

# Chlorine Trioxide, $\text{Cl}_2\text{O}_6$ , a Most Efficient Perchlorating Reagent in New Syntheses of Anhydrous Metal Perchlorates, Chloryl and Nitryl Perchloratometalates of Cobalt(II), Nickel(II), and Copper(II). Reactivity of Chlorine Trioxide with Anhydrous or Hydrated Chlorides and Nitrates †

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Anhydrous transition-metal perchlorates,  $\text{M}(\text{ClO}_4)_2$  ( $\text{M} = \text{Ni}, \text{Co}, \text{or Cu}$ ), and their chloryl and nitryl salts,  $\text{ClO}_2\text{M}(\text{ClO}_4)_3$ ,  $\text{NO}_2\text{M}(\text{ClO}_4)_3$ , and  $(\text{NO}_2)_2\text{M}(\text{ClO}_4)_4$ , have been prepared by the action of  $\text{Cl}_2\text{O}_6$  on the corresponding anhydrous or hydrated metal chloride or nitrate. The intermediate chloryl salts,  $\text{ClO}_2\text{M}(\text{ClO}_4)_3$ , can be isolated. The formation of  $\text{NO}_2^+$  is due to the highly acidic medium. The vibrational spectra of the compounds  $\text{M}(\text{ClO}_4)_2$  suggest a strong metal-perchlorate interaction and are consistent with the presence of two types of bidentate perchlorate group in  $\text{Cu}(\text{ClO}_4)_2$  and tridentate perchlorate in  $\text{Ni}(\text{ClO}_4)_2$  and  $\text{Co}(\text{ClO}_4)_2$ . The electronic spectra indicate an octahedral environment around the metal atom, and a polymeric structure.

A large part of perchlorate chemistry is essentially the chemistry of ionic perchlorates and until recently, except for a few examples such as  $\text{Cu}(\text{ClO}_4)_2$ ,<sup>1</sup> the co-ordinating ability of the  $\text{ClO}_4$  ligand was disputable.<sup>2</sup> New horizons were opened about ten years ago by the use of efficient perchlorating agents such as anhydrous perchloric acid, chlorine trioxide, or chlorine perchlorate,<sup>3-17</sup> which resulted in the isolation of numerous perchlorato-complexes. However, although the synthesis and study of the bivalent metal perchlorates  $\text{M}(\text{ClO}_4)_2$  ( $\text{M} = \text{Cu}$ ,<sup>18</sup>  $\text{Ni}$ ,<sup>19</sup> or  $\text{Co}$ <sup>20</sup>) are still tediously complex, they lead to an understanding of the influence of the metal centre on  $\text{ClO}_4$  co-ordination.

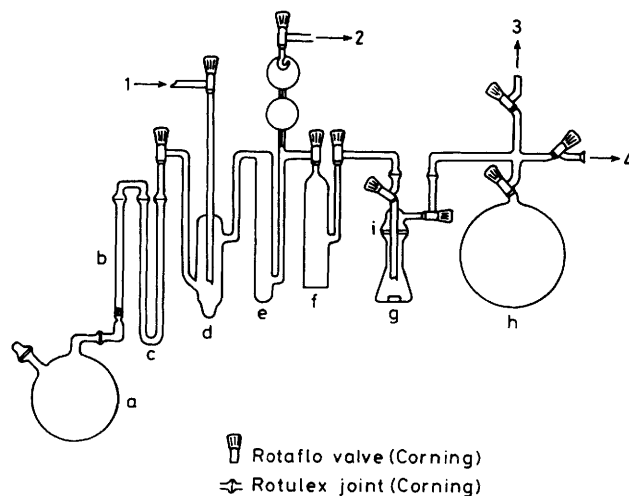
In this work, the perchlorating properties of chlorine trioxide ( $\text{Cl}_2\text{O}_6$ ) are used as the easiest route to the synthesis of metal perchlorates. In the two new methods proposed,  $\text{Cl}_2\text{O}_6$  exchanges  $\text{ClO}_4$  with  $\text{Cl}$  or  $\text{NO}_3$  and acts simultaneously as a dehydrating reagent. The electronic and vibrational spectra of the resulting compounds have allowed a structural approach to the nature of the  $\text{ClO}_4$  co-ordination.

## Experimental

**Caution:** Chlorine trioxide and anhydrous perchlorates are highly reactive and explosive compounds, particularly on contact with organic compounds and under shock; they must be handled with care. The reactions must be continuously monitored. All the products are very hygroscopic and must be handled in a vacuum line or in a dry-box filled with dry nitrogen or argon.

**Materials.**—The synthesis and the purification of  $\text{Cl}_2\text{O}_6$  have been described previously.<sup>14,15</sup> The purity and origin of anhydrous or hydrated chlorides and nitrates used in this work are given in Table 1.

**The Vacuum Line (Figure 1).**—The  $\text{Cl}_2\text{O}_6$  and perchlorato-complexes were synthesized in a Pyrex greaseless vacuum line equipped with Rotaflo valves and Rotulex joints (Corning) with Teflon coated O rings. The double-stage vacuum pump (*ca.* 1.33 Pa) and the Pirani vacuum gauge were protected by three traps cooled to  $-180^\circ\text{C}$ . The 41/35 ground-glass joints of these traps



**Figure 1.** Pyrex vacuum line for the synthesis of chlorine trioxide and anhydrous perchlorates: a, synthesis of  $\text{ClO}_2$  at  $50^\circ\text{C}$  [ $2\text{KClO}_3 + 2\text{H}_2\text{SO}_4$  (5N) +  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow 2\text{ClO}_2 + 2\text{CO}_2 + 4\text{H}_2\text{O} + 2\text{KHSO}_4$ ]; b, flowmeter; c,  $\text{P}_4\text{O}_{10}$  columns; d, synthesis of  $\text{Cl}_2\text{O}_6$  ( $2\text{ClO}_2 + 2\text{O}_3 \rightarrow \text{Cl}_2\text{O}_6 + 2\text{O}_2$ ) at  $-10^\circ\text{C}$ ; e,  $\text{Cl}_2\text{O}_6$  trap ( $0^\circ\text{C}$ ); f, distilled  $\text{Cl}_2\text{O}_6$  ( $-20^\circ\text{C}$ ); g, perchlorate synthesis; h, 4 l bulb to collect evolved gases; i, 29/15 Rotulex joint; 1,  $\text{O}_3$ - $\text{O}_2$  mixture from a Siemens type ozonizer; 2, to  $\text{H}_2\text{SO}_4$  traps and fume hood; 3, to vacuum line; 4, to i.r. cell (matrix type)

were greased with Voltalef, a Kelf grease. These traps were disconnected at  $-180^\circ\text{C}$  and gently warmed to room temperature after each experiment.

**Physicochemical Analysis.**—Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer. For Raman spectra a Dilor spectrometer linked to a Tracor TN 1710 modular multichannel computer (Northern Instruments) was used with a Spectra Physics argon laser (5 145 Å line and 140 mW). The electronic spectra were run on a Beckman DK 2A instrument equipped with an integrating sphere. The sensitivity and calibration of the spectrometers were described elsewhere.<sup>10</sup> The X-ray diffraction patterns were obtained on a Philips goniometer PW 1965/30.

† Supplementary data available (No. SUP 56074, 8 pp.): Raman and i.r. data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii-xix.

