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Electronic Spectra and Magnetic Properties of Some Rhenium(IV) and Rhenium(III) Complexes

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The electronic spectra and magnetic properties of the compounds $[ReX_5PPh_3][PPh_3H]$ ($X=Cl$, Br) of C_{4v} symmetry, $[ReX_4(PPh_3)_2]$ ($X=Cl$, Br) and $[ReX_2(DPE)_2]X$ ($X=Cl$, Br; DPE=diphenylphosphinoethane) of D_{4h} symmetry, have been investigated. The d–d transitions have been correlated using point charge model calculations in which the monoelectronic energies have been calculated according to the angular overlap method. The composition of ground states derived from calculations has been confirmed by magnetic measurements. Values for the optical electronegativities have been derived from the charge transfer transitions.

Introduction

The spectroscopic and magnetic properties of halogenorhenate(IV) ions of O_h symmetry have been investigated previously,[1,2] and recently, Leigh and Mingos[3] examined the charge transfer bands of $[ReCl_4(PMe_2Ph)_2]$. The aim of the present paper is the interpretation of the electronic spectra, in particular the *d–d* transitions, and magnetic properties of the compounds: $[ReX_5PPh_3][PPh_3H]$ ($X=Cl$, Br) of C_{4v} symmetry, $[ReX_4(PPh_3)_2]$ ($X=Cl$, Br) and $[ReX_2(DPE)_2]X$ ($X=Cl$, Br; DPE=diphenylphosphinoethane) of D_{4h} symmetry, (if the internal geometry of the ligand is ignored).

The spectra have been correlated using a point charge model calculation[4,5] which takes account of perturbations due to the ligand field, interelectronic repulsion and spin-orbit interaction, utilizing previously calculated[6,7] energy matrices. The monoelectronic energy levels of the *d* orbitals have been calculated according to the angular overlap method.

Magnetic measurements have confirmed the composition of the ground state, derived from the angular overlap method, for all the complexes examined.

Determination of Geometry

The IR spectrum of $[ReCl_5PPh_3][PPh_3H]$in nujol presents three bands (at 337(m), 308(vs), and 283(s) cm^{-1}), due to the Re–Cl stretching modes. This is in agreement with a C_{4v} symmetry, for which three IR active ($2A_1+E$), Re–Cl stretching bands are predicted, of which at least one has low intensity.

The IR spectra of $[ReCl_4(PPh_3)_2]$ and $[ReCl_2(DPE)_2]Cl$ in nujol present only a single Re–Cl stretch at 323 and 322 cm^{-1}, respectively. This is consistent with D_{4h} symmetry for which only one IR active (E_u) Re–Cl stretching mode would be predicted.

It appears reasonable that the bromoderivatives have the same geometry as the analogous chlorides.

Electronic Spectra

The bands between 4.0 and 20.0 kK are of low intensity and are therefore attributed to *d–d* transitions. Spectra in reflectance (Figures 1-4) and in chloroform solution have been recorded in this energy range. Those in reflectance are more suitable for observation of *d–d* bands, since they may easily be correlated with the spectra both of phosphinic ligands, and of several d^{10} complexes with these ligands. Intensities of the bands were obtained from solution

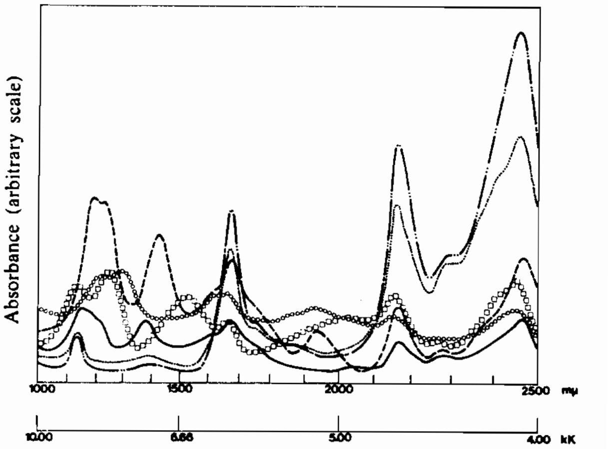

Figure 1. Reflectance spectra. —— $[ReCl_5(PPh_3)][PPh_3H]$; - - - - $[ReBr_5(PPh_3][PPh_3H]$; □□□ $[ReCl_4(PPh_3)_2]$; ○○○ $[ReBr_4(PPh_3)_2]$; · · · $[QuClPPh_3]$; —··— PPh_3.

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Table I. Calculated and observed *d—d* transitions (kK).

