Oxo Transfer and Metal Oxidation in the Reaction of $[Ru(PPh_3)_3Cl_2]$ with *m*-Chloroperbenzoic Acid: Structure of $[Ru(PPh_3)_2(m\text{-}ClC_6H_4CO_2)Cl_2]$†

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One mol and 0.5 mol of peracid are consumed for oxo transfer to PPh_3 and oxidation of metal, respectively, in the reaction of $[Ru(PPh_3)_3Cl_2]$ with *m*-$ClC_6H_4CO_3H$. The active oxo-transfer agent is metal-bound peracid. After oxo transfer the carboxylate residue remains chelated to the metal centre as shown by an *X*-ray structure determination of the product $[Ru(PPh_3)_2(m\text{-}ClC_6H_4CO_2)Cl_2]$ (**1**). The *trans, cis, cis*-$RuP_2O_2Cl_2$ co-ordination sphere has two-fold symmetry. Its e.s.r. and near-i.r. spectra are in agreement with the energy order $d_{xy} > d_{xz}, d_{yz}$. The complex undergoes one-electron quasi-reversible reduction but only at low potentials ($E_{298}°$ −0.40 V *vs.* saturated calomel electrode).

A number of ruthenium species undergo the model oxo-transfer reaction $PPh_3 + [M'O] \longrightarrow OPPh_3 + [M']$ where [M′O] symbolises the active metal reagent.[1] Herein we describe the facile and stoicheiometric reaction between $[Ru(PPh_3)_3Cl_2]$ and *m*-chloroperbenzoic acid affording $OPPh_3$ and a carboxylate chelated ruthenium(III) complex which has been structurally characterised. The active oxo-transfer agent contains the ligated peracid fragment $Ru(m\text{-}ClC_6H_4CO_3)$.

Results and Discussion

In dichloromethane or benzene solution *m*-$ClC_6H_4CO_3H$ rapidly oxidises $[Ru(PPh_3)_3Cl_2]$ at ambient temperature. An anaerobic environment is used since $[Ru(PPh_3)_3Cl_2]$ is redox labile in air.[1a,2,3] From the dark brown reaction mixture $OPPh_3$ and a paramagnetic e.s.r.-active ruthenium complex (**1**) can be isolated in excellent yields.

The composition of complex (**1**) is $[Ru(PPh_3)_2(m\text{-}ClC_6H_4CO_2)Cl_2]$. Its *X*-ray structure is shown in Figure 1 and selected bond parameters are listed in Table 1. The two *trans* PPh_3 ligands are related by a crystallographic two-fold symmetry with the C_2 axis passing through Ru, C(19), C(20), and C(23); the Cl(2) atom shows two-fold disorder. The carboxylato function is symmetrically chelated. The *trans, cis, cis*-$RuP_2Cl_2O_2$ co-ordination sphere shows large deviations from octahedral geometry, much of it originating from the acute bite angle of the carboxylate chelate.

