Electron Paramagnetic Resonance Spectra of Rhenium Tetrachloride Oxide and some of its Adducts

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X-Band e.p.r. spectra of $Re(O)Cl_4$, $[Re(O)Cl_4(NCMe)]$, $[Re(O)Cl_4(OPCl_3)]$, and $[Ph_4As][Re(O)Cl_5]$ have been recorded at 77 K and are analysed in detail. The metal-ion spin–orbit coupling constant and the parameter $P = 2{\cdot}002 g_{Re}\beta_e\beta_N\langle\psi|r^{-3}|\psi\rangle$ have been estimated to be *ca.* 2 400 and 0·033 cm^{-1} respectively. Spin-Hamiltonian parameters are listed for each substance and are equated to the atomic-orbital coefficients in some of the molecular orbitals involved in bonding in these molecules. The unpaired electron lies in the metal-ion $5d_{xy}$ orbital and is strongly delocalised (33%) on to the chloride ligands. $g_{\parallel}$ Is greater than $g_{\perp}$ and this is shown to be essentially due to charge-transfer mixing through spin–orbit coupling at the chlorine atoms. Changes in the spin-Hamiltonian parameters when a sixth ligand is added to $Re(O)Cl_4$ are accounted for. Hückel LCAO molecular-orbital calculations on $Re(O)Cl_4$ appear to give a reasonable description of its ground state.

DETAILED investigations of electronic and e.p.r. spectra, and of the relations connecting these branches of spectroscopy with bonding, have been made for d^1 complexes derived from the oxo-ions of vanadium, niobium, chromium, molybdenum, and tungsten.[1,2] Much less information is available for corresponding complexes of the sexivalent states of the Group 7A elements. In this context, in the case of rhenium(VI), e.p.r. absorption has only been observed in magnetically concentrated samples containing the rhenate ion,[3] $[ReO_4]^{2-}$, and in rhenium tetrachloride oxide and some of its adducts,[4,5] but detailed analyses of these observ-

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[1] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, and refs. therein.

[2] J. R. Shock and M. T. Rogers, *J. Chem. Phys.*, 1973, **58**, 3356.

[3] A. Carrington, D. J. E. Ingram, and M. C. R. Symons, *J. Chem. Soc.*, 1956, 4710.

[4] N. S. Garif'yanov, *Zhur. eksp. teor. Fiz.*, 1963, **45**, 1819; *Soviet Phys. JETP* (*English Translation*), 1964, **18**, 1246.

[5] N. S. Garif'yanov, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1968, 1902.

ations have not been reported. Here we describe e.p.r. spectra obtained from glasses containing rhenium tetrachloride oxide or its adducts, and discuss the conclusions that can be drawn about electron distributions within these complexes when such spectra are analysed in detail.

