Chlorine Trioxide, Cl₂O₆, 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, $M(ClO_4)_2$ (M = Ni, Co, or Cu), and their chloryl and nitryl salts, $ClO_2M(ClO_4)_3$, $NO_2M(ClO_4)_3$, and $(NO_2)_2M(ClO_4)_4$, have been prepared by the action of Cl_2O_6 on the corresponding anhydrous or hydrated metal chloride or nitrate. The intermediate chloryl salts, $ClO_2M(ClO_4)_3$, can be isolated. The formation of NO_2^+ is due to the highly acidic medium. The vibrational spectra of the compounds $M(ClO_4)_2$ suggest a strong metal–perchlorate interaction and are consistent with the presence of two types of bidentate perchlorate group in $Cu(ClO_4)_2$ and tridentate perchlorate in $Ni(ClO_4)_2$ and $Co(ClO_4)_2$. 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 $Cu(ClO_4)_2$,[1] the co-ordinating ability of the ClO_4 ligand was disputable.[2] 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,[3–17] which resulted in the isolation of numerous perchlorato-complexes. However, although the synthesis and study of the bivalent metal perchlorates $M(ClO_4)_2$ (M = Cu,[18] Ni,[19] or Co[20]) are still tediously complex, they lead to an understanding of the influence of the metal centre on ClO_4 co-ordination.

In this work, the perchlorating properties of chlorine trioxide (Cl_2O_6) are used as the easiest route to the synthesis of metal perchlorates. In the two new methods proposed, Cl_2O_6 exchanges ClO_4 with Cl or 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 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 Cl_2O_6 have been described previously.[14,15] 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 Cl_2O_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 °C. The 41/35 ground-glass joints of these traps
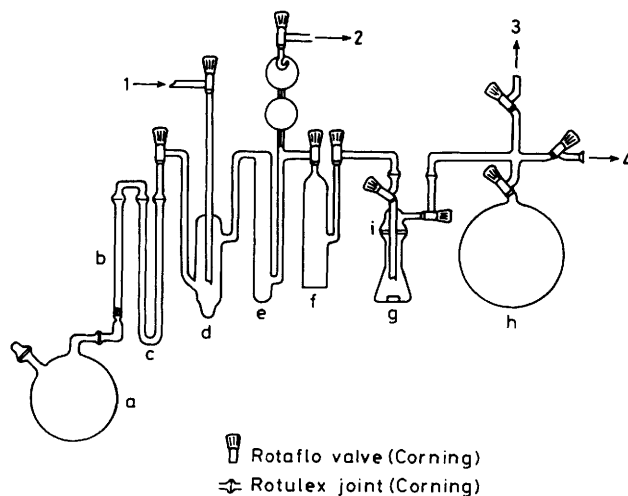

Figure 1. Pyrex vacuum line for the synthesis of chlorine trioxide and anhydrous perchlorates: a, synthesis of ClO_2 at 50 °C [$2KClO_3$ + $2H_2SO_4$ (5N) + $H_2C_2O_4$·$2H_2O$ → $2ClO_2$ + $2CO_2$ + $4H_2O$ + $2KHSO_4$]; b, flowmeter; c, P_4O_{10} columns; d, synthesis of Cl_2O_6 ($2ClO_2$ + $2O_3$ → Cl_2O_6 + $2O_2$) at −10 °C; e, Cl_2O_6 trap (0 °C); f, distilled Cl_2O_6 (−20 °C); g, perchlorate synthesis; h, 4 l bulb to collect evolved gases; i, 29/15 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 i.r. cell (matrix type)

🔲 Rotaflo valve (Corning)
⚖ Rotulex joint (Corning)

were greased with Voltalef, a Kelf grease. These traps were disconnected at −180 °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.[10] The X-ray diffraction patterns were obtained on a Philips goniometer PW 1965/30.

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

Starting reagent (amount/g)		Cl_2O_6 [a]	Reaction temperature (°C)	Product	Colour	Analysis [b] (%) M	ClO_4	ClO_2, NO_2
$NiCl_2$ [c]	(1.3425)	12	18	$ClO_2Ni(ClO_4)_3 \cdot xNiCl_2$	Orange			d
$NiCl_2$ [e]	(0.3681)	5 + 1 [f]	18	} $ClO_2Ni(ClO_4)_3$	Orange	13.75	70.35	15.9
$NiCl_2 \cdot 6H_2O$ [g]	(0.9827)	2	15			(13.85)	(70.3)	(15.9)
$CoCl_2$ [h]	(0.5488)	3		} $ClO_2Co(ClO_4)_3$	Orange-brown	13.75	70.05	16.2
$CoCl_2 \cdot 2H_2O$ [i]	(0.6635)	3	5—7			(13.85)	(70.25)	(15.9)
$CuCl_2$ [j]	(0.5100)	5		} $ClO_2Cu(ClO_4)_3$	Orange	14.35	69.55	
$CuCl_2 \cdot 2H_2O$ [k]	(1.9400)	2	10			(14.80)	(69.5)	
$Ni(NO_3)_2 \cdot 2H_2O$ [l]	(0.7254)	3 [m]	15	$(NO_2)_2Ni(ClO_4)_4$	Yellow-green	10.45	72.7	
						(10.7)	(72.5)	
$Co(NO_3)_2 \cdot 2H_2O$ [n]	(0.3698)	4 [o]]		$(NO_2)_2Co(ClO_4)_4$ [p]	Dirty pink	10.9	72.55	
			} 3			(10.75)	(72.5)	
$Co(NO_3)_2 \cdot 6H_2O$ [q]	(1.2870)	4 [r]]		$(NO_2)_x(ClO_2)_{1-x}Co(ClO_4)_3$ [s]	Brown	14.15	73.25	
$Cu(NO_3)_2$ [t]	(0.1719)	4		} $(NO_2)_2Cu(ClO_4)_4$	Pale green	11.5	72.55	15.95
$Cu(NO_3)_2 \cdot 3H_2O$ [u]	(1.3146)	3	10			(11.5)	(71.9)	(16.65)

