

The existence of $\text{Co}(\text{NCS})_2(\text{NO})(\text{PMe}_3)_2$ as an intermediate is substantiated by the presence in the IR spectrum of the solution of $\nu(\text{NO})$ at 1760 cm^{-1} together with the two $\nu(\text{NO})$ vibrations of the dinitrosyl cation, which indicates a mechanism similar to the one proposed for Co-phosphite complexes.⁹ In this case, a strong field stabilization effect resulting from the electronegative phosphite ligands able to stabilize a Co(III) species cannot be invoked, since PMe_3 is known as a good σ -donor ligand. Thus, the peculiar role of the NCS anion, not yet clear, has to be emphasized.

Conclusion

The redox reaction of NO with $\text{Co}(\text{NCS})_2(\text{PMe}_3)_2$ occurs through the formation of $\text{Co}(\text{NCS})_2(\text{NO})(\text{PMe}_3)_2$ as an unstable intermediate. It has been observed in solution and characterized by its $\nu(\text{NO})$ but isolated only as the PET_3 complex.

This complex dismutates to give a Co^- , Co^{2+} , and Co^{3+} species (formally if NO coordinates as NO^+), following a mechanism

probably similar to the one observed in $\text{Co}(\text{NO})(\text{sacsac})$ and $[\text{Co}(\text{NCS})(\text{NO})(\text{P}(\text{OR})_3)_4]^+$, that is, in complexes where hard donor ligands (O, N) are present. Although the use of NO as an oxidizing agent is known, its ability to readily produce a Co(III)- PMe_3 complex in good yield under mild conditions was unexpected.

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Registry No. $\text{Co}(\text{NCS})_2(\text{NO})(\text{PET}_3)_2$, 101011-29-4; $\text{Co}(\text{NCS})_3(\text{PMe}_3)_3$, 101011-30-7; $[\text{Co}(\text{NO})_2(\text{PMe}_3)_2]_2[\text{Co}(\text{NCS})_4]$, 101011-32-9; $[\text{Co}(\text{NO})_2(\text{PMe}_3)_2]\text{BPh}_4$, 101011-33-0; $\text{Co}(\text{NCS})_2(\text{PET}_3)_2$, 14916-34-8; NO, 10102-43-9.

Supplementary Material Available: Listings of X-ray crystallographic data for $\text{Co}(\text{NCS})_3(\text{PMe}_3)_3$, including structure factors, anisotropic thermal parameters, hydrogen parameters, and equations for least-squares planes (15 pages). Ordering information is given on any current masthead page.

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A Strongly Chelating Bidentate ClO_4^- . New Synthesis Route and Crystal Structure Determination of $\text{Ti}(\text{ClO}_4)_4$

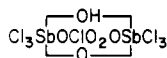
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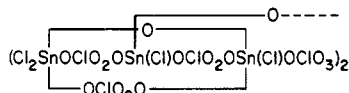
Reaction of Cl_2O_6 with TiCl_4 leads to $\text{Ti}(\text{ClO}_4)_4 \cdot x\text{Cl}_2\text{O}_6$. When this complex is warmed to $42\text{--}55\text{ }^\circ\text{C}$ under dynamic vacuum (1.33 Pa), colorless single crystals of $\text{Ti}(\text{ClO}_4)_4$ sublime. This compound crystallizes in the monoclinic system ($C2/c$): $Z = 4$, $a = 12.451(3)\text{ \AA}$, $b = 7.814(1)\text{ \AA}$, $c = 12.826(3)\text{ \AA}$, $\alpha = 108.13(3)^\circ$, $V = 1186(3)\text{ \AA}^3$ at $-100\text{ }^\circ\text{C}$. The structure was solved by direct methods and refined by full-matrix least squares to a final $R(F) = 0.051$ for 96 variables and 909 reflections. The asymmetric unit contains one independent molecule. The metal center is strongly chelated by four perchlorato ligands (mean Ti-O distance $d(\text{Ti}-\text{O}) = 2.069\text{ \AA}$). The eight oxygen atoms adopt a slightly flattened dodecahedral arrangement with C_2 symmetry. The ClO_4 ligands are distorted with mean observed Cl-O distances $d(\text{Cl}-\text{O}_b) = 1.51\text{ \AA}$ and $d(\text{Cl}-\text{O}_f) = 1.39\text{ \AA}$ and angles $\text{O}_b\text{ClO}_b = 97.2^\circ$ and $\text{O}_f\text{ClO}_f = 115.4^\circ$ (O_b is bonded oxygen; O_f is free oxygen). Vibrational spectroscopic data are consistent with the crystal structure and the molecular shape of $\text{Ti}(\text{ClO}_4)_4$.

