Crystal and Molecular Structure of Anhydrous Copper(II) Perchlorate†

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The structure of the pale blue-green $Cu(ClO_4)_2$ obtained by sublimation has been determined from single-crystal X-ray diffraction data. The structure was refined in the monoclinic space group $P2_1/c$, $Z = 2$, $a = 4.584(1)$, $b = 8.326(2)$, $c = 8.015(1)$ Å and $\beta = 114.21(1)°$, $R = 0.044$ for 894 observed reflections. The copper has a distorted-octahedral environment with four equatorial oxygen atoms at short distances [1.96(1) Å] and two long Cu–O axial interactions [2.46(1) Å]. Perchlorate groups are bridging bidentate, and can be regarded as pseudo-tridentate, leading to a three-dimensional polymeric network of infinite cross-linked chains interacting through long Cu–O contacts.

The preparation of anhydrous copper(II) perchlorate, $Cu(ClO_4)_2$, was an important historical step in the study of perchlorate salts.[1] Interpretation of its infrared spectra by Hathaway and Underhill in 1961[1] demonstrated, for the first time, the co-ordinating ability of the perchlorate group. Since then, numerous perchlorate complexes of transition- and non-transition-metals have been prepared by reliable synthetic routes,[2–5] emphasising the versatile co-ordinating properties of ClO_4: perchlorate can act as a mono-, bi- (chelating or bridging) or tri-dentate (bridging) ligand. On the other hand, ClO_4 acts as a good assembling ligand in the absence of strong bases such as organic solvents or water. Layered (Ni, Co, Zn, Mn, Cd, Ga, In)[6,7] or channelled (lanthanoids)[5] structures have been described. However, new perspectives in the reactivities of perchlorate complexes are unfortunately deeply restricted owing to the strong oxidative properties of ClO_4. Although $Cu(ClO_4)_2$ has been generally taken as a reference for the co-ordination of the perchlorate ligand, its crystal structure has, so far, remained relatively obscure. Some structural results have been provided by Pascal *et al.*[8] using EXAFS spectroscopy, which indicated bridged bidentate, pseudo-tridentate ClO_4 groups. In this paper we report the crystal and molecular structure of the copper perchlorate complex, $Cu(ClO_4)_2$, of which single crystals were grown by sublimation at 438 K.

Experimental

CAUTION: Chlorine oxides and perchlorates are highly reactive compounds particularly on contact with organic substances and under shock. They must be handled with care and reactions must be continuously monitored.

General methods of synthesis, purification and handling of reagents as well as perchlorates have been described elsewhere.[2–5] Methods and apparatus for chemical analysis and vibrational characterization (Raman) of $Cu(ClO_4)_2$ follow those given in previous papers.[9] ESR spectra were recorded on a Bruker ER 200D spectrometer with X-band frequency at room temperature and at 77 K. Samples were sealed in 5 mm diameter tubes and 2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl was used as reference.

Preparation of $Cu(ClO_4)_2$.—Copper(II) perchlorate was synthesised by treating Cl_2O_6 with basic copper(II) carbonate $CuCO_3 \cdot Cu(OH)_2$ (Merck, extra pure). As previously described,[4] the chloryl salt, $Cu(ClO_2)(ClO_4)_3$, is obtained in a first step and decomposed further into $Cu(ClO_4)_2$ at 343 K under dynamic vacuum (10^3 Pa). At 430 K, the latter compound sublimes into a fine microcrystalline powder which is unfortunately not suitable for X-ray analysis. Incidently, some sizable single crystals of anhydrous $Cu(ClO_4)_2$ were grown while preparing YBaCuO at low temperature from a mixture of the perchlorates of yttrium, barium and copper (1 : 1 : 1). At 438 K, pale blue-green crystals sublime, under static vacuum, onto the upper part of the Pyrex reactor. The Raman spectrum of a single crystal as well as ESR powder spectra agree with previous work of Pascal *et al.*[8] and unambiguously characterize $Cu(ClO_4)_2$. Raman ($\tilde{\nu}$/cm^{-1}): 1273m, 1248s, 1122–1178m, 936vs, 917vs, 652m, 608s, 498m, 473s, 252vs, 233 (sh).

