approx$115°) while the O_t–Cl–O_b closes ($\approx$104°). Although the crystallographic determination of $(ClO_2)_2Sn(ClO_4)_6$ [144] was of limited quality, monodentate $[ClO_4]$ groups could be identified (see Fig. 2). Crystals of this compound were obtained by rapid sublimation at 125 °C of a freshly prepared product. The interatomic bond lengths, with d(Cl–O_b) = 1.49 Å and d(Cl–O_t) = 1.40 Å, are less perturbed upon coordination than in $HClO_4$ or Cl_2O_7, but as found in Cl_2O_6 [46,57], interactions occur between $[ClO_4]$ and ClO_2^+. The $d(O_2Cl\cdot\cdot\cdot O_3ClO)$ distances of approximately 2.85 Å are less than the sum of the Van der Waals radii ($r_{Cl}+r_O=3.2$ Å). The mean Sn–O distance, 2.03 Å, is considerably shorter than in $Cl_3SnOClO_3^-$ (2.90 Å) [145], and represents a strong metal to ligand interaction.

3.1.2. *Bridging bidentate $[ClO_4]$*

A regular bridging bidentate $[ClO_4]$ was first described in $Sb_2Cl_6(O)(OH)ClO_4$ [146]. This compound was obtained by keeping $Sb_8Cl_{24}O_5(ClO_4)_6$ standing for several weeks with slightly hydrated $SbCl_5$. As depicted in Fig. 3, the $[ClO_4]$ group in this complex shows ideal C_{2v} symmetry and Cl–O bond variations and angular distortions are as expected. The Sb–O distances (2.20–2.24 Å) are shorter than those

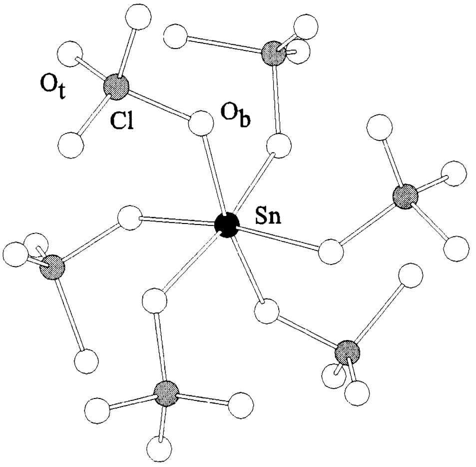


Fig. 2. Molecular structure of Sn(ClO$_4$)$_6^{2-}$ anion from Ref. [147]. Mean distances: Sn–O = 2.03 Å, Cl–O$_b$ = 1.49 Å; Cl–O$_t$ = 1.40 Å.

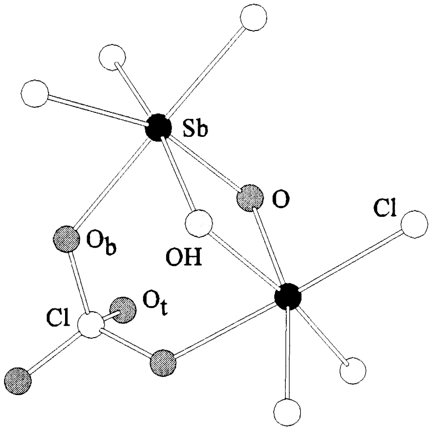


Fig. 3. Molecular structure of Sb$_2$Cl$_6$(O)(OH)ClO$_4$ from Ref. [150]. The crystal structure shows two independent units linked to each other through medium strength hydrogen bonds (O· · ·O = 2.65 Å) in an approximate cross arrangement. Mean distances and angles: Sb–Cl = 2.28 Å, Sb–O(OH) = 2.00 Å, Sb–Ob = 2.22 Å, Cl–O$_b$ = 1.48 Å; Cl–O$_t$ = 1.39 Å; O$_b$–Cl–O$_b$ = 106°; O$_t$–Cl–O$_t$ = 115°.

found in [(CH$_3$)$_2$SbClO$_4$]$_2$O at 2.60 Å [161] and bond strengths are comparable with those in parent trichloroacetato or acetato complexes [162,163].

Analysis by EXAFS, X-ray powder diffraction data and vibrational spectra of Ga(ClO$_4$)$_3$ and In(ClO$_4$)$_3$ indicated bridging bidentate [ClO$_4$]. The polymeric structures, in which [ClO$_4$] is a building block in the layered arrangements, can be related to AsI$_3$ (R$\bar{3}$) and BiI$_3$ (P$\bar{3}$m) respectively. Ga and In are in octahedral environments with Ga–O and In–O distances of 1.95 and 2.19 Å, respectively.

In Sn$_3$O$_2$(ClO$_4$)$_4$Cl$_4$, monodentate and bridging bidentate [ClO$_4$] groups coexist in the same structural edifice (Fig. 4) [143]. This compound is prepared by dissolution of $(ClO_2)_2Sn(ClO_4)_6$ in an excess of $SnCl_4$ [97]. The structure is built around a Sn_4O_6 skeleton of the rutile type. Internal cohesion of the molecule is ensured by six bridging bidentate groups. Two other monodentate $[ClO_4]$ and eight chlorine atoms give the electroneutrality of the molecule. Two tin atoms per formula unit are five-coordinate while the other are in an octahedral environment. In good agreement with the HSAB concept, the presence of an oxygen atom in the coordination sphere of the metal leads to longer Sn–O(ClO_4) bond distances (2.16 Å) than in the chloryl salt (2.04 Å). The geometry of the perchlorato group is poorly determined owing to high thermal motion of terminal oxygen atoms. However, the expected deformation from ideal C_{2v} symmetry is observed.

3.1.3. Chelating bidentate [ClO$_4$]

Because of the high constraints introduced in the perchlorato group and the natural propensity of the $[ClO_4]$ ligand to build a polymeric structure rather than individual molecular units, this particular mode of bonding seems to be the least common for perchlorato complexes. Chelating bidentate $[ClO_4]$ was first described in $Zr(ClO_4)_4$ [89], but a more accurate determination of $[ClO_4]$ geometrical deformations was given in $Ti(ClO_4)_4$ [65]. Since these studies, it has been shown that $Hf(ClO_4)_4$ is isostructural with the corresponding zirconium and titanium complexes [93]. From Raman data, $Ce(ClO_4)_4$ adopts the same structure [78]. A chelating bidentate arrangement has also been postulated for terminal perchlorato groups in $Rb_4Bi_2(ClO_4)_{10}$ [149], but in view of the low accuracy of the structural determination, this cannot be definitively asserted.

In $Ti(ClO_4)_4$, titanium is chelated by four bidentate perchlorato ligands (Fig. 5). The eight oxygen atoms surrounding the metal form a slightly flattened dodecahe-

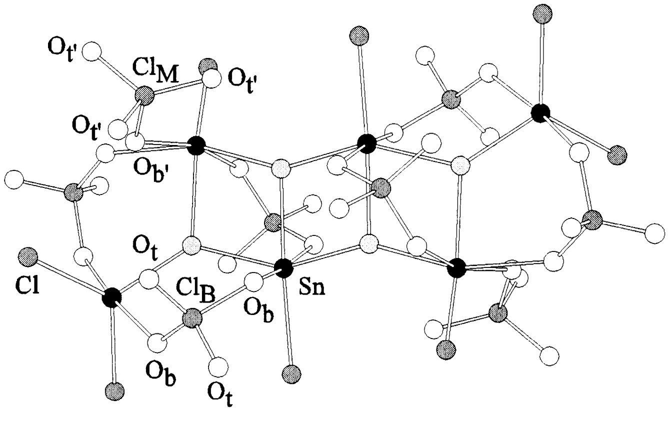


Fig. 4. Molecular structure of dimeric $Sn_3O_2Cl_4(ClO_4)_4$ from Ref. [146]. Cl_M and Cl_B correspond to mono and bidentate $[ClO_4]$, respectively. The mean Sn–O distances in the rutile type skeleton with planar tricoordinated oxygen atoms lie around 2.06 Å. Other characteristic mean distances and angles: $Sn–O_b = 2.11$ Å, $Sn–O_{b'} = 2.09$ Å, $Cl_B–O_b = 1.47$ Å; $Cl_M–O_{b'} = 1.50$ Å; $Cl_B–O_t = 1.34$ Å; $Cl_M–O_{t'} = 1.39$ Å; $O_b–Cl_B–O_b = 107°$; $O_t–Cl_B–O_t = 150°$, $O_{t'}–Cl_M–O_{b'} = 107°$; $O_{t'}–Cl_M–O_{t'} = 180°$.

