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The Structure of Rhenium Pentacarbonyl Chloride,* $Re(CO)_5Cl$

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Abstract. $M_r = 361\cdot7$, orthorhombic, *Pnma*, $a = 11\cdot686\ (2)$, $b = 11\cdot661\ (3)$, $c = 6\cdot069\ (2)$ Å, $V = 827\cdot1\ (6)$ Å^3, $Z = 4$, $D_x = 1\cdot444$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot7093$ Å, $\mu(\text{Mo } K\alpha) = 8\cdot816$ cm^{-1}, $F(000) = 648\cdot0$, $T = 296$ K, $R = 0\cdot022$ for 600 ($I > 3\sigma$) reflections. The molecules are discrete monomeric units having required mirror symmetry but non-crystallographic $4mm$ symmetry. Important distances are: Re—Cl 2·515 (2) Å; Re—C(*cis* to Cl) 2·005 (7) and 2·031 (8) Å; Re—C(*trans*) 1·912 (14) Å.

Introduction. The pentacarbonyl halides, $M(CO)_5X$, with M = Mn, Tc and Re and X = Cl, Br, I, have long been of interest for the study of bonding in metal carbonyls and their spectra have been extensively investigated (Wozniak & Sheline, 1972; Ceasar, Milazzo, Cihonski & Levenson, 1974; Hall, 1975; Wrighton, Morse, Gray & Ottesen, 1976; Behrens, 1978). In view of this it is surprising that their structures have not been studied much. Only that of $MnCl(CO)_5$ has been determined accurately and reported (Greene & Bryan, 1971). That of $Re(CO)_5I$ has also been determined (Russell & Ruff, 1982). In the course of some chemical studies we found ourselves with a very nicely diffracting crystal of $Re(CO)_5Cl$ mounted and aligned and we considered it worth while to carry through the structure determination.

Experimental. Material from reaction of $[n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ in acetonitrile with CO at 9·6 GPa and 353 K, crystals taken from cooled reaction vessel; well-shaped crystal 0·2 × 0·2 × 0·3 mm, Enraf–Nonius CAD-4 automated diffractometer, graphite monochromator, automatic search routine located and centered 25 intense reflections, $19 < 2\theta < 38°$, from which unit-cell dimensions derived; systematic absences $0kl$, $k + l \neq 2n$, and $hk0$, $h \neq 2n$, indicated *Pnma* (No. 62) or $Pna2_1$ (No. 33), *Pnma* chosen since crystals are isomorphous with $Mn(CO)_5Cl$ and $MnBr(CO)_5$, for which the centric space group was confirmed by measurements of the orientation of the field-gradient tensor for the ^{55}Mn and halogen nuclei (Greene & Bryan, 1971); 814 unique reflections, $0 < 2\theta < 50°$, 600 ($I > 3\sigma$) collected, $0 < h < 12$, $0 < k < 13$, $0 < l < 7$, three intensity standards checked every hour of exposure: no decay, random fluctuations of *ca* 2% during collection; empirical absorption correction, ψ scan for each of the nine reflections near $\chi = 90°$ measured, each reflection measured at 10° intervals from $\psi = 0$ to $\psi = 360°$, normalized transmission factors 1·00 to 0·79; approximate positions of the eight independent atoms taken from the isotypic $Mn(CO)_5Cl$ structure, F magnitudes for refinement of positions, anisotropic temperature factors, scale factor and secondary extinction coefficient; $R = 0\cdot022$, $R_w = 0\cdot035$, $w = 1/\sigma^2(|F_o|)$, $S = 1\cdot19$; $\Delta_{\max}/\sigma = 0\cdot01$, max. $\Delta\rho$ excursion in final difference Fourier 0·736 e Å^{-3}, refined secondary extinction coefficient $4\cdot3\ (2) \times 10^{-7}$; atomic scattering factors and f', f'' values from *International Tables for X-ray Crystallography*.† All calculations performed with the Enraf–Nonius *Structure Determination Package* on the PDP 11/60 computer at B. A. Frenz and Associates, Inc., College Station, Texas.

Discussion. The positional parameters and equivalent isotropic thermal parameters are given in Table 1. The structure of the molecule is given in Fig. 1, together with the atom numbering used.

The molecular structure (Fig. 1) is qualitatively as expected. The interatomic distances and angles are listed in Table 2. The molecule has an essentially octahedral distribution of ligands about the central rhenium atom; the Cl—Re—C(1)—O(1) chain is strictly linear while the equatorial CO groups are bent *ca* 1·0° away from the axial CO group and toward the Cl atom.