**Table 1.** Syntheses of perchlorato-complexes from anhydrous and hydrated chlorides and nitrates

Starting reagent (amount/g)	Cl <sub>2</sub> O <sub>6</sub> <sup>a</sup>	Reaction temperature (°C)	Product	Colour	Analysis <sup>b</sup> (%)		
					M	ClO <sub>4</sub>	ClO <sub>2</sub> , NO <sub>2</sub> <sup>d</sup>
NiCl <sub>2</sub> <sup>c</sup> (1.3425)	12	18	ClO <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>3</sub> ·xNiCl <sub>2</sub>	Orange			
NiCl <sub>2</sub> <sup>c</sup> (0.3681)	5 + 1 <sup>f</sup>	18	ClO <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>3</sub>	Orange	13.75 (13.85)	70.35 (70.3)	15.9 (15.9)
NiCl <sub>2</sub> ·6H <sub>2</sub> O <sup>g</sup> (0.9827)	2	15					
CoCl <sub>2</sub> <sup>h</sup> (0.5488)	3	5–7	ClO <sub>2</sub> Co(ClO <sub>4</sub> ) <sub>3</sub>	Orange-brown	13.75 (13.85)	70.05 (70.25)	16.2 (15.9)
CoCl <sub>2</sub> ·2H <sub>2</sub> O <sup>i</sup> (0.6635)	3						
CuCl <sub>2</sub> <sup>j</sup> (0.5100)	5	10	ClO <sub>2</sub> Cu(ClO <sub>4</sub> ) <sub>3</sub>	Orange	14.35 (14.80)	69.55 (69.5)	
CuCl <sub>2</sub> ·2H <sub>2</sub> O <sup>k</sup> (1.9400)	2						
Ni(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O <sup>l</sup> (0.7254)	3 <sup>m</sup>	15	(NO <sub>2</sub> ) <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>4</sub>	Yellow-green	10.45 (10.7)	72.7 (72.5)	
Co(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O <sup>n</sup> (0.3698)	4 <sup>o</sup>	3	(NO <sub>2</sub> ) <sub>2</sub> Co(ClO <sub>4</sub> ) <sub>4</sub> <sup>p</sup>	Dirty pink	10.9 (10.75)	72.55 (72.5)	
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O <sup>q</sup> (1.2870)	4 <sup>r</sup>						
Cu(NO <sub>3</sub> ) <sub>2</sub> <sup>t</sup> (0.1719)	4	10	(NO <sub>2</sub> ) <sub>2</sub> Cu(ClO <sub>4</sub> ) <sub>4</sub>	Pale green	11.5 (11.5)	72.55 (71.9)	15.95 (16.65)
Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O <sup>u</sup> (1.3146)	3						

<sup>a</sup> Number of successive additions (ca. 8 g) of Cl<sub>2</sub>O<sub>6</sub>. <sup>b</sup> Required values are given in parentheses. <sup>c</sup> Merck Schuchardt, for synthesis. <sup>d</sup> Raman analysis; only the decomposition product Ni(ClO<sub>4</sub>)<sub>2</sub>·xNiCl<sub>2</sub> was chemically analysed (see Table 2). <sup>e</sup> NiCl<sub>2</sub>·6H<sub>2</sub>O (Merck, pure) dehydrated by freshly distilled SOCl<sub>2</sub> (Merck Schuchardt) according to Pray.<sup>27</sup> <sup>f</sup> The first five additions gave an incomplete reaction; the mixture was warmed to 80 °C to obtain predominantly Ni(ClO<sub>4</sub>)<sub>2</sub> and small amounts of unreacted NiCl<sub>2</sub>. Further addition of Cl<sub>2</sub>O<sub>6</sub> yielded the expected pure product. <sup>g</sup> Merck, pure. <sup>h</sup> CoCl<sub>2</sub>·6H<sub>2</sub>O (Merck Schuchardt, for synthesis)  $\xrightarrow[\text{vacuum}]{135^\circ\text{C}}$  CoCl<sub>2</sub>. <sup>i</sup> CoCl<sub>2</sub>·6H<sub>2</sub>O + nH<sub>2</sub>O  $\xrightarrow[\text{vacuum}]{40^\circ\text{C}}$  CoCl<sub>2</sub>·2H<sub>2</sub>O. <sup>j</sup> Alfa Ventron. <sup>k</sup> Labosi, for analysis. <sup>l</sup> Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Prolabo RP)  $\xrightarrow[\text{vacuum}]{80^\circ\text{C}}$  Ni(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O. <sup>m</sup> The mixture of Cl<sub>2</sub>O<sub>6</sub> and Ni(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O had to be stirred vigorously for at least 32 h to obtain complete reaction. <sup>n</sup> Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Merck Schuchardt)  $\xrightarrow[\text{vacuum}]{50^\circ\text{C}}$  Co(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O. <sup>o</sup> One addition of Cl<sub>2</sub>O<sub>6</sub> ca. 2 g. <sup>p</sup> One mixture exploded after 1 h of stirring. <sup>q</sup> Merck Schuchardt. <sup>r</sup> One addition of Cl<sub>2</sub>O<sub>6</sub> ca. 4 g. <sup>s</sup> Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O reacts vigorously with Cl<sub>2</sub>O<sub>6</sub>, the final product being a mixture of ClO<sub>2</sub>Co(ClO<sub>4</sub>)<sub>3</sub> and NO<sub>2</sub>Co(ClO<sub>4</sub>)<sub>3</sub>. <sup>t</sup> Synthesized according to Wallwork and Addison (*J. Chem. Soc.*, 1965, 2925). <sup>u</sup> Cu(NO<sub>3</sub>)<sub>2</sub>·nH<sub>2</sub>O (Prolabo, pure)  $\xrightarrow[\text{vacuum}]{40^\circ\text{C}}$  Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O.

**Table 2.** Decomposition of chloryl or nitryl perchlorate salts

Starting material	Decomposition temperature (°C) <sup>a</sup>	Final product	Colour	Analysis (%)	
				M	ClO <sub>4</sub>
ClO <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>3</sub> ·xNiCl <sub>2</sub>	80	Ni(ClO <sub>4</sub> ) <sub>2</sub> ·xNiCl <sub>2</sub>	Yellow	23.3 (22.8)	72.95 (77.2) <sup>b</sup>
ClO <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>3</sub>	80	Ni(ClO <sub>4</sub> ) <sub>2</sub>	Yellow	22.95 (22.8)	77.1 (77.2)
ClO <sub>2</sub> Co(ClO <sub>4</sub> ) <sub>3</sub>	75	Co(ClO <sub>4</sub> ) <sub>2</sub>	Pink	23.1 (22.85)	76.9 (77.15)
ClO <sub>2</sub> Cu(ClO <sub>4</sub> ) <sub>3</sub>	65–70	Cu(ClO <sub>4</sub> ) <sub>2</sub> <sup>c</sup>	Blue-white	24.2 (24.2)	75.75 (75.8)
(NO <sub>2</sub> ) <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>4</sub>	140–150	NO <sub>2</sub> Ni(ClO <sub>4</sub> ) <sub>3</sub> <sup>d</sup>	Yellow	14.15 (14.55)	73.55 <sup>e</sup> (74.0)
(NO <sub>2</sub> ) <sub>2</sub> Co(ClO <sub>4</sub> ) <sub>4</sub>	100–105	NO <sub>2</sub> Co(ClO <sub>4</sub> ) <sub>3</sub> <sup>d</sup>	Pink	14.35 (14.6)	72.55 (74.0)
(NO <sub>2</sub> ) <sub>x</sub> (ClO <sub>2</sub> ) <sub>1-x</sub> Co(ClO <sub>4</sub> ) <sub>3</sub>	90	(NO <sub>2</sub> ) <sub>x</sub> Co(ClO <sub>4</sub> ) <sub>2+x</sub>	Pink	20.55	79.45 <sup>f</sup>
(NO <sub>2</sub> ) <sub>2</sub> Cu(ClO <sub>4</sub> ) <sub>4</sub>	115	NO <sub>2</sub> Cu(ClO <sub>4</sub> ) <sub>3</sub> <sup>g</sup>	White	15.85 (15.6)	74.05 (73.15)

<sup>a</sup> Under vacuum. <sup>b</sup> Required values are those of Ni(ClO<sub>4</sub>)<sub>2</sub>; 3.25% Cl<sup>-</sup> was found. <sup>c</sup> An irreversible colour change from blue-white to pale green was noted on warming a sample to 190 °C. The X-ray diffraction patterns and u.v., e.s.r., i.r., and Raman spectra gave no evidence for a change in the molecular or crystal structure. <sup>d</sup> On increasing the temperature this compound can decompose into M(ClO<sub>4</sub>)<sub>2</sub>. <sup>e</sup> The existence of NO<sub>2</sub><sup>+</sup> was checked by i.r. and Raman spectroscopy. <sup>f</sup> x ca. 0.3; the product is a mixture of Co(ClO<sub>4</sub>)<sub>2</sub> and NO<sub>2</sub>Co(ClO<sub>4</sub>)<sub>3</sub>. <sup>g</sup> Sublimes.

A Pyrex matrix i.r. cell built in the laboratory<sup>15</sup> was used to check the purity of Cl<sub>2</sub>O<sub>6</sub> and to analyse the gases evolved during the course of the reactions. The crude solid perchlorates were pressed between silicon plates [(111) cleavage, thickness 1 mm]. Neutral perchlorates or nitryl perchloratometalates can be milled with Nujol distilled and dried over sodium. For Raman spectroscopy the samples were generally introduced

into a Pyrex tube (outside diameter 5 mm) and sealed under vacuum. A spinning cell and a sealed Pyrex tube (outside diameter 2 mm) were used to record Raman spectra of Cu(ClO<sub>4</sub>)<sub>2</sub> (blue-white form) and Co(ClO<sub>4</sub>)<sub>2</sub>. The nitryl salts and Ni(ClO<sub>4</sub>)<sub>2</sub> were cooled to -180 °C to minimize their decomposition. We could not record the spectra of chloryl and nitryl perchloratocobaltates.