At both 298 and 77 K, the ESR spectra of $Cu(ClO_4)_2$ exhibit a very strong quadruplet signal ($\Delta H = 50$ G) without hyperfine structure, characteristic of the presence of a large number of copper(II) paramagnetic centres. The spectrum gives three anisotropic g values, independent of temperature and very close to those reported by Pascal *et al.*,[8] $g_x = 2.092$, $g_y = 2.225$ and $g_z = 2.335$.

Owing to their high hygroscopicity, crystals of $Cu(ClO_4)_2$ were examined inside a glove-box filled with purified extra-dry argon[6d] and inserted into sealed thin-walled Lindemann glass capillaries to be checked by X-ray methods.

Crystallography.—Crystal data. Cl_2CuO_8, $M = 262.44$, monoclinic, space group $P2_1/c$, $a = 4.584(1)$, $b = 8.326(2)$, $c = 8.015(1)$ Å, $\beta = 114.21(1)°$, $U = 279.05$ Å^3 (by least-squares refinement of the angular positions of 25 reflections automatically centred on the diffractometer, $\lambda = 0.7107$ Å), $Z = 2$, $D_c = 3.12$ g cm^{-3}, $F(000) = 254$. Pale blue-green air- and light-sensitive plates. Crystal dimensions 0.1 × 0.3 × 0.1 mm.

Data collection and processing. Enraf–Nonius CAD-4 diffractometer, ω–$\frac{2}{3}\theta$ mode with ω scan width $= 1 + 0.35 \tan\theta$, graphite-monochromated Mo-Kα radiation; 1003 reflections measured ($2 \leqslant \theta \leqslant 30°$, octants hkl and $hk-l$) giving 894 with $I > 3\sigma(I)$. No significant loss in intensities was observed. Data collection at 175 K and absorption corrections did not improve refinement substantially.

Structure analysis and refinement. The structure was solved in the monoclinic space group $P2_1/c$ by direct methods provided by SHELXS 86.[10a] Full-matrix least-squares refinements were

