The Chemistry of Rhenium Alkyls. Part IV.[1] Electron Spin Resonance Spectra of Hexamethylrhenium(VI) and the Octamethylrhenate(VI) Ion †

By **John F. Gibson, Gordon M. Lack, Konstantinos Mertis, and Geoffrey Wilkinson,*** Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY

Well-resolved e.s.r. spectra of hexamethylrhenium(VI) and the octamethylrhenate(VI) ion are analysed. For $ReMe_6$ the resulting Hamiltonian parameters are consistent with distorted octahedral symmetry. For the octamethylrhenate(VI) ion, $[ReMe_8]^{2-}$, a square antiprism structure best fits the parameters. The g values in both cases are inflated, probably through participation of excited charge-transfer states from high-lying bonding orbitals and good agreement with existing theory is not obtained. The nuclear-spin electron-orbit interaction, which is commonly neglected, is found to give an appreciable contribution to A_{iso} in these compounds.

Electron Spin Resonance Spectra of Hexamethylrhenium.—Solutions of hexamethylrhenium[1] in petroleum or toluene gave well resolved e.s.r. spectra showing hyperfine structure from one rhenium nucleus. Petroleum solutions were almost completely free of traces of tetramethyloxorhenium(VI),[2] $ReOMe_4$, but toluene solutions usually contained small amounts of the oxo-compound. The frozen solution Q-band spectrum at 85 K is shown in Figure 1. After spectra had been recorded down to 97 K an X-band sample was warmed when the individual hyperfine lines were first seen to broaden and diminish in intensity. The whole spectrum then intensified and changed into a sextet typical of a freely rotating molecule. This spectrum was observable over the temperature range 170 ± 20 K and the hyperfine spacing showed marked second-order effects, which were allowed for in estimating the isotropic parameters listed in Table 1. When this sample was inspected at room temperature a black solid was seen to have been deposited. This precipitate was paramagnetic giving a weak, broad, featureless e.s.r. line of width 120 mT at room temperature. The solution above the deposit gave no e.s.r. spectrum at 293 K but, even after some days, still gave the intense original spectrum at 77 K.

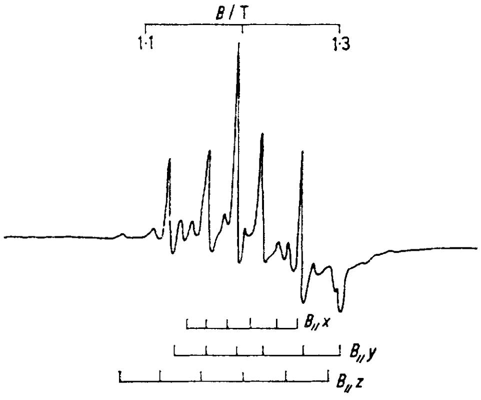

FIGURE 1 Q-Band spectrum of hexamethylrhenium in light petroleum at 85 K; ν = 35.72 GHz

TABLE 1

E.s.r. parameters for hexamethylrhenium

$g_x = 2.122$ $P_x = -0.0004$
$g_y = 2.095$ $P_y = +0.0012$
$g_z = 2.155$ $P_z = -0.0008$

$A_x = +0.0217$ $g_{iso} = 2.112$
$A_y = -0.0328$ $A_{iso} = -0.0181$
$A_z = -0.0428$

A and P are in cm^{-1}.

The analysis of the Q-band spectrum was simplified after it had been established that the weak lines on the

---

† No reprints available.

[1] Part III, K. Mertis and G. Wilkinson, preceding paper.

[2] J. F. Gibson, K. Mertis, and G. Wilkinson, *J.C.S. Dalton*, 1975, 1093.

right in Figure 1 were derived from tetramethyloxorhenium(VI) and that, even though their presence required assignment of other features in the body of the spectrum also to the oxo-compound, these were coincident with genuine parts of the hexamethylrhenium(VI) spectrum. After assignment of the six major features of this spectrum to one principal direction of the g and A tensors, the parameters from the isotropic spectrum were used to estimate reasonable values of the other two principal values of each tensor, allowing for the fact that strong second-order effects would be expected, particularly along the direction of smallest A value. Several assignments were then tested using the program MNES * to fit the spectrum to the usual Hamiltonian:

$$\mathcal{H} = \beta B . \boldsymbol{g} . S + S . \boldsymbol{A} . I + I . \boldsymbol{P} . I - \beta_n B . \boldsymbol{g}_n . I$$

The best fit was the one in which one of the principal A values was of opposite sign to the other two with all tensors coincident. The data are given in Table 1 and the assignment is represented by stick diagrams below the spectrum in Figure 1.