For u.v. spectroscopy samples were analysed by a diffuse reflectance method, using either crude materials or samples diluted in dry MgO, pressed between a Teflon plate and an Infrasil window. In X-ray analysis the powdered crude material was placed on an aluminium plate and protected by a beryllium, Kapton, or Parafilm window (respectively 0.25, 0.0025, and 0.015 mm thick). The cell was sealed with Voltaef grease.

**Chemical Analysis.**—Great care must be taken when the anhydrous perchlorates are dissolved. They react quickly and vigorously with water and can therefore be partly decomposed: this is especially pronounced for the chloryl salts. The perchlorates must be dissolved at low temperature and the solution slowly warmed to room temperature.<sup>14,16</sup>

Metallic cations were titrated by a complexometric method using 0.1 or 0.01 mol dm<sup>-3</sup> ethylenediaminetetra-acetate (edta).<sup>21</sup> Perchlorate ion was analysed by a potentiometric method using an Orion specific electrode and 0.04 mol dm<sup>-3</sup> tetraphenylarsonium solution (Merck for analysis) as titrant.<sup>22</sup> When possible ClO<sub>2</sub><sup>+</sup> was titrated as ClO<sub>3</sub><sup>-</sup> by a standard redox method.<sup>23</sup>

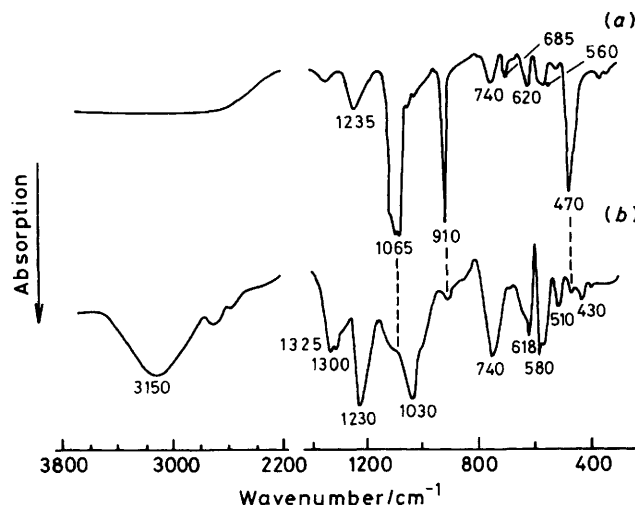
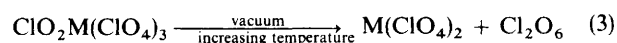
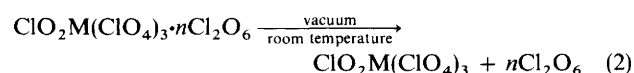
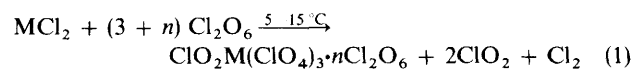
**Synthesis of Anhydrous Perchlorates.**—Chlorine trioxide (2–4 g) was added at –180 °C in the reactor (g) (Figure 1) to anhydrous or hydrated chloride or nitrate (0.3–2 g). The mixture was allowed to warm slowly until the reaction started (3 to 10 °C). Evolved gases (ClO<sub>2</sub>, Cl<sub>2</sub>, and sometimes ClOClO<sub>3</sub>) were collected in the 4 l bulb (h). This bulb was evacuated from time to time to avoid too high a concentration of explosive ClO<sub>2</sub>. If the reaction was smooth, the temperature was increased to 10 or 15 °C and up to 8 g of distilled Cl<sub>2</sub>O<sub>6</sub> introduced. The Cl<sub>2</sub>O<sub>6</sub> and the salt can be stirred using a Teflon-coated magnetic bar. However, the mixtures have to be carefully ground periodically in a dry-box to ensure complete reaction. Successive additions of Cl<sub>2</sub>O<sub>6</sub> were made until the reaction was complete. The progress of the reaction was checked by the colour, change in weight, qualitative tests, and spectroscopic or X-ray analysis.

In every case the product of the first step is a chloryl or a nityl salt. These salts can lose ClO<sub>2</sub>ClO<sub>4</sub> or NO<sub>2</sub>ClO<sub>4</sub> on heating under vacuum to give directly a neutral salt or, for the nityl salt, an intermediate with a smaller NO<sub>2</sub>–M ratio. The specific experimental procedures are summarized in Tables 1 and 2.

## Discussion

**Synthesis of Anhydrous Perchlorates.**—As previously shown<sup>3,5,7,11,15,24</sup> the formation of perchlorato-complexes using Cl<sub>2</sub>O<sub>6</sub> as perchlorating reagent is attributed to its ionic character, being ClO<sub>2</sub><sup>+</sup>ClO<sub>4</sub><sup>-</sup> in the solid state<sup>25</sup> but in equilibrium, Cl<sub>2</sub>O<sub>6</sub> (covalent) ⇌ ClO<sub>2</sub><sup>+</sup>ClO<sub>4</sub><sup>-</sup>, in the liquid state.<sup>26</sup>

**From metal chlorides.** (a) *Anhydrous chlorides.* Whatever the source of the anhydrous metal chloride used (commercial or obtained using the Pray method<sup>27</sup>) the synthetic route in equations (1)–(3) can be written. Starting from commercial



**Figure 2.** I.r. spectra of the evolved gases trapped on a cold (–180 °C) silicon window in a matrix cell during the reaction of NiCl<sub>2</sub>·6H<sub>2</sub>O and Cl<sub>2</sub>O<sub>6</sub>. The ClO<sub>2</sub> vibrations are indicated by dashed lines. The other bands are due to HClO<sub>4</sub>. (a) Reaction of Cl<sub>2</sub>O<sub>6</sub> with Cl<sup>-</sup>; (b) dehydration

anhydrous chlorides, the synthesis of pure chloryl salts is generally slow and impossible with anhydrous NiCl<sub>2</sub>. The best yield is obtained with anhydrous MCl<sub>2</sub> synthesized according to Pray, but for nickel chloride this route is unsatisfactory (see Table 1).

(b) *Hydrated chlorides.* Chlorine trioxide reacts readily with all the hydrated chlorides including NiCl<sub>2</sub>·6H<sub>2</sub>O. Although the final products are identical to those obtained with anhydrous chlorides, the synthetic pathway evidently differs. The i.r. analysis (Figure 2) of evolved gases shows, at the beginning of the reaction, mainly ClO<sub>2</sub> bands<sup>28</sup> while HClO<sub>4</sub> bands<sup>29</sup> appear subsequently. It is significant that the dehydration process occurs after the replacement of Cl by ClO<sub>4</sub>.

(c) *Comments on the different reactivities of chlorides as starting materials.* The higher reactivity of hydrated chlorides can be explained first by the differences in the co-ordination shell of chlorine atoms around the metal atom, as previously noted in the syntheses of anhydrous aluminium perchlorates;<sup>3b,9</sup> in hydrated chlorides Cl<sup>-</sup> ions are free or weakly bound to the metal atom while in anhydrous chlorides they are often part of a compact lattice. The high reactivity of dehydrated chlorides synthesized according to Pray can be attributed to the existence of a disordered lattice or to residual water molecules. The importance of the crystal lattice is emphasized by the different reactivity of CuCl<sub>2</sub>, where the octahedral distortion around the Cu atoms (in CuCl<sub>2</sub>) favours the reaction, but the differences in the reactivities of CoCl<sub>2</sub> and NiCl<sub>2</sub>, which have the same structure, requires consideration of the following factors: (i) the electronic configuration of the metal cation (respectively d<sup>7</sup> and d<sup>8</sup>) which is responsible for the relative stability of MX<sub>2</sub> in the order Cu < Co < Ni normally expected, (ii) the ionic radii of the metal cations (respectively 0.73 and 0.69 Å).