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

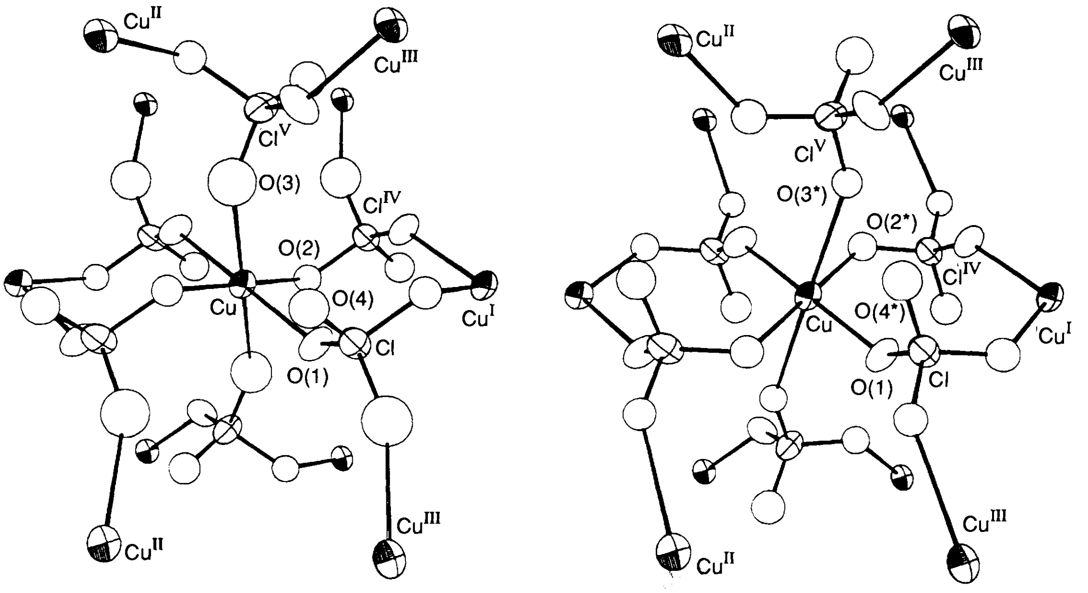

Fig. 1 ORTEP diagrams of $Cu(ClO_4)_2$ for the two sets of disordered atoms

Table 1 Refined positional parameters for $Cu(ClO_4)_2$ [asterisked atoms are the alternatives for disordered atoms O(2)–O(4)]

Atom	*x*	*y*	*z*
Cu	0.0	0.0	0.0
Cl	0.6837(6)	−0.1138(3)	0.2560(4)
O(1)	0.388(2)	−0.131(1)	0.0896(4)
O(2)	0.076(3)	0.009(2)	−0.223(2)
O(2*)	0.071(5)	0.124(3)	−0.186(3)
O(3)	0.170(5)	0.231(3)	0.209(3)
O(3*)	0.278(3)	0.254(2)	0.127(2)
O(4)	0.639(4)	−0.035(2)	0.400(2)
O(4*)	0.664(4)	0.031(2)	0.337(2)

carried out using the program SHELX 76.[10b] Finally, all atomic positional parameters, anisotropic thermal parameters for copper, chlorine and one oxygen atom and isotropic thermal parameters for the two sets of disordered oxygen atoms (see discussion below) were refined by minimizing the function $w(|F_o| - |F_c|)^2$ and using the weighting scheme $w = 0.9358/[\sigma^2(F_o) + 0.0006\ F_o^2]$ to final agreement factors $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R'(F)$ of 0.044 and 0.045. The last Fourier difference map was flat except for a few residuals < 1 e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

Refined positional parameters of all atoms are listed in Table 1. Main interatomic distances and angles are collected in Table 2. Corresponding ORTEP diagrams of $Cu(ClO_4)_2$ molecular units are given in Fig. 1.

Crystal Structure.—The unit cell contains two formula units $Cu(ClO_4)_2$. The copper atoms lie on the 2(a) special position (0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$). An interesting feature of the crystal structure is the orientational disorder of the ClO_4 group around the Cl–O(1) axis. Such disorder problems have already been encountered in some perchlorate complexes,[6a] but in this work, it could be fortunately resolved into two equally distributed sets of oxygen atoms. Fig. 2 presents the two sets of oxygen atoms, and the corresponding angular values of rotation and distortion. Further X-ray investigation did not give evidence of extra peaks for doubling or tripling the cell parameters compatible with a large superstructure.

