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- [29] Structure analysis of 1 (T = 295 K): Data were collected from a dry crystal mounted on a glass fiber by using a Enraf-Nonius CAD4 diffractometer.  $M_r = 966.2 (C_{53}H_{71}N_7O_{10})$ , monoclinic, space group  $P2_1$ , a = 10.953(2),  $b = 20.065(2), c = 12.862(2) \text{ Å}, \beta = 95.1(1), V = 2815.3(7) \text{ Å}^3, Z = 2,$  $\rho_{coled} = 1.14 \text{ g cm}^{-3}$ ;  $Cu_{kx}$  radiation,  $\lambda = 1.5418 \text{ Å}$ ,  $\mu = 6.109 \text{ cm}^{-1}$ ; F(000) =1036.0,  $2\theta = 130^\circ$ ,  $(\omega - 2\theta)$  scans; 4926 independent reflections, of which 4674 with  $|F_0| > 4\sigma(|F_0|)$  were considered as independent. Lorentz and polarization corrections were applied to the data, but no absorption correction was made. The structure was determined using the direct methods employing the SHELXS86 [29] computer program and full-matrix least-squares refinement was carried out using the software SHELXL93 [30]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms fixed on the basis of stereochemistry were used only for structure factor calculations. The atoms of the benzene ring in residue  $\Delta Phe^6$  (except C6G) were found to be disordered between two positions (see Fig. 1). These five atoms were refined isotropically with the effective occupancy adding up to 1. Final R-values (based on  $|F_0|$ ) for the observed reflections 0.046, for all reflections 0.048, (based on I) for all reflections 0.136, GoF = 1.049. Crystallographic data (excluding structure factors) for the structure described in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-5". Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: Int. code +(1223)336-033; e-mail: teched(a chemcrys.cam.ac.uk).
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## **Chlorine Tetraoxide\*\***

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The existence of the  $\text{ClO}_4$  radical, one of the simplest chlorine oxides  $\text{ClO}_x$  (x = 1-4), has not yet been unequivocally established. Yet it has been postulated as a reactive intermediate in several reactions and should be a binary compound of fundamental significance.  $\text{ClO}_4$  is probably an intermediate in the photochemical formation of  $\text{Cl}_2\text{O}_7$  from  $\text{Cl}_2$  and  $\text{O}_3$ ,<sup>[1]</sup> as well as in the thermal decomposition of  $\text{Cl}_2\text{O}_6^{[2]}$  and  $\text{Cl}_2\text{O}_7$ ,<sup>[3]</sup> and in the anodic oxidation of  $\text{ClO}_4^-$  ions.<sup>[4]</sup> An indication of the existence of  $\text{ClO}_4$  was obtained from ESR measurements on KClO<sub>4</sub> crystals that had been irradiated with X-rays.<sup>[5]</sup> However, the assignment and analysis of the ESR signals is still controversial.<sup>[6,7]</sup> The formation enthalpy of the endothermic ClO<sub>4</sub>, derived from mass spectrometric and kinetic measurements on  $\text{Cl}_2\text{O}_7$ , amounts to 200–270 kJ mol<sup>-1</sup>.<sup>[8,9]</sup>

The successful synthesis and spectroscopic identification of ClO<sub>3</sub> in the vacuum thermolysis of ClOClO<sub>3</sub> and matrix isolation of the products<sup>[10]</sup> encouraged us to generate a ClO<sub>4</sub> radical in the same way. For this purpose a sample of  $Cl_2O_6$  (or  $Cl_2O_7$ ) in a U-tube was cooled to -35 (or -105 °C) such that the partial pressure was roughly  $10^{-3}$  mbar. Neon or argon was passed over the cold sample to give a 1:500 mixture of starting material and noble gas. This gas stream was thermolyzed at 230 °C (410 °C) at the orifice of the nozzle. Under these conditions 95% of the molecules decay within a few milliseconds. The construction of the vacuum thermolysis and the matrix isolation apparatus is described elsewhere.<sup>[11]</sup> IR and UV/Vis spectra of the matrix-isolated thermolysis products were recorded. The proportion of decayed starting material was calculated by comparison with reference spectra of pure matrix-isolated starting material. In a total of 25 experiments we found five new bands in the IR spectra of the thermolysis products of Cl<sub>2</sub>O<sub>6</sub> and  $Cl_2O_7$  (Fig. 1, Table 1). These reproducible bands belonging to an



Fig. 1. Difference spectrum before and after the photolysis ( $\lambda > 495$  nm) from the IR spectra of the thermolysis products of Cl<sub>2</sub>O<sub>6</sub> isolated in a neon matrix. The bands of ClO<sub>4</sub> point upwards and those of the photolysis products downwards. Some noncompensated bands disrupt the spectrum. Bands arising from the by-products OCIO (o). ClO<sub>3</sub> (•), and the starting material Cl<sub>2</sub>O<sub>6</sub> (\*) are labeled. Cl<sub>2</sub>O<sub>4</sub> is formed in the photolysis of Cl<sub>2</sub>O<sub>6</sub> [2].

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Table 1.	Wavenumb	ers i [cm <sup>-1</sup>	<sup>1</sup> ]. intensities	in paren	theses). and	assignments of
the func	lamental vib	rations of <b>C</b>	CIO <sub>4</sub> . CIO <sub>3</sub> F	, and SO <sub>3</sub> I	F radical.	