**From chlorine trioxide and nitrates.** Although the reactions of Cl<sub>2</sub>O<sub>6</sub> with N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub> have been studied,<sup>24</sup> none with metallic nitrates has been reported until now. Whatever the M(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O used, the final product is (NO<sub>2</sub>)<sub>2</sub>M(ClO<sub>4</sub>)<sub>4</sub>. Spectra of samples recorded during the course of the reaction showed the presence of the nityl perchlorate complex and some

\* However some irregularities were encountered with cobalt complexes (Table 1) depending upon the value of x, and perhaps related to their unpredictable stability.<sup>30</sup>

Table 3. X-Ray diffraction patterns\*

A		B		C		D		F		G		I		J		K		L	
<i>I</i>	<i>d/Å</i>	<i>I</i>	<i>d/Å</i>	<i>I</i>	<i>d/Å</i>	<i>I</i>	<i>d/Å</i>	<i>I</i>	<i>d/Å</i>	<i>I</i>	<i>d/Å</i>	<i>I</i>	<i>d/Å</i>	<i>I</i>	<i>d/Å</i>	<i>I</i>	<i>d/Å</i>	<i>I</i>	<i>d/Å</i>
22	6.30	34	6.30	38	6.27	100	7.39	m	6.36	m	6.27	74	9.12	72	8.18	35	6.65	8	6.80
13	4.47	4	4.48	7	4.43	40	4.07	m	4.85	w	4.48	36	6.96	38	7.36	30	5.67	75	5.48
12	4	8	4.46	14	4.00	40	3.58	m	4.05	m	3.98	33	6.15	34	5.67	15	4.17	8	4.29
8	3.81	25	4.25	20	3.96	30	3.36	m	4.02	w	3.81	7	5.71	56	4.87	30	3.91	41	4.14
36	3.61	17	4.01	33	3.65	5	2.44	w	3.77	s	3.65	7	5.46	60	3.98	15	3.81	8	4.04
12	3.38	22	3.96	20	3.61	60	2.38	m	3.69	s	3.63	17	4.82	41	3.86	13	3.75	46	3.74
100	3.17	17	3.78	20	3.38	15	2.35	m	3.65	m	3.33	28	4.48	87	3.59	30	3.59	93	3.61
17	2.84	33	3.66	100	3.15	5	2.27	m	3.40	s	3.16	16	4.30	43	3.52	30	3.49	64	3.57
7	2.61	24	3.61	6	2.87	20	2.03	s	3.36	s	3.15	13	3.90	79	3.49	15	3.37	38	3.28
3	2.59	10	3.49	16	2.84	5	1.99	m	3.34	w	3.08	85	3.80	87	3.48	100	3.27	13	3.05
4	2.44	100	3.37	26	2.81	10	1.70	s	3.20	m	2.85	10	3.67	76	3.36	70	3.17	100	2.99
5	2.32	sh	3.33	4	2.58	10	1.44	s	3.19	m	2.82	50	3.56	100	3.23	40	2.95	5	2.80
14	2.24	100	3.11	4	2.55	5	1.43	s	3.17	14	3.53	93	3.10	93	3.10	30	2.85	13	2.75
7	2.14	15	2.85	6	2.52	20	1.37	m	3.10	14	3.49	49	3.08	49	3.08	15	2.76	13	2.71
		26	2.82	8	2.42	5	1.35	w	2.91	80	3.25	26	3.03	26	3.03	46	2.34	22	2.51
		5	2.75	4	2.31			m	2.87	90	3.22	96	2.99	96	2.99	20	2.28	22	2.36
		3	2.70	4	2.30			m	2.84	100	3.10	19	2.97	19	2.97	30	2.05	9	2.24
		4	2.59	12	2.23			w	2.59	30	4.75	14	3.00	39	2.74	20	1.97	27	2.20
		11	2.56	10	1.99			w	2.55	50	4.13	15	2.94	34	2.72			8	2.07
		8	2.53	4	1.91			w	2.44	30	3.91	14	2.93	13	2.67			15	1.87
		8	2.42	9	1.74			w	2.32	90	3.33	15	2.91	39	2.63			15	1.83
		19	2.23					w	4.08	40	3.12	27	2.88	43	2.49			12	1.79
		31	2.18					m	3.73	20	3.01	23	2.85	24	2.46			9	1.67
		7	2.13					w	3.50	90	2.42	46	2.78	15	2.41			9	1.66
		14	1.98					s	3.22	30	2.29	24	2.72	15	2.39			4	1.56
		3	1.91					w	3.12	15	2.02	24	2.27	24	2.27			6	1.30
		56	1.87					m	2.88	20	1.45			44	2.16				
		5	1.82					w	2.60	30	1.39								
								w	2.45										
								w	2.27										
								w	1.87										

\* A =  $\text{ClO}_2\text{Ni}(\text{ClO}_4)_3$ ; B =  $(\text{NO}_2)_2\text{Ni}(\text{ClO}_4)_4$ ; C =  $\text{NO}_2\text{Ni}(\text{ClO}_4)_3$ ; D =  $\text{Ni}(\text{ClO}_4)_2$ ; E =  $\text{ClO}_2\text{Co}(\text{ClO}_4)_3$ ; F =  $(\text{NO}_2)_2\text{Co}(\text{ClO}_4)_4$ ; G =  $\text{NO}_2\text{Co}(\text{ClO}_4)_3$ ; H =  $\text{Co}(\text{ClO}_4)_2$ ; I =  $\text{ClO}_2\text{Cu}(\text{ClO}_4)_3$ ; J =  $(\text{NO}_2)_2\text{Cu}(\text{ClO}_4)_4$ ; K =  $\text{NO}_2\text{Cu}(\text{ClO}_4)_3$ ; L =  $\text{Cu}(\text{ClO}_4)_2$ . Italicized values belong to  $\text{NO}_2\text{ClO}_4$ . The symbols s, w, and m having their usual meaning, are used for poor X-ray patterns in which relative intensities cannot be measured accurately. For D and H the lines were recorded using a Kapton (Du Pont) window, however, the quality of spectra is hard to improve.

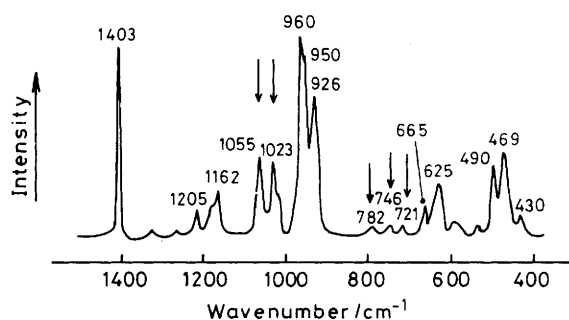
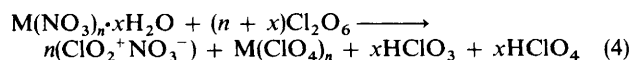


Figure 3. Raman spectrum of a mixture sampled in the course of the reaction of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  with  $\text{Cl}_2\text{O}_6$ . Arrows indicate the existence of unreacted  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , while the other bands (slightly shifted by crystal effects) are due to the final product  $(\text{NO}_2)_2\text{Cu}(\text{ClO}_4)_4$ .

unreacted hydrated nitrate (Figure 3). Unlike the chloride reaction, there is a progressive elimination of water and simultaneous formation of nitryl perchloratometalate.

A chemical pathway can be proposed to explain the  $\text{NO}_2^+$  formation. In a transient step, while  $\text{NO}_3^-$  is substituted by  $\text{ClO}_4^-$ ,  $\text{ClO}_2^+$  associates with  $\text{NO}_3^-$  according to equation (4).

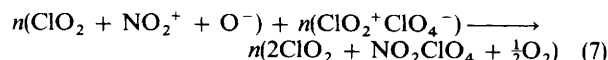
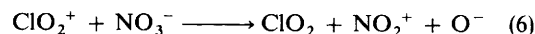
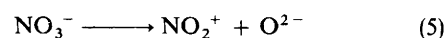


Two mechanisms can explain the formation of  $\text{NO}_2^+$ . In a strong acidic medium, according to ref. 31,  $\text{NO}_3^-$  undergoes a

Table 4. U.v. data ( $\text{cm}^{-1}$ )

$\text{Ni}(\text{ClO}_4)_2$	6 670 (sh), 7 190s, 11 905s, 14 490 (sh), 22 430s
$\text{Co}(\text{ClO}_4)_2$	6 620s, 7 140s, 13 510 (sh), 18 540s, 20 520 (sh)
$\text{Cu}(\text{ClO}_4)_2$	7 220 (sh), 9 600 (sh), 11 760s, 21 200w, br
$\text{ClO}_2\text{Ni}(\text{ClO}_4)_3$	6 780 (sh), 7 250s, 12 350s, 14 490 (sh)
$\text{ClO}_2\text{Co}(\text{ClO}_4)_3$	6 800—7 140s
$\text{ClO}_2\text{Cu}(\text{ClO}_4)_3$	7 520 (sh), 10 640s
$(\text{NO}_2)_2\text{Ni}(\text{ClO}_4)_4$	7 140s, 7 500 (sh), 14 400 (sh)
$\text{NO}_2\text{Ni}(\text{ClO}_4)_3$	6 755 (sh), 7 195s, 7 575 (sh), 12 195 (sh), 17 840 (sh), w, 20 575 (sh), 23 150s
$(\text{NO}_2)_2\text{Co}(\text{ClO}_4)_4$	6 670 (sh), 7 140s, 14 290 (sh), 18 940 (sh), s
$\text{NO}_2\text{Co}(\text{ClO}_4)_3$	6 710 (sh), 7 140s, 13 790w, 18 130s, 20 570 (sh)
$(\text{NO}_2)_2\text{Cu}(\text{ClO}_4)_4$	8 850 (sh), 11 240s, br
$\text{NO}_2\text{Cu}(\text{ClO}_4)_3$	7 300 (sh), 11 100s, br

self-ionization process [equations (5)–(7)]. Secondly, the instabilities of  $\text{NO}_2^+\text{ClO}_3^-$  and  $\text{ClO}_2^+\text{ClO}_3^-$  result in



reactions (8)–(10). By either mechanism the total balance is as in equation (11).