In the last 15 years, the knowledge of perchlorato complexes has expanded with the discovery of convenient syntheses¹ and the systematic studies of their molecular structures using vibrational² and more recently EXAFS³ spectroscopies; on the other hand, the X-ray structural approach has been less successful. Up to now, generally, it has been believed that the low basicity of the ligand ClO_4^- would allow only weak coordination⁵ (or semicoordination in reference to Hathaway⁴) to metal centers; nevertheless, it has recently been possible to isolate and characterize a few perchlorato complexes with strong metal- ClO_4^- interactions.⁶ In some of these complexes, this type of coordination is greatly aided by the presence of porphyrin ligands.^{6a-d}

In $\text{Sb}_2\text{Cl}_6(\text{O})(\text{OH})(\text{ClO}_4)_6^f$



and $[\text{Sn}_3\text{O}_2\text{Cl}_4(\text{ClO}_4)_4]_2^{6e}$



the ClO_4^- ligand is able to strongly coordinate to metal centers ($d(\text{M}-\text{O}) = 1.95\text{--}2.24\text{ \AA}$) as a monodentate or bridging bidentate

group, without the help of electron-draining coligands such as porphyrin rings.

Some recent structural EXAFS investigations on $\text{Cu}(\text{ClO}_4)_2^{3a}$ and $\text{M}(\text{ClO}_4)_n$ ($n = 2$, $\text{M} = \text{Ni}$, Co ,^{3b} Zn ,^{3c} $n = 3$, $\text{M} = \text{Ga}$, In ^{3c}) have revealed strongly coordinated ClO_4^- groups acting between

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Table I. IR and Raman Frequencies and Their Assignments for Ti(ClO₄)₄

Raman			IR			assignments
a*	b	c	a	b	c	
1320 (5)	1320 (10)		1285 (sh, s)	1300 (m)		} ν _{as} (ClO ₄)
		1316 (m)	1270 (s)	1300 (s, br)	1286 (m)	
1305-1292 (2)	1300 (5)		1250 (sh)			} ν _s (ClO ₄)
1201 (40)	1200 (55)	1198 (vs)		1200 (sh)	1195 (vs)	
1169-1153 (2)	1157 (3)	1165 (w)	1165 (s)	1165 (s)	1155 (s)	} ν _s (ClO ₄)
890 (20)	890 (20)	887 (m)	1040 (sh)	1030 (sh)	1080 (w, sh)	
880-870 (5)	878 (8)	881 (sh)	1000 (sh)		1030 (w, sh)	} ν _s (ClO ₄)
			970 (sh)	970 (sh)		
			920 (s)	915 (s)	906 (w, sh)	} ν _{as} (ClO ₄)
880-846 (15)	850 (20)	849 (7)	865 (sh)	870 (s)	867 (s)	
822-814 (w)			845 (s)	853 (s)	844 (s)	} ν _{as} (ClO ₄)
			825 (s)			
			790 (s)		740 (sh)	
702 (30)	700 (35)	700 (m)				ρ _r
675-660 (5)	660 (10)	662 (w)	665 (s)	660 (s, br)	660 (s)	ρ _w
610-604 (5)	607 (7)	605 (w)	620 (sh)			} δ(Cl(O ₄) ₂)
			605 (sh)	605 (sh)	605 (sh)	
590 (5)	590 (5)	590 (w)	590 (m)	590 (s)	582 (m)	} ρ _t
546-555 (20)	553 (20)	555 (m)				
539-529 (5)	526 (10)	534 (w)	535 (m)	540 (s)	542 (w)	} δ(Cl(O ₄) ₂)
					530 (sh)	
					465 (m)	
411 (15)	410 (20)	411 (s)		405 (sh)		} ν _{as} (TiO ₈)
396-391 (10)	398 (15)	398 (w)	385 (s, br)	380 (s)	380 (m, br)	
383-370 (5)	378 (10)	377 (w)	350 (sh)			} ν _s (TiO ₈)
269 (10)	268 (15)					
234 (100)	234 (100)	239 (s)	240 (sh)		225 (w)	} TiO ₈ def
201 (20)	202 (30)	203 (w)	215 (sh)			
196, 190 (sh)		170 (w)				} lattice
157 (10)	157 (20)					
115-110 (20)	110 (45)	116 (w)				
75-71 (sh)						
64 (40)						
50-44 (25)						
24 (20)						

*This work. The asterisk indicates that for broad lines or groups of lines only the main intensity is given. ^bReferences 1c and 12. ^cReference 7.

metal atoms as bridging bidentate or tridentate ligands, forming polymeric arrangements.

In the meantime Rosolovskii et al. have discovered a chelating bidentate ClO₄ in Zr(ClO₄)₄,^{6g} but this structure does not appear accurate enough to permit a good chelating process description.

In this paper, we present the structure of Ti(ClO₄)₄, which was analyzed at -100 °C to avoid instability of the crystal inside the X-ray beam and to limit atomic thermal motions. This compound has been found to be a rare example of an ordered ClO₄ ligand. This complex was previously obtained by Christe et al.^{1c} and Rosolovskii et al.⁷ by action of ClOClO₃ or HClO₄ on TiCl₄. We report in this work a new synthesis using the most efficient perchlorating reagent: Cl₂O₆.