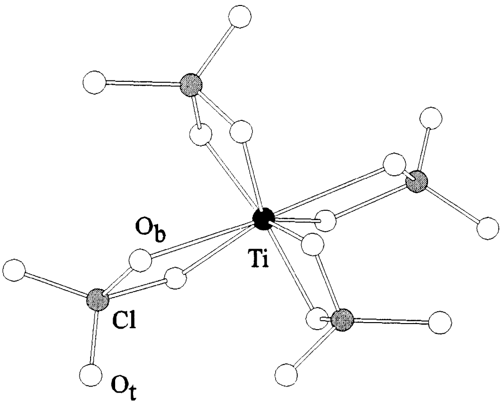


Fig. 5. Molecular structure of $Ti(ClO_4)_4$ from Ref. [67]. Mean distances and angles: Ti–O_b=2.07 Å, Cl–O_b=1.39 Å; Cl–O_t=1.51 Å; O_b–Cl–O_b=97°; O_t–Cl–O_t=115°.

dron. The mean Ti–O distance of 2.068 Å indicates strong metal to ligand interactions. The $[ClO_4]$ geometry is relatively distorted, although Cl–O_t distances of approximately 1.39 Å, are comparable with those found in other complexes. In contrast, Cl–O_b distances are the longest ever reported for bidentate perchlorato groups (about 1.51 Å against 1.48 Å for the Sb complex described earlier). The most striking fact concerns the observed deformation of the O_b–Cl–O_b angle which is lower than the normal tetrahedral angle by 12°. This constraint leads to a characteristic vibrational spectroscopic feature (see later) and enhances the reactivity of this compound [65].

3.1.4. Bridging tridentate [ClO4]

The first reference to tridentate coordination of the $[ClO_4]$ group was in 1980 by Loginov et al. on the basis of an IR analysis and magnetic measurements performed on $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ [37]. Such an arrangement was subsequently confirmed by the structure characterization of both complexes (Fig. 6) [107]. The structure of cobalt and nickel perchlorates derives from that of $CdCl_2$ and $NiCl_2$ [63]. Metal–oxygen, metal–chlorine and metal–metal distances were extracted from EXAFS data. Lattice parameters, determined by X-ray powder diffraction, imply a rotation of the $[ClO_4]$ group around the threefold axis and a loss of crystal symmetry towards the related $NiCl_2$ ($R\bar{3}m \rightarrow R\bar{3}$). Owing to the high symmetry, it was possible to locate all the atoms in the lattice. Co and Ni are in regular octahedral surroundings. Metal–oxygen distances of 2.09 Å (Co) and 2.04 Å (Ni) and the observed deformations of the perchlorate are characteristic of a weaker coordination than with monodentate or bidentate $[ClO_4]$ groups.

We recently observed symmetrical tridentate $[ClO_4]$, depicted in Fig. 7, in rare earth complexes of Y and La to Yb. The ClO_4 geometry could be accurately determined by Rietveld analysis of high-resolution X-ray powder diffraction data recorded at the ESRF synchrotron line in Grenoble [32]. This geometry, with

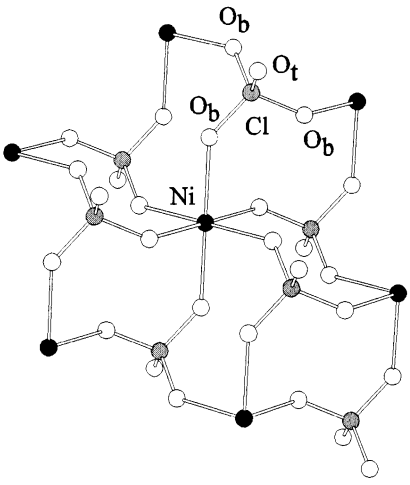


Fig. 6. Coordination shell around Ni and Co in $Ni(ClO_4)_2$ and $Co(ClO_4)_2$ from Ref. [110]. The $[ClO_4]$ bridging tridentate is characterized by: $Ni–O_b = 2.04$ Å, $Cl–O_b = 1.44$ Å, $Cl–O_t = 1.39$ Å; $Co–O_b = 2.09$ Å; $Ni\cdots Ni = 4.80$ Å; Ni or $Co\cdots Cl = 3.25$ Å. The interplanar metallic distance in the layered arrangement is 7.28 Å.

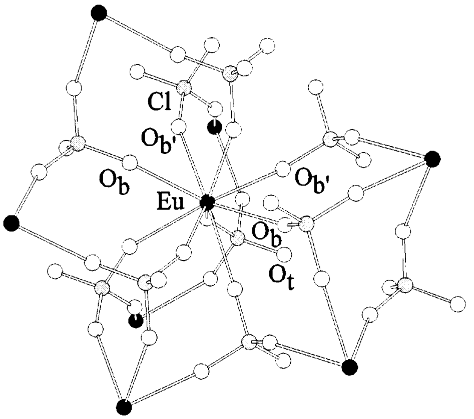


Fig. 7. Molecular structure of $Eu(ClO_4)_3$ displaying the Eu coordination shell, a slightly distorted tricapped trigonal prism, and bridging tridentate $[ClO_4]$ groups [33]. Characteristic distances are: $Eu–O_b = 2.47$ Å, $Eu–O_{b'} = 2.40$ Å, $Cl–O_b = 1.45$ Å, $Cl–O_t = 1.39$ Å, $Cl–O_{b'} = 1.47$ Å, $Eu\cdots Eu = 5.73$ Å.

$d(Cl–O_t) = 1.39$ Å and averaged $d(Cl–O_b) = 1.45$ Å, is similar to that found in $Ni(ClO_4)_2$. A nine-fold surrounding of the rare earth atoms builds a slightly distorted tricapped trigonal prism. The mean M–O distance lies around 2.45 Å and is consistent with the effective ionic radii. The bridging tridentate $[ClO_4]$ groups create hexagonal rings $[d(M\cdots M) \approx 5.7$ Å$]$ which develop through the structure to give a channel arrangement. One or several $M–O(ClO_4)$ bonds can be broken by hydrolysis. A study of $Yb(ClO_4)_3 \cdot H_2O$ (Fig. 8) shows that two of three bridging tridentate per Yb atom, transform into bridging bidentate on hydrolysis [158].

These bridging bidentate groups form a hexagonal ring very similar to that in the anhydrous parent complex. The rings are linked to each other through tridentate $[ClO_4]$ giving large channels containing water molecules. Although Yb–O(ClO_4) distances suggest strong interactions, the ClO_4 bond lengths show little variation and angular deformations are relatively weak. For bidentate and tridentate groups the mean d(Cl–O_t) of 1.40 Å and d(Cl–O_b) of 1.44 Å are equal and very close to those previously given. When the number of basic ligands, such as OH or H_2O, increases in the coordination sphere of the metal, perturbation of the perchlorato group decreases. Good examples of this are in $Pr_2(OH)_3H_2O(ClO_4)_3$ [80] or $Nd_2(OH)_3(ClO_4)_3 \cdot 5H_2O$ [81] where $[ClO_4]$ remains an important building block.

3.1.5. *Bridging chelating tridentate $[ClO_4]$*

A simultaneously bridging and chelating tridentate perchlorato group was described for the first time by Ivanova et al. in $Rb_4Bi_2(ClO_4)_{10}$ [149]. However, the geometrical parameters of $[ClO_4]$ were poorly determined and since the Cl–O and Bi–O distances cited contradict expected values, such an arrangement seems unlikely.