<sup>35</sup> Cl <sup>16</sup> O <sub>4</sub> [b]	<sup>35</sup> Cl <sup>18</sup> O <sub>4</sub> [b]	CIO <sub>3</sub> F [c]	SO <sub>3</sub> F [d]	Assignment [a] XO <sub>3</sub> Y
1234 (s)	1196 (s)	1315.6 (vs)	1177.4 (m)	$v_4(e) = v_{as}(XO)$
1161 (vs)	1118 (vs)	1062.3 (m)	1053.0 (s)	$v_s(a_1) = v_s(XO)$
874 (w)	832 (w)	712.4 (s)	832.8 (s)	$v_2(a_1) = v(XY)$
646 (m)	609 (m)	588.3 (m)	601 (w)	$v_5(e) = \delta_{as}$
576 (m)	548 (m)	547.5 (w) 405.9 (w)	531.2 (m) 366 (vw)	$\begin{aligned} v_3(a_1) &= \delta_s \\ v_6(e) &= \rho \end{aligned}$

[a] Assignment for point group  $C_{3v}$ , [b] In Ne matrix, [c] In Ne matrix [14], [d] In Ar matrix [15].

unknown chlorine oxide are remarkable because their full width at half maximum is up to  $10 \text{ cm}^{-1}$ . This partly obscures the <sup>35/37</sup>Cl isotopic pattern, which is typical of species with one Cl atom. Since the relative intensities of the bands were the same in all experiments and since the bands decreased uniformly after photolysis of the matrix (tungsten-halogen lamp, cutoff filter,  $\lambda > 495$  nm), all bands must belong to one single species. By IR spectroscopy we identified only ClOO as a product of the photolysis; it is probably formed by the primary decomposition of ClO<sub>4</sub> to give OClO and O<sub>2</sub> and subsequent photoisomerization of OClO.<sup>[12]</sup> In the UV/Vis spectra ClO<sub>4</sub> shows a wide absorption band ranging from 380 to 510 nm (maximum at 425 nm) with vibrational fine structure. The intensity of this band on photolysis decreases in the same fashion as the infrared bands of ClO<sub>4</sub>. Below 380 nm the UV spectrum is obscured by the bands of ClO<sub>3</sub>, ClO<sub>2</sub>, and the starting material.

 $ClO_2$  and  $ClO_3$  are the most important by-products formed in the thermolysis of  $Cl_2O_6$  and  $Cl_2O_7$ , respectively. Thus the primary decomposition can be described according to Equations (a) and (b), and the new bands can be assigned to the

$$Cl_2O_6 \rightarrow ClO_4 + ClO_2$$
 (a)

 $Cl_2O_- \longrightarrow ClO_4 + ClO_3$ 

 $\text{ClO}_4$  radical. Experiments with  $\text{Cl}_2^{18}\text{O}_6$  and the calculation of the vibrational frequencies with the program NORCOR<sup>[13]</sup> verify the existence of  $\text{ClO}_4$ . There are numerous possibilities for the arrangement of atoms in a  $\text{ClO}_4$  molecule and for its symmetry. Based on the mode of formation, it can be assumed that  $\text{ClO}_4$  has a tetrahedral or distorted tetrahedral structure with  $T_d$ ,  $C_{3v}$ ,  $C_{2v}$ , or  $C_s$  symmetry. Therefore two, six, eight, or nine corresponding bands can be expected in the range of fundamental vibrations in the IR spectrum. Comparison of the five new vibrations with the fundamentals of the similarly built FClO<sub>3</sub> and the isosteric FSO<sub>3</sub> radical clearly indicates a  $\text{ClO}_4$  molecule with  $C_{3v}$  symmetry (Table 1). We have not yet been able to detect the missing  $v_6(e)$  vibration, which is expected as a weak band around 400 cm<sup>-1</sup>.

Our assignment of the bands to the vibrational modes is supported by the product rule for the mode  $a_1$ . The wavenumbers of the three  $a_1$  vibrations of  ${}^{35}Cl^{16}O_4$  and  ${}^{35}Cl^{18}O_4$  were used to calculate the quotient of the wavenumber products (observed: 1.311; calculated: 1.308). In addition, a normal coordinate analysis of the vibrational data was performed with the bond lengths listed and a bond angle of 116° between the short ClO bonds of OCIO. The results are three strong  $(8.7 \times 10^2 \text{ Nm}^{-1})$  and one weak ClO bond  $(5.3 \times 10^2 \text{ Nm}^{-1})$ . The correlation of the force constant with the bond length (Fig. 2) leads to the structure of the ClO<sub>4</sub> radical shown in Figure 3.

The distortion of the  $ClO_4$  radical to  $C_{3v}$  symmetry is dynamic (Jahn – Teller effect). One electron switches from an antibond-



Fig. 2. Plot of the length of the Cl- O versus the force constant in  $10^2$  N m<sup>-1</sup> for the Cl- O bond for a) FClO<sub>3</sub>, b) FClO<sub>2</sub>, c) ClO<sub>4</sub>, d) OClO, e) ClO<sub>3</sub>, and f) ClO. An exponential function was fitted to the data. The broken lines relate the force constants of the ClO<sub>4</sub> radical with the corresponding bond lengths.

ing  $\sigma^*$  orbital of one ClO bond to that of another, resulting in the broadening of the IR bands.

The ClO<sub>4</sub> radical completes the series of mononuclear binary chlorine oxides known, which can combined formally to give the binuclear species  $Cl_2O_2$ ,  $Cl_2O_3$ ,  $Cl_2O_4$ ,  $Cl_2O_6$ , and  $Cl_2O_7$ . We have demonstrated that the primary thermal



Fig. 3. Structure of  $ClO_4$ .

decay of two binuclear chlorine oxides yields the corresponding mononuclear radicals, with a preference for the formation of OCIO. The chemistry of NO<sub>x</sub> is analogous: the radicals NO, NO<sub>2</sub>, and NO<sub>3</sub> participate in the formation and the decomposition of N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, and N<sub>2</sub>O<sub>5</sub>, respectively.

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