Experimental Section

Caution! Cl₂O₆ and perchlorates are highly explosive compounds particularly on contact with organic substances and under shock.⁸ The reactions must be carried out with caution and continuously checked. Only small amounts of products should be prepared and handled.

Synthesis of Ti(ClO₄)₄·xCl₂O₆ (x < 0.05). The synthesis of chlorine trioxide and its use for the preparation of perchlorato complexes have been described elsewhere.^{1a}

TiCl₄ (Prolabo, Rectapur, 99.5%) was used without purification and poured into the Pyrex reactor under dry-nitrogen atmosphere, and the reaction was carried out on a vacuum line.^{1a}

In a typical experiment, small fractions of Cl₂O₆ (0.5-1 g, 0.003-0.006 mol) were added by vacuum distillation onto 1.7 g (0.009 mol) of TiCl₄

at -180 °C. The mixture was allowed to warm slowly to 10 °C and then stirred until a yellow precipitate was formed; then the excess TiCl₄ was pumped out. The precipitate was treated with a new fraction of Cl₂O₆ (≈0.5-1 g) until a red liquid formed; this liquid was vigorously stirred for 15 min and then concentrated by vacuum evaporation until a pale yellow powder formed.

If the red liquid obtained in the second step is stirred more than 15 min and if the evaporation process is too slow, the formation of an orange-yellow solid Ti₂O(ClO₄)₆ is observed.

For the chemical analysis, the product was gently hydrolyzed at low temperature^{1a} and its chemical content was determined by gravimetry of TiO₂⁹ and potentiometry of ClO₄⁻¹⁰. The product was formulated as Ti(ClO₄)₄. Anal. Calcd for Ti(ClO₄)₄: Ti, 10.74; ClO₄, 89.25. Found: Ti, 10.84; ClO₄, 89.89.

The facts that the product appeared pale yellow instead of white as expected and that the typical line of ClO₂⁺ (1062 cm⁻¹)¹¹ was observed in the Raman spectrum indicated that this compound incorporates some traces of Cl₂O₆ undetectable by the chemical analysis.

Ti(ClO₄)₄ Crystal Growth. When Ti(ClO₄)₄·xCl₂O₆ is gently warmed to 42-55 °C under dynamic vacuum, colorless crystals rapidly sublime onto the wall of the tube. By reference to the previous studies of Rosolovskii and Christe,^{1c,7,12} Raman and IR spectra unambiguously charac-

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(13) Ti(ClO₄)₄ reacted with CCl₄ to give CO₂, COCl₂, ClO₂, and a white residue that was a mixture of TiO₂ and TiO(ClO₄)₂.

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Table II. X-ray, Crystal, and Least-Squares Refinement Parameters

Crystal Parameters ^a			
cryst syst	monoclinic	$V, \text{\AA}^3$	1186
space group	$C2/c$	$T, ^\circ\text{C}$	-100
$a, \text{\AA}$	12.451 (3)	Z	4
$b, \text{\AA}$	7.814 (1)	mol wt	445.7
$c, \text{\AA}$	12.826 (3)	$d_{\text{calcd}}, \text{g/cm}^3$	2.49 ^c
α, deg	108.13 (3)		
Intensity Data and Least-Squares Refinement ^b			
diffractometer	Nonius CAD-4		
radiation	Mo $K\alpha$		
$\lambda(K\alpha), \text{\AA}$	0.71073		
monochromator	graphite		
2θ range, deg	4-50		
scan type	$\omega-\theta$		
scan range, deg	$1.2 + 0.35 \tan \theta$		
reflens measd	$h, k, \pm l$		
no. of reflens colld	1198		
no. of obsd. unique reflens with $I > 3\sigma(I)$	909		
cryst shape	truncated hexagonal pyramid		
cryst size, mm	0.3×0.2		
cryst color	colorless		
abs coeff, cm^{-1}	17.4		
$R(F)$	0.034		
$R_w(F)$	0.051		

^aCell parameters were obtained by least-squares refinement of the angular positions of 25 reflections automatically centered on the diffractometer. ^bThe profile analysis of a few low-angle reflections indicated that an $\omega-\theta$ scan method was the most appropriate for data collection. Scan ranges were calculated from the formula $S_r = A + B \tan \theta$, where A depends on the mosaic spread of the crystal and B allows for increasing peak width due to K_1 and K_2 splitting: A and B were chosen as 1.2 and 0.35° , respectively. For each reflection, the calculated scan angle was extended by 25% on either side to estimate the background count. ^cOwing to its high chemical reactivity, it has not been possible to determine the density of the compound.¹³

terize the compound as $\text{Ti}(\text{ClO}_4)_4$. We must emphasize that single crystals of the compound could not be obtained by sublimation of pure $\text{Ti}(\text{ClO}_4)_4$ free from Cl_2O_6 .