Table 2 Distances (Å) and angles (°) in $Cu(ClO_4)_2$

Cu ··· Cu^I	4.584(3)	Cu ··· Cl	3.107(3)
Cu ··· Cu^{II}	5.778(3)	Cu ··· Cl^{IV}	3.107(3)
Cu ··· Cu^{III}	6.272(3)	Cu ··· Cl^V	3.734(3)
Cu–O(1)	1.956(8)		
Cu–O(2)	1.96(1)	Cu–O(2*)	1.95(1)
Cu–O(3)	2.46(2)	Cu–O(3*)	2.46(1)
Cl–O(1)	1.465(8)		
Cl–O(2)	1.51(1)	Cl–O(2*)	1.45(1)
Cl–O(3)	1.43(2)	Cl–O(3*)	1.41(1)
Cl–O(4)	1.42(2)	Cl–O(4*)	1.39(2)
O(1)–Cu–O(2)	83.1(4)	O(1)–Cu–O(2*)	99.3(4)
O(1)–Cu–O(3)	101.5(4)	O(1)–Cu–O(3*)	94.8(3)
O(2)–Cu–O(3)	117.7(5)	O(2*)–Cu–O(3*)	69.2(4)
O(1)–Cl–O(2)	111.1(6)	O(1)–Cl–O(2*)	102.6(5)
O(1)–Cl–O(3)	106.0(9)	O(1)–Cl–O(3*)	110.1(6)
O(1)–Cl–O(4)	113.6(8)	O(1)–Cl–O(4*)	107.1(7)
O(2)–Cl–O(3)	103.7(11)	O(2*)–Cl–O(3*)	107.9(7)
O(2)–Cl–O(4)	103.7(8)	O(2*)–Cl–O(4*)	115.9(7)
O(3)–Cl–O(4)	118.2(11)	O(3*)–Cl–O(4*)	112.7(9)
Cu–O(1)–Cl	101.5(3)		
Cu–O(2)–Cl^{IV}	126.8(6)	Cu–O(2*)–Cl^{IV}	131.9(7)
Cu–O(3)–Cl^V	146.6(11)	Cu–O(3*)–Cl^V	148.3(8)

Symmetry operations: I $1 + x, y, z$; II $-x, \frac{1}{2} + y, \frac{1}{2} - z$; III $1 - x, \frac{1}{2} + y, +\frac{1}{2} - z$, IV $1 - x, -y, -z$; V $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The following discussion will be carried on the analysis of a single set [Cl, O(1), O(2), O(3), O(4)] of the perchlorate group, however all results and remarks can be transposed to the alternative set [Cl, O(1), O(2*), O(3*), O(4*)] without significant differences.

As in $CuCl_2$,[11] $CuBr_2$,[12] α- and γ-$Cu(IO_3)_2$,[13] $Cu(NO_3)_2$[14] and $Cu(O_2PF_2)_2$,[15] the copper atom has a distorted-octahedral co-ordination: four oxygen atoms [2 × O(1) and 2 × O(2)] form a rectangle around Cu [Cu–O(1), Cu–O(2) 1.96(1) Å; O(1)–Cu–O(2) 83.1(4) °]; two axial oxygen atoms [2 × O(3)] complete the six-co-ordination of the copper atom through longer interactions [2.46(1) Å]. However, the Cu–O(3) axis is not quite perpendicular to the rectangular plane of atoms O(1) and O(2) with O(1)–Cu–O(3) 101.5(4) ° and O(2)–Cu–O(3) 117.7(5) °.

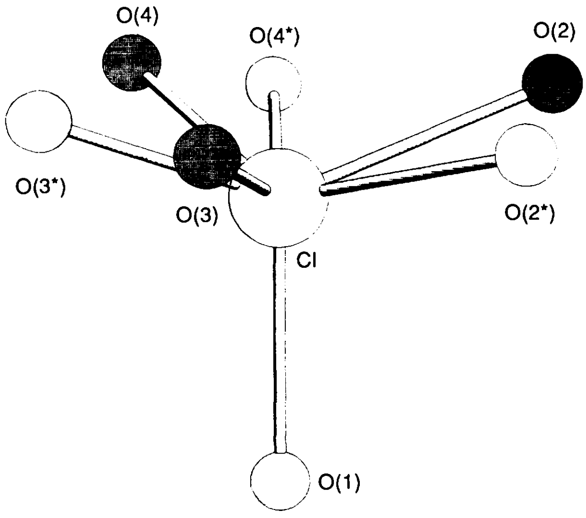

Fig. 2 Diagram of the two sets of the perchlorate group. Angular values (°) of rotation and distortion are O(2)–Cl–O(2*) 39.3(6), O(3)–Cl–O(3*) 40.7(10), O(4)–Cl–O(4*) 32.5(9), Δ[O(2), O(2*)] 8.6(6), Δ[O(3), O(3*)] −4.1(9), Δ[O(4), O(4*)] 6.4(8) where Δ(X,Y) is the angular difference between O(1)–Cl–X and O(1)–Cl–Y, where X and Y respectively refer to O(2, 3, 4) and O(2*, 3*, 4*) atoms