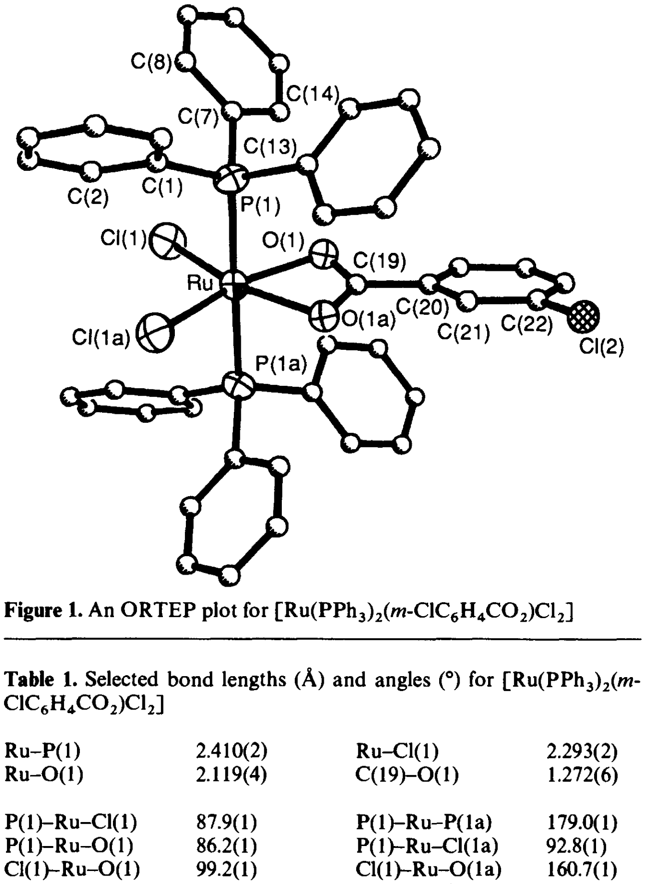

Figure 1. An ORTEP plot for $[Ru(PPh_3)_2(m\text{-}ClC_6H_4CO_2)Cl_2]$

Table 1. Selected bond lengths (Å) and angles (°) for $[Ru(PPh_3)_2(m\text{-}ClC_6H_4CO_2)Cl_2]$

Ru–P(1)	2.410(2)	Ru–Cl(1)	2.293(2)
Ru–O(1)	2.119(4)	C(19)–O(1)	1.272(6)
P(1)–Ru–Cl(1)	87.9(1)	P(1)–Ru–P(1a)	179.0(1)
P(1)–Ru–O(1)	86.2(1)	P(1)–Ru–Cl(1a)	92.8(1)
Cl(1)–Ru–O(1)	99.2(1)	Cl(1)–Ru–O(1a)	160.7(1)
Cl(1)–Ru–Cl(1a)	99.9(1)	P(1)–Ru–O(1a)	93.0(1)
O(1)–Ru–O(1a)	61.6(2)		

The magnetic moment (1.84 μ_B) of complex (**1**) corresponds to one unpaired electron. Its e.s.r. spectrum in a dichloromethane–toluene glass (77 K) [Figure 2(*a*)] is compatible with the *X*-ray structure of rhombic symmetry (two-fold axis only). The spectrum was analysed using the *g*-tensor theory[4,5] for low-spin d^5 ions. This afforded values of the axial distortion (Δ) which splits the t_2 shell into *e* + *b* and of the rhombic distortion (*V*) which splits *e* further into two non-degenerate components. The value of the orbital reduction factor *k* is also furnished by the analysis. A pair of optical transitions ν_1 and ν_2 among the Kramers doublets is predicted (Table 2) to lie at ≈4 200 and ≈5 700 cm^{-1} [the spin–orbit coupling constant λ of Ru^{III} is taken as 1 000 cm^{-1} (ref. 6)]. Two weak transitions are indeed observed at 4 600 and 6 500 cm^{-1} [Table 2, Figure 2(*b*)]. Strong *trans* binding of the phosphine ligands is believed to be responsible for the large and positive axial distortion which corresponds to the energy-level order $d_{xy} > d_{xz}, d_{yz}$ (unpaired electron in d_{xy}).

The quasi-reversible redox couple (1) is observable by cyclic

$$(1) + e \rightleftharpoons (1^-) \qquad (1)$$

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† Dichloro(*m*-chlorobenzoato-κ*O,O′*)bis(triphenylphosphine)ruthenium(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