IR and Raman Vibrational Analysis. IR and Raman spectrometers and their calibrations as well as the sampling techniques were described elsewhere.^{1a} The IR spectrum of $\text{Ti}(\text{ClO}_4)_4$ shows an important "Christiansen" effect when crude powdered polycrystalline samples are pressed between silicon plates (111). On the other hand, mulling agents react quickly with the complex. In order to obtain an accurate spectrum, the product was sublimed on a silicon plate as previously described.²⁵ The results are reported in the Table I. They are compared to those obtained previously by Christe et al.^{1a,12} and Rosolovskii et al.⁷

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Table III. Final Atomic Positional Parameters for $\text{Ti}(\text{ClO}_4)_4$

	x	y	z
Ti	0.0	0.0345 (1)	0.250
Cl1	0.8249 (1)	-0.1867 (1)	0.1640 (1)
Cl2	0.9410 (1)	0.2693 (1)	0.0849 (1)
O11	0.4296 (3)	0.3540 (4)	0.1316 (2)
O12	0.3239 (3)	0.1428 (4)	0.1917 (3)
O13	0.3523 (2)	0.4260 (3)	0.2642 (2)
O14	0.2274 (3)	0.3728 (5)	0.0833 (3)
O21	0.8687 (3)	0.2349 (5)	-0.0206 (2)
O22	0.0375 (2)	0.1448 (4)	0.1166 (2)
O23	0.9804 (3)	0.4370 (4)	0.1022 (3)
O24	0.8868 (3)	0.2172 (4)	0.1705 (2)

Table IV. Bond Distances (\AA) and Angles (deg) in $\text{Ti}(\text{ClO}_4)_4$

Ti-O11	2.058 (3)	Cl1-O13	1.507 (3)
Ti-O13	2.084 (3)	Cl1-O11	1.520 (3)
Ti-O22	2.094 (3)	Cl2-O23	1.392 (4)
Ti-O24	2.042 (3)	Cl2-O21	1.399 (4)
Cl1-O12	1.380 (3)	Cl2-O22	1.500 (3)
Cl1-O14	1.408 (3)	Cl2-O24	1.512 (4)
O24-Ti-O22	66.3 (1)	O13-Cl1-O11	97.2 (2)
O11-Ti-O13	66.4 (1)	O23-Cl2-O21	115.1 (2)
O12-Cl1-O14	115.7 (2)	O23-Cl2-O22	110.8 (2)
O12-Cl1-O13	111.2 (2)	O23-Cl2-O24	110.6 (2)
O12-Cl1-O11	110.5 (2)	O21-Cl2-O22	110.9 (2)
O14-Cl1-O11	110.3 (2)	O21-Cl2-O24	110.6 (2)
O14-Cl1-O13	110.4 (2)	O22-Cl2-O24	97.4 (2)

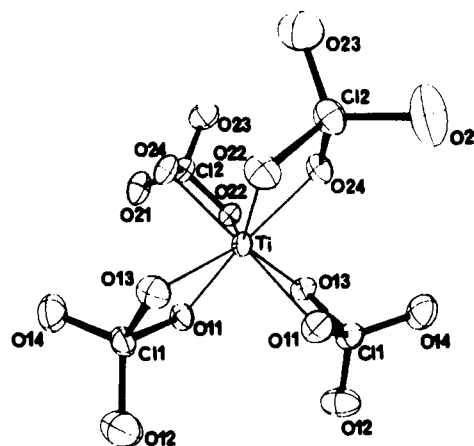
**Figure 1.** ORTEP diagram of the $\text{Ti}(\text{ClO}_4)_4$ unit. Thermal ellipsoids are shown at the 50% probability level.

Figure 4 shows the Raman spectrum from which were made the main assignments.

X-ray Data Collection. The crystals were examined with a microscope inside a drybox (JACOMEX) filled with a purified-argon atmosphere (water content less than 1 ppm). Most of crystals appeared large and generally twinned. These crystals could not be cut appropriately owing to their brittleness. About 20 crystals were mounted in thin-wall Lindemann glass capillaries and analyzed through preliminary oscillation photographs. Only three crystals appeared suitable for a complete X-ray study.

Preliminary X-ray analysis showed the crystals to possess monoclinic symmetry, and it appeared very quickly that these crystals were not stable at room temperature to X-ray radiation. Therefore, it was decided to record the data at -100°C on the automatic diffractometer.

The crystal data and the details of the crystallographic analysis are given in Table II.

During data collection the intensities of 3 standard reflections were checked after every 75 reflections. The loss in intensity was less than 4% but was taken into account in data reduction. The data were corrected for the effects of Lorentz polarization. The effect of absorption was neglected.

The systematic absence of reflections hkl with $h+k$ odd and $h0l$ with l odd indicated two possible space groups, $C2/c$ and Cc .