[a] Number of successive additions (ca. 8 g) of Cl_2O_6. [b] Required values are given in parentheses. [c] Merck Schuchardt, for synthesis. [d] Raman analysis; only the decomposition product $Ni(ClO_4)_2 \cdot xNiCl_2$ was chemically analysed (see Table 2). [e] $NiCl_2 \cdot 6H_2O$ (Merck, pure) dehydrated by freshly distilled $SOCl_2$ (Merck Schuchardt) according to Pray.[27] [f] The first five additions gave an incomplete reaction; the mixture was warmed to 80 °C to obtain predominantly $Ni(ClO_4)_2$ and small amounts of unreacted $NiCl_2$. Further addition of Cl_2O_6 yielded the expected pure product. [g] Merck, pure. [h] $CoCl_2 \cdot \varepsilon H_2O$ (Merck Schuchardt, for synthesis) $\xrightarrow[\text{vacuum}]{135\,°C}$ $CoCl_2$. [i] $CoCl_2 \cdot \varepsilon H_2O + nH_2O \xrightarrow[\text{vacuum}]{40\,°C} CoCl_2 \cdot 2H_2O$. [j] Alfa Ventron. [k] Labosi, for analysis. [l] $Ni(NO_3)_2 \cdot 6H_2O$ (Prolabo RP) $\xrightarrow[\text{vacuum}]{80\,°C}$ $Ni(NO_3)_2 \cdot 2H_2O$. [m] The mixture of Cl_2O_6 and $Ni(NO_3)_2 \cdot 2H_2O$ had to be stirred vigorously for at least 32 h to obtain complete reaction. [n] $Co(NO_3)_2 \cdot 6H_2O$ (Merck Schuchardt) $\xrightarrow[\text{vacuum}]{50\,°C}$ $Co(NO_3)_2 \cdot 2H_2O$. [o] One addition of Cl_2O_6 ca. 2 g. [p] One mixture exploded after 1 h of stirring. [q] Merck Schuchardt. [r] One addition of Cl_2O_6 ca. 4 g. [s] $Co(NO_3)_2 \cdot 6H_2O$ reacts vigorously with Cl_2O_6, the final product being a mixture of $ClO_2Co(ClO_4)_3$ and $NO_2Co(ClO_4)_3$. [t] Synthesized according to Wallwork and Addison (J. Chem. Soc., 1965, 2925). [u] $Cu(NO_3)_2 \cdot nH_2O$ (Prolabo, pure) $\xrightarrow[\text{vacuum}]{40\,°C}$ $Cu(NO_3)_2 \cdot 3H_2O$.

Table 2. Decomposition of chloryl or nitryl perchlorate salts

Starting material	Decomposition temperature (°C) [a]	Final product	Colour	Analysis (%) M	ClO_4
$ClO_2Ni(ClO_4)_3 \cdot xNiCl_2$	80	$Ni(ClO_4)_2 \cdot xNiCl_2$	Yellow	23.3	72.95
				(22.8)	(77.2) [b]
$ClO_2Ni(ClO_4)_3$	80	$Ni(ClO_4)_2$	Yellow	22.95	77.1
				(22.8)	(77.2)
$ClO_2Co(ClO_4)_3$	75	$Co(ClO_4)_2$	Pink	23.1	76.9
				(22.85)	(77.15)
$ClO_2Cu(ClO_4)_3$	65—70	$Cu(ClO_4)_2$ [c]	Blue-white	24.2	75.75
				(24.2)	(75.8)
$(NO_2)_2Ni(ClO_4)_4$	140—150	$NO_2Ni(ClO_4)_3$ [d]	Yellow	14.15	73.55 [e]
				(14.55)	(74.0)
$(NO_2)_2Co(ClO_4)_4$	100—105	$NO_2Co(ClO_4)_3$ [d]	Pink	14.35	72.55
				(14.6)	(74.0)
$(NO_2)_x(ClO_2)_{1-x}Co(ClO_4)_3$	90	$(NO_2)_xCo(ClO_4)_{2+x}$	Pink	20.55	79.45 [f]
$(NO_2)_2Cu(ClO_4)_4$	115	$NO_2Cu(ClO_4)_3$ [g]	White	15.85	74.05
				(15.6)	(73.15)

[a] Under vacuum. [b] Required values are those of $Ni(ClO_4)_2$; 3.25% Cl^- was found. [c] 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. [d] On increasing the temperature this compound can decompose into $M(ClO_4)_2$. [e] The existence of NO_2^+ was checked by i.r. and Raman spectroscopy. [f] x ca. 0.3; the product is a mixture of $Co(ClO_4)_2$ and $NO_2Co(ClO_4)_3$. [g] Sublimes.

A Pyrex matrix i.r. cell built in the laboratory[15] was used to check the purity of Cl_2O_6 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 mulled 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 $Cu(ClO_4)_2$ (blue-white form) and $Co(ClO_4)_2$. The nitryl salts and $Ni(ClO_4)_2$ 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 Voltalef 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.[14,16]

Metallic cations were titrated by a complexometric method using 0.1 or 0.01 mol dm^{-3} ethylenediaminetetra-acetate (edta).[21] Perchlorate ion was analysed by a potentiometric method using an Orion specific electrode and 0.04 mol dm^{-3} tetraphenylarsonium solution (Merck for analysis) as titrant.[22] When possible ClO_2^+ was titrated as ClO_3^- by a standard redox method.[23]

Synthesis of Anhydrous Perchlorates.—Chlorine trioxide (2—4 g) was added at $-180\ ^\circ C$ 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 $^\circ C$). Evolved gases (ClO_2, Cl_2, and sometimes $ClOClO_3$) 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_2. If the reaction was smooth, the temperature was increased to 10 or 15 $^\circ C$ and up to 8 g of distilled Cl_2O_6 introduced. The Cl_2O_6 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_2O_6 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 nitryl salt. These salts can lose ClO_2ClO_4 or NO_2ClO_4 on heating under vacuum to give directly a neutral salt or, for the nitryl salt, an intermediate with a smaller NO_2–M ratio. The specific experimental procedures are summarized in Tables 1 and 2.