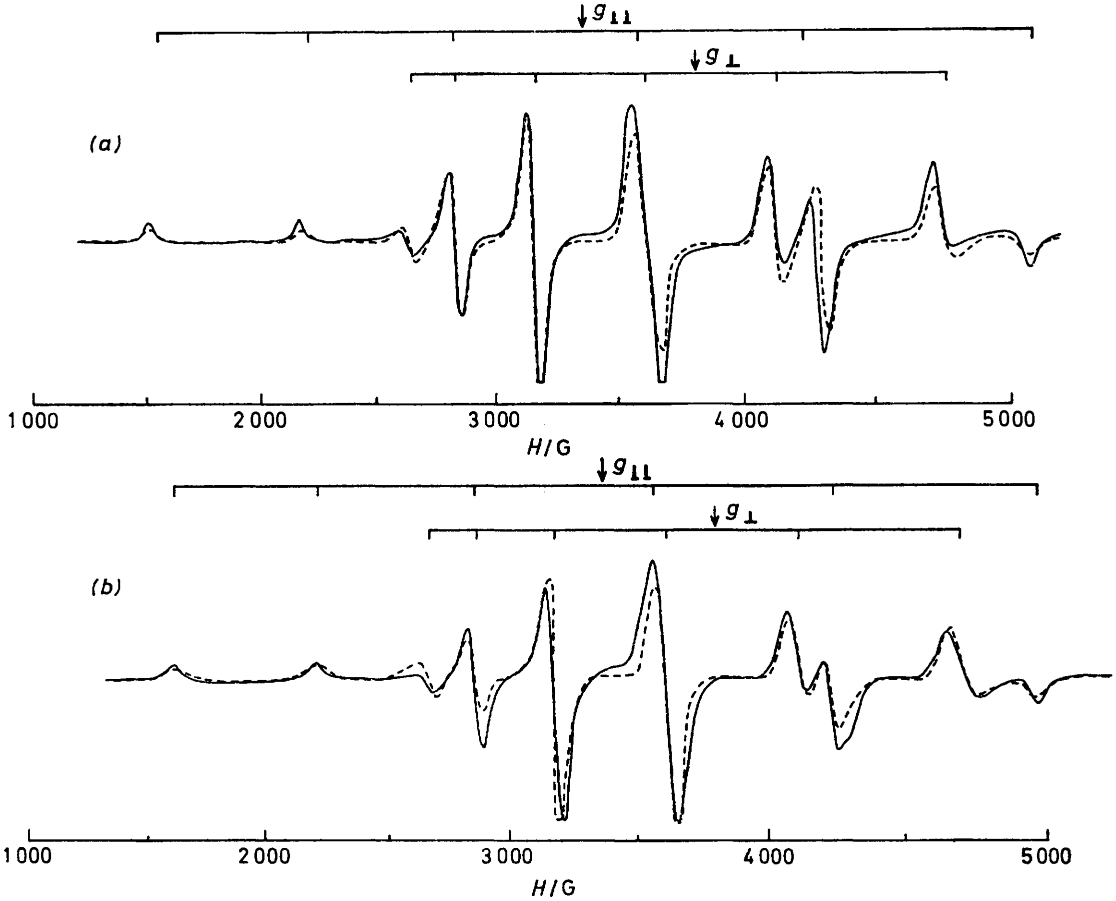

FIGURE 1 Observed (——) and calculated (– – –) e.p.r. spectra of 10^{-3}M solutions of $Re(O)Cl_4$, (*a*), and $[Ph_4As][Re(O)Cl_5]$, (*b*), in dioxan at 77 K

EXPERIMENTAL

Tetrachloro-oxorhenium(VI), $Re(O)Cl_4$, was prepared[6] by treating rhenium metal with purified sulphuryl chloride inside an evacuated sealed tube held at 340 °C for 3 d. After allowing the reaction mixture to cool to room temperature, excess of SO_2Cl_2 was distilled off under vacuum at 273 K and volatile $Re(O)Cl_4$ was separated from unreacted rhenium by subliming it *in vacuo* at 290 K. The resublimed $Re(O)Cl_4$ was then used to prepare[7-9] the ' adducts ' $[Re(O)Cl_4(NCMe)]$, $[Re(O)Cl_4(OPCl_3)]$, and $[Ph_4As][Re(O)Cl_5]$.

Visible–u.v. absorption spectra of solutions of each of these complexes were recorded on Unicam SP 700C and 800 spectrophotometers, using matched 1 cm quartz cells; $\tilde{\nu}_{max.}$ values are listed in Table 1. Thoroughly outgassed 10^{-3}M solutions of each complex were also examined at 290 and 77 K in a Decca X-3 e.p.r. spectrometer combined with a Newport Instruments 11 in magnet system, all resonant fields being calibrated by standard proton magnetic resonance techniques.* Typical derivative spectra are shown in Figure 1.

TABLE 1

Band maxima (cm^{-1}) in the visible–u.v. absorption spectra of rhenium tetrachloride oxide and some of its ' adducts '

Complex	Solvent	*d*←*d* Transitions	Metal ion←chloride charge transfer	Other bands
$Re(O)Cl_4$	CCl_4	12 800 17 500	23 800	32 000
	Dioxan	12 600, 17 400	23 700	32 000
$[Re(O)Cl_4(NCMe)]$	Nitromethane	12 500, 17 200	23 600	25 000, 31 200
$[Re(O)Cl_4(OPCl_3)]$	$POCl_3$	12 400, 17 200	23 600	31 500
$[Ph_4As][Re(O)Cl_5]$	Dioxan	12 000, 17 000	23 600	29 000

Analysis of E.p.r. Spectra.—These spectra were all characteristic of one unpaired electron moving in an axially

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* 1M = 1 mol dm^{-3}.

[6] D. A. Edwards and A. A. Woolf, *J. Chem. Soc.* (*A*), 1966, 91.

[7] D. A. Edwards and R. T. Ward, *J.C.S. Dalton*, 1972, 89.