We have recently shown that $Ln(ClO_4)_3$ (Ln = Tm, Yb and Lu) crystallize in a high temperature form upon warming. Depending on the reaction temperature, the low (LT) and high temperature (HT) forms were detected for Er, Tm and Yb complexes while Lu showed only the HT form. From Er to Yb, the temperature of the irreversible transformation decreases from 280 °C to 202 °C. For the Er complex, this is very close to its decomposition temperature, at about 300 °C, and the LT and HT forms could not be separated. The HT form should exist in the whole series of

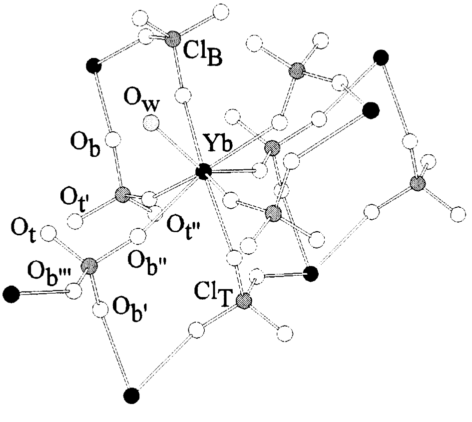


Fig. 8. Molecular structure of $Yb(ClO_4)_3 \cdot H_2O$ from Ref. [162], displaying the ytterbium coordination shell, a fairly distorted square antiprism, and the bridging bidentate and tridentate $[ClO_4]$ groups. $Yb–O_w(H_2O)$ 2.25 Å; bridging bidentate: $Yb–O_b = 2.29$ Å, $Cl_B–O_b = 1.44$ Å, $Cl_B\text{-}O_{t'(t'')} = 1.41$ Å, $O_{t'}–Cl_B–O_{t''} = 114°$, $O_b–Cl_B–O_b = 106°$; bridging tridentate: $Yb–O_{b'} = 2.31$ Å, $Yb–O_{b''} = 2.49$ Å, $Yb–O_{b'''} = 2.35$ Å, $Cl_T–O_t = 1.40$ Å, $Cl_T–O_{b'} = 1.45$ Å, $Cl_T–O_{b''} = 1.42$ Å, $Cl_T–O_{b'''} = 1.45$ Å, $O_t\text{-}Cl_T–O_{b''} = 112°$, $O_{b''}\text{-}Cl_T–O_{b'''} = 107°$.

lanthanides but below Er, the LT to HT temperature transformations are higher than the decomposition temperature. Noteworthy is the fact that in the reaction of Cl_2O_6 with LaOCl, the decomposition product of $La(ClO_4)_3$ (LT) leads, in a first step, to La_3O_4Cl which corresponds to the stoichiometry observed for the decomposition products of HT lanthanide perchlorato complexes. In an excess of chlorine trioxide, La_3O_4Cl slowly transforms into the HT form of $La(ClO_4)_3$, but progressively rearranges, at the same time, into the LT form.

Although the layered HT form structure of $Ln(ClO_4)_3$ contains bridging chelating tridentate $[ClO_4]$ groups, the Cl–O bond distances, $d(Cl–O_t) = 1.37$ Å and $d(Cl–O_b) = 1.44$ Å, are very close to those observed in a symmetrical bridging tridentate group. The O_b–Cl–$O_{b'}$ angle of the chelating part of 103.7° is very close to the corresponding angle in a bridging tridentate group (103.3°). However, the angular constraints are much weaker than in chelating bidentate group (O_b–Cl–$O_b = 97°$ in $Ti(ClO_4)_4$). A schematic representation of the structure of $Lu(ClO_4)_3$ is depicted in Fig. 9. Nine oxygen atoms build a deformed tricapped trigonal antiprism and Lu–O distances ranging from 2.28 to 2.45 Å are characteristic of strong metal to perchlorate interactions.

3.1.6. *Bridging bidentate pseudo-tridentate [ClO$_4$]. The particular case of copper perchlorate*

The bidentate coordination of $[ClO_4]$ in $Cu(ClO_4)_2$ was postulated by Hathaway and Underhill in 1961. By comparison of the infrared band splitting in the spectra of anhydrous, dihydrated and hexahydrated copper complexes, they were able to establish precise rules based on group theory and to confirm the coordinating ability

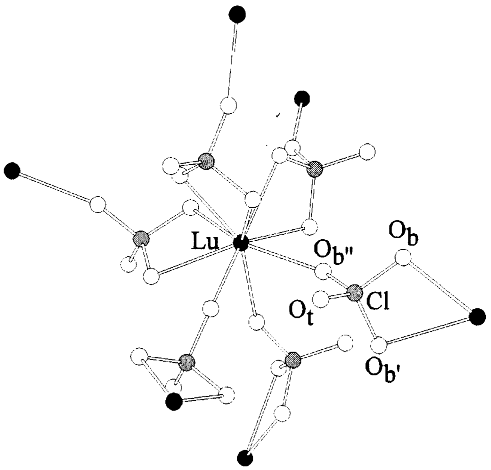


Fig. 9. Molecular structure of $Lu(ClO_4)_3$, from Ref. [33], displaying the lutetium coordination shell, a tricaped trigonal antiprism, and the bridging chelating tridentate $[ClO_4]$ groups. $Lu–O_{b'} = 2.45$ Å, $Lu–O_{b''} = 2.40$ Å, $Lu–O_{b'''} = 2.28$ Å, $Cl–O_t = 1.37$ Å, $Cl–O_b$ and $Cl–O_{b'} = 1.43$ Å, $Cl–O_{b''} = 1.45$ Å, $Ob–Cl–O_{b'} = 103.7°$, $O_t–Cl–O_{b'} = 113.9°$, $O_t–Cl–O_{b''} = 111.7°$. The structure is layered with mean Lu· · ·Lu distances = 6.16 Å.

of [ClO_4]. They unambiguously allowed distinctions to be made between ionic, monodentate and bidentate perchlorato groups.

Although $Cu(ClO_4)_2$ is a still-used model for the coordination of the perchlorato group, its structure remained unknown until recently. In 1985, using EXAFS data, ESR, IR and Raman spectroscopies, a first model based on the $CuSO_4$ structure was proposed [111]: bridging bidentate [ClO_4] groups link Cu atoms into two non-linear chains, one with short Cu–Cu distances (3.01 Å), the other with long Cu· · ·Cu distances up to 6 Å. The metal atoms are located in a distorted octahedral surrounding with four short Cu–O contacts at 1.96 Å and two longer at 2.68 Å.

In 1994, we were able to grow single crystals of $Cu(ClO_4)_2$ by warming under vacuum, an equimolar mixture of Y, Ba and Cu perchlorates at 160 °C [112]. The crystal structure showed orientational disorder of [ClO_4], and was solved considering two sets of oxygen atoms of equal site occupancy. One set is depicted in Fig. 10. The structure is made up of infinite chains in which copper atoms are doubly bridged by [ClO_4] groups. These chains are linked together through an oxygen atom of these same perchlorato groups. We have christened such a bonding mode "bidentate pseudo-tridentate" because the bridging bidentate character prevails and the third interaction is found only through a long Cu–O bond. The resulting distortions of the [ClO_4] group could not be accurately determined owing to the orientational disorder, but they lie between those observed for a pure bidentate group as in $Sb_2Cl_6(O)(OH)ClO_4$ [146] and a tridentate group as in $Ni(ClO_4)_2$ [107] for example. The immediate environment of Cu atoms agrees with that derived from EXAFS data. No short Cu–Cu distances were observed.

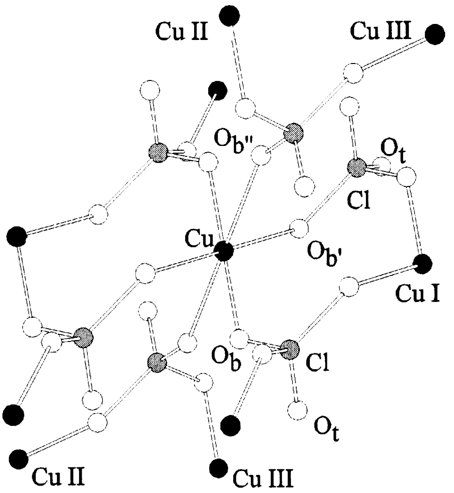


Fig. 10. One set of the disordered atoms in $Cu(ClO_4)_2$ from Ref. [115]. Mean bond lengths and angles: $Cu–O_b = Cu–O_{b'} = 1.96$ Å, $Cu–O_{b''} = 2.46$ Å, $Cl–O_b = 1.46$ Å, $Cl–O_{b'} = 1.51$ Å, $Cl–O_{b''} = 1.43$ Å, $Cl–O_t = 1.42$ Å, $O_b–Cl–O_{b'} = 111°$, $O_{b''}–Cl–O_t = 118°$, $O_{b'}–Cl–O_t = 104°$. Cu· · ·Cu distances range from 4.58 to 6.27 Å.