Discussion

Synthesis of Anhydrous Perchlorates.—As previously shown[3,5,7,11,15,24] the formation of perchlorato-complexes using Cl_2O_6 as perchlorating reagent is attributed to its ionic character, being $ClO_2^+ClO_4^-$ in the solid state[25] but in equilibrium, Cl_2O_6 (covalent) $\rightleftharpoons ClO_2^+ClO_4^-$, in the liquid state.[26]

From metal chlorides. (a) *Anhydrous chlorides.* Whatever the source of the anhydrous metal chloride used (commercial or obtained using the Pray method[27]) the synthetic route in equations (1)—(3) can be written. Starting from commercial
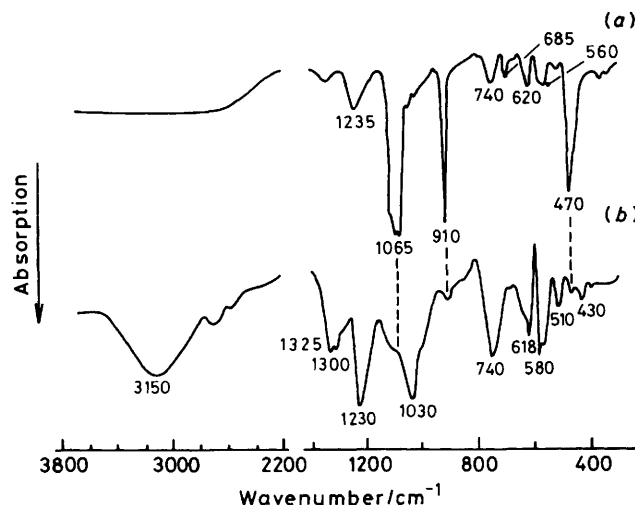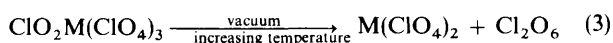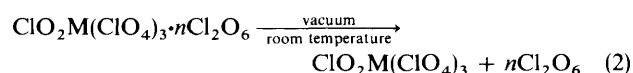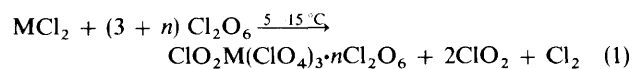
$$MCl_2 + (3 + n)\ Cl_2O_6 \xrightarrow{5\ 15\ ^\circ C}$$
$$ClO_2M(ClO_4)_3 \cdot nCl_2O_6 + 2ClO_2 + Cl_2 \quad (1)$$

$$ClO_2M(ClO_4)_3 \cdot nCl_2O_6 \xrightarrow[\text{room temperature}]{\text{vacuum}}$$
$$ClO_2M(ClO_4)_3 + nCl_2O_6 \quad (2)$$

$$ClO_2M(ClO_4)_3 \xrightarrow[\text{increasing temperature}]{\text{vacuum}} M(ClO_4)_2 + Cl_2O_6 \quad (3)$$

Figure 2. I.r. spectra of the evolved gases trapped on a cold $(-180\ ^\circ C)$ silicon window in a matrix cell during the reaction of $NiCl_2 \cdot 6H_2O$ and Cl_2O_6. The ClO_2 vibrations are indicated by dashed lines. The other bands are due to $HClO_4$. (*a*) Reaction of Cl_2O_6 with Cl^-; (*b*) dehydration

anhydrous chlorides, the synthesis of pure chloryl salts is generally slow and impossible with anhydrous $NiCl_2$. The best yield is obtained with anhydrous MCl_2 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 $NiCl_2 \cdot 6H_2O$. 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_2 bands[28] while $HClO_4$ bands[29] appear subsequently. It is significant that the dehydration process occurs after the replacement of Cl by ClO_4.

(*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;[3b,9] in hydrated chlorides Cl^- 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 $CuCl_2$, where the octahedral distortion around the Cu atoms (in $CuCl_2$) favours the reaction, but the differences in the reactivities of $CoCl_2$ and $NiCl_2$, which have the same structure, requires consideration of the following factors: (*i*) the electronic configuration of the metal cation (respectively d^7 and d^8) which is responsible for the relative stability of MX_2 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_2O_6 with N_2O_4 and N_2O_5 have been studied,[24] none with metallic nitrates has been reported until now. Whatever the $M(NO_3)_2 \cdot xH_2O$ used, the final product is $(NO_2)_2M(ClO_4)_4$.* Spectra of samples recorded during the course of the reaction showed the presence of the nitryl perchlorate complex and some

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

Table 3. X-Ray diffraction patterns *

A		B		C		D		F		G		I		J		K		L	
I	$d/\text{Å}$	I	$d/\text{Å}$	I	$d/\text{Å}$	I	$d/\text{Å}$	I	$d/\text{Å}$	I	$d/\text{Å}$	I	$d/\text{Å}$	I	$d/\text{Å}$	I	$d/\text{Å}$	I	$d/\text{Å}$
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	*4.47*	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	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	15	2.76	13	2.71
		26	*2.82*	8	2.42	5	1.35	w	2.91			80	3.25	26	3.03	46	2.34	22	2.51
		5	*2.75*	4	2.31			m	2.87			90	3.22	96	2.99	20	2.28	22	2.36
		3	*2.70*	4	2.30			m	*2.84*			100	3.10	19	2.97	30	2.05	9	2.24
		4	*2.59*	12	2.23			w	2.59			14	3.00	39	2.74	20	1.97	27	2.20
		11	*2.56*	10	1.99			w	*2.55*			15	2.94	34	2.72			8	2.07
		8	2.53	4	1.91			w	2.44			14	2.93	13	2.67			15	1.87
		8	2.42	9	1.74			w	2.32			15	2.91	39	2.63			15	1.83
		19	2.23					m	2.25			27	2.88	43	2.49			12	1.79
		31	2.18									23	2.85	24	2.46			9	1.67
		7	2.13									46	2.78	15	2.41			9	1.66
		14	*1.98*									24	2.72	15	2.39			4	1.56
		3	1.91											24	2.27			6	1.30
		56	1.87											44	2.16				
		5	1.82																