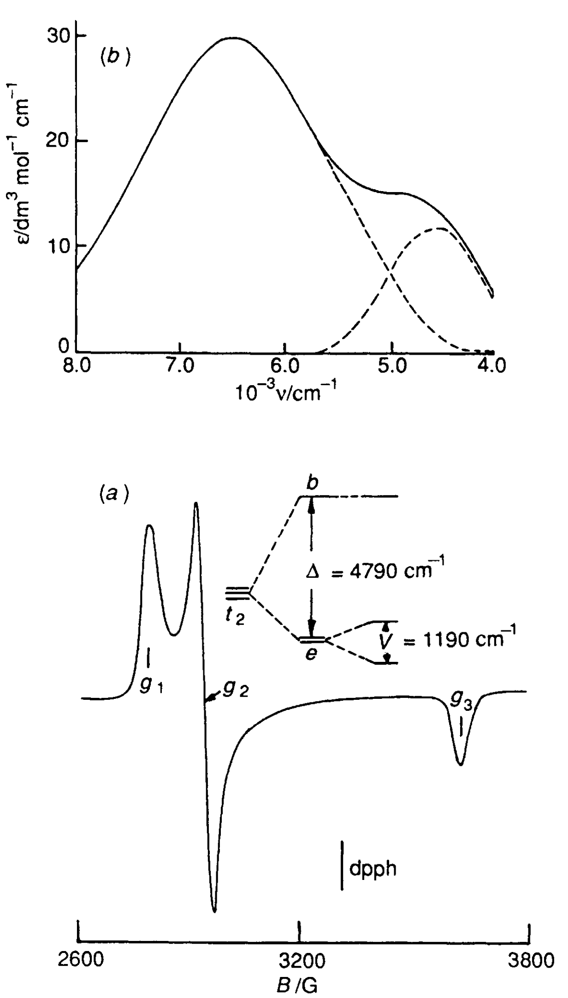


Figure 2. (*a*) *X*-Band e.s.r. spectrum and t_2 splittings of [Ru(PPh$_3$)$_2$(*m*-ClC$_6$H$_4$CO$_2$)Cl$_2$] in a dichloromethane–toluene (1:1) glass (77 K), dpph = diphenylpicrylhydrazyl. (*b*) Near-i.r. spectrum of the complex in dichloromethane. The broken curves represent Gaussian components.

Table 2. Assignments of e.s.r. *g* values, distortion parameters, and near-i.r. transitions for compound (**1**)[a]

g_x	−2.399	ν_1/λ	
g_y	−2.289	Calc.	4.223
g_z	1.850	Obs.[b]	4.6
k	0.883		
Δ/λ	4.786	ν_2/λ	
V/λ	−1.189	Calc.	5.695
		Obs.[b]	6.5

[a] Symbols have the same meaning as in the text. [b] Observed frequencies converted into ν/λ by setting λ = 1 000 cm^{-1}.

voltammetry near −0.4 V *vs.* saturated calomel electrode (s.c.e.) in dichloromethane solution. This stoicheiometry is supported by coulometric data. It is believed that (**1**$^-$) is the ruthenium(II) congener of (**1**). It is unstable and has eluded isolation. The low reduction potential of couple (1) explains the facile metal oxidation in the oxo-transfer reaction.

We can now examine the stoicheiometry and nature of the oxo-transfer reaction. For a given concentration of [Ru(PPh$_3$)$_3$Cl$_2$] the intensity of the PO stretch at 1 175 cm^{-1} increases with the concentration of *m*-ClC$_6$H$_4$CO$_3$H till the [metal]:[peracid] ratio reaches 1:1.5 (Figure 3). This is also consistent with the growth of (**1**) as a function of peracid concentration as ascertained spectrophotometrically (intensity of band at 1 540 nm) and voltammetrically [current height of the couple (1)]. The oxidation reaction is represented by equation (2).

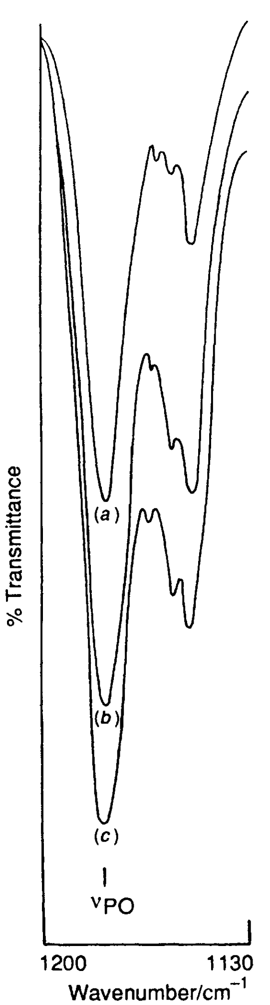


Figure 3. Solution i.r. spectra of mixtures of [Ru(PPh$_3$)$_3$Cl$_2$] and *m*-ClC$_6$H$_4$CO$_3$H in different concentration ratios in dichloromethane, [metal]:[peracid] (*a*) 1:0.5, (*b*) 1:1, and (*c*) 1:1.5

$$[\mathrm{Ru(PPh_3)_3Cl_2}] + 1.5m\text{-}\mathrm{ClC_6H_4CO_3H} \longrightarrow (\mathbf{1}) + \mathrm{OPPh_3} + 0.5m\text{-}\mathrm{ClC_6H_4CO_2H} + 0.5\mathrm{H_2O} \quad (2)$$

Oxidations of the phosphine and metal respectively consume 1 and 0.5 mol of the oxidant. Reaction (2) proceeds *via* an intermediate in which the peracid is bound to the metal centre. It is however necessary first to consider a plausible alternative.