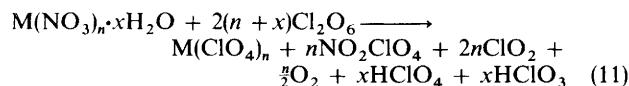
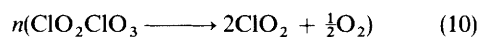
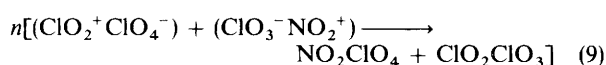
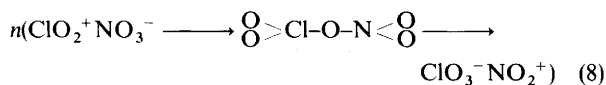
**Table 5.** Spectrochemical series for ligands bound to nickel

Ligand	NH <sub>3</sub>	CH <sub>3</sub> CN	O <sup>2-</sup>	H <sub>2</sub> O	NO <sub>3</sub> <sup>-</sup>	Me <sub>2</sub> SO	S <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	SO <sub>3</sub> F <sup>-</sup>	Cl <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>	Br <sup>-</sup>
<i>Dq/cm<sup>-1</sup></i>	1 080	1 070	860	850	801	773	757	734	720	690	680
Ref.	33	33	33	<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>c</i>	33	<i>d</i>	33

<sup>a</sup> C. C. Addison, *Chem. Rev.*, 1980, **80**, 21. <sup>b</sup> F. M'Ba, Thesis Université des Sciences et Techniques du Languedoc, Montpellier, 1983. <sup>c</sup> D. A. Edwards, M. J. Stiff, and A. A. Wolf, *Inorg. Nucl. Chem. Lett.*, 1967, **3**, 427. <sup>d</sup> This work.

**Table 6.** Assignments for the stretching modes (cm<sup>-1</sup>) of Ni(ClO<sub>4</sub>)<sub>2</sub> and Co(ClO<sub>4</sub>)<sub>2</sub> compared to previous work

	Ni(ClO <sub>4</sub> ) <sub>2</sub>			Co(ClO <sub>4</sub> ) <sub>2</sub>		
	I.r.		Raman	I.r.		Raman
	Ref. 19	This work		Ref. 20	This work	This work
<i>v</i> <sub>sym</sub> (ClO <sub>b</sub> )	980	960	965	948	944	953
<i>v</i> <sub>asym</sub> (ClO <sub>b</sub> )	1 010	1 030	1 011—1 057	1 025	1 000	985
<i>v</i> (ClO <sub>t</sub> )	1 290	1 300	1 308	1 260	1 278	



**Structures of the Isolated Complexes.**—The synthesized complexes crystallize poorly and no solvent was found in which single crystals could be grown for structural determination. The X-ray diffraction patterns, u.v., vibrational (i.r. and Raman), and more recently extended X-ray absorption fine structure (EXAFS) spectroscopy gave some structural information.

**X-Ray diffraction patterns.** In spite of the poor crystalline quality of Ni(ClO<sub>4</sub>)<sub>2</sub> and Co(ClO<sub>4</sub>)<sub>2</sub>, experimental data (Table 3) show that: (i) Ni(ClO<sub>4</sub>)<sub>2</sub> prepared from the reaction of Cl<sub>2</sub>O<sub>6</sub> with NiCl<sub>2</sub>·nH<sub>2</sub>O is identical to the material previously obtained by dehydrating Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O;<sup>32</sup> (ii) Ni(ClO<sub>4</sub>)<sub>2</sub> and Co(ClO<sub>4</sub>)<sub>2</sub> are isomorphous, which has not been previously demonstrated; (iii) the structure of these two perchlorates differs from that of Cu(ClO<sub>4</sub>)<sub>2</sub>; (iv) lines characteristic of NO<sub>2</sub>ClO<sub>4</sub> and NO<sub>2</sub>M(ClO<sub>4</sub>)<sub>3</sub> in the diffraction pattern of (NO<sub>2</sub>)<sub>2</sub>M(ClO<sub>4</sub>)<sub>4</sub> (M = Co or Ni) (Table 3) indicate the formation of a mixture of NO<sub>2</sub>M(ClO<sub>4</sub>)<sub>3</sub> and NO<sub>2</sub>ClO<sub>4</sub> {these lines are absent in the spectrum of (NO<sub>2</sub>)<sub>2</sub>Cu(ClO<sub>4</sub>)<sub>4</sub> suggesting a definite complex containing the [Cu(ClO<sub>4</sub>)<sub>4</sub>]<sup>2-</sup> ion}; (v) the compounds AM(ClO<sub>4</sub>)<sub>3</sub> (A = NO<sub>2</sub><sup>+</sup> or ClO<sub>2</sub><sup>+</sup>, M = Ni or Co) have the same kind of crystal structure and are isotopic with NO<sub>2</sub>Zn(ClO<sub>4</sub>)<sub>3</sub>;<sup>12</sup> however the perchloratocopper complexes ACu(ClO<sub>4</sub>)<sub>3</sub> (A = ClO<sub>2</sub><sup>+</sup> or NO<sub>2</sub><sup>+</sup>) do not have isotopic crystal structures and differ from the salts of Co and Ni.

**U.v. spectroscopy.** U.v. spectra show that in all the complexes studied the central atom is in an octahedral environment (Table 4), resulting in a polymeric structure for the metal complexes M(ClO<sub>4</sub>)<sub>2</sub>. For Ni and Co the shape of the octahedron is regular,<sup>33</sup> but for the copper complexes the u.v. spectra suggest that the octahedra are distorted, with an elongated axial symmetry.<sup>34</sup> The observed frequencies show that, as expected, the ClO<sub>4</sub> group is a weak ligand. This is clearly demonstrated by the spectrochemical series found for several ligands bonded to nickel (Table 5).