$[ReCl_5PPh_3][PPh_3H]$			$[ReBr_5PPh_3][PPh_3H]$			$[ReCl_4(PPh_3)_2]$			$[ReBr_4(PPh_3)_2]$			$[ReCl_2(DPE)_2]Cl$			$[ReBr_2(DPE)_2]Br$		
Calc.	Γ;Γ'	Obs.	Calc.	Γ;Γ'	Obs.	Calc.	Γ;Γ'	Obs.	Calc.	Γ;Γ'	Obs.	Calc.	Γ;Γ'	Obs.	Calc.	Γ;Γ'	Obs.
0,023	$^4B_1;E'$	—	0,038	$^4B_1E'$	—	0,153	$^4B_1;E'$	—	0,242	$^4B_1E'$	—	1,08	$^3A_2;E$	—	1,13	$^3A_2;E$	—
5,38	$^2E;E''$	—	4,83	$^2E;E''$	5,16	2,73	$^2E;E''$	—	2,47	$^2E;E''$	—	4,96	$^1B_2;B_2$	4,88	4,92	$^1B_2;B_2$	5,00
6,89	$^2E;E'$	6,32	6,36	$^2E;E'$	6,25	4,66	$^2E;E'$	4,92	4,35	$^2E;E'$	5,19	5,21	$^1B_1;B_1$	5,26	5,15	$^1B_1;B_1$	5,49
7,86	$^2B_1;E''$	7,27	7,40	$^2B_1;E''$	7,06	7,60	$^2B_1;E''$	6,49	7,38	$^2B_1;E''$	6,21	5,63	$^3E;A_2$	5,53	5,79	$^3E;A_2$	5,67
8,07	$^2A_1;E'$	—	7,61	$^2A_2;E'$	8,06	7,86	$^2A_1;E'$	8,00	7,64	$^2A_1;E'$	7,69	5,80	$^3E;A_1$	5,88	5,95	$^3E;A_1$	5,99
8,33	$^2E;E'$	8,33	7,86	$^2E;E'$	8,33	8,12	$^2A_2;E'$	8,69	7,89	$^2A_2;E'$	8,33	6,65	$^3E;E$	6,17	6,82	$^3E;E$	—
13,62	$^2B_2;E''$	13,33	12,83	$^2B_2;E''$	12,5	13,14	$^2B_2;E''$	13,33	12,67	$^2B_2;E''$	11,90	9,05	$^3E;B_1$	8,69	9,22	$^3E;B_1$	9,06
14,88	$^2E;E'$	14,40	14,21	$^2E;E'$	13,6	16,60	$^2E;E'$	—	16,33	$^2E;E'$	13,79	9,08	$^3E;B_2$	—	9,26	$^3E;B_2$	—
16,50	$^2E;E''$	15,90	15,86	$^2E;E''$	15,15	18,74	$^2E;E''$	—	18,47	$^2E;E''$	—	10,27	$^1A_1;A_1$	10,56	10,17	$^1A_1;A_1$	10,25
												11,94	$^1E;E$	14,81	12,01	$^1E;E$	14,30

Table II. Values of the parameters used (cm^{-1}).

	A	*B*	*A'*	*B'*	B	C	ζ
$[ReCl_5PPh_3][PPh_3H]$	4857	—3607	20233	—6835	360	1520	2300
$[ReBr_5PPh_3][PPh_3H]$	4696	—3544	20233	—6835	340	1400	2300
$[ReCl_4(PPh_3)_2]$	4857	—3607	20233	—6835	330	1400	2300
$[ReBr_4(PPh_3)_2]$	4690	—3544	20233	—6835	310	1320	2300
$[Re(DPE)_2Cl_2]Cl$	4857	—3607	20233	—6335	330	1400	2300
$[Re(DPE)_2Br_2]Br$	4690	—3544	20233	—6335	300	1400	2350

Table III. Composition of the ground state.

$[ReCl_5PPh_3][PPh_3H]$	$0.9586(e^2b_2,{}^4B_1)—0.1897(e^3,{}^2E)+0.1717(e^2b_2,{}^2B_2)$
$[ReBr_5PPh_3][PPh_3H]$	$0.9493(e^2b_2,{}^4B_1)—0.2176(e^3,{}^2E)+0.1855(e^2b_2,{}^2B_2)$
$[ReCl_4(PPh_3)_2]$	$0.8617(e^2b_2,{}^4B_1)—0.4492(e^3,{}^2E)+0.1952(e^2b_2,{}^2B_2)$
$[ReBr_4(PPh_3)_2]$	$0.8060(e^2b_2,{}^4B_1)—0.5363(e^3,{}^2E)+0.2054(e^2b_2,{}^2B_2)$
$[Re(DPE)_2Cl_2]Cl$	$0.88921(b_2{}^2e^2,{}^3A_2)—0.3558(b_2e^3,{}^3E)—0.2708(b^2{}_2e^2,{}^1A_1)$
$[Re(DPE)_2Cl_2]Br$	$0.8858(b_2{}^2e^2,{}^3A_2)—0.3554(b_2e^3,{}^3E)—0.2814(b^2{}_2e^2,{}^1A_1)$

spectra and values of ε between 10 and 50 were found.