[8] A. Guest and C. J. L. Lock, *Canad. J. Chem.*, 1971, **49**, 603.

[9] B. R. Brisdon and D. A. Edwards, *Inorg. Chem.*, 1968, **7**, 1898.

symmetric orbital, and so the spin Hamiltonian has the form (1). The nuclear spin quantum numbers, I, for

$$\mathscr{H} = g_{\parallel}\beta H_zS_z + g_{\perp}\beta(H_xS_x + H_yS_y) + AS_zI_z + B(S_xI_x + S_yI_y) + Q'[I_z^2 - \tfrac{1}{3}I(I+1)] \quad (1)$$

^{185}Re (natural abundance 37·07%) and ^{187}Re (natural abundance 62·93%) are both $\frac{5}{2}$. The magnetic dipole moments of these isotopes differ by only 1% and, since we were not able to resolve any rhenium isotopic fine structure, all absorption spectra were analysed by fitting them to curves of the form (2) where S_{m_I} is a Kneubühl function [10]

$$\mathrm{f}(H') = (2\pi)^{-\frac{1}{2}} \sum_{m_I=-\frac{5}{2}}^{m_I=+\frac{5}{2}} \int_{H=-\infty}^{+\infty} \beta^{-1}S_{m_I}(H)\exp[-(H'-H)^2(2\beta^2)^{-1}]\mathrm{d}H \quad (2)$$

and β an appropriate Gaussian broadening factor. The forms of the contributions to the polycrystalline spectrum originating from complexes in which $m_I = \frac{3}{2}$ puzzled us until it was realised that for these species the relative magnitudes of the spin-Hamiltonian parameters are such that the resonant field values do not vary smoothly as the orientations of these molecules in the applied field are altered. As already reported for some copper(II) complexes,[11,12] discontinuities therefore appear in the Kneubühl functions $S_{m_I}(H)$, ($m_I = \frac{3}{2}$), in addition to those that are observed when the magnetic field lies along the principal axes directions. For Re(O)Cl$_4$ in dioxan, $S_{m_I}(H)$, ($m_I = \frac{3}{2}$), is shown in Figure 2.

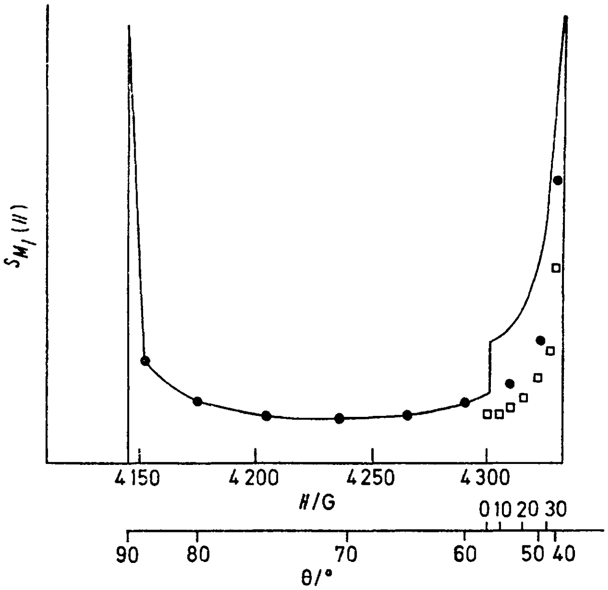

FIGURE 2 The Kneubühl curve $S_{m_I}(H)$ for Re(O)Cl$_4$ when $m_I = \frac{3}{2}$: θ is the angle between the applied magnetic field and the molecular C_4 axis, and H is the corresponding resonant field; (□), contributions from molecules for which 0° ⩽ θ ⩽ 35°; (●), contributions for which 40° ⩽ θ ⩽ 90°

RESULTS AND DISCUSSION

Iterative computation of the e.p.r. spectra led to the spin-Hamiltonian parameters listed in Table 2, and some derivative spectra computed from these parameters are shown in Figure 1. The quantity $g_{\parallel}$ was greater than $g_{\perp}$, a situation which is unusual in d^1 species subjected to a tetragonal ligand field, and it therefore follows [13-15] that charge transfer from chloride ligands to the central metal ion must be considered in accounting for the spin-Hamiltonian parameters. The analyses showed that A and B in equation (1) must have the same sign, and the theoretical treatment which follows shows that this is negative. Since 'forbidden' transitions were not observed, the sign of Q' could not be obtained from these spectra.