E

I	$d/\text{Å}$
w	5.02
w	4.45
w	4.08
m	3.73
w	3.50
s	3.22
w	3.12
m	2.88
w	2.60
w	2.45
w	2.27
w	1.87

H

I	$d/\text{Å}$
100	7.35
30	4.75
50	4.13
30	3.91
90	3.33
40	3.12
20	3.01
90	2.42
30	2.29
15	2.02
20	1.45
30	1.39

* A $= \text{ClO}_2\text{Ni(ClO}_4)_3$; B $= (\text{NO}_2)_2\text{Ni(ClO}_4)_4$; C $= \text{NO}_2\text{Ni(ClO}_4)_3$; D $= \text{Ni(ClO}_4)_2$; E $= \text{ClO}_2\text{Co(ClO}_4)_3$; F $= (\text{NO}_2)_2\text{Co(ClO}_4)_4$; G $= \text{NO}_2\text{Co(ClO}_4)_3$; H $= \text{Co(ClO}_4)_2$; I $= \text{ClO}_2\text{Cu(ClO}_4)_3$; J $= (\text{NO}_2)_2\text{Cu(ClO}_4)_4$; K $= \text{NO}_2\text{Cu(ClO}_4)_3$; L $= \text{Cu(ClO}_4)_2$. Italicized values belong to NO_2ClO_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.
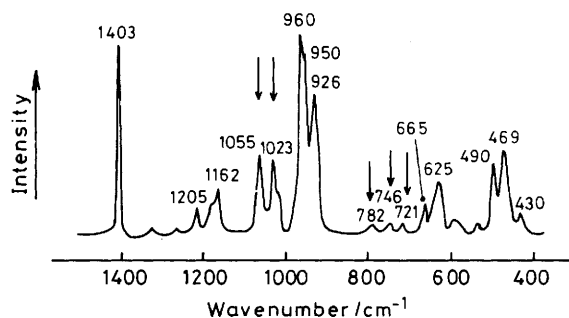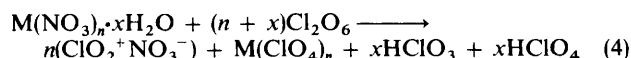

Figure 3. Raman spectrum of a mixture sampled in the course of the reaction of $\text{Cu(NO}_3)_2\cdot 3\text{H}_2\text{O}$ with Cl_2O_6. Arrows indicate the existence of unreacted $\text{Cu(NO}_3)_2\cdot 3\text{H}_2\text{O}$, while the other bands (slightly shifted by crystal effects) are due to the final product $(\text{NO}_2)_2\text{Cu(ClO}_4)_4$

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

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

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 NO_2^+ formation. In a transient step, while NO_3^- is substituted by ClO_4^-, ClO_2^+ associates with NO_3^- according to equation (4).

$$\text{M(NO}_3)_n\cdot x\text{H}_2\text{O} + (n + x)\text{Cl}_2\text{O}_6 \longrightarrow$$
$$n(\text{ClO}_2^+\text{NO}_3^-) + \text{M(ClO}_4)_n + x\text{HClO}_3 + x\text{HClO}_4 \quad (4)$$

Two mechanisms can explain the formation of NO_2^+. In a strong acidic medium, according to ref. 31, NO_3^- undergoes a

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

$$\text{NO}_3^- \longrightarrow \text{NO}_2^+ + \text{O}^{2-} \quad (5)$$

$$\text{ClO}_2^+ + \text{NO}_3^- \longrightarrow \text{ClO}_2 + \text{NO}_2^+ + \text{O}^- \quad (6)$$

$$n(\text{ClO}_2 + \text{NO}_2^+ + \text{O}^-) + n(\text{ClO}_2^+\text{ClO}_4^-) \longrightarrow$$
$$n(2\text{ClO}_2 + \text{NO}_2\text{ClO}_4 + \tfrac{1}{2}\text{O}_2) \quad (7)$$
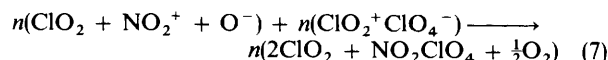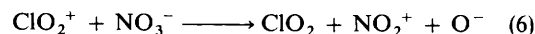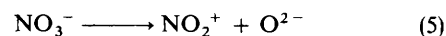
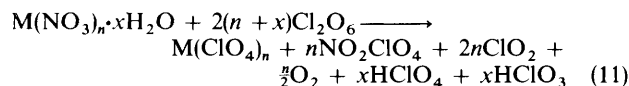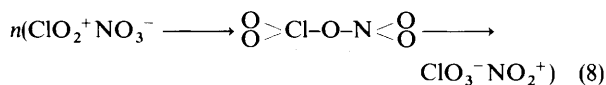reactions (8)—(10). By either mechanism the total balance is as in equation (11).