Since six-co-ordination is not the potential maximum for rhenium(VI), solvent co-ordination is a possibility. However, the addition of pyridine or tetrahydrofuran to solutions of $ReMe_6$ causes no change in the electronic or e.s.r. spectra so we can be confident that we are dealing with a six-co-ordinate compound of octahedral or near octahedral symmetry. Furthermore, except for one extra band at low energy corresponding to the extra electron in hexamethylrhenium, the photoelectron spectrum [4] is very similar to that of hexamethyltungsten,[5] which may be analysed in terms of O_h symmetry. Apart from the dithiolates [6], *e.g.*, $Re(S_2C_2Ph_2)_3$, which are trigonal prismatic, the only other ReX_6 species known is hexafluororhenium. Raman spectra [7] suggest that ReF_6 may be described as a dynamically distorted octahedron at room temperature. However, it gives no e.s.r. spectrum down to 77 K,[8] whereas that of $ReMe_6$ is still visible above 190 K, indicating that the degeneracy of the t_{2g} orbitals is lifted more in $ReMe_6$ than in ReF_6. Furthermore, once the anisotropic spectrum is frozen out, it does not change down to 12 K. Hence the distortion from strict O_h symmetry is not dynamic in the temperature range we have covered and the e.s.r. parameters of Table 1 are not averaged out by such a mechanism. Thus we might expect that Griffith's approach [9] in analysing this $(t_{2g})^1$ system might be appropriate. Here the distortion of the molecule and spin–orbit coupling will combine to lift the degeneracy of the t_{2g} orbitals to give the three orbitals ξ, η, and ζ of energy Δ, $V/2$, and $-V/2$ respectively. We can assume that in a third-row transition element of high oxidation state the e_g orbitals will lie very high indeed and that configuration interaction between them and the ground state may be neglected, as required by this approach. However, the experimental g values do not yield coefficients a, b, c, and orbital reduction factor k which form a satisfactory solution corresponding to the lowest orbital. Only when quantities as large as 0.12 are subtracted from each g value do we find solutions which are remotely satisfactory. Thus it appears that if hexamethylrhenium is a slightly distorted octahedron the g values are unusually inflated relative to those appropriate for a pure $(t_{2g})^1$ configuration. Such a situation has already been shown to arise for tetramethyloxorhenium(VI) where positive g shifts result from an admixture of charge-transfer states involving high-lying bonding orbitals. A similar explanation is appropriate here because the solutions are intensely coloured and the photoelectron spectrum has several bands at low energy.[4]

A further interesting point is the small value of A_{iso} relative to those found in other rhenium compounds.[2,8,10,11] On the basis that contributions to A_{iso} from spin polarization are expected to be negative,[12] it seems clear that there must be also a positive contribution from some other mechanism in this case. We note that a positive contribution could arise from admixture of 6*s* if the symmetry were low enough to permit it but, since rhenium has a very high spin–orbit coupling constant, there is another mechanism, the much neglected direct interaction between nuclear spin and electron orbital motion which might be important for this compound. Its contribution to A_{iso} is of the order $\Delta g \beta g_n \beta_n \langle r^{-3} \rangle$ and will be positive for the two compounds reported in this paper and for those of ref. 2 because in all these cases the g shift is positive. Assuming a value of 12.6 a.u. for $\langle r^{-3} \rangle$ [13] this contribution amounts to *ca.* 0.003 cm^{-1} which, being *ca.* 17% of A_{iso}, is thus not negligible.

Electron Spin Resonance Spectra of the Octamethylrhenate(VI) *Ion.*—Solutions of the lithium salt [1] $Li_2[ReMe_8]$ in toluene or tetrahydrofuran gave well-resolved e.s.r. spectra at room temperature or below. In all of these, sets of hyperfine lines typical of interaction of an unpaired electron with one rhenium nucleus were seen. The frozen solution spectra at X and Q band frequencies are shown in Figures 2 and 3.