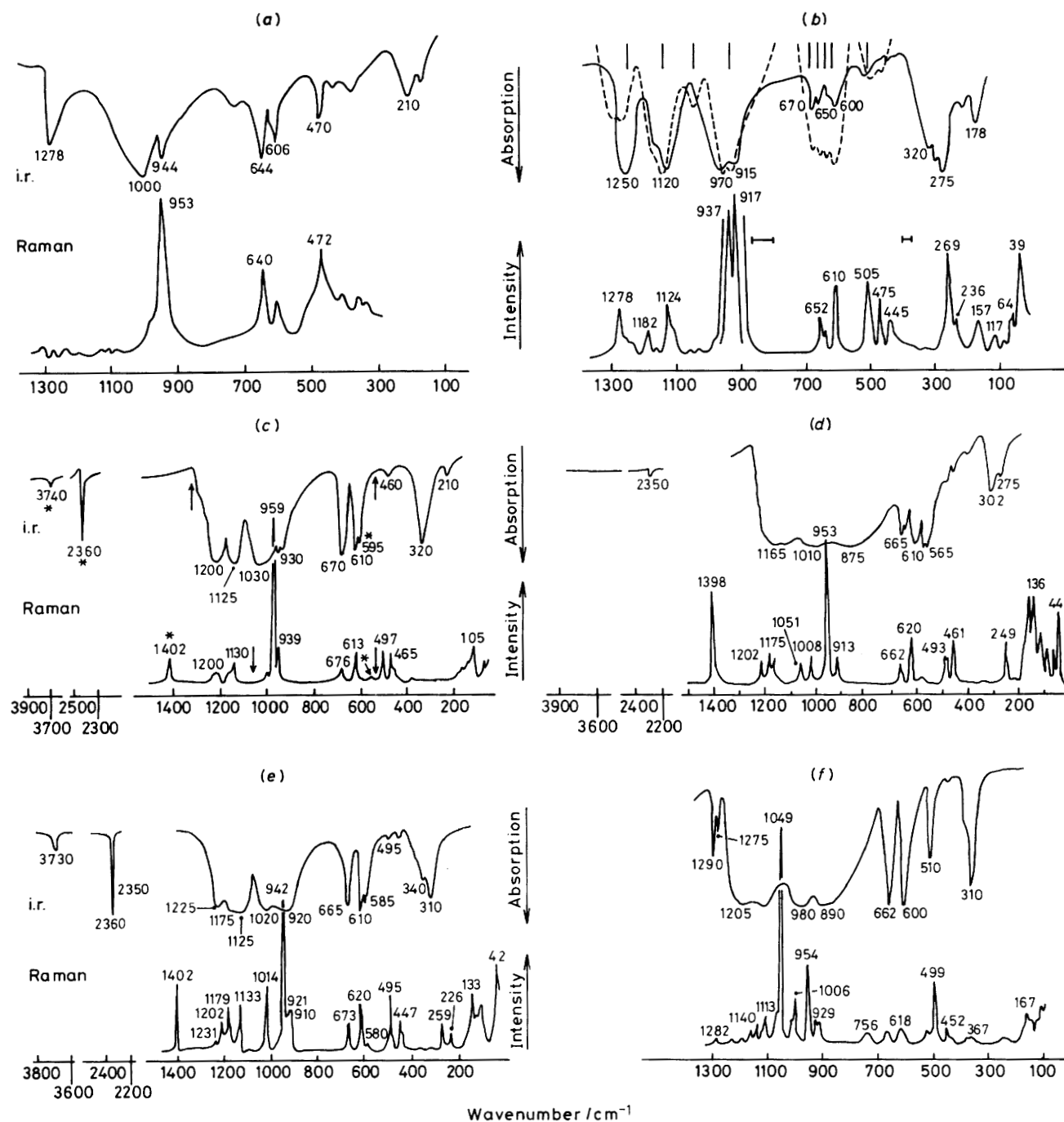
**Vibrational spectroscopy.** Typical i.r. and Raman spectra of the perchlorato-complexes isolated in this study are shown in the Figure 4. The splitting of the degenerate modes and the relaxation of selection rules, particularly for the stretching vibrations, show that the ClO<sub>4</sub> group interacts with the central atom.<sup>1,3-20</sup> The co-ordination of the ClO<sub>4</sub> group is corroborated by the existence of bands or lines in the range of the M—O stretching modes (350—200 cm<sup>-1</sup>).<sup>35</sup> According to the experimental spectra, five types of complex can be defined: (a) M(ClO<sub>4</sub>)<sub>2</sub> (M = Ni or Co); (b) Cu(ClO<sub>4</sub>)<sub>2</sub>; (c) AM(ClO<sub>4</sub>)<sub>3</sub> (A = NO<sub>2</sub><sup>+</sup> or ClO<sub>2</sub><sup>+</sup>, M = Ni or Co); (d) (NO<sub>2</sub>)<sub>2</sub>Cu(ClO<sub>4</sub>)<sub>4</sub>; (e) ACu(ClO<sub>4</sub>)<sub>3</sub> (A = NO<sub>2</sub><sup>+</sup> or ClO<sub>2</sub><sup>+</sup>).

(a) M(ClO<sub>4</sub>)<sub>2</sub> (M = Ni or Co). The spectra [Figure 4(a) and ref. 6] differ from those observed for complexes containing uni- or bi-dentate (bridging or chelating) ClO<sub>4</sub> groups previously studied<sup>3-17</sup> and from that of Cu(ClO<sub>4</sub>)<sub>2</sub><sup>1</sup> re-examined in this work (see below). The presence of three bands or lines for the stretching modes in the range 500—1 300 cm<sup>-1</sup> leads to the assumption of C<sub>3v</sub> symmetry for the ClO<sub>4</sub> group with three co-ordinated oxygen atoms. This analysis is consistent with recent EXAFS experiments on M(ClO<sub>4</sub>)<sub>2</sub> (M = Ni or Co).<sup>36</sup>

The correlation diagram T<sub>d</sub>-C<sub>3v</sub> allows specific assignments of the different stretching modes (Table 6): it should nevertheless be noted that the three co-ordinated oxygen atoms lead to a lowering of *v*<sub>asym</sub>(ClO<sub>b</sub>)(E) [O<sub>b</sub> = co-ordinated (bridging) oxygen atom] compared with *v*<sub>asym</sub>(ClO<sub>t</sub>) [O<sub>t</sub> = unco-ordinated (terminal) oxygen atom] observed in a classical unidentate perchlorate.<sup>10</sup> The low intensity of the Raman line assigned to *v*(ClO<sub>t</sub>) is surprising compared with the intensity of the line assigned to *v*(ClO<sub>b</sub>). The only likely explanation lies in its origin; *v*(ClO<sub>t</sub>) derives from *v*<sub>3</sub>(F<sub>2</sub>) in free ClO<sub>4</sub><sup>-</sup>. In the range of M—O(ClO<sub>3</sub>) stretching modes, *v*(Co—O) appears at 210 cm<sup>-1</sup> and Ni—O at 220 cm<sup>-1</sup>, i.e. the metal—oxygen interaction is stronger in the nickel complex and is consistent with the M—O distances observed in EXAFS, 2.04 (Ni) and 2.09 Å (Co).<sup>36</sup>

(b) Cu(ClO<sub>4</sub>)<sub>2</sub>. The i.r. spectrum differs slightly from that previously given;<sup>1,18</sup> in particular, the line at 1 030 cm<sup>-1</sup> does not appear in the i.r. spectrum of Figure 4(b). This does not seem to be due to differences in the synthetic methods (Table 2) but to a slight hydration occurring either during the synthesis or handling; this band is very strong in the i.r. spectrum of Cu(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O.<sup>1</sup> An analysis of the vibrational spectra of the metal—oxygen skeleton has recently been given by some of us.<sup>13</sup>

The observed splittings for the stretching modes in the Raman and i.r. spectra [Figure 4(b)] are compatible with bidentate ClO<sub>4</sub>, as previously proposed.<sup>1</sup> Nevertheless, the multiplicity is much more important for the stretching and



**Figure 4.** Typical i.r. and Raman spectra of: (a)  $\text{Co}(\text{ClO}_4)_2$ ; (b)  $\text{Cu}(\text{ClO}_4)_2$  (— — —, ref. 1), (—, ref. 18, relative intensities not given); (c)  $\text{NO}_2\text{Ni}(\text{ClO}_4)_3$  (the  $\text{NO}_2^+$  bands are indicated by asterisks,  $\text{ClO}_2^+$  bands of the chloryl salt by arrows); (d)  $(\text{NO}_2)_2\text{Cu}(\text{ClO}_4)_4$ ; (e)  $\text{NO}_2\text{Cu}(\text{ClO}_4)_3$ ; (f)  $\text{ClO}_2\text{Cu}(\text{ClO}_4)_3$

deformation modes ( $\nu_3$  and  $\nu_2$  in  $T_d$ ): six principal lines appear in the Raman spectrum for the first and three for the second (four and two are expected) so that the existence of two types of  $\text{ClO}_4$  ligand in  $\text{Cu}(\text{ClO}_4)_2$  is assumed. This hypothesis has recently been supported by an EXAFS determination.<sup>13</sup> The proposed structure of  $\text{Cu}(\text{ClO}_4)_2$  is shown in Figure 5. One  $\text{ClO}_4$  is bonded to a non-linear chain of copper atoms, while the other is involved in interchain interactions. Around the copper, the co-ordination shell is (4 + 2), each type of  $\text{ClO}_4$  participates in four Cu—O short bonds; the two longer Cu—O bonds come from the  $\text{ClO}_4$  involved in the Cu—Cu chain. The

elongated rhombic symmetry is consistent with the  $g$  values ( $g_1 = 2.09$ ,  $g_2 = 2.22$ , and  $g_3 = 2.33$ ) derived from the e.s.r. spectrum. The two types of  $\text{ClO}_4$  are somewhat different; the intrachain  $\text{ClO}_4$  groups bridging the Cu atoms exhibit three Cu—O interactions, two at 1.96 and one at 2.67 Å, and are partially tridentate, while the interchain  $\text{ClO}_4$  groups are purely bidentate, so that the perturbations observed for each type will be quite different.