Table 5. Spectrochemical series for ligands bound to nickel

Ligand	NH_3	CH_3CN	O^{2-}	H_2O	NO_3^-	Me_2SO	$S_2O_7^{2-}$	SO_3F^-	Cl^-	ClO_4^-	Br^-
Dq/cm^{-1}	1 080	1 070	860	850	801	773	757	734	720	690	680
Ref.	33	33	33	a	a	a	b	c	33	d	33

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

Table 6. Assignments for the stretching modes (cm^{-1}) of $Ni(ClO_4)_2$ and $Co(ClO_4)_2$ compared to previous work

	$Ni(ClO_4)_2$			$Co(ClO_4)_2$		
	I.r.		Raman	I.r.		Raman
	Ref. 19	This work		Ref. 20	This work	This work
$v_{sym}(ClO_b)$	980	960	965	948	944	953
$v_{asym}(ClO_b)$	1 010	1 030	1 011—1 057	1 025	1 000	985
$v(ClO_t)$	1 290	1 300	1 308	1 260	1 278	

$$n(ClO_2^+NO_3^-) \longrightarrow \begin{matrix} O \\ O \end{matrix} > Cl-O-N < \begin{matrix} O \\ O \end{matrix} \longrightarrow$$

$$ClO_3^-NO_2^+) \quad (8)$$

$$n[(ClO_2^+ClO_4^-) + (ClO_3^-NO_2^+)] \longrightarrow$$
$$NO_2ClO_4 + ClO_2ClO_3] \quad (9)$$

$$n(ClO_2ClO_3 \longrightarrow 2ClO_2 + \tfrac{1}{2}O_2) \quad (10)$$

$$M(NO_3)_n \cdot xH_2O + 2(n + x)Cl_2O_6 \longrightarrow$$
$$M(ClO_4)_n + nNO_2ClO_4 + 2nClO_2 +$$
$$\tfrac{n}{2}O_2 + xHClO_4 + xHClO_3 \quad (11)$$
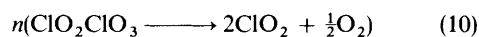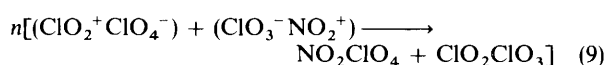
Structures of the Isolated Complexes.—The synthesized complexes crystallize poorly and no solvent was found in which single crystals could be grown for structural determination. The X-ray diffraction patterns, u.v., vibrational (i.r. and Raman), and more recently extended X-ray absorption fine structure (EXAFS) spectroscopy gave some structural information.

X-*Ray diffraction patterns.* In spite of the poor crystalline quality of $Ni(ClO_4)_2$ and $Co(ClO_4)_2$, experimental data (Table 3) show that: (i) $Ni(ClO_4)_2$ prepared from the reaction of Cl_2O_6 with $NiCl_2 \cdot nH_2O$ is identical to the material previously obtained by dehydrating $Ni(ClO_4)_2 \cdot 6H_2O$;[32] (ii) $Ni(ClO_4)_2$ and $Co(ClO_4)_2$ are isomorphous, which has not been previously demonstrated; (iii) the structure of these two perchlorates differs from that of $Cu(ClO_4)_2$; (iv) lines characteristic of NO_2ClO_4 and $NO_2M(ClO_4)_3$ in the diffraction pattern of $(NO_2)_2M(ClO_4)_4$ (M = Co or Ni) (Table 3) indicate the formation of a mixture of $NO_2M(ClO_4)_3$ and NO_2ClO_4 {these lines are absent in the spectrum of $(NO_2)_2Cu(ClO_4)_4$ suggesting a definite complex containing the $[Cu(ClO_4)_4]^{2-}$ ion}; (v) the compounds $AM(ClO_4)_3$ (A = NO_2^+ or ClO_2^+, M = Ni or Co) have the same kind of crystal structure and are isotypic with $NO_2Zn(ClO_4)_3$;[12] however the perchloratocopper complexes $ACu(ClO_4)_3$ (A = ClO_2^+ or NO_2^+) do not have isotypic 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 $M(ClO_4)_2$. For Ni and Co the shape of the octahedron is regular,[33] but for the copper complexes the u.v. spectra suggest that the octahedra are distorted, with an elongated axial symmetry.[34] The observed frequencies show that, as expected, the ClO_4 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_4 group interacts with the central atom.[1,3–20] The co-ordination of the ClO_4 group is corroborated by the existence of bands or lines in the range of the M–O stretching modes (350—200 cm^{-1}).[35] According to the experimental spectra, five types of complex can be defined: (a) $M(ClO_4)_2$ (M = Ni or Co); (b) $Cu(ClO_4)_2$; (c) $AM(ClO_4)_3$ (A = NO_2^+ or ClO_2^+, M = Ni or Co); (d) $(NO_2)_2Cu(ClO_4)_4$; (e) $ACu(ClO_4)_3$ (A = NO_2^+ or ClO_2^+).

(a) $M(ClO_4)_2$ (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_4 groups previously studied[3–17] and from that of $Cu(ClO_4)_2$[1] 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^{-1} leads to the assumption of C_{3v} symmetry for the ClO_4 group with three co-ordinated oxygen atoms. This analysis is consistent with recent EXAFS experiments on $M(ClO_4)_2$ (M = Ni or Co).[36]

The correlation diagram $T_d–C_{3v}$ 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 $v_{asym}(ClO_b)(E)$ [O_b = co-ordinated (bridging) oxygen atom] compared with $v_{asym}(ClO_t)$ [O_t = unco-ordinated (terminal) oxygen atom] observed in a classical unidentate perchlorate.[10] The low intensity of the Raman line assigned to $v(ClO_t)$ is surprising compared with the intensity of the line assigned to $v(ClO_b)$. The only likely explanation lies in its origin; $v(ClO_t)$ derives from $v_3(F_2)$ in free ClO_4^-. In the range of M–O(ClO_3) stretching modes, $v(Co–O)$ appears at 210 cm^{-1} and Ni–O at 220 cm^{-1}, 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).[36]

(b) $Cu(ClO_4)_2$. The i.r. spectrum differs slightly from that previously given;[1,18] in particular, the line at 1 030 cm^{-1} 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 $Cu(ClO_4)_2 \cdot 2H_2O$.[1] An analysis of the vibrational spectra of the metal–oxygen skeleton has recently been given by some of us.[13]