The analysis of the spectra was made by the method used for hexamethylrhenium except that axial symmetry was assumed and the program MNES [3] sought the

---

* MNES is a least-squares procedure using ESRS, described by Dowsing and Gibson.[3] Both programs were written in their present form by R. D. Dowsing, Department of Computer Science, University College of Swansea, Swansea SA2 8PP.

[3] R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, 1969, **50**, 294.

[4] J. C. Green, personal communication.

[5] L. Galyer, G. Wilkinson, and D. R. Lloyd, *J.C.S. Chem. Comm.*, 1975, 497.

[6] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1966, **5**, 411.

[7] I. W. Levin, S. Abramowitz, and A. Müller, *J. Mol. Spectroscopy*, 1972, **41**, 415; H. H. Claassen and H. Selig, *Israel J. Chem.*, 1969, **7**, 499.

[8] J. H. Holloway and J. B. Raynor, *J.C.S. Dalton*, 1975, 737.

[9] J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, Cambridge, 1961.

[10] A. H. Al-Mowali and A. L. Porte, *J.C.S. Dalton*, 1975, 50.

[11] P. T. Meiklejohn, M. T. Pope, and R. A. Prados, *J. Amer. Chem. Soc.*, 1974, **96**, 6779.

[12] B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51.

[13] J. A. McMillan and T. Halpern, *J. Chem. Phys.*, 1971, **55**, 33.

parameters which gave a best fit at X and Q band simultaneously. The results are given in Table 2 and the assignments are shown beneath the spectra in Figures 2 and 3. The contribution to A_{iso} from the nuclear-spin electron-orbit interaction is much smaller than for $ReMe_6$ being only *ca.* 5% of A_{iso} in this case.

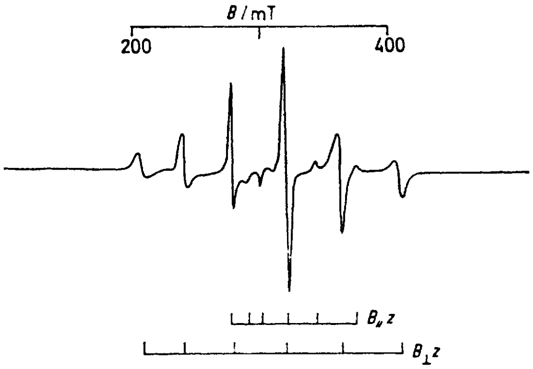

FIGURE 2 X-Band spectrum of lithium octamethylrhenate(VI) in toluene at 85 K; $\nu = 9.149$ GHz

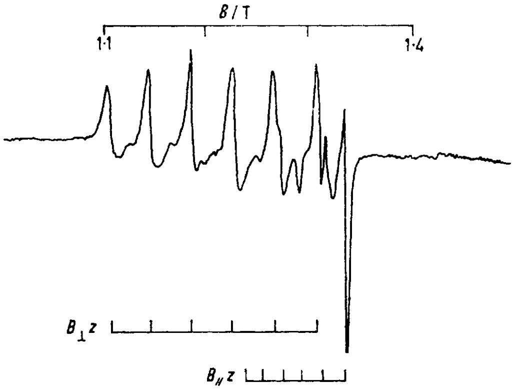

FIGURE 3 Q-Band spectrum of lithium octamethylrhenate(VI) in toluene at 85 K; $\nu = 35.74$ GHz

It is clear from the e.s.r. data that the complex is axially symmetric. Also, since we have seen a well resolved spectrum at room temperature, there must be no low-lying excited state through which spin–orbit coupling can connect the spin to the lattice and give a fast relaxation. McGarvey[14] has observed the resonance from $[Mo(CN)_8]^{3-}$ and, after considering five geometries, square antiprism, dodecahedron, cube, and trigonal prism with the remaining two ligands in the middle of either each end or two sides, has rejected the latter three geometries because each would cause a fast spin-lattice relaxation. For the remaining two structures the ground state must have its single electron in a $d_{x^2-y^2}$, d_{xy}, or d_{z^2} orbital, but the first two only differ in the choice of axes, one set being rotated 45° from the other. Ligand field theory then leads to the following criteria for small values of the spin–orbit coupling constant.