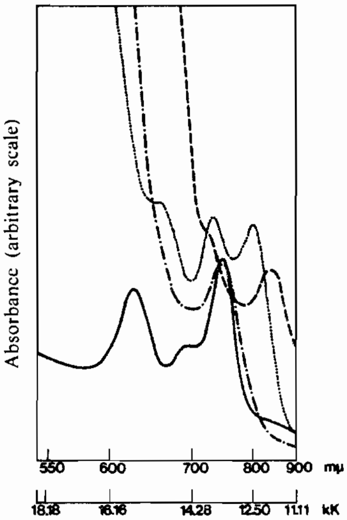

Figure 2. Reflectance spectra. —— $[ReCl_5(PPh_3)][PPh_3H]$; ····$[ReBr_5(PPh_3)][PPh_3H]$; —·—·— $[ReCl_4(PPh_3)_2]$; ---- $[ReBr_4(PPh_3)_2]$.

The calculation was initially carried out using the crystal field model. However, the monoelectronic energy level schemes and the composition of the ground states calculated as a function of G(k) and G'(k), characteristic of the halogens and the phosphines, respectively, could not rationalize the magnetic behaviour with temperature.

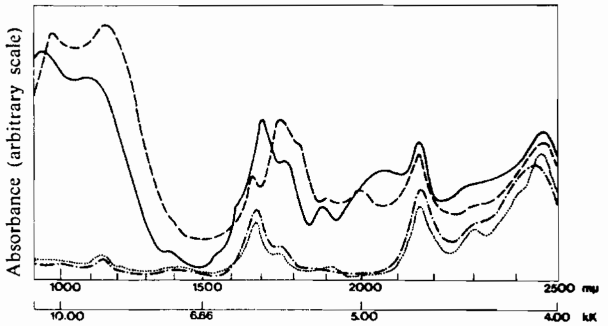

Figure 3. Reflectance spectra. ——— $[ReCl_2(DPE)_2]Cl$; ---- $[ReBr_2(DPE)_2]Br$; —·—·— DPE; ···· [CuClDPE).

It is known[8] that the crystal field model, while capable of interpreting the properties of complexes having cubic symmetries, is not easily adapted to lower symmetries. Because of this we have adopted the angular overlap scheme to calculate the perturbation of the field and ignored δ bonding. This method takes account of differences between the σ and π properties of the ligands by means of the parameters *A*, *B* for the halogens, and *A'*, *B'* for the phosphines, respectively. We have thus calculated monoelectronic energy levels and ground states which may be confirmed by magnetic measurements. Values for *A*, *B*, *A'* and *B'* have been chosen assuming that the phospines have σ—donor powers greater than the halogens and, in contrast to the latter, behave also as weak π—acceptors. On this basis it is necessary that $|A'|>|A|$ and $|B'|>|B|$. For the interelectronic repulsion parameters B and C, and the spin-orbit coupling constant ζ, initial values similar to those for halogenorhenate(IV)[2] have been chosen. Analogously, initial parameters *A* and *B* were obtained using the relation: $10Dq_{(ReX_6^{2-})}=3A–4B$. The parameters *A′* and *B′*, as mentioned previously, take account of the differences in chemical properties between the halides and the phosphines. The values of all the parameters have been modified so to obtain agreement between the calculated and experimental frequencies. It is necessary to point out that these values, taken singularly, have little chemical significance, but they are sufficient to determine, to a reasonable approximation, the number of bands predicted by the geometry and also the ground state of the compounds.

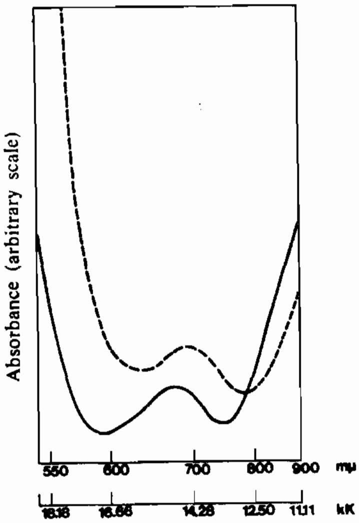

Figure 4. Reflectance spectra. ——— $[ReCl_2(DPE)_2]Cl$; - - - - $[ReBr_2(DPE)_2]Br$.

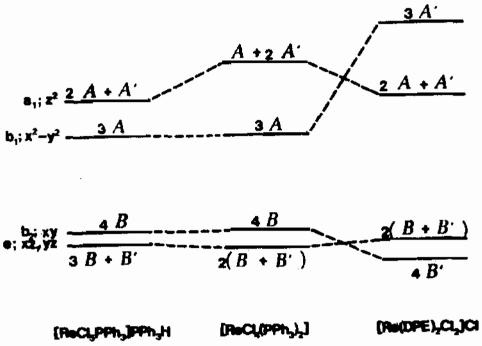

Figure 5. Monoelectronic levels.