The observed splittings for the stretching modes in the Raman and i.r. spectra [Figure 4(b)] are compatible with bidentate ClO_4, as previously proposed.[1] Nevertheless, the multiplicity is much more important for the stretching and
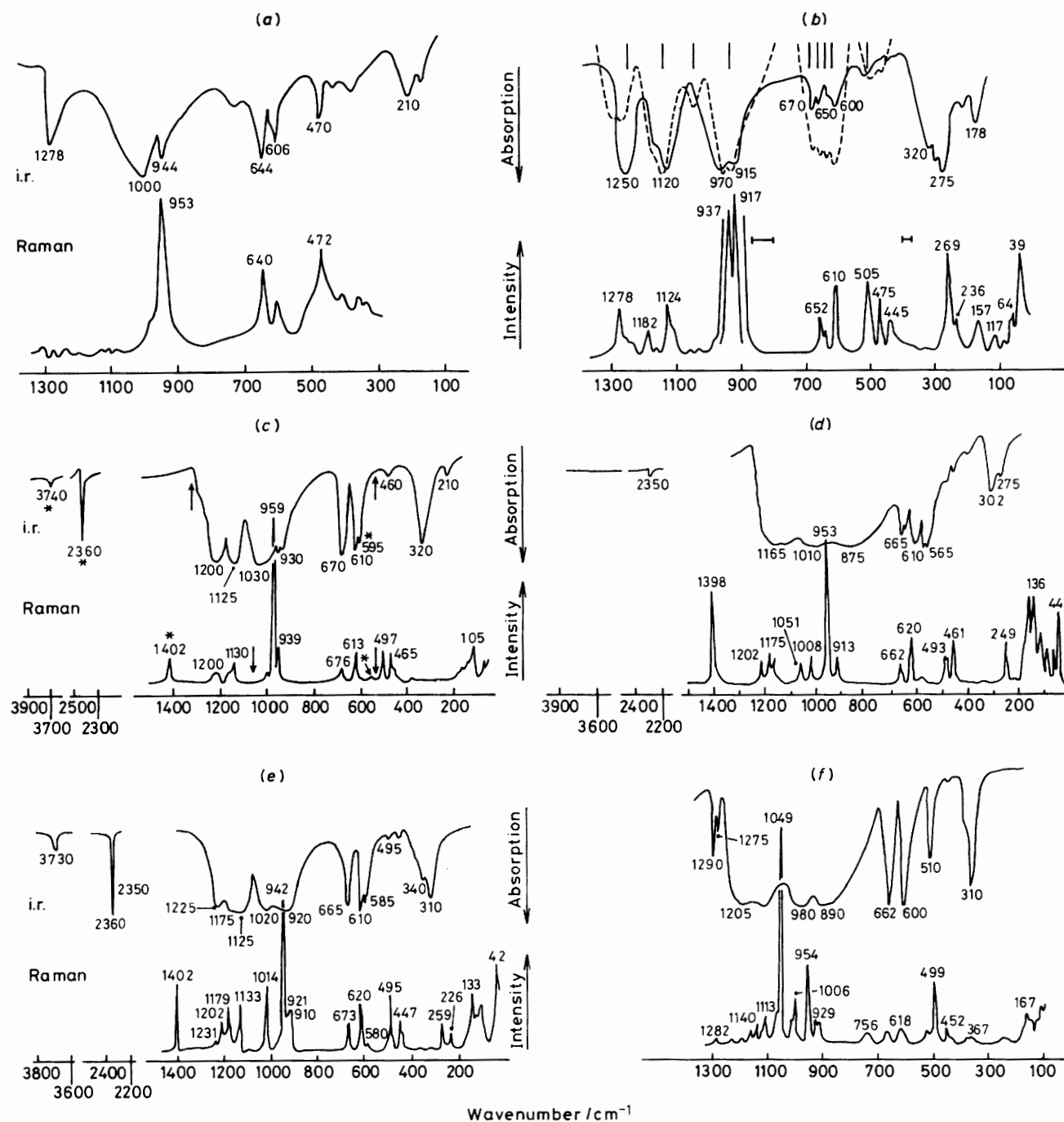
Figure 4. Typical i.r. and Raman spectra of: (a) $Co(ClO_4)_2$; (b) $Cu(ClO_4)_2$ (— — —, ref. 1), (———, ref. 18, relative intensities not given); (c) $NO_2Ni(ClO_4)_3$ (the NO_2^+ bands are indicated by asterisks, ClO_2^+ bands of the chloryl salt by arrows); (d) $(NO_2)_2Cu(ClO_4)_4$; (e) $NO_2Cu(ClO_4)_3$; (f) $ClO_2Cu(ClO_4)_3$

deformation modes (v_3 and v_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 ClO_4 ligand in $Cu(ClO_4)_2$ is assumed. This hypothesis has recently been supported by an EXAFS determination.[13] The proposed structure of $Cu(ClO_4)_2$ is shown in Figure 5. One 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 ClO_4 participates in four Cu–O short bonds; the two longer Cu–O bonds come from the 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 ClO_4 are somewhat different; the intrachain 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 ClO_4 groups are purely bidentate, so that the perturbations observed for each type will be quite different.

Intrachain 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
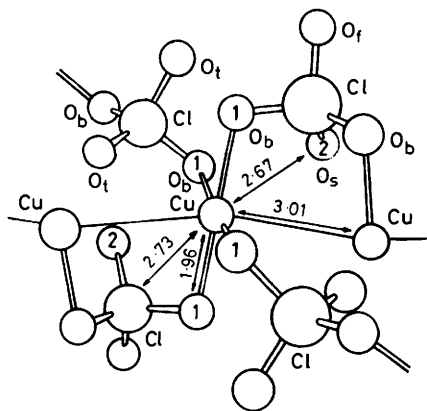
Figure 5. Structure of $Cu(ClO_4)_2$ according to an EXAFS study[13]

lowering of symmetry. The secondary co-ordination of O(2) (O_s) implies a shorter ClO_f bond (O_f = free oxygen atom). The line at 1 278 cm^{-1} in the Raman might be assigned to $v(ClO_f)$; the i.r. component appears at 1 250 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 $v(ClO_t)$ in $Ni(ClO_4)_2$ and $Co(ClO_4)_2$ (see above).