TABLE 2

E.s.r. parameters for the octamethylrhenate(VI) anion

$g_\parallel = 1.977$	$P_\parallel = 0.0012$
$g_\perp = 2.109$	
	$g_{iso} = 2.065$
$A_\parallel = -0.0179$	$A_{iso} = -0.0307$
$A_\perp = -0.0396$	

A and $P_\parallel$ are in cm^{-1}. $P_\parallel = 3P_z/2$.

For a d_{xy} ground state (B_2) in a dodecahedron (D_{2d})

$$2.0023 > g_\perp > g_\parallel \quad |A_\perp| < |A_\parallel|$$

For a d_{z^2} ground state (A_1) in a square antiprism (D_{4d})

$$2.0023 = g_\parallel > g_\perp \quad |A_\parallel| < |A_\perp| \text{ or } |A_\parallel| > |A_\perp|$$

A similar analysis for $[W(CN)_8]^{3-}$ has appeared more recently.[15]

There is an immediate difficulty in attempting to apply such an analysis to $[ReMe_8]^{2-}$ because one of the g values is greater than the free-spin value. However, we have seen before, in tetramethyloxorhenium(VI),[2] that anomalously high g values can arise through contributions from excited charge-transfer states in which an electron is excited up to the d_{xy} ground state from a bonding orbital. (This also seems to be encountered in hexamethylrhenium.) We might, therefore, expect similar contributions here which means that the g value criterion is not very helpful in deciding between D_{2d} and D_{4d}. However, the magnitude of the principal g values affects the anisotropic hyperfine values to a lesser degree and so we expect the A values to be more reliable as a guide to the structure. Since $|A_\perp| > |A_\parallel|$ we favour the square antiprism (D_{4d}) as the structure. This agrees with the prediction of Orgel[16] that, on electrostatic grounds, eight-co-ordinate species will be square antiprismatic but that if π-acceptor ligands are present they will tend towards a dodecahedral structure to increase π-bonding. Thus $K_4[Mo(CN)_8]$,[17] $K_4[Nb(CN)_8]$,[18] and $K_3[Re(OH)_4(CN)_4]$[19] are dodecahedral whereas $K_2[ReF_8]$[20] and $Li_2[ReMe_8]$ are square antiprismatic.

EXPERIMENTAL

Hexamethylrhenium and lithium octamethylrhenate(VI) were synthesized as before.[1] Solutions were prepared on a standard vacuum line, transferred to quartz e.s.r. tubes, frozen, and then stored in the dark. E.s.r. spectra were obtained at X band (*ca.* 9.2 GHz) using a Varian E12 spectrometer and at Q band using a Varian 36 GHz bridge and cavity with a Newport Instruments type F magnet.

---

[14] B. R. McGarvey, *Inorg. Chem.*, 1966, **5**, 476.

[15] R. A. Pribush and R. D. Archer, *Inorg. Chem.*, 1974, **13**, 2556.

[16] L. E. Orgel, *J. Inorg. Nuclear Chem.*, 1960, **14**, 136.

[17] J. L. Hoard and H. H. Nordsieck, *J. Amer. Chem. Soc.*, 1939, **61**, 2853.

[18] P. Kiernan, J. F. Gibson, and W. P. Griffith, *J.C.S. Chem. Comm.*, 1973, 816.

[19] M. Basu and S. Basu, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3669.

[20] P. A. Koz'min, *J. Struct. Chem.*, 1964, **5**, 70.

Samples were cooled in a stream of nitrogen or helium gas. Spin Hamiltonian parameters and e.s.r. line analyses were derived by a trial and error method using the computer programs MNES and ESRS.[3] The d^1 analysis described by Griffith [9] was performed using the method described by Hudson and Kennedy.[21]

We thank the S.R.C. for financial support (to K. M.) and for a studentship (to G. M. L.).

[5/1869 *Received, 29th September,* 1975]

[21] A. Hudson and M. J. Kennedy, *J. Chem. Soc. (A)*, 1969, 1116.