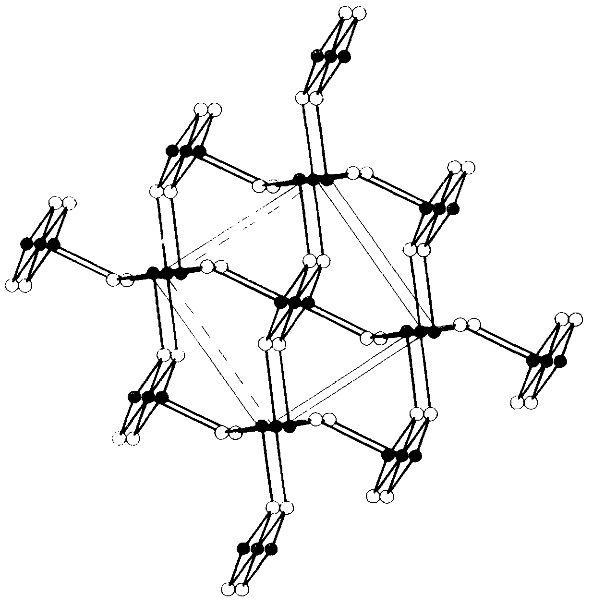

Fig. 3 Schematic representation of $Cu(ClO_4)_2$ viewed along the *a* axis; (●) Cu, (○) ClO_4

Fig. 3 shows a schematic representation of the stacking. Copper atoms (dark circles), aligned along the *a* axis, are bridged by perchlorate groups (white circles) and are involved in eight-membered $Cu_2O_4Cl_2$ rings. The resulting chains, at the centre and along the edges of the cell, are interconnected through long Cu–O interactions. This arrangement as cross-linked chains can be compared to those in $CuCl_2$, $CuBr_2$, α-$Cu(IO_3)_2$ and $Cu(NO_3)_2$, but differs from those previously observed in γ-$Cu(IO_3)_2$ and $Cu(O_2PF_2)_2$ (parallel chains). Thus, this three-dimensional polymeric structure implies three different Cu ··· Cu distances: 4.584(3) Å between copper atoms along the *a* axis, 5.778(3) and 6.272(3) Å between central copper atoms and those of adjacent chains. These Cu ··· Cu distances are too long to yield exchange interactions as demonstrated by the ESR spectra and a previous magnetic measurement.[8]

Owing to its co-ordination, the perchlorate group is fairly distorted. Unfortunately the disordered positions of the O(2,3,4) atoms introduce errors that substantially mask the expected lengthening of Cl–O relative to the co-ordinated oxygen atoms and shortening of the free Cl–O bonds as generally observed for bi- or tri-dentate ClO_4.[5,6] However, the Cl–O(1,2,3) bonds in $Cu(ClO_4)_2$ (1.41–1.51 Å) are to be compared with those found in the bidentate complexes $Ti(ClO_4)_4$ (1.50–1.52 Å)[6d] and $[Sb_2Cl_6O(OH)(ClO_4)]$ (1.48 Å)[6b] or in the tridentate perchlorate: $Ni(ClO_4)_2$ (1.44 Å) and $Co(ClO_4)_2$ (1.44 Å).[6c] The Cl–O(4) bond (1.39, 1.42 Å) is slightly longer than free Cl–O in complexes of Ti, Co, Ni or Sb (1.38–1.38 Å).

The above crystallographic results concerning the local environment around copper are in excellent agreement with those previously obtained by X-ray absorption spectroscopy[8] for the first-shell distance in $Cu(ClO_4)_2$ (four Cu–O at 1.96 Å). Differences between the model suggested from EXAFS and that determined from X-ray diffraction data for more distant co-ordination shells are due to the limited long-range information available in the former technique which probably results from multiple scattering effects.

Acknowledgements

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