X-Ray analysis [16] of the crystal structure of Re(O)Cl$_4$ shows that the molecule is a square pyramid with C_{4v} symmetry, the four chlorine atoms forming the base of the pyramid and the rhenium atom being raised slightly out of this plane. Using the co-ordinate system shown in Figure 3, molecular orbitals (m.o.s) in this complex may be described in terms of basis orbitals derived from (*i*) the 5*d*, 6*s*, and 6*p* orbitals of the rhenium ion, (*ii*) the chloride ion 3*s* and 3*p* orbitals, and (*iii*) the oxide ion 2*s* and 2*p* orbitals. In the C_{4v} group, these 29 basis orbitals can themselves be grouped as shown in Table 3 and Hückel calculations carried out on linear combinations of orbitals belonging to the same representation then led to the energies and forms of m.o.s given in the Appendix and to the energy-level scheme shown in Figure 4. These calculations also showed that the rhenium-ion configuration is Re ($\cdots 5d^{4\cdot880}6s^{0\cdot714}6p^{0\cdot939}$) and that the resultant charges in units of the proton charge are distributed as follows:

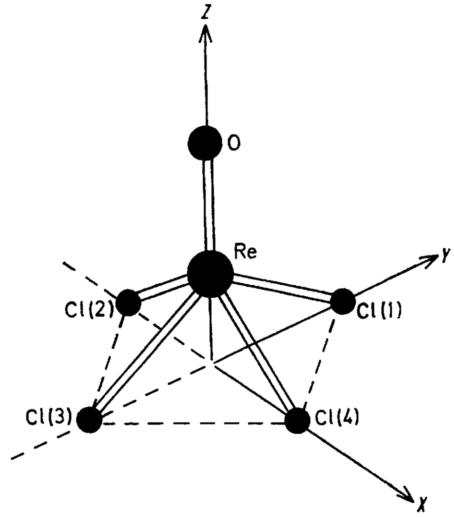

FIGURE 3

Atom	Re	0	Cl
Charge	+0·476	−0·431	−0·011

The unpaired electron is in the antibonding B_2 orbital numbered (21) in Figure 4 and given an asterisk in

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[10] F. K. Kneubühl, *J. Chem. Phys.*, 1960, **33**, 1074.

[11] R. Neiman and D. Kivelson, *J. Chem. Phys.*, 1961, **35**, 156.

[12] H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, 1962, **36**, 3221.

[13] H. Kon and N. E. Sharpless, *J. Chem. Phys.*, 1965, **42**, 906.

[14] K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, 1965, **42**, 1019.

[15] H. Kon and N. E. Sharpless, *J. Phys. Chem.*, 1966, **70**, 105.

[16] A. J. Edwards, *J.C.S. Dalton*, 1972, 582.

TABLE 2

Spin-Hamiltonian parameters for Re(O)Cl$_4$ and its ' adducts ' at 77 K. All hyperfine-tensor components are in units of cm^{-1}. Limits of error for $g_{\parallel}$, $g_{\perp}$, and $\langle g \rangle$ are $\pm 0{\cdot}004$, for A, B, and $\langle a \rangle$ $\pm 0{\cdot}0004$ cm^{-1}, and for Q' $\pm 0{\cdot}0001$ cm^{-1}

Complex	Solvent	$g_{\parallel}$	$g_{\perp}$	A	B	Q'	$\langle g \rangle$	$\langle a \rangle$
Re(O)Cl$_4$	CCl$_4$	1·974	1·708	−0·0636	−0·0323	±0·0020	1·796	−0·0419
Re(O)Cl$_4$	Dioxan	1·968	1·720	−0·0630	−0·0320	±0·0020	1·803	−0·0417
[Re(O)Cl$_4$(NCMe)]	Nitromethane	1·970	1·732	−0·0621	−0·0315	±0·0020	1·811	−0·0406
[Re(O)Cl$_4$(OPCl$_3$)]	POCl$_3$	1·970	1·734	−0·0616	−0·0308	±0·0019	1·813	−0·0397
[Ph$_4$As][Re(O)Cl$_5$]	Dioxan	1·975	1·740	−0·0609	−0·0305	±0·0020	1·818	−0·0392