The dissociation of [Ru(PPh$_3$)$_3$Cl$_2$] in solution, equation (3),

$$[\mathrm{Ru(PPh_3)_3Cl_2}] \rightleftharpoons [\mathrm{Ru(PPh_3)_2Cl_2}] + \mathrm{PPh_3} \quad (3)$$

is well documented.[2,3] On the other hand, i.r. data (ν_{PO}) reveal that PPh$_3$ is smoothly oxidised to OPPh$_3$ by *m*-ClC$_6$H$_4$CO$_3$H in dichloromethane, equation (4). Further, aliphatic and aromatic carboxylic acids are known[7] to convert [Ru(PPh$_3$)$_3$Cl$_2$] into [Ru(PPh$_3$)$_2$(RCO$_2$)Cl$_2$] (R = alkyl or aryl) and free PPh$_3$

$$\mathrm{PPh_3} + m\text{-}\mathrm{ClC_6H_4CO_3H} \longrightarrow \mathrm{OPPh_3} + m\text{-}\mathrm{ClC_6H_4CO_2H} \quad (4)$$

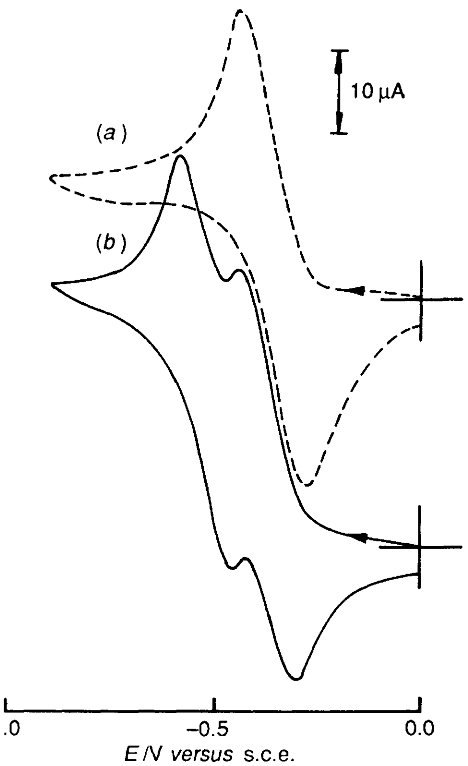


Figure 4. Cyclic voltammograms (298 K) in dichloromethane (0.1 mol dm^{-3} [NEt_4][ClO_4]) at a platinum electrode of: (*a*) the ruthenium(III) complex ($\approx 10^{-3}$ mol dm^{-3}) isolated from the oxidation of [$Ru(PPh_3)_3Cl_2$] by *m*-$ClC_6H_4CO_3H$ in the presence of $PhCO_2H$; (*b*) a 1 : 1 mixture of [$Ru(PPh_3)_2$(*m*-$ClC_6H_4CO_2)Cl_2$] and [$Ru(PPh_3)_2(PhCO_2)Cl_2$] ($\approx 10^{-3}$ mol dm^{-3})

(not $OPPh_3$) in hot benzene under aerobic conditions, equation (5). The *X*-ray structure of [$Ru(PPh_3)_2(PhCO_2)Cl_2$] prepared by this reaction is known;[8] it is isostructural with (**1**). Reaction (2) could therefore be the sum total of the reactions (3) and (4) followed by carboxylate chelation and metal oxidation (oxidant *m*-$ClC_6H_4CO_3H$) similar to reaction (5).

$$[Ru(PPh_3)_3Cl_2] + RCO_2H + 0.25O_2 \longrightarrow [Ru(PPh_3)_2(RCO_2)Cl_2] + 0.5H_2O + PPh_3 \quad (5)$$

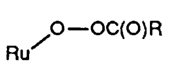
In terms of the above scheme the reaction of [$Ru(PPh_3)_3Cl_2$] with *m*-$ClC_6H_4CO_3H$ carried out in presence of the carboxylic acid RCO_2H ($R \neq$ *m*-ClC_6H_4) must produce both (**1**) and [$Ru(PPh_3)_2(RCO_2)$ Cl_2]. In practice this does *not* happen. For example when [$Ru(PPh_3)_3Cl_2$] is treated with *m*-$ClC_6H_4CO_3H$ (1.5 mol) in the presence of $PhCO_2H$ (1.5 mol), under conditions used for reaction (2), [$Ru(PPh_3)_2(PhCO_2)Cl_2$] is not formed; (**1**) is the sole ruthenium(III) product. The yield of (**1**) is also unaffected by the presence of $PhCO_2H$. The cyclic voltammogram of the complex isolated from the *m*-$ClC_6H_4CO_3H$ + $PhCO_2H$ reaction is compared with that of a mixture (prepared by simply mixing the two compounds) of (**1**) and [$Ru(PPh_3)_2(PhCO_2)Cl_2$] [prepared as in equation (5)] in Figure 4. The reduction potential of the [$Ru(PPh_3)_2(PhCO_2)Cl_2$] complex is more negative (−0.55 V *vs.* s.c.e. in dichloromethane) than that of (**1**) as expected. The response due to this complex is absent in the ruthenium(III) product obtained by *m*-$ClC_6H_4CO_3H$ oxidation in the presence of $PhCO_2H$.