The bond distances that may be of interest in connection with questions of bonding and spectroscopic analysis are the Re—C and C—O distances. The two equatorial Re—C distances, 2·005 (7) and 2·031 (8) Å, have a mean value of 2·018 (13) Å. The difference between them, 0·026 (11) Å, is not significant at the 3σ level. However, the differences between each of them

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* Pentacarbonylchlororhenium.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38726 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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and the axial Re—C distance, 0·119 (15) and 0·083 (15) Å, are statistically significant. The mean shortening of the Re—C axial bond relative to the Re—C equatorial bond lengths, 0·10 (2) Å, is in accord with the generally accepted concept that there is more $Md\pi \rightarrow CO\pi^*$ bonding to the axial CO group than to one of the equatorial CO groups (Hall, 1975).

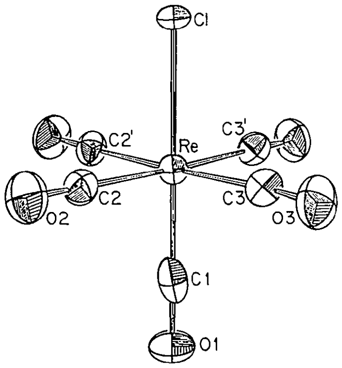

Fig. 1. A view of the molecule showing the atom-labeling scheme.

Table 1. *Positional parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B (Å^2)
Re	0·37553 (4)	0·250	0·44946 (6)	1·999 (8)
Cl	0·2478 (2)	0·250	0·1160 (4)	2·15 (4)
O(1)	0·5329 (7)	0·250	0·861 (2)	4·5 (2)
O(2)	0·2204 (4)	0·4414 (4)	0·655 (1)	4·2 (1)
O(3)	0·5227 (5)	0·4442 (5)	0·236 (1)	4·2 (1)
C(1)	0·473 (1)	0·250	0·703 (2)	3·4 (2)
C(2)	0·2745 (6)	0·3726 (7)	0·586 (1)	2·6 (2)
C(3)	0·4704 (6)	0·3721 (6)	0·305 (1)	2·4 (1)

Table 2. *Bond distances* (Å) *and angles* (°) *in* $Re(CO)_5Cl$ *with e.s.d.'s in parentheses*

Re—C(1)	1·912 (14)	C(1)—O(1)	1·189 (15), 1·240,* 1·279†
Re—C(2)	2·031 (8)	C(2)—O(2)	1·103 (8), 1·145, 1·204
Re—C(3)	2·005 (7)	C(3)—O(3)	1·122 (8), 1·159, 1·214
Re—Cl	2·515 (2)		

Cl—Re—C(1)	179·9 (3)	C(2)—Re—C(2′)	89·5 (4)
—C(2)	89·0 (2)	—C(3)	177·7 (3)
—C(3)	88·7 (2)	C(3)—Re—C(3′)	90·5 (4)
C(1)—Re—C(2)	91·0 (3)	Re—C(1)—O(1)	179·7 (9)
—C(3)	91·3 (3)	Re—C(2)—O(2)	177·9 (7)
		Re—C(3)—O(3)	175·9 (6)

* Bond lengths corrected by riding model (O riding on C).

† Bond lengths corrected assuming independent thermal motion for C and O.

Table 3. *Comparison of some bond lengths* (Å) *for* $Re(CO)_5Cl$, $Mn(CO)_5Cl$ *and* $Re(CO)_5I$

	$Re(CO)_5Cl$	$Mn(CO)_5Cl$	$Re(CO)_5I$
M—C(ax)	1·912 (14)	1·807 (9)	1·96 (3)
Mean M—C(eq)	2·018 (13)	1·892 (4)	2·021 (14)
Δ(eq—ax)	0·10 (2)	0·085 (10)	0·06 (3)
M—X(X=Cl, I)	2·515 (2)	2·367 (4)	2·779 (2)
$d(M-X)-r(X)$*	1·53	1·38	1·45
C—O(ax)	1·189 (15)	1·122 (11)	1·149 (16)
Mean C—O(eq)	1·112 (9)	1·109 (6)	1·10 (3)
Δ(ax—eq)	0·077 (16)	0·013 (12)	0·05 (4)

* Using r(Cl) = 0·99 Å and r(I) = 1·33 Å.

On the basis of the $Md\pi \rightarrow CO\pi^*$ explanation for the difference in Re—C bond lengths, it would follow that the CO bond should be longer in the axial CO group than in the equatorial ones. This, too, is clearly shown. The two equatorial CO bonds do not differ significantly in length, 0·019 (11) Å, and have a mean value of 1·112 (9) Å. This is significantly less, by 0·077 (16) Å, than the axial CO bond length, where we use values uncorrected for thermal motion. Corrected CO bond lengths, also given in Table 3, show virtually the same relationship.

Within the rather large experimental errors, the pattern of bond lengths for $Re(CO)_5Cl$ is consistent with those in $Mn(CO)_5Cl$ and $Re(CO)_5I$, as shown by the figures collected in Table 3, although the trends are more clearly defined here. The difference between the two values of the Re radius obtained from Re—Cl and Re—I bonds is such as to suggest that the Re—I bond may have some π character.

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