TABLE 3

	A_1	A_2
Rhenium-ion orbitals	$6s$, $6p_z$, $5d_{z^2}$	—
Chloride-ion orbitals	$3s[A_1] = \frac{1}{2}[3s_1 + 3s_2 + 3s_3 + 3s_4]$ $3p_z[A_1] = \frac{1}{2}[3p_{z_1} + 3p_{z_2} + 3p_{z_3} + 3p_{z_4}]$ $3p_\sigma[A_1] = \frac{1}{2}[-3p_{y_1} + 3p_{x_2} + 3p_{y_3} - 3p_{x_4}]$	$3p[A_2] = \frac{1}{2}[3p_{x_1} + 3p_{y_2} - 3p_{x_3} - 3p_{y_4}]$
Oxide-ion orbitals	$2s$, $2p_z$	—
	B_1	B_2
Rhenium-ion orbitals	$5d_{x^2-y^2}$	$5d_{xy}$
Chloride-ion orbitals	$3s[B_1] = \frac{1}{2}[3s_1 - 3s_2 + 3s_3 - 3s_4]$ $3p_z[B_1] = \frac{1}{2}[3p_{z_1} - 3p_{z_2} + 3p_{z_3} - 3p_{z_4}]$ $3p_\sigma[B_1] = \frac{1}{2}[3p_{y_1} + 3p_{x_2} - 3p_{y_3} - 3p_{x_4}]$	$3p[B_2] = \frac{1}{2}[3p_{x_1} - 3p_{y_2} - 3p_{x_3} + 3p_{y_4}]$
Oxide-ion orbitals	—	—
	E	
Rhenium-ion orbitals	$6p_x$, $6p_y$, $5d_{xz}$, $5d_{yz}$	
Chloride-ion orbitals	$3s_1[E] = 2^{-\frac{1}{2}}[3s_1 - 3s_3]$ $3s_2[E] = 2^{-\frac{1}{2}}[3s_2 - 3s_4]$ $3p_{xz}[E] = 2^{-\frac{1}{2}}[3p_{z_2} - 3p_{z_4}]$ $3p_{yz}[E] = 2^{-\frac{1}{2}}[3p_{z_1} - 3p_{z_3}]$ $3p_{\pi x}[E] = 2^{-\frac{1}{2}}[3p_{x_1} + 3p_{x_3}]$ $3p_{\sigma x}[E] = 2^{-\frac{1}{2}}[3p_{x_2} + 3p_{x_4}]$ $3p_{\sigma y}[E] = 2^{-\frac{1}{2}}[3p_{y_1} + 3p_{y_3}]$ $3p_{\pi y}[E] = 2^{-\frac{1}{2}}[3p_{y_2} + 3p_{y_4}]$	
Oxide-ion orbitals	$2p_x$, $2p_y$	

Table 5. The methods outlined in the Appendix also show that the spin–orbit coupling constants ξ_{Re} and ξ_{Cl} for rhenium and chlorine in Re(O)Cl$_4$ are 2 400 and 587 cm^{-1} respectively, and that the value of $P = 2{\cdot}002 g_{Re}\beta_e\beta_N\langle\psi|r^{-3}|\psi\rangle$ for the orbital containing the unpaired electron is 0·033 cm^{-1}.

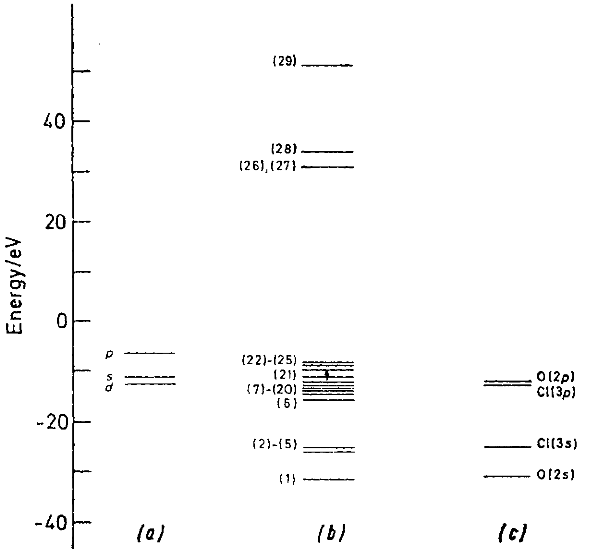

FIGURE 4 M.o. energy-level diagram for Re(O)Cl$_4$; (*a*), metal-ion orbitals; (*b*), m.o.s; and (*c*), ligand orbitals