Table 3. Atomic co-ordinates ($\times 10^4$) for [$Ru(PPh_3)_2$(*m*-$ClC_6H_4CO_2)Cl_2$]

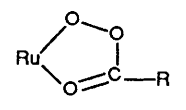
Atom	*x*	*y*	*z*
Ru	0	2 274(1)	7 500
P(1)	−1 009(1)	2 292(1)	6 438(1)
Cl(1)	712(1)	1 006(1)	6 999(1)
C(7)	−608(3)	2 263(6)	5 672(3)
C(1)	−1 729(3)	1 120(6)	6 315(3)
C(2)	−1 445(4)	−9(5)	6 388(3)
C(6)	−2 557(4)	1 293(6)	6 156(3)
C(5)	−3 068(4)	342(8)	6 079(3)
C(4)	−2 770(5)	−755(8)	6 161(3)
C(13)	−1 636(3)	3 593(5)	6 346(3)
C(20)	0	5 677(7)	7 500
C(19)	0	4 409(7)	7 500
C(15)	−2 229(5)	5 260(6)	5 740(4)
C(17)	−2 458(4)	4 841(7)	6 838(4)
C(22)	−607(4)	7 460(5)	7 684(3)
C(23)	0	8 037(7)	7 500
C(18)	−1 986(3)	3 870(6)	6 878(3)
C(14)	−1 764(4)	4 297(6)	5 778(3)
C(8)	−851(5)	1 466(7)	5 158(3)
C(12)	−27(4)	3 058(8)	5 614(3)
C(16)	−2 584(4)	5 537(7)	6 268(4)
C(11)	297(5)	3 044(9)	5 038(3)
C(10)	64(5)	2 237(9)	4 540(4)
C(21)	−605(4)	6 272(5)	7 695(3)
C(9)	−510(6)	1 458(9)	4 601(4)
C(3)	−1 969(5)	−929(7)	6 303(4)
O(1)	410(2)	3 839(3)	7 163(2)
Cl(2)	−1 348(2)	8 106(3)	7 869(2)

In the peracid oxidation of [$Ru(PPh_3)_3Cl_2$] the chelated carboxylate function in the product ruthenium(III) complex (**1**) is thus derived directly from the peracid and not indirectly *via* preformation of free carboxylic acid. A logical conclusion is that the *peracid binds to the metal centre before oxo transfer to* PPh_3 *occurs.* After formation of $OPPh_3$ the carboxylate moiety remains tightly bound to the metal centre thus blocking further oxo-transfer activity. Because of the low Ru^{III}–Ru^{II} reduction potential the metal in the carboxylate complex naturally appears in the trivalent state.

The present work does not reveal the binding mode of the peracid to the ruthenium centre in the active intermediate. However on the basis of currently available information[9] on peracid complexes of transition metals the monodentate (**2a**) and bidentate (**2b**) models are plausible (co-ordinated PPh_3 and Cl^- not shown). A species such as [$Ru(PPh_3)_2(RCO_3)Cl_2$] (R = aryl) is expected to react rapidly with PPh_3 [arising from equation (3)] affording $OPPh_3$ and (**1**).



(2a)



(2b)

Experimental

Starting Materials.—Commercial ruthenium trichloride (Arora Matthey, Calcutta), was purified by repeated evaporation to dryness with concentrated hydrochloric acid.[10] The complex [$Ru(PPh_3)_3Cl_2$] was prepared according to the reported procedure.[11] Commercial *m*-chloroperbenzoic acid was purified by a reported procedure and was used after determining the active oxygen content by iodometric titrations.[12,13] The purification of dichloromethane and the preparation of tetraethylammonium perchlorate for electrochemical work were done as before.[4] All other chemicals and solvents used for preparative work were of reagent grade and were used without further purification.