$v(ClO_b)$ is expected around 900 cm^{-1}. The splitting 970—937 cm^{-1} (Δv = 33 cm^{-1}) is similar to that observed for v_{asym}- and v_{sym}-(ClO_b) in antimony(v)[11] and tin(IV) complexes[8] where a ClO_4 ligand bridges two metal centres (Δv = 40 cm^{-1}) with d(M–O) = 2.20 instead of the 1.95 Å here. Thus, these bands and lines are assigned to the stretching ClO_b modes of intrachain ClO_4, while those of 1 182 (Raman) and 1 152 cm^{-1} (i.r.) are to be assigned to $v(ClO_s)$ (with Δv = 30 cm^{-1}).

Interchain ClO_4. This ClO_4 ligand has a C_{2v} or C_s symmetry and the classical correlation diagrams T_d–C_{2v} or T_d–C_s predict four stretching modes: v_{asym}- and v_{sym}-(ClO_t) and v_{asym}- and v_{sym}-(ClO_b). In the Raman and i.r. spectra a strong line appears at 917 cm^{-1} and a strong band at 915 cm^{-1}, which are assigned to $v(ClO_b)$. The medium-intensity line at 1 124 cm^{-1} (1 120 cm^{-1} in i.r.) could be assigned to $v_{sym}(ClO_t)$, the large band at 1 250 cm^{-1} to $v_{asym}(ClO_t)$. 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) $AM(ClO_4)_3$ (A = NO_2^+ or ClO_2^+, M = Co or Ni). After assignment of the stretching and deformations modes belonging to the NO_2^+ and ClO_2^+ cations [for example in nickel salts: NO_2^+, i.r., 3 740 (v_{sym} + v_{asym}), 2 360—2 350 (v_{asym}); Raman, 1 402 (v_{sym}), 549 (δ); ClO_2^+, i.r., 1 305—1 295 (with isotopic $^{35}Cl^{37}Cl$ splitting), 515 (δ); Raman, 1 048 (v_{sym}) and 518 cm^{-1} (δ)], the i.r. and Raman spectra [Figure 4(c)] can be interpreted on the basis of discrete anions $M(ClO_4)_3^-$ with bidentate chelating (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[5b] in the neutral $Ga(ClO_4)_3$ or $Fe(ClO_4)_3$ complexes [i.e. $\Delta v(ClO_t)$ = 70 cm^{-1} in $M(ClO_4)_3^-$ but 125 cm^{-1} in $Ga(ClO_4)_3$] which probably results from cation–anion interactions.

(d) $(NO_2)_2Cu(ClO_4)_4$. The frequencies observed for NO_2^+ vibrational modes are similar to those found for the other nitryl salts isolated in this work, Figure 4(d). When $(NO_2)_2Cu(ClO_4)_4$ is warmed to give $NO_2Cu(ClO_4)_3$ which results from the loss of NO_2ClO_4, the most significant change in the Raman spectrum is the disappearance of the lines at 953 and 1051 cm^{-1}. These frequencies are not identical to those found for NO_2ClO_4 in $(NO_2)_2Ni(ClO_4)_4$ (945, 1 042—1 063 cm^{-1}). Simultaneously the Raman lines characteristic of $NO_2Cu(ClO_4)_3$ cannot be found

Table 7. Assignments for the stretching modes (cm^{-1}) of $Cu(ClO_4)_2$

I.r.	Raman	Assignments
915		$v(ClO_b)$ Interchain
	917	
	937	$v(ClO_b)$ Intrachain
970		
1 120		
	1 124	$v_{sym}(ClO_t)$ Interchain
1 152		
	1 182	$v(ClO_s)$ Intrachain
1 250	1 250	$v_{asym}(ClO_t)$ Interchain + $v(ClO_f)$ intrachain (i.r.)
	1 278	$v(ClO_f)$ Intrachain

Table 8. Assignments for the stretching modes (cm^{-1}) of $M(ClO_4)_3^-$ based on an octahedral environment for the metal atoms

$NO_2Ni(ClO_4)_3$	$NO_2Cu(ClO_4)_3$		
939	910—921	$v_{sym}(ClO_b)$	(E)
959	942	$v_{sym}(ClO_b)$	(A_1)
980	1 014	$v_{asym}(ClO_b)$	(E)
1 130	1 133	$v_{sym}(ClO_t)$	(A_1)
1 148	1 179—1 202	$v_{sym}(ClO_t)$	(E)
1 200—1 214	1 231	$v_{asym}(ClO_t)$	(E)