The question remains: are there two kinds of arrangement for $Cu(ClO_4)_2$? As a starting point for an answer and as a conclusion, we note that Rosolovskii et al. showed that $Cu(ClO_4)_2$ undergoes a polymorphic phase transformation at 150–160 °C [42]. However, in our work, we found no apparent vibrational spectroscopic, powder X-ray diffraction or electronic spectral differences between the pale blue solid prepared in a first step and the pale green material obtained at $T > 160$ °C [31].

The crystal data provided above allow us to correlate M–O(ClO4) distances with effective ionic radii of M atoms in a given surroundings (Fig. 11). Therefore, the shortest M–O(ClO_4) distances corresponding to the strongest bonding to ClO_4 can be predicted.

Although data are limited, analysis of the various crystal structures shows the diversity of the mode of coordinations of the [ClO_4] group. The variety does not end with the arrangements described above since, for example, a double bridging oxygen atom has been reported in $Pr_2(OH)_3H_2O(ClO_4)_3$ [80]. More recently a twelve-coordinated bonding mode was observed for an encapsulated [ClO_4] in a Dawson mixed valence octodecatungstate perchlorate [164]. Furthermore, in view of the peculiarities encountered in some IR and Raman spectra, one can predict that new [ClO_4] bonding modes will yet be identified.

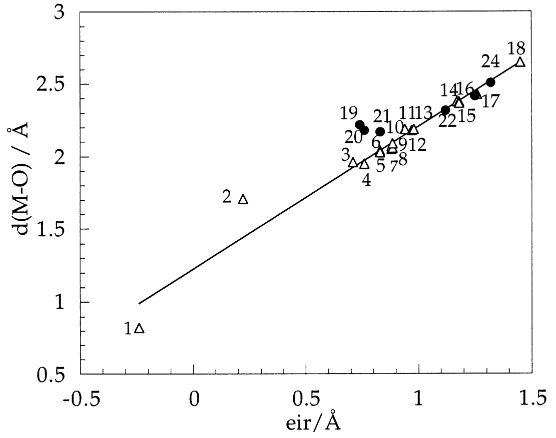


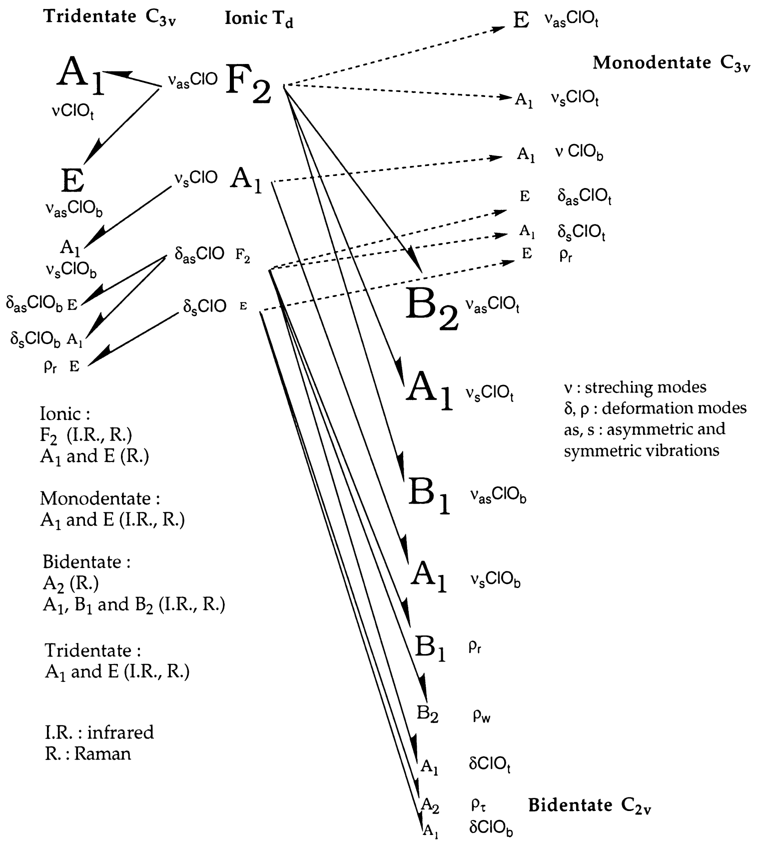
Fig. 11. Plot of M–O distances related to effective ionic radii (eir) [164]. 1—$HClO_4$, 2—Cl_2O_7, 3—$Cu(ClO_4)_2$, 4—$Ga(ClO_4)_3$, 5—$Sn(ClO_4)_6^{2-}$, 6—$Ni(ClO_4)_2$, 7—$Zn(ClO_4)_2$, 8—$Co(ClO_4)_3^-$, 9—$Ti(ClO_4)_4$, 10—$Co(ClO_4)_2$, 11—$In(ClO_4)_3$, 12—$Hf(ClO_4)_4$, 13—$Zr(ClO_4)_4$, 14—$Lu(ClO_4)_3$, 15—$Yb(ClO_4)_3$ (LT), 16—$Yb(ClO_4)_3$ (HT), 17—$Eu(ClO_4)_3$, 18—$Bi_2(ClO_4)_{10}^{4-}$, 19—$Sb_2Cl_6O(OH)ClO_4$, 20—$Sn_3O_2Cl_4(ClO_4)_4$ (five-coordination around Sn), 21—$Sn_3O_2Cl_4(ClO_4)_4$ (six-coordination around Sn), 22—$Yb(ClO_4)_3 \cdot H_2O$, 23—$Nd_2(OH)_3(ClO_4)_3 \cdot 5H_2O$, 24—$Pr_2(OH)_3H_2O(ClO_4)_3$. The curve fit, $dM\text{–}O = 1.23 + 0.98$ eir, was calculated from complexes including exclusively ClO_4 as a ligand (open triangles). Shaded circles correspond to complexes incorporating more basic ligands than ClO_4: O, OH, H_2O, and it is clearly show that with small metallic eir, [ClO_4] is scattered out the coordination sphere while with greater eir, [ClO_4] draws nearer.

3.2. From vibrational analysis

Vibrational spectroscopies remain precious tools for the study of the bonding modes of [ClO_4] groups and, since perchlorato complexes crystallize poorly, a good approach to the molecular structure of the complexes can be obtained.

Upon coordination, ClO_4 loses its T_d symmetry to adopt a C_{3v} geometry in the case of monodentate or tridentate bonding modes, C_{2v} for chelating or bridging bidentate groups and C_s for bridging chelating tridentate. Selection rules based on group theory gives for each bonding mode the splittings of the various vibrational modes (Table 7). Since in inorganic perchlorato complexes, [ClO_4] is strongly bonded to the metal, the splitting is expected to be significant and largely greater than those induced by lattice or polarization effects.

Table 7
Normal modes of vibration of perchlorate



3.2.1. *Ionic [ClO_4]*

Although ionic perchlorates are not the main purpose of this review, some inorganic perchlorates, such as $HgClClO_4$ [115] or $TeCl_3ClO_4$ [61], include ionic [ClO_4] groups.

The frequencies and intensities of Raman lines of [ClO_4] in $HgClClO_4$ (see Fig. 12) are very close to those observed in alkali or alkaline earth metal perchlorates [168]. The mean frequency of the symmetrical mode $\nu_sClO_4^-$ at 924–935 cm^{-1}; split by crystal field effects, indicates a pure unpolarized ClO_4^-. In $TeCl_3ClO_4$, the lowering of this frequency is characteristic of weak interactions between $TeCl_3^+$ and ClO_4^-.