Physical Measurements.—U.v.–visible–near-i.r. spectra were recorded by using a Hitachi 330 spectrophotometer. Gaussian analysis of near-i.r. bands was performed as before.[4c,14] Infrared spectra were taken on a Perkin-Elmer 783 spectrophotometer. The magnetic susceptibility was measured on a PAR 155 vibrating-sample magnetometer. Electrochemical, e.s.r., and microanalytical measurements were done as before.[4]

Treatment of E.S.R. Data.—The details of the method used for assigning the observed e.s.r. signals can be found in our recent publications.[4] We note that a second solution also exists which is different from that chosen, having small values of Δ, V, ν_1, and ν_2. The near-i.r. results clearly eliminate this solution.

*Preparation of Dichloro(*m*-chlorobenzoato)bis(triphenylphosphine)ruthenium*(III), $[Ru(PPh_3)_2(m\text{-}ClC_6H_4CO_2)Cl_2]$.—Nitrogen gas was passed for 15 min through a dichloromethane (30 cm^3) solution of *m*-chloroperbenzoic acid (50 mg, 0.20 mmol). To this was added $[Ru(PPh_3)_3Cl_2]$ (100 mg, 0.10 mmol) and the mixture was stirred magnetically at room temperature for 0.5 h under a dinitrogen atmosphere. The colour of the solution turned to dark red-brown. The solvent was then evaporated under reduced pressure. The solid mass was collected by filtration and washed thoroughly with dilute NaOH solution and finally with water to remove excess of acids. The dried crude product was dissolved in a small volume of dichloromethane and was subjected to chromatography on a silica gel (BDH, 60—120 mesh) column (20 × 1 cm). With benzene a deep red-brown band was rapidly eluted and was collected. The complex (**1**) was obtained from the eluant in crystalline form by slow evaporation (yield *ca.* 90%) (Found: C, 60.70; H, 4.05. Calc. for $C_{43}H_{34}Cl_3O_2P_2Ru$: C, 60.60; H, 4.00%). Electronic spectral data in dichloromethane [$\lambda_{max.}$/nm(ε/dm^3 mol^{-1} cm^{-1})]: 2 180(12), 1 540(30), 540(1 500), and 270(22 800).

The above reaction was also carried out by adding benzoic acid (26 mg, 0.20 mmol) along with *m*-chloroperbenzoic acid. Complex (**1**) was again isolated, in 90% yield.

The complex $[Ru(PPh_3)_2(PhCO_2)Cl_2]$ was prepared according to a reported method.[7]

X-Ray Structure Determination.—Single crystals were grown by slow diffusion of a dichloromethane solution of complex (**1**) into hexane.

Crystal data. $C_{43}H_{34}Cl_3O_2P_2Ru$, $M = 852.1$, monoclinic, space group $C2/c$, $a = 17.148(8)$, $b = 11.633(6)$, $c = 20.094(8)$ Å, $\beta = 103.61(3)°$, $U = 3\,896(3)$ Å^3 (by least-squares refinement of diffractometer angles for 25 automatically centred reflections), $Z = 4$, $D_c = 1.451$ g cm^{-3}, red prismatic (0.22 × 0.12 × 0.18 mm), $\mu(\text{Mo-}K_\alpha) = 7.17$ cm^{-1}, $\lambda = 0.710\,73$ Å, $F(000) = 1\,728$.

Data collection and processing. Nicolet R3m/V diffractometer, ω-scan method ($2 \leqslant 2\theta \leqslant 55°$), graphite-monochromated Mo-K_α radiation; 4 481 independent measured reflections, 2 901 observed [$F > 6\sigma(F)$], corrected for Lorentz and polarisation factors; semiempirical absorption correction (transmission 0.8095—0.8784). Three standard reflections monitored showed no significant variations.

Solution and refinement. The structure was solved by direct methods and subsequently refined by full-matrix least-squares procedures. All non-hydrogen atoms except the disordered Cl(2) atom were made anisotropic. Hydrogen atoms were included in calculated positions with U values (isotropic thermal parameters) of 0.08 Å^2. The final residuals R and R' were 0.052 and 0.063 respectively. The function minimised was $\Sigma w(|F| - |F_c|)^2$ with the weight $w = 1/[\sigma^2(F) + 0.0003F^2]$. The maximum and minimum residual electron densities in the final ΔF map were 1.13 and 0.00 e Å^{-3} respectively. Positional parameters for the non-hydrogen atoms are collected in Table 3. Computations were carried out on a MicroVAX II computer using the SHELXTL-PLUS program system.[15]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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