Structure Solution and Refinement. The structure was solved by direct methods. By analogy with $\text{Zr}(\text{ClO}_4)_4$, whose structure was previously determined by Rosolovskii,^{6b} the cell was assumed to contain four formula

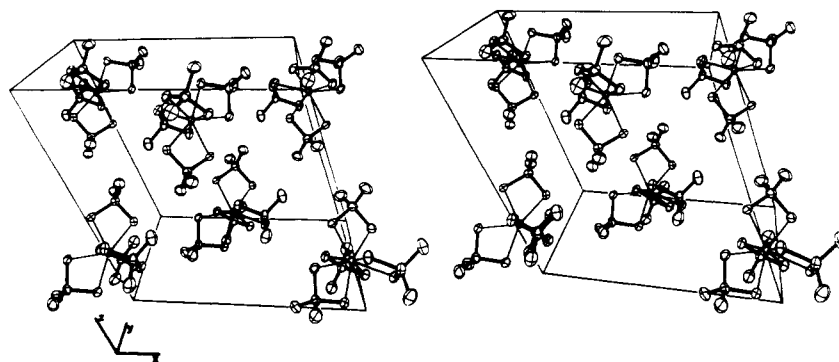


Figure 2. Stereoscopic packing of Ti(ClO₄)₄ in the unit cell.

Table V. Comparison of Mean Values of Structural Parameters^a of TiX₈ (X = O, S) in TiL₄ Complexes (L = ClO₄⁻, NO₃⁻, H₁₀C₅NS₂⁻) and ZrO₈ in Zr(ClO₄)₄

compd	bite	ϕ_A	ϕ_B	α	a/r	m/r	g/r	b/r	MO _A /MO _B
Ti(ClO ₄) ₄ ^b	1.09	35.9	104.2	1	1.167	1.095	1.292	1.430	1.02
Ti(NO ₃) ₄ ^c	1.03	37.2	100.1	6	1.214	1.030	1.320	1.426	1.01
Ti(H ₁₀ C ₅ NS ₂) ₄ ^d	1.11	35.5	103.0	7.5	1.181	1.107	1.305	1.420	1.04
Zr(ClO ₄) ₄ ^e	1.04	36.6			1.192	1.042	1.314	1.436	1.05
HSM		36.9	110.5		1.199	1.199	1.199	1.499	1

^aStructural parameters (distances in Å; angles in deg) are specified in ref 17–19: bite is the X–X distance relative to the M–X distance (M = Ti, Zr; X = O, S); ϕ_A and ϕ_B are the angles made by the M_A and M_B bonds, respectively, with the main axis (for TiO₈ in Ti(ClO₄)₄ (Figure 3), the corners of type A are O₁₃ and O₂₂ while the corners of type B are O₁₁ and O₂₄, and M is defined as above; the reference axis spans the edges *a* (Figure 3)); α is the twist in the BAAB trapezoid (the edges between B and A are the edges *m* (Figure 3)); *r* is the mean M–O distance; MO_A/MO_B is the mean bond length ratio. The hard-sphere model (HSM) according to Hoard and Silverston¹⁷ is relative to a regular dodecahedron. ^bThis work. ^cReference 16. ^dReference 20. ^eCalculated from ref 6g.

units, giving a calculated density of 2.49 g/cm³. The Wilson test of MULTAN¹⁵ gave a strong indication of centricity, so the structure solution was attempted in the space group *C2/c*, which proved later to be the correct one.

The output from the Fourier step of MULTAN contained three peaks of high weight, one occurring on a special 4(e) position and the others occurring in general 8(f) positions. These peaks were attributed respectively to titanium and chlorine atoms. After a few cycles of positional and isotropic parameter refinement, $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.54$ with negative temperature factors for all atoms. However, the phasing was good enough to allow location of the oxygen atoms on the subsequent Fourier map.

All atoms were refined with anisotropic thermal parameters. Convergence was obtained by minimizing the function $w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma_{\text{count}}^2(F_o^2)/4F_o^2 + 0.05F_o^2$. The final agreement factors were $R(F) = 0.034$ and $R_w(F) = 0.051$ for 96 variables and 909 reflections.

The scattering factors were taken from Doyle and Turner,¹⁴ and the crystallographic programs¹⁵ used were MULTAN 80 for the automatic solution of the crystal structure, FORDAP for Fourier summations, ORXFLS 3 for least-squares refinement, ORFFE 3 for molecular and error functions, and ORTEP II for the thermal ellipsoid program for molecular plots.

Results and Discussion

Crystal Structure. The final positional parameters for the 11 crystallographically unique atoms in Ti(ClO₄)₄ are listed in Table III, and bond distances and bond angles are given in Table IV. Listings of observed and calculated structure factors as well as temperature factors are given in the supplementary material.

In Figure 1 is depicted the geometry of the independent molecule of Ti(ClO₄)₄. Figure 2 represents a stereoscopic view of the unit cell. The molecular packing is relatively compact with distances between oxygens of independent molecules on the order of 3.33 Å.