3.2.2. *Monodentate [ClO_4]*

The symmetry of a monodentate [ClO_4] group is C_{3v}, but when the M-$OClO_3$ entity is considered, the symmetry is lowered to C_s. The consequent degeneracy of the δ_s, ν_{as} and δ_{as} modes is shown in Table 7. The splitting of bands and lines and the variation of frequencies with respect to those observed for ClO_4^-, are related to the bond length variations. Monodentate groups are found in $GeCl_3ClO_4$ [159], $Sn(ClO_4)_6^{2-}$ [144] as well as in monomeric $SnCl_2(ClO_4)_2$ [144], $GeCl_2(ClO_4)_2$ [159] and in boron perchlorates [59]. IR and Raman spectra of $GeCl_3ClO_4$ are reproduced in Fig. 13. Typical bands and lines, allowing at once the characterization of monodentate [ClO_4] groups, appear around 1250, 1040, 750 and 300 cm^{-1}. They are, respectively, assigned to $\nu_{as}ClO_{3t}$ (E or A′+A″), ν_sClO_{3t} (A_1 or A′), νClO_b (A_1 or A″) and ρ_rClO_{3t} (E or A′+A″). In the range of bending vibrations additional lines νGe–O (675 cm^{-1}) and νGe–Cl (420 cm^{-1}) are also identified according to the literature [169]. For $(ClO_2)_2Sn(ClO_4)_6$ strong [ClO_4]–[ClO_2] interaction occurs and some monodentate groups should be considered as pseudo-bidentate. Detailed analysis is given in Ref. [144].

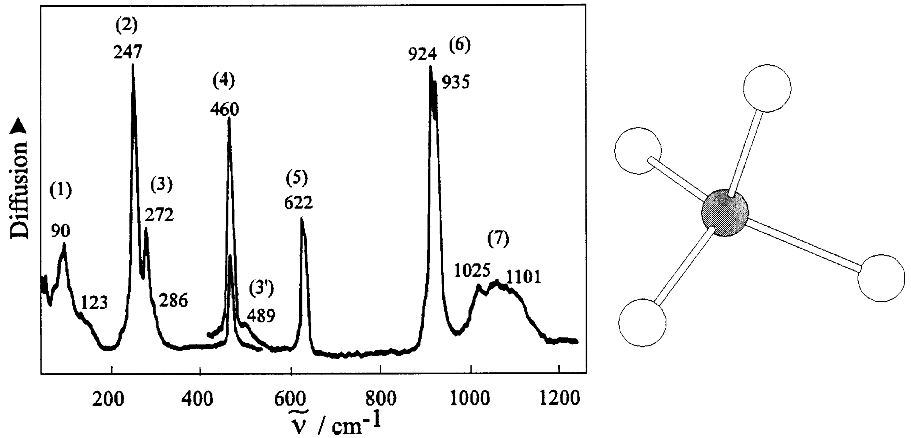


Fig. 12. Raman spectrum of $HgClClO_4$. (1) lattice vibrations, (2) ν_sHgCl^+, (3) $\nu_{as}HgCl^+$, (3) $\nu HgCl$(?), (4) $\delta_sClO_4^-$, (5) $\delta_{as}ClO_4^-$, (6) $\nu_sClO_4^-$, (7) $\nu_{as}ClO_4^-$, $HgCl^+$ was assumed to be polymeric cation $(HgCl)_n^{n+}$ [118].

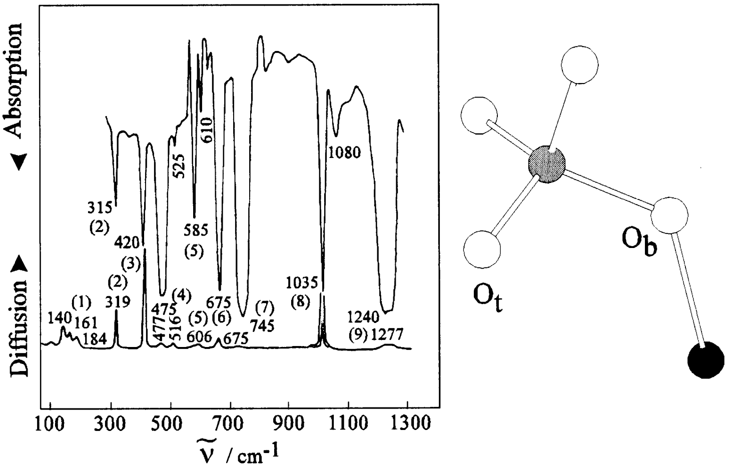


Fig. 13. IR and Raman spectra of $GeCl_3ClO_4$. (1) lattice vibrations + def. $GeCl_3 + \delta GeOCl$, (2) $\rho_r ClO_3$, (3) $\nu_s GeCl_3$, (4) $\nu_{as} GeGl_3 + \delta_s ClO_4$, (5) $\delta_{as} ClO_4$, (6) $\nu GeO(ClO_4)$, (7) νClO_b, (8) $\nu_s ClO_t$, (9) $\nu_{as} ClO_t$. def: deformation including δ and ρ; O_b: bridging oxygen; O_t: non bonded Cl–O.

3.2.3. *Bridging bidentate [ClO$_4$]*

The symmetry of a bidentate [ClO_4] group is C_{2v}. The distribution of vibrational modes is given in Table 7. The main stretching modes are characteristically located around 1300, 1200 and 900–800 cm^{-1} (ν_{as}, $\nu_s ClO_t$ and ν_{as}, $\nu_s ClO_p$). As for monodentate and other geometries described below, the splittings observed are related to bond length variations. Bridging bidentate is a common arrangement encountered in $Sc(ClO_4)_3$ [74], $Cr(ClO_4)_3$ [97], $Fe(ClO_4)_3$ [102], $Ga(ClO_4)_3$ [135], $GaCl_2ClO_4$ [134], $In(ClO_4)_3$ [137], $Tl(ClO_4)_3$ [138], $SnCl_2(ClO_4)_2$ [144], $Sn_3O_2Cl_4(ClO_4)_4$ [143], $Sb_2Cl_6(O)(OH)ClO_4$ [146], etc. Typical IR and Raman spectra are shown in Fig. 14. Main general features are observed for $Ga(ClO_4)_3$ and $Sc(ClO_4)_3$ (see Fig. 15). Although these spectra are characteristic of bidentate [ClO_4], as identified from the EXAFS of $Ga(ClO_4)_3$, variations between the spectra of these compounds must reflect different geometries and distortions of the perchlorato group.

3.2.4. *Chelating bidentate [ClO$_4$]*

This bonding mode is exclusively found in group 14 complexes and in $Ce(ClO_4)_4$ [78], and the C_{2v} geometry is retained. The frequency distribution as well as the band and line shapes of the stretching modes are similar from one to another of these complexes. Due to significant angular variation, the main splitting appears in the range of bending vibrations. For $Ti(ClO_4)_4$ (see Fig. 16), the rocking and twisting modes move, respectively, to 702 and 555 cm^{-1}, which are the highest observed frequencies for such modes. Note that the strong intensity and breadth of these Raman lines is the best means of characterizing chelating bidentate [ClO_4].

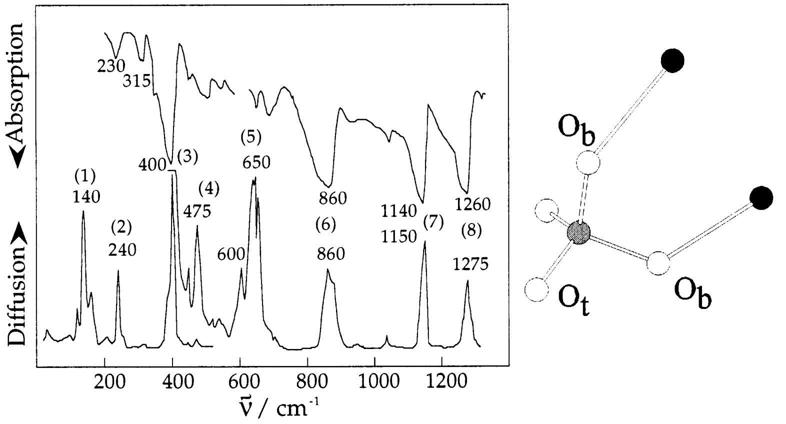


Fig. 14. IR and Raman spectra of $Sb_2Cl_6(O)(OH)ClO_4$. (1) lattice vibrations, (2) $\nu SbO(ClO_4)$, (3)+(4) ν_s, $\nu_{as}SbCl+\nu SbO[SbO(OH)Sb\ ring]+\delta ClO_b+\rho_t$, (5) $\delta ClO_t+\rho_w+\rho_r$, (6) ν_s, $\nu_{as}ClO_b$, (7) ν_sClO_t, (8) $\nu_{as}ClO_t$. Formulae units are linked together through medium strength hydrogen bonds ($O\cdots O=2.65$ Å) with corresponding broad bands between 2000 and 3600 cm^{-1} and lines in the range 2550–3500 cm^{-1}.