**Intrachain  $\text{ClO}_4$ .** For this pseudo-tridentate ligand it is more convenient to analyse the spectra in terms of decoupled ClO vibrations, especially for the stretching modes, than in terms of

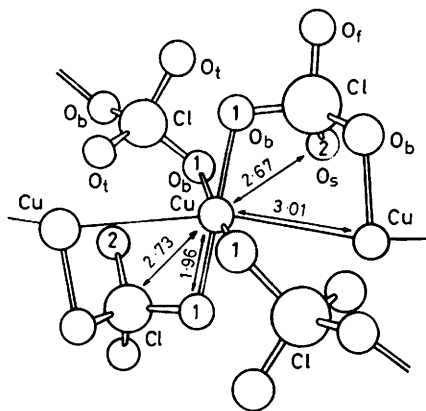


Figure 5. Structure of  $\text{Cu}(\text{ClO}_4)_2$  according to an EXAFS study<sup>13</sup>

lowering of symmetry. The secondary co-ordination of O(2) ( $\text{O}_s$ ) implies a shorter  $\text{ClO}_f$  bond ( $\text{O}_f$  = free oxygen atom). The line at  $1\,278\text{ cm}^{-1}$  in the Raman might be assigned to  $\nu(\text{ClO}_f)$ ; the i.r. component appears at  $1\,250\text{ cm}^{-1}$  but perhaps this mode is not the only one responsible for this large band. These relatively high frequencies are close to those observed for  $\nu(\text{ClO}_i)$  in  $\text{Ni}(\text{ClO}_4)_2$  and  $\text{Co}(\text{ClO}_4)_2$  (see above).

$\nu(\text{ClO}_b)$  is expected around  $900\text{ cm}^{-1}$ . The splitting  $970\text{--}937\text{ cm}^{-1}$  ( $\Delta\nu = 33\text{ cm}^{-1}$ ) is similar to that observed for  $\nu_{\text{asym}}^-$  and  $\nu_{\text{sym}}^-(\text{ClO}_b)$  in antimony(v)<sup>11</sup> and tin(IV) complexes<sup>8</sup> where a  $\text{ClO}_4$  ligand bridges two metal centres ( $\Delta\nu = 40\text{ cm}^{-1}$ ) with  $d(\text{M--O}) = 2.20$  instead of the  $1.95\text{ \AA}$  here. Thus, these bands and lines are assigned to the stretching  $\text{ClO}_b$  modes of intrachain  $\text{ClO}_4$ , while those of  $1\,182$  (Raman) and  $1\,152\text{ cm}^{-1}$  (i.r.) are to be assigned to  $\nu(\text{ClO}_s)$  (with  $\Delta\nu = 30\text{ cm}^{-1}$ ).

**Interchain  $\text{ClO}_4$ .** This  $\text{ClO}_4$  ligand has a  $C_{2v}$  or  $C_s$  symmetry and the classical correlation diagrams  $T_d\text{--}C_{2v}$  or  $T_d\text{--}C_s$  predict four stretching modes:  $\nu_{\text{asym}}^-$  and  $\nu_{\text{sym}}^-(\text{ClO}_i)$  and  $\nu_{\text{asym}}^-$  and  $\nu_{\text{sym}}^-(\text{ClO}_b)$ . In the Raman and i.r. spectra a strong line appears at  $917\text{ cm}^{-1}$  and a strong band at  $915\text{ cm}^{-1}$ , which are assigned to  $\nu(\text{ClO}_b)$ . The medium-intensity line at  $1\,124\text{ cm}^{-1}$  ( $1\,120\text{ cm}^{-1}$  in i.r.) could be assigned to  $\nu_{\text{sym}}^-(\text{ClO}_i)$ , the large band at  $1\,250\text{ cm}^{-1}$  to  $\nu_{\text{asym}}^-(\text{ClO}_i)$ . The weakness of the mechanical coupling between the chains is probably responsible for the absence of a correlation effect. Table 7 summarizes these assignments.

(c)  $\text{AM}(\text{ClO}_4)_3$  ( $\text{A} = \text{NO}_2^+$  or  $\text{ClO}_2^+$ ,  $\text{M} = \text{Co}$  or  $\text{Ni}$ ). After assignment of the stretching and deformations modes belonging to the  $\text{NO}_2^+$  and  $\text{ClO}_2^+$  cations [for example in nickel salts:  $\text{NO}_2^+$ , i.r.,  $3\,740$  ( $\nu_{\text{sym}} + \nu_{\text{asym}}$ ),  $2\,360\text{--}2\,350$  ( $\nu_{\text{asym}}$ ); Raman,  $1\,402$  ( $\nu_{\text{sym}}$ ),  $549$  ( $\delta$ );  $\text{ClO}_2^+$ , i.r.,  $1\,305\text{--}1\,295$  (with isotopic  $^{35}\text{Cl}/^{37}\text{Cl}$  splitting),  $515$  ( $\delta$ ); Raman,  $1\,048$  ( $\nu_{\text{sym}}$ ) and  $518\text{ cm}^{-1}$  ( $\delta$ )], the i.r. and Raman spectra [Figure 4(c)] can be interpreted on the basis of discrete anions  $\text{M}(\text{ClO}_4)_3^-$  with bidentate chelating ( $\text{ClO}_4$ ) groups. The maximum symmetry of this anion is  $D_3$  and the Ni or Co atoms are octahedrally co-ordinated. In these anions the splittings in the stretching-mode range are weaker than those observed<sup>5b</sup> in the neutral  $\text{Ga}(\text{ClO}_4)_3$  or  $\text{Fe}(\text{ClO}_4)_3$  complexes [i.e.  $\Delta\nu(\text{ClO}_i) = 70\text{ cm}^{-1}$  in  $\text{M}(\text{ClO}_4)_3^-$  but  $125\text{ cm}^{-1}$  in  $\text{Ga}(\text{ClO}_4)_3$ ] which probably results from cation-anion interactions.

(d)  $(\text{NO}_2)_2\text{Cu}(\text{ClO}_4)_4$ . The frequencies observed for  $\text{NO}_2^+$  vibrational modes are similar to those found for the other nitryl salts isolated in this work, Figure 4(d). When  $(\text{NO}_2)_2\text{Cu}(\text{ClO}_4)_4$  is warmed to give  $\text{NO}_2\text{Cu}(\text{ClO}_4)_3$  which results from the loss of  $\text{NO}_2\text{ClO}_4$ , the most significant change in the Raman spectrum is the disappearance of the lines at  $953$  and  $1\,051\text{ cm}^{-1}$ . These frequencies are not identical to those found for  $\text{NO}_2\text{ClO}_4$  in  $(\text{NO}_2)_2\text{Ni}(\text{ClO}_4)_4$  ( $945$ ,  $1\,042\text{--}1\,063\text{ cm}^{-1}$ ). Simultaneously the Raman lines characteristic of  $\text{NO}_2\text{Cu}(\text{ClO}_4)_3$  cannot be found

Table 7. Assignments for the stretching modes ( $\text{cm}^{-1}$ ) of  $\text{Cu}(\text{ClO}_4)_2$

I.r.	Raman	Assignments
915	917	$\nu(\text{ClO}_b)$ Interchain
	937	
970		$\nu(\text{ClO}_b)$ Intrachain
1 120		
1 120	1 124	$\nu_{\text{sym}}^-(\text{ClO}_i)$ Interchain
1 152	1 182	$\nu(\text{ClO}_s)$ Intrachain
1 250	1 250	$\nu_{\text{asym}}^-(\text{ClO}_i)$ Interchain + $\nu(\text{ClO}_f)$ intrachain (i.r.)
	1 278	$\nu(\text{ClO}_f)$ Intrachain

Table 8. Assignments for the stretching modes ( $\text{cm}^{-1}$ ) of  $\text{M}(\text{ClO}_4)_3^-$  based on an octahedral environment for the metal atoms

$\text{NO}_2\text{Ni}(\text{ClO}_4)_3$	$\text{NO}_2\text{Cu}(\text{ClO}_4)_3$		
939	910—921	$\nu_{\text{sym}}^-(\text{ClO}_b)$	(E)
959	942	$\nu_{\text{sym}}^-(\text{ClO}_b)$	( $A_1$ )
980	1 014	$\nu_{\text{asym}}^-(\text{ClO}_b)$	(E)
1 130	1 133	$\nu_{\text{sym}}^-(\text{ClO}_i)$	( $A_1$ )
1 148	1 179—1 202	$\nu_{\text{sym}}^-(\text{ClO}_i)$	(E)
1 200—1 214	1 231	$\nu_{\text{asym}}^-(\text{ClO}_i)$	(E)

in the spectrum of  $(\text{NO}_2)_2\text{Cu}(\text{ClO}_4)_4$ ;  $[\text{Cu}(\text{ClO}_4)_4]^-$  appears to be a specific anion, consistent with X-ray data. It is difficult to propose a molecular structure for the complexes, however using results found for complexes containing the anions  $\text{M}(\text{NO}_3)_4^{2-}$  ( $\text{M} = \text{Ni}$ ,  $\text{Zn}$ , or  $\text{Cu}$ )<sup>37</sup> it is possible that the ligands are weakly bonded in a manner intermediate between bi- and uni-dentate but closer to the latter [ $\nu_{\text{sym}}^-(\text{ClO}_b)$   $913$  and  $953$ ,  $\nu_{\text{sym}}^-(\text{ClO}_i)$   $1\,008$  and  $1\,051$ , and  $\nu_{\text{asym}}^-(\text{ClO}_i)$   $1\,156\text{--}1\,205\text{ cm}^{-1}$ ]. The same conclusion has been deduced from spectroscopic analyses for  $\text{ClO}_2^+[\text{Ga}(\text{ClO}_4)_4]^-$ .<sup>5a,16</sup>