While in tetrakis(nitrato)titanium¹⁶ the metal centers constitute parallel corrugated hexagonal sheets, in the perchlorato complex the metal centers are arranged in a weakly corrugated rectangular packing of parallelepipeds, allowing each individual titanium to adopt a flattened pseudooctahedral environment. The distances between titanium atoms are equal to 7.35 Å in the equatorial plane (*xy*). Along the *z* axis, titanium atoms form zigzag chains (Ti–Ti distances of 6.44 Å and Ti–Ti–Ti angles of 170.4°).

In Ti(ClO₄)₄, the metal center is chelated by four bidentate perchlorato ligands. So far, after Zr(ClO₄)₄, it is the second example of this type.

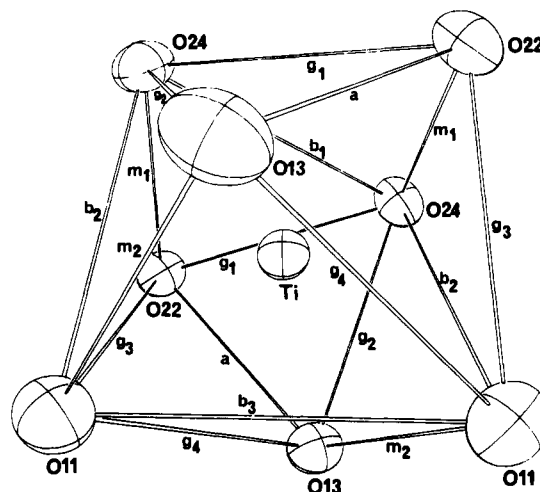


Figure 3. TiO₈ dodecahedron in Ti(ClO₄)₄. Definitions of the edges *a*, *b*, *g*, and *m* and angles $\delta(x_i)$ are given respectively in ref 17 and 18 ($\delta(x_i)$ is the dihedral angle between the faces containing the edge as labeled). Distances (Å): $a = 2.146$ (3); $b_1 = 2.920$ (6); $b_2 = 2.959$ (4); $b_3 = 2.997$ (6); $g_1 = 2.658$ (4); $g_2 = 2.670$ (4); $g_3 = 2.677$ (6); $g_4 = 2.687$ (4); $m_1 = 2.263$ (4); $m_2 = 2.270$ (4). Angles (deg): $\delta(a) = 65.3$ (1); $\delta(b_1) = \delta(b_2) = \delta(b_3) = 33.5$ (2); $\delta(g_1) = 55.5$ (1); $\delta(g_2) = 54.6$ (1); $\delta(g_3) = 56.2$ (1); $\delta(g_4) = 54.4$ (1); $\delta(m_1) = 75.9$ (1); $\delta(m_2) = 77.2$ (1). For the ideal dodecahedron the expected values are as follows: $a = m = 2.42$ Å; $b = 3.08$ Å; $g = 2.56$ Å; $\delta(a) = \delta(m) = 43^\circ$; $\delta(b) = 29.5^\circ$; $\delta(g) = 62.5^\circ$.

Chlorine atoms are arranged around the titanium center in a highly distorted tetrahedron at distances close to 2.73 Å, with Cl–Ti–Cl angles varying from 95.3 to 136.7°.

Therefore, in its first coordination shell, the metal atom is coordinated to eight oxygen atoms adopting a slightly flattened dodecahedron arrangement with *C₂* symmetry according to space group *C2/c*, as can be seen in Figure 3.

Very fine and detailed analyses of dodecahedral coordination have been reported by different authors.^{17–19} Using Kepert's criteria,¹⁹ we have compared some structural parameters of Ti(ClO₄)₄ to those of Zr(ClO₄)₄ and other titanium complexes (Table V). Among the different complexes of titanium reported in this table, the distortion from the ideal dodecahedral symmetry is