If spin–orbit coupling is ignored then the unpaired electron is located in an antibonding orbital

$$\psi^*(B_2) = \beta_2 d_{xy} + \beta_2^{(1)} 3p[B_2] \tag{3}$$

but when spin–orbit interactions are considered then mixing of excited states into the ground state of the molecule must be taken into account. These excited states are produced either by promoting the unpaired electron into empty antibonding orbitals of B_1 or E symmetry which lie immediately above $\psi^*(B_2)$ in Figure 4, or by promoting an electron from the filled bonding orbitals of B_1 or E symmetry into $\psi^*(B_2)$: only mixing of the m.o.s numbered (7), (22), (23), and (24) need be considered in this context. M.o. calculations show that in Re(O)Cl$_4$ ligand *s* orbitals contribute little to the magnetically important m.o.s so that these may be written in the forms (4). Mixing of the orbitals

$$\begin{aligned}\psi(B_1) &= \beta_1 d_{x^2-y^2} + \beta_1^{(1)} 3p_\sigma[B_1] + \beta_1^{(11)} 3p_z[B_1]\\ \psi(E_{xz}) &= e_{xz} d_{xz} + e_{xz}^{(1)} 3p_{xz}[E] + e_{xz}^{(11)} 3p_{\sigma x}[E] +\\ &\qquad e_{xz}^{(111)} 2p_x[E]\\ \psi(E_{yz}) &= e_{yz} d_{yz} + e_{yz}^{(1)} 3p_{yz}[E] + e_{yz}^{(11)} 3p_{\sigma y}[E] +\\ &\qquad e_{yz}^{(111)} 2p_y[E]\end{aligned} \tag{4}$$

(3) and (4) under the influence of spin–orbit coupling at the rhenium and chlorine atoms, together with Zeeman interactions and hyperfine interactions, then leads to the relations (5)—(9) for the principal components of the *g* and hyperfine-coupling tensors.[17,14]

$$g_{\parallel} = 2{\cdot}0023 \pm \sum \frac{2\xi_{Re}}{|\Delta E(B_1)|}[2\beta_1\beta_2 - \beta_1^{(1)}\beta_2^{(1)}V_{Cl}][2\beta_1\beta_2 - \beta_1^{(1)}\beta_2^{(1)}] \tag{5}$$

In equation (5) orbitals (7) and (24) contribute to the sum, and the positive sign refers to orbital (7) and the negative sign to orbital (24); $V_{Cl} = (\xi_{Cl}/\xi_{Re})$. In

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[17] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 1958, **29**, 31.

equation (6) the second term is due to mixing of orbital (22). $g_{\parallel}$ is greater than $g_{\perp}$ in Re(O)Cl$_4$ and therefore in

$$g_{\perp} = 2{\cdot}0023 - \frac{2\xi_{\mathrm{Re}}}{|\Delta E(E)|}\,[\beta_2 e_{xz} + \beta_2{}^{(1)} e_{xz}{}^{(1)}]^2 \qquad (6)$$

equation (5) we have allowed for mixing of states obtained by exciting bonding electrons but have not considered similar effects in equation (6). In equation (7) orbitals (7) and (24) contribute to the sum, the

$$A = P\left[-\kappa - \frac{4}{7}\beta_2{}^2 \pm 8\xi_{\mathrm{Re}}\beta_2{}^2\left(\sum\frac{\beta_1{}^2}{|\Delta E(B_1)|}\right) - \frac{6}{7}\frac{\xi_{\mathrm{Re}}\beta_2{}^2 e_{xz}{}^2}{|\Delta E(E)|}\right] \qquad (7)$$

positive sign referring to orbital (7) and the negative sign to orbital (24); orbital (22) contributes to the last term.

$$B = P\left[-\kappa + \frac{2}{7}\beta_2{}^2 - \frac{11}{7}\frac{\xi_{\mathrm{Re}}\beta_2{}^2 e^2{}_{xz}}{|\Delta E(E)|}\right] \qquad (8)$$

$$\langle a\rangle = -P\kappa - (2{\cdot}0023 - \langle g\rangle)P \qquad (9)$$

The relative intensities, effects of solvents on the positions of the maxima, m.o. calculations, and consistency with the e.p.r. data, all indicate that the band maxima in the visible–u.v. absorption spectra listed in Table 1 should be assigned to the transitions listed below.