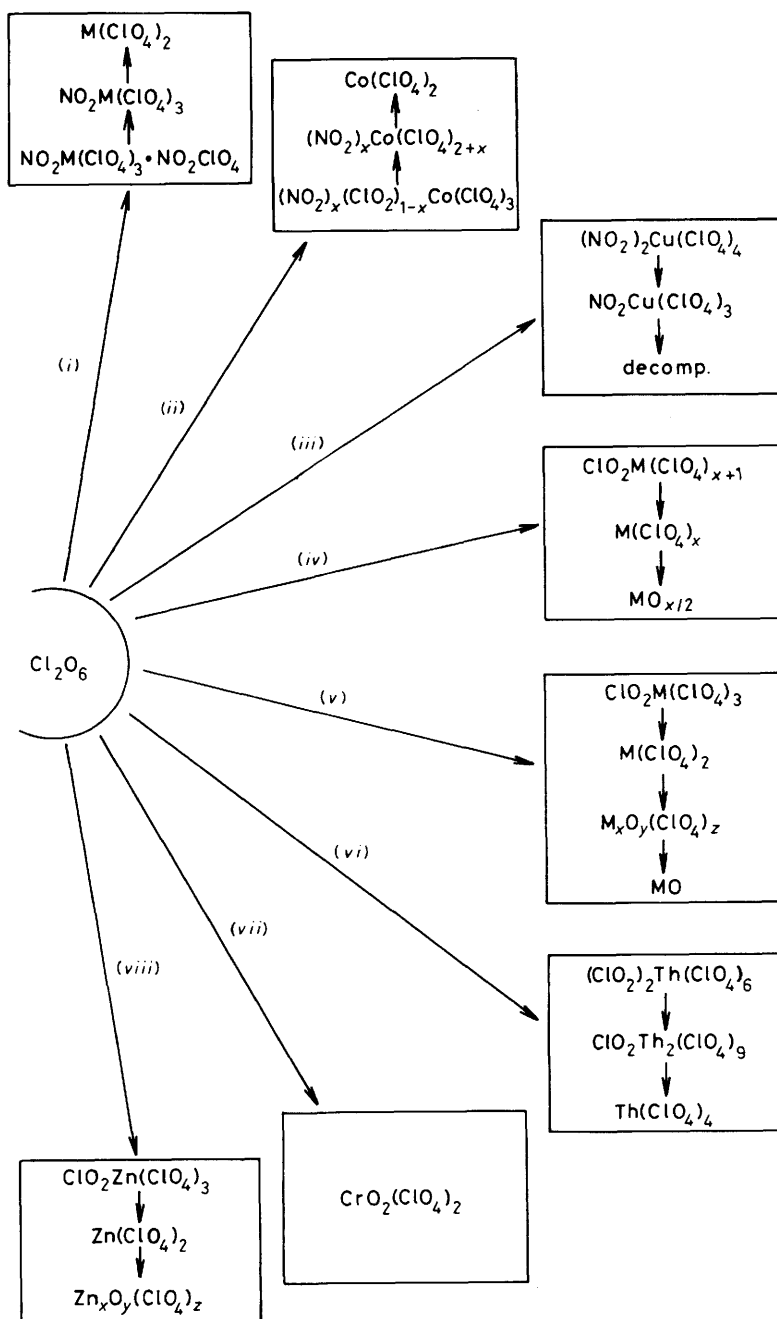
(e)  $\text{NO}_2\text{Cu}(\text{ClO}_4)_3$  and  $\text{ClO}_2\text{Cu}(\text{ClO}_4)_3$ . The X-ray diffraction patterns indicate that the two compounds do not belong to the same structural type, a conclusion supported by vibrational spectroscopy [Figure 4(e) and (f)]. For instance, the spectrum of  $\text{ClO}_2\text{Cu}(\text{ClO}_4)_3$  contains extra lines around  $756$  and  $1\,113\text{ cm}^{-1}$ . For the nitryl salt a reasonable interpretation of the Raman spectrum can be given, involving a discrete anion with three bidentate  $\text{ClO}_4$  groups and  $D_3$  symmetry as in  $\text{Ni}(\text{ClO}_4)_3^-$  or  $\text{Co}(\text{ClO}_4)_3^-$ . The assignments of the stretching modes are given in Table 8.

The structure imposes a regular octahedron around the copper atom which is rarely found. A more complicated framework can be proposed where Cu is in a non-octahedral regular environment of unidentate ( $910$ ,  $1\,014$ , and  $1\,231\text{ cm}^{-1}$ ) and bidentate ( $921$ ,  $942$ ,  $1\,133\text{--}1\,179$ , and  $1\,202\text{ cm}^{-1}$ )  $\text{ClO}_4$  groups. A similar structure was found in  $[\text{NOZn}(\text{NO}_3)_3]_n$ .<sup>37</sup>

For the chloryl salt, some frequencies, in the stretching-mode range, are close to those observed for the nitryl salt and they therefore suggest a similar type of  $\text{ClO}_4$  group. The extra lines at  $1\,113$  and  $756\text{ cm}^{-1}$  may belong to a unidentate<sup>16</sup>  $\text{ClO}_4$  group interacting strongly with a  $\text{ClO}_2^+$  cation. Thus,  $\text{ClO}_2\text{Cu}(\text{ClO}_4)_3$  has a more complex structure than  $\text{NO}_2\text{Cu}(\text{ClO}_4)_3$ .

## Conclusions

Although perchlorato-complexes of nickel, cobalt, and copper have been studied previously, this work offers a new chemical pathway more suitable than those previously described for the preparation of these complexes. If the synthesis based on the reactivity of  $\text{Cl}_2\text{O}_6$  with hydrated chlorides appears logical owing to the highly hygroscopic character of  $\text{Cl}_2\text{O}_6$ , that using



**Scheme.** Reactions of  $\text{Cl}_2\text{O}_6$ : (i)  $\text{M}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ; (ii)  $\text{Co}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ; (iii)  $\beta\text{-Cu}(\text{NO}_3)_2$ ; (iv)  $\text{MCl}_x$ ; <sup>3a,5,6</sup> (v)  $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ ; (vi)  $\text{ThCl}_4 \cdot \epsilon\text{ThO}_2$  (A. M. Koulkes-Puyo, D. Martin-Rovet, G. Folcher, M. Plissonnier, and J. L. Pascal, *Nouv. J. Chim.*, 1982, **6**, 571; J. L. Pascal, unpublished work); (vii)  $\text{CrO}_3$ ; <sup>8,24</sup> (viii)  $\text{Zn}^{12}$

nitrates as starting material is more surprising but illustrates the behaviour of  $\text{NO}_3^-$  in an acidic medium. These two new routes extend the known reactivities of chlorine trioxide as shown in the Scheme. Chlorine trioxide therefore appears to be the most efficient perchlorating reagent known.

Using spectroscopic and X-ray powder methods, some progress has been made towards deducing the structures of the perchlorates and a new type of tridentate arrangement of  $\text{ClO}_4^-$  shown to appear in  $\text{Ni}(\text{ClO}_4)_2$  and  $\text{Co}(\text{ClO}_4)_2$ . Copper(II) perchlorate, until now considered as a classical bidentate  $\text{ClO}_4^-$  model, shows a complex molecular structure, in which both bidentate and pseudo-tridentate  $\text{ClO}_4^-$  are found. The copper

has a distorted octahedral environment which leads to a three-dimensional framework, in contrast with the tendency of Ni and Co to be surrounded by a regular octahedral shell which leads to a  $\text{CdCl}_2$ -type array.

#### Acknowledgements

Financial support from the CNRS is gratefully acknowledged. C. S. Zhang thanks the French Government for a research fellowship. We also thank Professor J. Roziere for helpful discussions and Dr. D. J. Jones for linguistic corrections to the manuscript.



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Received 13th December 1983; Paper 3/2202