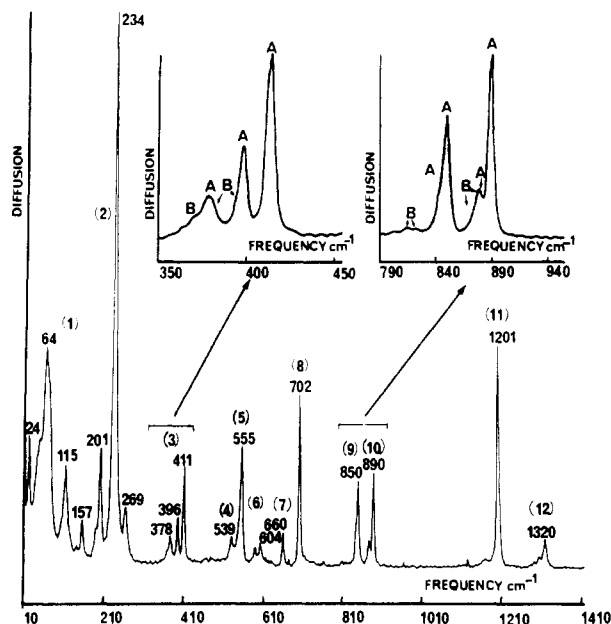


Figure 4. Raman spectrum of $\text{Ti}(\text{ClO}_4)_4$. Inserts show respectively the A and B splitting for $\nu_{\text{as}}(\text{TiO}_8)$, $\nu_{\text{s}}(\text{ClO}_4)$, and $\nu_{\text{as}}(\text{ClO}_4)$: (1) lattice modes + TiO_8 deformations; (2) $\nu_{\text{s}}(\text{TiO}_8)$; (3) $\nu_{\text{as}}(\text{TiO}_8)$; (4) $\delta(\text{Cl}(\text{O}_b)_2)$; (5) ρ_{t} ; (6) $\delta(\text{Cl}(\text{O}_i)_2)$; (7) ρ_{w} ; (8) ρ_{r} ; (9) $\nu_{\text{as}}(\text{ClO}_4)$; (10) $\nu_{\text{s}}(\text{ClO}_4)$; (11) $\nu_{\text{s}}(\text{ClO}_4)$; (12) $\nu_{\text{as}}(\text{ClO}_4)$.

obviously the weakest for the perchlorato complex.

As the Ti–O distances show (Table IV), the perchlorato group is strongly coordinated to the metal atom. The mean Ti–O distance of 2.069 Å is very close to that found in the nitrate complex¹⁶ (2.068 Å). This value is relatively shorter than the M–O distances encountered in $\text{Sb}_2\text{Cl}_6(\text{O})(\text{OH})(\text{ClO}_4)^{6f}$ and $\text{Zr}(\text{ClO}_4)_4^{6g}$ (respectively 2.23 and 2.19 Å). As expected for the Ti and Zr complexes, this is in agreement with the effective ionic radii of the metal ions (0.88 and 0.98 Å).²¹ However, Ti–O distances are longer than M–O distances found in $\text{Cu}(\text{ClO}_4)_2$ (1.95 Å) containing bridging ClO_4 groups;^{3a} though the effective ionic radii of the elements are very similar, the slight lengthening of Ti–O distances tends to minimize the repulsions among the four chelating perchlorato groups.

As it is generally observed for bidentate groups,^{3,6} the ClO_4 geometry is relatively distorted in $\text{Ti}(\text{ClO}_4)_4$. This leads to a lengthening of Cl–O_b (O_b is bonded oxygen) by about 0.07 Å and a shortening of Cl–O_i (O_i is free oxygen) by 0.05 Å. The mean $d(\text{Cl}-\text{O}_i)$ for $\text{Ti}(\text{ClO}_4)_4$ is very close to the value observed in complexes of Ni^{3b} and Sb^{6f} (1.38 and 1.39 Å).

The Cl–O_b bonds in $\text{Ti}(\text{ClO}_4)_4$ (1.50–1.52 Å) are the longest ever found for bidentate ClO_4 groups (1.48 Å in the Sb^{6f} complex); however, the Cl–O_b bonds are quite short compared to single bonds observed for monodentate ClO_4 ligands (1.64–1.70 Å).²⁹

It is worth noting that O_i–Cl–O_i angles are quite similar ($\approx 115^\circ$) within the Ti and Sb complexes while the O_b–Cl–O_b angle decreases to 97° in the titanium complex (106° in the Sb complex). On the other hand, very slight folding is observed between the O_bO_bTi and O_bO_bCl planes (dihedral angles of 2.4 and 4.2°).

Vibrational Spectroscopy. Vibrational spectra are consistent with the crystal symmetry (C_{2h}), as shown by the observed splitting of IR and Raman frequencies (Table I). Owing to the high difficulty of obtaining untwinned single crystals suitable for precise Raman study, no complete spectroscopic assignments have been attempted.

A first interpretation of vibrational spectra has been previously given by Rosolovskii et al.⁷ In this work, better resolution of the

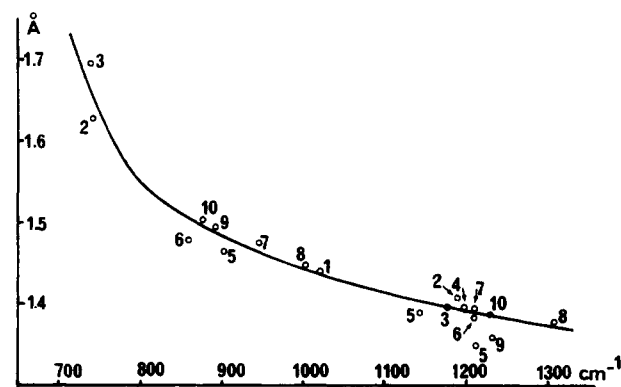


Figure 5. Plot of Cl–O bond lengths against $((\nu_{\text{s}}^2 + \nu_{\text{as}}^2)/2)^{1/2}$: (1) ClO_4^- ; (2) HClO_4 ; (3) Cl_2O_7 ; (4) ClO_3F ; (5) $(\text{Sn}_3\text{O}_2\text{Cl}_4(\text{ClO}_4)_4)_2$; (6) $\text{Sb}_2\text{Cl}_6(\text{O})(\text{OH})(\text{ClO}_4)^{6f}$; (7) $\text{Cu}(\text{ClO}_4)_2$; (8) $\text{Ni}(\text{ClO}_4)_2$; (9) $\text{Zr}(\text{ClO}_4)_4$; (10) $\text{Ti}(\text{ClO}_4)_4$ (this work).