in the spectrum of $(NO_2)_2Cu(ClO_4)_4$; $[Cu(ClO_4)_4]^-$ 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 $M(NO_3)_4^{2-}$ (M = Ni, Zn, or Cu)[37] it is possible that the ligands are weakly bonded in a manner intermediate between bi- and uni-dentate but closer to the latter [$v_{sym}(ClO_b)$ 913 and 953, $v_{sym}(ClO_t)$ 1 008 and 1 051, and $v_{asym}(ClO_t)$ 1 156—1 205 cm^{-1}]. The same conclusion has been deduced from spectroscopic analyses for $ClO_2^+[Ga(ClO_4)_4]^-$.[5a,16]
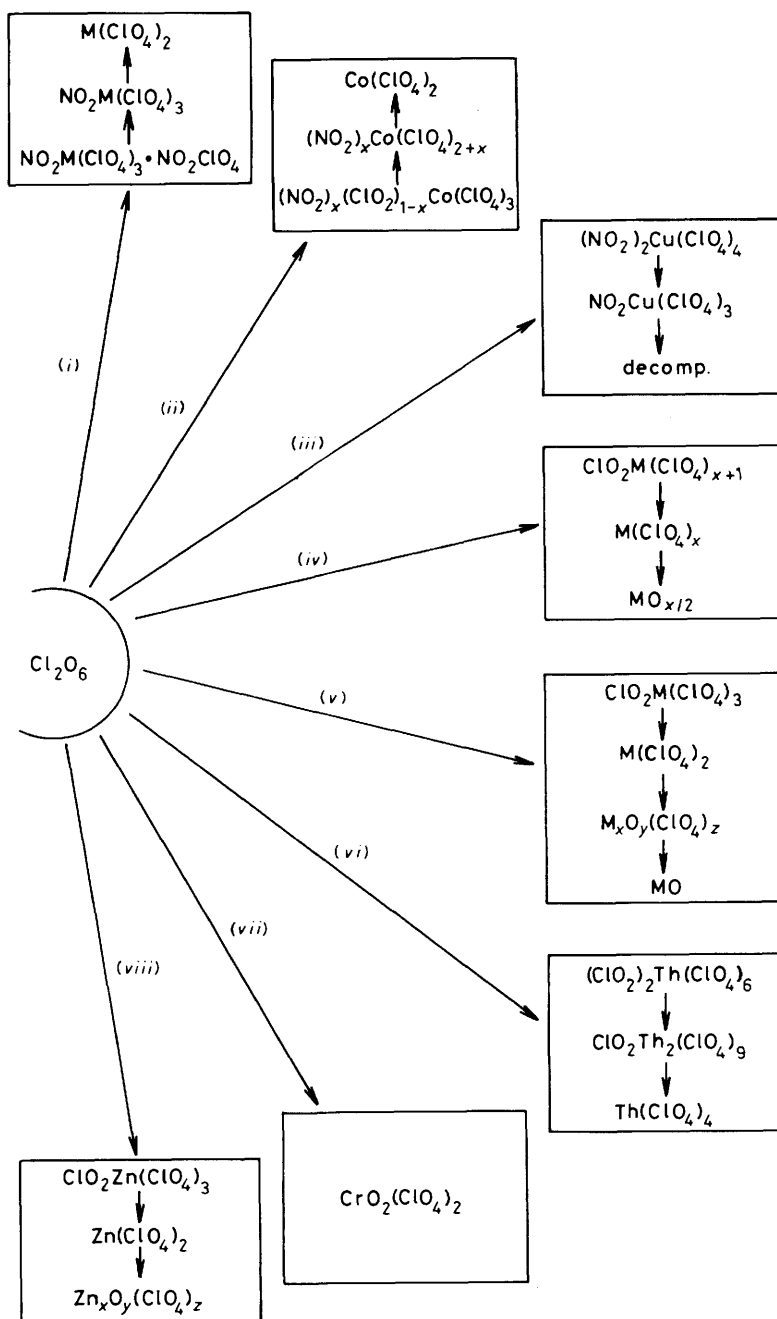
(e) $NO_2Cu(ClO_4)_3$ and $ClO_2Cu(ClO_4)_3$. The X-ray diffraction patterns indicate that the two compounds do not belong to the same structural type, a conclusion supported by vibrational spectroscopy [Figure 4(e) and (f)]. For instance, the spectrum of $ClO_2Cu(ClO_4)_3$ contains extra lines around 756 and 1 113 cm^{-1}. For the nitryl salt a reasonable interpretation of the Raman spectrum can be given, involving a discrete anion with three bidentate ClO_4 groups and D_3 symmetry as in $Ni(ClO_4)_3^-$ or $Co(ClO_4)_3^-$. 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 cm^{-1}) and bidentate (921, 942, 1 133—1 179, and 1 202 cm^{-1}) ClO_4 groups. A similar structure was found in $[NOZn(NO_3)_3]_n$.[37]

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 ClO_4 group. The extra lines at 1 113 and 756 cm^{-1} may belong to a unidentate[16] ClO_4 group interacting strongly with a ClO_2^+ cation. Thus, $ClO_2Cu(ClO_4)_3$ has a more complex structure than $NO_2Cu(ClO_4)_3$.

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 Cl_2O_6 with hydrated chlorides appears logical owing to the highly hygroscopic character of Cl_2O_6, that using

$M(ClO_4)_2$
↑
$NO_2M(ClO_4)_3$
↑
$NO_2M(ClO_4)_3 \cdot NO_2ClO_4$

$Co(ClO_4)_2$
↑
$(NO_2)_x Co(ClO_4)_{2+x}$
↑
$(NO_2)_x (ClO_2)_{1-x} Co(ClO_4)_3$

$(NO_2)_2 Cu(ClO_4)_4$
↓
$NO_2Cu(ClO_4)_3$
↓
decomp.

$ClO_2M(ClO_4)_{x+1}$
↓
$M(ClO_4)_x$
↓
$MO_{x/2}$

$ClO_2M(ClO_4)_3$
↓
$M(ClO_4)_2$
↓
$M_xO_y(ClO_4)_z$
↓
MO

$(ClO_2)_2Th(ClO_4)_6$
↓
$ClO_2Th_2(ClO_4)_9$
↓
$Th(ClO_4)_4$

Cl_2O_6

(i) (ii) (iii) (iv) (v) (vi) (vii) $(viii)$

$ClO_2Zn(ClO_4)_3$
↓
$Zn(ClO_4)_2$
↓
$Zn_xO_y(ClO_4)_z$

$CrO_2(ClO_4)_2$

Scheme. Reactions of Cl_2O_6: (i) $M(NO_3)_2 \cdot nH_2O$; (ii) $Co(NO_3)_2 \cdot nH_2O$; (iii) β-$Cu(NO_3)_2$; (iv) MCl_x;[3a,5,6] (v) $MCl_2 \cdot nH_2O$; (vi) $ThCl_4 \cdot \varepsilon ThO_2$ (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) CrO_3;[8,24] (viii) Zn[12]

nitrates as starting material is more surprising but illustrates the behaviour of 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 ClO_4^- shown to appear in $Ni(ClO_4)_2$ and $Co(ClO_4)_2$. Copper(II) perchlorate, until now considered as a classical bidentate ClO_4 model, shows a complex molecular structure, in which both bidentate and pseudo-tridentate 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 $CdCl_2$-type array.

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