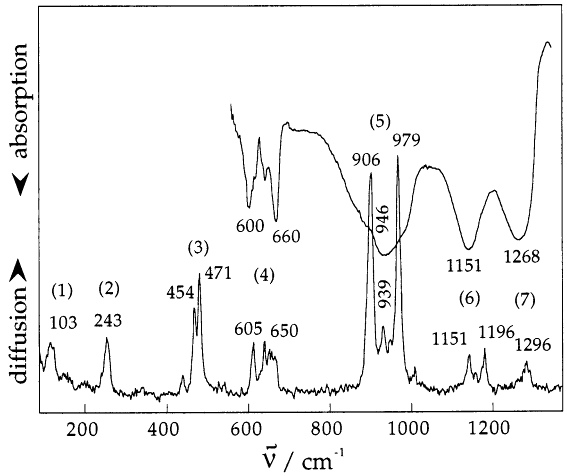


Fig. 15. IR and Raman spectra of $Sc(ClO_4)_3$. Bridging bidentate $[ClO_4]$ involved in a layered bidimentional polymeric unit (c.f. $Ga(ClO_4)_3$ [140]) (1) lattice vibrations, (2) $\nu ScO(ClO_4)$, (3) $\delta ClO_b+\rho_t$, (4) $\delta ClO_t+\rho_w+\rho_r$, (5) ν_s, $\nu_{as}ClO_b$, (6) ν_sClO_t, (7) $\nu_{as}ClO_t$.

3.2.5. Bridging tridentate [ClO$_4$]

As for a monodentate group, the symmetry of a bridging tridentate $[ClO_4]$ group is C_{3v}. However, since three oxygens per chlorine atom are bonded to the metal instead of one, the distribution of vibrational modes is completely different, as shown in Table 7. Particular shapes of bands and lines appear in the stretching range. Since the first description of such a bonding mode in $Ni(ClO_4)_2$ [23] and $Co(ClO_4)_2$ [105], numerous other examples have been found: $Mn(ClO_4)_2$ [101],

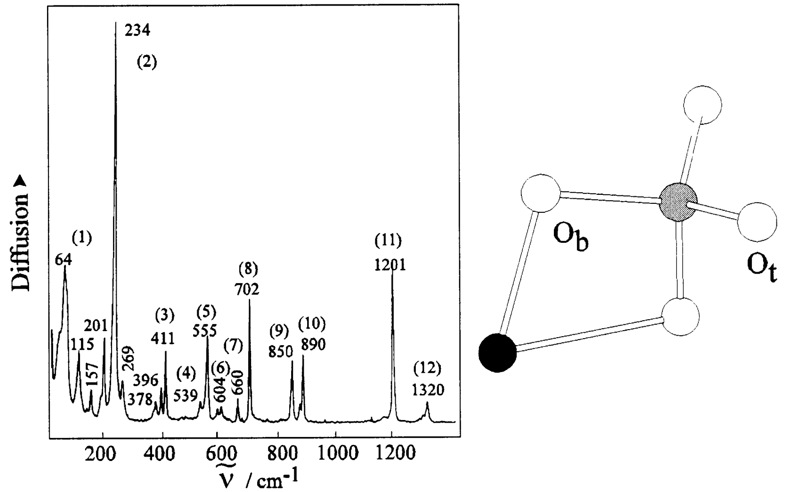


Fig. 16. Raman spectra of $Ti(ClO_4)_4$. (1) lattice vibrations + TiO_8 deformations, (2) $\nu_sTiO(ClO_4)$, (3) $\nu_{as}TiO(ClO_4)$, (4) δClO_b, (5) ρ_t, (6) δClO_t, (7) ρ_w, (8) ρ_r, (9) $\nu_{as}ClO_b$, (10) ν_sClO_b, (11) ν_sClO_t, (12) $\nu_{as}ClO_t$. The high frequencies of ρ_t and ρ_r are characteristic of chelating bidentate $[ClO_4]$.

$Zn(ClO_4)_2$ [113], $Cd(ClO_4)_2$ [115] and $Ln(ClO_4)_3$ [32] (with Ln = Y and from La to Yb). A typical spectrum, of $Ni(ClO_4)_2$, is shown in Fig. 17. The νClO_{3p} vibrations are characterized by a strong Raman line and a medium intensity IR band at frequencies up to 940 cm^{-1} (mean frequency for ν_s in an ionic ClO_4^-) and a broad IR band arising from two absorptions around 1010–1050 cm^{-1}. νClO_t appears as

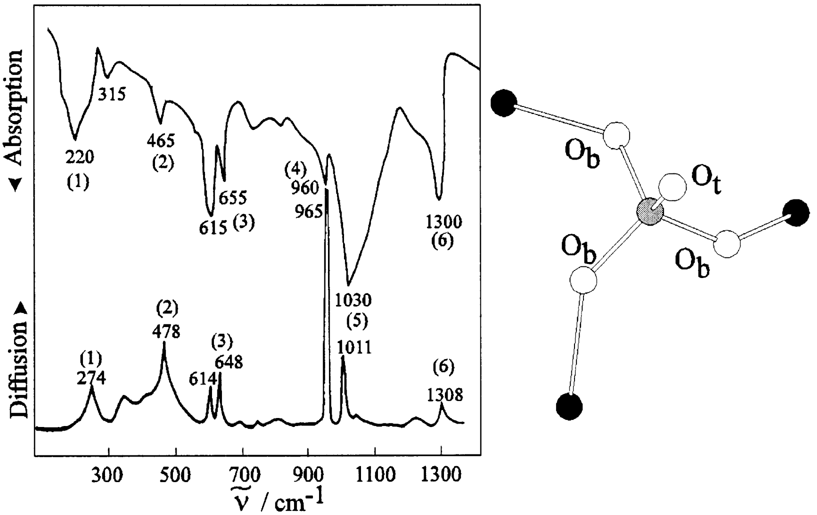


Fig. 17. IR and Raman spectra of $Ni(ClO_4)_2$. (1) $\nu NiO(ClO_4)$, (2) ρ_r, (3) δ_s, $\delta_{as}ClO_b$, (4) ν_sClO_b, (5) $\nu_{as}ClO_b$, (6) νClO_t.

medium intensity band and weak line up to 1200 cm^{-1}. The mean frequency of the stretching mode ($\nu_s + \nu_{as}$) in the ClO_{3b} unit is lower than that in an ionic ClO_4^- (around 1010 instead of 1060 cm^{-1}). This difference is characteristic of a lengthening of the Cl–O$_b$ bond, consistent with the crystallographic results.

3.2.6. *Bridging chelating tridentate [ClO$_4$]*

Until now, simultaneously bridging chelating tridentate perchlorato groups were only identified in the high temperature form of $Ln(ClO_4)_3$ complexes (M = Yb, Tm and Lu). The Raman spectrum of $Yb(ClO_4)_3$ [82] in its high temperature form is depicted in Fig. 18. The C_{3v} symmetry of the conventional bridging tridentate [ClO$_4$] is lowered to a C_s symmetry. Because of the chelating character, constraints occur and the vibrational modes are perturbed. The bending vibrations show a larger splitting than observed in tridentate C_{3v} and the frequency of the $\nu_s ClO_{3t}$ decreases ($\Delta\nu = 50$ cm^{-1}).

3.2.7. *Chloryl salts*

Two types of chloryl salt were identified during the synthesis of some inorganic perchlorato complexes: definite salts, $(ClO_2)_xM(ClO_4)_{n+x}$, where an anion $[MClO_4)_{n+x}]^{x-}$ can be characterized; and double salts $M(ClO_4)_n \cdot xCl_2O_6$ where chlorine trioxide (covalent or/and ionic) is a guest between the layers or in the channels of $M(ClO_4)_n$.