Raman spectrum (Figure 4) allowed us to assign the observed frequencies to the different vibrational modes, using the correlation effect $T_d \rightarrow C_{2v} \rightarrow C_s \rightarrow D_{2d} \rightarrow C_2$. For example, $\nu_{\text{s}}(\text{ClO}_4)$ near 890 cm^{-1} is characterized by four Raman lines that correspond to the expected 2A and 2B components (insert in Figure 4).

Using the Cl–O bond lengths determined in different compounds, we have drawn a curve relating Cl–O bond lengths to their stretching frequencies according to the formula established by Garner et al. for complexes containing N–O bonds.²³

$d(\text{Cl}-\text{O})$ vs. $[(\nu_{\text{s}}^2 + \nu_{\text{as}}^2)/2]^{1/2}$ is shown in Figure 5. In the particular cases of the tetrakis(perchlorato)titanium and the bis(perchlorato)nickel^{3b} complexes, the points for ClO_i and ClO_b are very close to the best curve.

The ClO deformation modes appear in the range $500\text{--}720 \text{ cm}^{-1}$. The medium-intensity Raman line at 701 cm^{-1} , which occurs at a relatively high frequency, as also observed for nitrito-chelated complexes,²⁴ is assigned to the ρ_{r} mode according to the sequence $\rho_{\text{r}} > \rho_{\text{w}} > \delta(\text{Cl}(\text{O}_i)_2) > \rho_{\text{t}} > (\text{Cl}(\text{O}_b)_2)$ established elsewhere.²⁵

The ρ_{w} , ρ_{t} , $\delta(\text{Cl}(\text{O}_i)_2)$, and $\delta(\text{Cl}(\text{O}_b)_2)$ modes are found respectively around 665, 554, 595, and 529 cm^{-1} . The deformation mode $\delta(\text{Cl}(\text{O}_b)_2)$ is observed at higher frequencies than in the case of bridging bidentate perchlorato groups.^{1a,2c,6f,26}

Twenty-one vibrational modes are expected for the TiO_8 skeleton. According to the correlation path $O_h \rightarrow C_{4h} \rightarrow D_{2d} \rightarrow C_2$, the most important splitting is classically observed for the stretching mode, six lines for ν_{as} around 390 cm^{-1} (insert in Figure 4) and at least two lines around 251 cm^{-1} for ν_{s} . This last frequency is consistent with those observed in other perchlorato complexes: $\text{Cu}(\text{ClO}_4)_2$, 269 cm^{-1} ;^{1a} $\text{Ga}(\text{ClO}_4)_3$, 270 cm^{-1} ;²⁵ $(\text{Sn}_3\text{O}_2\text{Cl}_4(\text{ClO}_4)_4)_2$, 292 cm^{-1} .²⁷ On the other hand, the ν_{s} frequency can be correlated to that observed in $\text{Ti}(\text{NO}_3)_4$ (310 cm^{-1}).¹⁶ The difference in frequency is correctly accounted for by the mass shift $((62/99.5)^{1/2})$ between ClO_4^- and NO_3^- .

The accurate structure determination by X-ray diffraction has permitted the precise assignments of the main spectroscopic features of this novel coordination mode for the perchlorato ligand. The former conclusion that ClO_4 acted only as a bridging ligand^{3c} between metal centers has been invalidated. It must be emphasized that the high deformation of ClO_4 groups induced by the chelating coordination mode process is responsible for the poor stability of this type of compound.

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Registry No. $\text{Ti}(\text{ClO}_4)_4 \cdot x\text{Cl}_2\text{O}_6$ (coordination structure), 101310-90-1; $\text{Ti}(\text{ClO}_4)_4 \cdot x\text{Cl}_2\text{O}_6$ (salt structure), 101056-42-2; TiCl_4 , 7550-45-0; Cl_2O_6 , 12442-63-6; $\text{Ti}(\text{ClO}_4)_4$ (coordination structure), 60580-20-3; $\text{Ti}(\text{ClO}_4)_4$ (salt structure), 13498-15-2.

Supplementary Material Available: Listings of observed and calculated structure factors and final positional and temperature factor parameters for the atoms in $\text{Ti}(\text{ClO}_4)_4$ (6 pages). Ordering information is given on any current masthead page.

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