Band maximum (cm^{-1})	Transition	M.o. levels involved
12 800	$\psi^*(E) \leftarrow \psi^*(B_2)$	(22), (21)
17 500	$\psi^*(B_1) \leftarrow \psi^*(B_2)$	(24), (21)
23 800	$\psi^*(B_2) \leftarrow \psi(B_1)$	(21), (7)

These assignments enable values of κ and the magnitudes of some of the m.o. coefficients for orbitals (21)—(24) to be estimated, and parameters obtained in this way for Re(O)Cl$_4$ and for its ' adducts ' are listed in Table 4. In each case the unpaired electron is in an antibonding m.o. compounded out of the $5d_{xy}$ orbital of rhenium and chlorine $3p_x$ and $3p_y$ orbitals, and it is *ca.* 33% delocalised on to the chlorine atoms. We were not able to resolve chlorine hyperfine coupling in these spectra, but linewidth measurements are consistent with *ca.* 21% delocalisation in this orbital.

TABLE 4

κ Values and m.o. coefficients for Re(O)Cl$_4$ and some of its ' adducts '

M.o.	κ	(21) $\lvert\beta_2\rvert$	(24) $\lvert\beta_1\rvert$	(22) $\lvert e_{xz}\rvert$
Re(O)Cl$_4$ in CCl$_4$	1·064	0·820	0·780	0·920
Re(O)Cl$_4$ in dioxan	1·063	0·814	0·782	0·913
[Re(O)Cl$_4$(NCMe)]	1·041	0·809	0·781	0·907
[Re(O)Cl$_4$(OPCl$_3$)]	1·012	0·808	0·781	0·906
[Ph$_4$As][Re(O)Cl$_5$]	1·004	0·805	0·780	0·903

Addition of an extra ligand to the sixth co-ordination position of Re(O)Cl$_4$ has no measurable effect on σ-bonding to the metal-ion $5d_{x^2-y^2}$ orbital, and it has little effect on the transition energies $|\Delta E(B_1)|$. Hence co-ordinating a sixth ligand does not alter $g_{\parallel}$. On the other hand, in the case of in-plane π-bonding to the metal-ion $5d_{xy}$ orbital, and of out-of-plane π-bonding to the metal-ion $5d_{xz}$ and $5d_{yz}$ orbitals, the sixth ligand does cause very small additional drifts of electrons away from the central metal ion and also increases the magnitudes of the transition energies $|\Delta E(E)|$. The additional ligand therefore noticeably increases the magnitude of

TABLE 5

Energy levels (eV) and atomic-orbital coefficients in the LCAO m.o. description of Re(O)Cl$_4$. M.o.s are in symmetry classes appropriate to the C_{4v} group. The unpaired electron is in the asterisked B_2 orbital

Orbital	Energy	Atomic-orbital coefficients							
		$6s$	$6p_z$	$5d_{z^2}$	$3s[A_1]$	$3p_z[A_1]$	$3p_\sigma[A_1]$	$2s$	$2p_z$
A_1 Symmetry									
(1)	−31·21	0·139	0·077	0·091	0·032	−0·024	−0·011	0·888	0·035
(2)	−25·93	0·200	−0·063	−0·063	0·884	0·004	−0·036	−0·096	0·001
(6)	−15·50	0·234	0·015	−0·394	−0·246	0·079	0·674	−0·003	0·110
(10)	−13·90	0·192	−0·098	0·386	−0·127	0·227	0·198	−0·160	−0·721
(14)	−12·95	−0·011	0·125	−0·086	0·032	0·929	−0·166	−0·048	0·163
(25)	−8·5	0·065	−0·429	0·744	−0·071	0·166	0·243	0·014	0·594
(28)	33·4	−0·417	1·352	0·703	0·539	−0·345	0·918	−0·738	0·403
(29)	51·2	1·679	0·387	0·082	−0·694	−0·415	−0·975	−0·835	0·574
A_2 Symmetry		$3p[A_2]$							
(18)	−12·80	1·000							
B_1 Symmetry		$5d_{x^2-y^2}$	$3s[B_1]$	$3p_z[B_1]$	$3p_\sigma[B_1]$				
(5)	−25·14	−0·103	0·981	−0·001	0·002				
(7)	−14·35	−0·549	−0·141	0·270	−0·674				
(17)	−12·80	0·000	0·000	0·928	0·371				
(24)	−8·92	0·870	0·187	0·268	−0·671				
B_2 Symmetry		$5d_{xy}$	$3p[B_2]$						
(11)	−13·80	−0·603	−0·729						
(21 *)	−11·01	0·807	−0·696						
E Symmetry		$6p_x$ or $6p_y$	$5d_{xz}$ or $5d_{yz}$	$3s_2[E]$ or $3s_1[E]$	$3p_{xz}[E]$ or $3p_{yz}[E]$	$3p_{\sigma x}[E]$ or $3p_{\sigma y}[E]$	$3p_{\pi x}[E]$ or $3p_{\pi y}[E]$		$2p_x$ or $2p_y$
(3), (4)	−25·30	∓0·127	±0·037	±0·930	∓0·013	∓0·034	±0·017		±0·015
(8), (9)	−14·13	0·000	±0·619	∓0·062	∓0·233	±0·461	∓0·104		±0·431
(12), (13)	−13·41	∓0·204	∓0·122	∓0·136	±0·429	±0·582	∓0·351		∓0·310
(15), (16)	−12·80	0·000	0·000	0·000	±0·273	0·000	±0·899		0·000
(19), (20)	−12·66	±0·036	±0·122	±0·014	±0·789	∓0·296	∓0·127		±0·502
(22), (23)	−9·79	±0·048	±0·786	∓0·035	±0·216	±0·037	∓0·051		∓0·681
(26), (27)	+31·0	±1·627	∓0·103	±0·901	±0·349	∓0·888	±0·443		∓0·388