3.2.7.1. *Definite chloryl salts.*

The strong Raman line around 1050 cm^{-1} ($\nu_s ClO_2^+$) and the IR band (doublet, due to $^{35}Cl-^{37}Cl$ isotopic shift) around 1300 cm^{-1} ($\nu_{as} ClO_2^+$) allow unambiguous characterization of ClO_2^+. δClO_2^+ is close to 520 cm^{-1}.

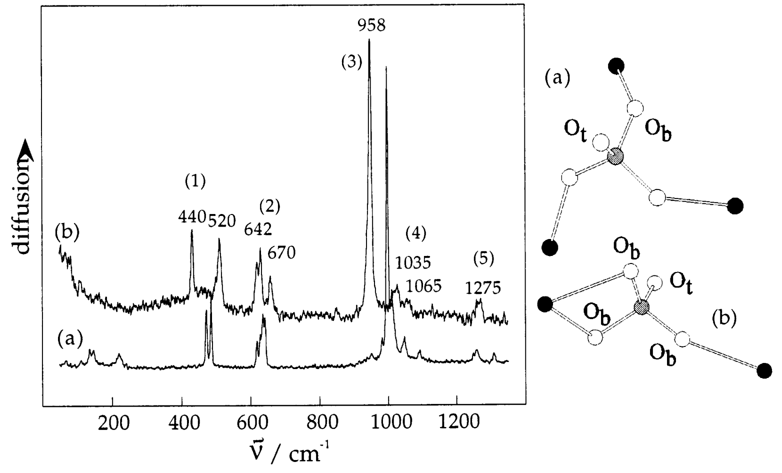


Fig. 18. Raman spectrum of the low temperature (a) and high temperature (b) forms of $Yb(ClO_4)_3$ showing the spectral differences between bridging tridentate (a) and bridging chelating tridentate (b) [ClO$_4$] groups. (1) ρ_r, (2) δ_s, $\delta_{as}ClO_b$, (3) $\nu_s ClO_b$, (4) $\nu_{as} ClO_b$, (5) νClO_t.

$(ClO_2)_2Sn(ClO_4)_6$ was described earlier and two particular facts are emphasized: (i) ClO_2^+ interacts with the $[ClO_4]$ ligand; and (ii) the octahedral surrounding of Sn, as in the neutral $Sn(ClO_4)_4$ [144], is conserved, but bridging bidentate groups become monodentate due to the introduction of two extra $[ClO_4]$ groups in the coordination sphere of the metal. The same observations can be made for some chloryl salts. For example, in $ClO_2Ni(ClO_4)_3$ and $ClO_2Co(ClO_4)_3$, $[ClO_4]$ groups are bridging bidentate and the structure can be related to $ANiCl_3$ salts (with A = alkali metal) [170]. In both cases, as well as in $ClO_2Er(ClO_4)_4$ (see Fig. 19) or $(ClO_2)_{.33}La(ClO_4)_{3.33}$ [61], the M–O bond strength is weaker than in corresponding $M(ClO_4)_n$ complexes in which perchlorates are tridentate.

In $ClO_2Cu(ClO_4)_3$ [23], $ClO_2Zn(ClO_4)_3$ [113], $ClO_2Cd(ClO_4)_3$ [115], $ClO_2Ga(ClO_4)_4$ [135], $ClO_2In(ClO_4)_4$ [138], $ClO_2Tl(ClO_4)_4$ [138], $ClO_2Fe_2(ClO_4)_7$ [102] and $(ClO_2)_2Th(ClO_4)_6$ (J.L. Pascal and F. Favier, unpublished results), well-characterized bridging bidentate and monodentate groups coexist.

3.2.7.2. Double salts $M(ClO_4)_n \cdot xCl_2O_6$. Two complexes have been reported in which chlorine trioxide is inserted or intercalated: $Sc(ClO_4)_3 \cdot 0.25Cl_2O_6$ [74] and $Pr(ClO_4)_3 \cdot Cl_2O_6$ [79] (see Fig. 20). In both, the structure of the host $M(ClO_4)_3$ complex is retained or is only distorted due to the intercalation. In $Sc(ClO_4)_3$, which has a layered structure similar to that of $Ga(ClO_4)_3$, Cl_2O_6 is spectroscopically purely ionic, but there is no anion to cation interaction as observed in the pure liquid. In the Pr salt, which has a channel structure [32,79], ionic Cl_2O_6 is in equilibrium with its covalent form.

3.2.8. Nitryl salts

Nitryl salts are generally characterized by NO_2^+ vibrational modes: $\nu_sNO_2^+ = 1400\ cm^{-1}$ (Raman), $\nu_{as} = 2360\ cm^{-1}$ (IR), $\delta \approx 580\ cm^{-1}$ (IR) [168] and a typical

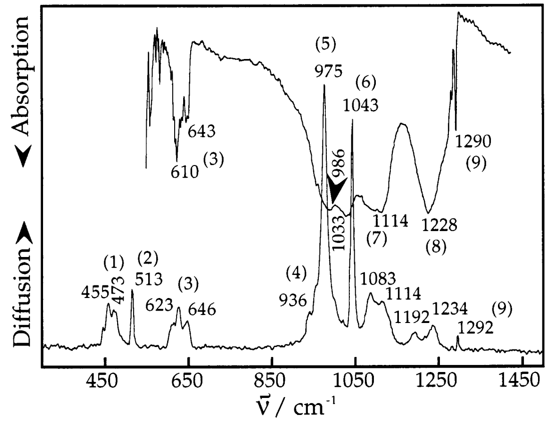


Fig. 19. IR and Raman spectra of $ClO_2Er(ClO_4)_4$. Characteristic ClO_2^+ bands and lines: (2) δClO_2, (6) ν_sClO_2, (9) $\nu_{as}ClO_2$, other bands and lines are assigned to a bidentate $[ClO_4]$: (1) $\delta ClO_b + \rho_t$, (3) $\delta ClO_t + \rho_w + \rho_r$, (4) $\nu_{as}ClO_b$, (5) ν_sClO_b, (7) ν_sClO_t, (8) &[nu];$_{as}ClO_t$.

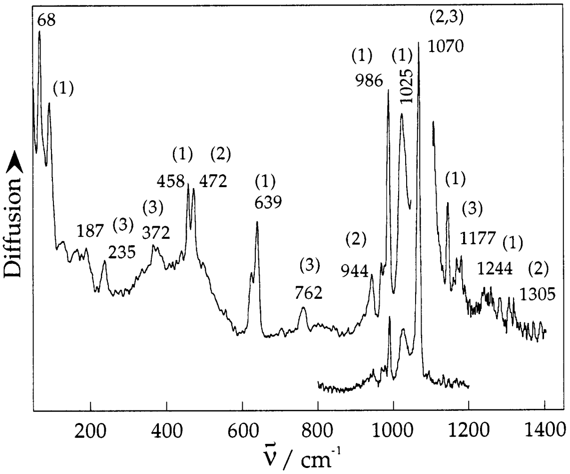


Fig. 20. Raman spectrum of $Pr(ClO_4)_3 \cdot Cl_2O_6$. (1) $Pr(ClO_4)_3$, (2) ionic Cl_2O_6, (3) covalent Cl_2O_6.

$\nu_s + \nu_{as}$ combination mode appearing as a weak and sharp IR band around 3740 cm^{-1} (see Fig. 21). No interaction occurs between NO_2^+ and $[ClO_4]$ ligands in contrast to chloryl salts.

General remarks about $M(ClO_4)_n^{x-}$ anions for chloryl salts apply also to nitryl salts. Thus, the molecular structure of $NO_2M(ClO_4)_3$ complexes with M = Mn, Co, Ni, Zn and Cd are very close to those found for the chloryl salts of the corresponding perchlorato complexes.