$g_\perp$ and reduces the magnitudes of the magnetic hyperfine-tensor components. This ligand should presumably have the greatest influence on σ-bonding to the metal-ion $5d_{z^2}$ orbital, but this involves m.o.s of A_1 symmetry which are inaccessible to us since they do not affect the paramagnetic properties of these complexes.

APPENDIX

Molecular-orbital Analysis of Re(O)Cl$_4$.—The dimensions used in our calculations were obtained from Edwards' *X*-ray analysis.[16] This shows that the molecule is a square pyramid with C_{4v} symmetry and that the rhenium atom is raised 0·59 Å above the plane containing the four chlorine atoms. The Re–O bond length is 1·63 Å, the Re–Cl bond length is 2·26 Å, and the O–Re–Cl bond angle is 105°. The m.o. calculations were of the standard type [18,19] cycled until the input and output charges associated with each atom were self consistent. The final estimated electronic configuration and charge at the rhenium atom were Re $(\cdots 5d^{4\cdot880}6s^{0\cdot714}6p^{0\cdot939})$ and +0·476, respectively. Final eigenvalues and eigenfunctions are listed in Table 5 and the resultant energy-level diagram is shown in Figure 4.

ξ and P *Values.*—Figure 5 is obtained when free-ion values of the spin–orbit coupling constant, ξ, for rhenium are plotted against ionic charge.[1] Since spin–orbit coupling constants for the third transition series are only approximately known, and since we did not have enough information to enable us to estimate the effects of changes in configuration on these values, we used the value of $\xi = 2\,400$ cm^{-1}, obtained directly from Figure 5, for Re$^{0\cdot476+}$ in rhenium tetrachloride oxide. The *P* value of 0·033 cm^{-1} was obtained by interpolating between the values of 0·0320 cm^{-1} for Re^0 $(\cdots 5d^5 6s^2)$ and 0·0500 cm^{-1} for Re^{6+} $(\cdots 5d^1)$, which were derived from values of $\langle r^{-3} \rangle$ given by McMillan and Halpern.[1,20]

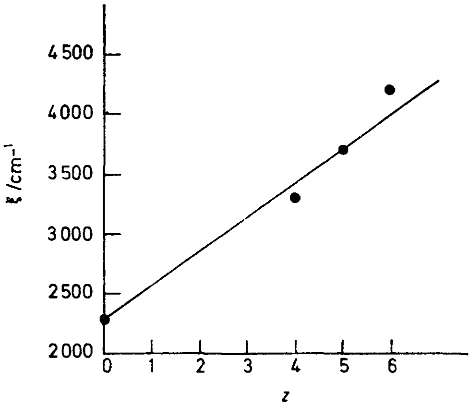

FIGURE 5 Spin-orbit coupling constants, ξ (cm^{-1}), for rhenium ions as a function of ionic charge, *z*

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