Particular comment should be made for $NO_2Pr(ClO_4)_4$ [79]. The molecular struc-

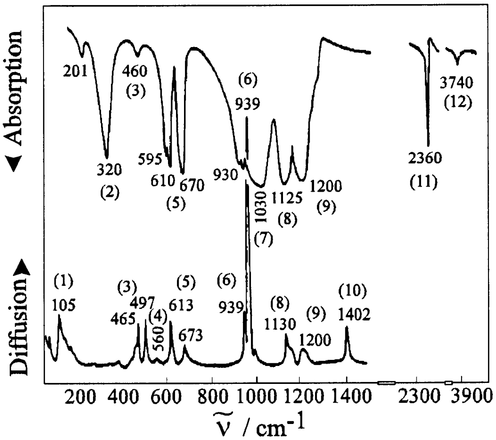


Fig. 21. IR and Raman spectra of $NO_2Ni(ClO_4)_3$. Characteristic NO_2^+ bands and lines: (4) δNO_2^+, (10) $\nu_s NO_2^+$, (11) $\nu_{as} NO_2^+$, (12) $\nu_s + \nu_{as} NO_2^+$, other bands and lines are assigned to a bidendate $[ClO_4]$: (1) lattice vibrations, (2) $\nu NiO(ClO_4)$, (3) $\delta_s ClO_b + \rho_t$, (5) $\delta_{as} ClO_t + \rho_w + \rho_r$, (6) $\nu_s ClO_b$, (7) $\nu_{as} ClO_b$, (8) $\nu_s ClO_t$, (9) $\nu_{as} ClO_t$.

ture of $Pr(ClO_4)_3$ is adopted, but is slightly disturbed by the additional weakly bonded $[ClO_4]$ for which Raman frequencies are very close to those observed for ClO_4 in solid Cl_2O_6.

3.2.9. Cl–O bond length and stretching frequencies

Differences between the frequencies of the stretching modes, the bending modes and generally those of the stretching modes of the MO_n skeleton are sufficiently large ($\Delta\nu > 300\ cm^{-1}$) to avoid coupling between these modes. Thus, it is possible to correlate the known bond lengths, determined by X-ray diffraction or EXAFS analysis, and the corresponding vibrational frequencies. One can predict a bond length when crystallographic data are missing. The relationship between Cl–O distances and $\nu_s^2 + \nu_{as}^2$ is given in Fig. 22.

4. Reactivity of inorganic perchlorato complexes

The difficulties encountered during the synthesis of perchlorato complexes, hazards and constraints in handling these compounds, the common use of perchlorate in the field of pyrotechnics and the generally bad reputation of organic perchlorates have largely restricted even ideas of any common use of this family of compounds. However, the use of ionic perchlorate as oxidants or propellants are largely described in the literature [10,11]. More recently, considerable interest was generated by complexes of weak and labile ligand such as trifluoromethanesulphonate (triflate) [171] or perchlorate [172] which can be used as reusable catalysts in organic synthesis.

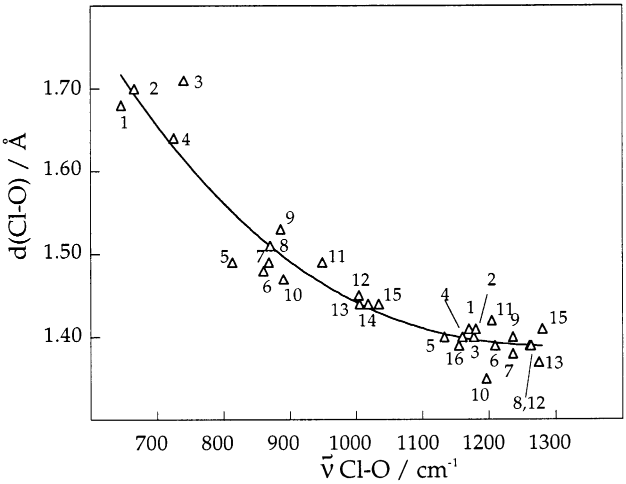


Fig. 22. Plot of Cl–O bond length against $[(\nu_s^2+\nu_{as}^2)/2]^{1/2}$. 1—$ClOClO_3$, 2—$FOClO_3$, 3—$Cl_2O_7$, 4—$HClO_4$, 5—$Sn(ClO_4)_6^{2-}$, 6—$Sb_2Cl_6O(OH)ClO_4$, 7—$Ti(ClO_4)_4$, 8—$Zr(ClO_4)_4$, 9—$Hf(ClO_4)_4$, 10—$Sn_3O_2Cl_4(ClO_4)_4$ (bidentate), 11—$Cu(ClO_4)_2$, 12—$Yb(ClO_4)_3$ (HT), 13—$Ni(ClO_4)_2$, 14—ClO_4^-, 15—$Yb(ClO_4)_3$ (LT), 16—$Sn_3O_2Cl_4(ClO_4)_4$ (monodentate).

In the same way, the rear cover of a recent issue of *Inorganic Chemistry* [36(8) (1997)] showed the advertisement of a chemical distributor for pure rare-earth perchlorates as catalysts, supported by numerous literature data. Anhydrous and dihydrated iron perchlorates, prepared by our group were successfully used as a starting reagent in a heterogeneous cationic polymerization process [24], with greater efficiency than other catalysts such as chlorides or triflates. Unfortunately, the unpredictable behaviour of perchlorates, particularly in organic media, limits such uses and triflates are often preferred [173,174].

More interesting facts should be exploited: $Ti(ClO_4)_4$ was shown to be as an exceptional oxidizing agent [65] and Cl_2O_6 inserted in layers or channels is a milder reagent than pure liquid or solid Cl_2O_6 (J.L. Pascal and F. Favier, unpublished results).

Since perchlorato complexes decompose at moderate temperature, generally below 300 °C, they could be the sources for nanosized ceramics, oxides, chlorides or oxychlorides. The decomposition of hydrated perchlorates is reported in the literature [12] but, due to the high temperature employed, the resulting products are crystalline. A recent study [25] of the thermal behaviour of anhydrous perchlorato complexes of lanthanides shows that, at $T \approx 300$ °C, they either yield LnOCl or Ln_3O_4Cl depending on the crystalline form of the precursors. As shown in Fig. 23, these oxychlorides are obtained as fine powders which can easily react in water to give hydroxides and, in a second step, by dehydration below 200 °C, the corresponding oxides.

5. Conclusion

This overview of perchlorato complexes supported by data gathered over the past 30 years underlines the richness of chemistry and structural diversities of these

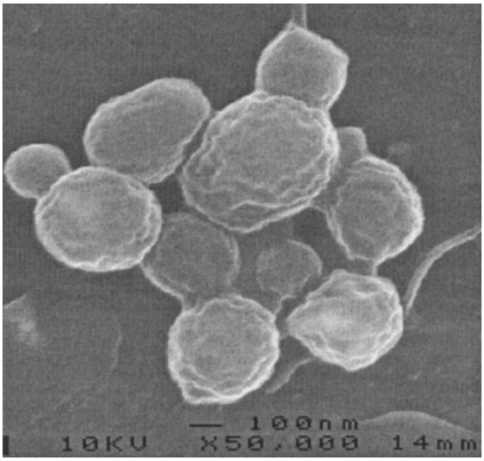


Fig. 23. Nanosized particles of EuOCl obtained from decomposition of $Eu(ClO_4)_3$ at 280 °C under vacuum (1.33 Pa).

compounds. The use of efficient reagents has allowed the synthesis of unsolvated perchlorato complexes of a majority of the elements of the periodic table. There are still gaps, but they are limited (see Table 6). The number of complexes synthezized is largely greater than that of the crystal structures solved. Vibrational spectroscopies remain a chosen tool providing a good approach to the molecular structure, but the details of the molecular arrangement cannot be derived. More crystal and molecular data must be obtained to relate structure and properties, and to extend the use of inorganic perchlorato complexes.

Note: it is a difficult task in the limited space available to provide what we would like to be able to call a complete review of the area of inorganic perchlorates. Additional details completing the information, and the references, given here, are to be found in the publications cited.

Acknowledgements

J. and A. Potier are gratefully thanked for their initiation of this work. This paper summarizes the work of Ph.D. students or of postdoctoral students and collaborators: M. Chaabouni, T. Chausse, C.S. Zhang, H. Abduljabbar, M. Fourati. Special thanks to M. Tillard Charbonnel, C. Belin for X-ray diffraction studies on single crystal, D.J. Jones, A. Michalowicz, J. Roziere for EXAFS studies, A. Fitch, C. Vaughan for Rietveld analysis. LURE (Orsay) and ESRF (Grenoble) are acknowledged for the use of their experimental facilities and the CNRS for financial support.

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