It may be noted from the calculations that all the *d–d* transitions observed are those concerning configurations derived from the octahedral ones t^3_{2g} and t^4_{2g}, respectively. The bands derived from higher octahedral configurations are not observed because they have maxima in the energy range expected for charge transfer bands. The order of the monoelectronic energy levels of the chloroderivatives is shown in Figure 5. The calculated and observed *d–d* transitions are in Table I. Values of parameters are in Table II and ground state compositions including spin-orbit coupling, limited the configurations present with eigenvectors>0.1, are in Table III. The ground states of the d^3 compounds have symmetry E″, while the d^4 ones have symmetry A_1. The values in Table III refer to calculations restricted to configurations derived from the octahedral t^3_{2g}, $t^2_{2g}e_g$ ones in the case of d^3, and t^4_{2g}, $t^3_{2g}e_g$ for d^4 cases. This was done because the calculations extended to all the possible configurations did not give rise to significant variations neither in the transition energies nor in the composition of the ground states. The calculated electronic transitions suffer from all the criticisms that may be levelled against such methods. Despite this, it appears that the good agreement between calculated and observed values is not totally casual.

Magnetic Properties

The halogenorhenates(IV) with O_h symmetry have magnetic moments, at room temperature, of c.3.4. B.M., which decrease with temperature[9] and show magnetic exchange. The rhenium(IV) complexes examined here show, at room temperature, $\mu=3.46$ and 3.53 B.M. for D_{4h} and C_{4v} symmetry, respectively, and do not appear to show magnetic exchange. These values are close to those of halogenorhenate, and this similarity is caused by the predominant partecipation of a quartet state into the ground state, not only for O_h but also for D_{4h} and C_{4v} symmetries. Such behaviour is also found in $[ReI_4(py)_2]$.[9] Instead, the apparently anomalous properties of $[Re(OH)Cl_3(PEt_2Ph)_2]$,[9] in view of the above considerations, may be attributed to the important contribution of the doublet state to the ground state in a symmetry very different from the O_h one.

Magnetic measurements have been performed down to liquid nitrogen temperature by the Gouy method for all the compounds (Table IV and V). The rhenium(IV) complexes with C_{4v} symmetry have a temperature independent magnetic moment and their magnetic behaviour agrees with the presence of the energy levels E″ (fundamental) and E′ (excited state), both of which are magnetic, as calculated by the angular overlap method. In fact, the calculated energy difference between the two states, of ~ 30 cm^{-1} (see Table I) suggests that, in the temperature range investigated, the population of these two states remains approximately constant. The D_{4h} compounds, in contrast, show a temperature dependent magnetic moment. This also agrees with the calculated values of the energy levels E″ (fundamental) and E′ (excited) (see Table I). The calculated difference between these states, of ~ 200 cm^{-1}, indicates small variations in Boltzmann population, even within the restricted temperature range.

The magnetic measurements have also been elaborated according to the method of Figgis,[10] which, using a simplified Hamiltonian and measuring the average magnetic susceptibility, determines the values

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[10] B. N. Figgis, Trans Faraday Soc., *56*, 1553 (1960).

of the zero field splitting. Values for the C_{4v} compounds lower than 30 cm^{-1} and for the D_{4h} one lower than 130 cm^{-1} are obtained, (allowing for small errors due to the limited temperature interval). We thus conclude that the energy values obtained by the magnetic measurements are in agreement with those calculated in Table I. It is not possible to verify the composition of the magnetic ground state from the measurements of average susceptibility since $\bar{\chi}_M$ depends only on the absolute value of the zero field splitting:

$$\bar{\chi}_M = \frac{N\beta^2}{3kT}\,\frac{\bar{g}^2}{2}\,\frac{9+9e^{-X}+\frac{12}{X}(1-e^{-X})}{1+e^{-X}}$$

where $X = \frac{\delta}{KT}$ and δ = zero field splitting.

Table IV. Magnetic data over a temperature range for $[ReCl_5(PPh_3)][PPh_3H]$.

T(°K)	$\chi_M^{corr}10^6$	μ_{eff}	T(°K)	$\chi_M^{corr}10^6$	μ_{eff}
103	15090	3.52	203	7776	3.55
113	13676	3.51	213	7414	3.55
123	12591	3.52	223	7079	3.55
133	11734	3.53	233	6757	3.55
143	10950	3.54	243	6476	3.55
153	10267	3.54	253	6215	3.55
163	9604	3.54	263	5967	3.54
173	9055	3.54	273	5739	3.54
183	8593	3.55	283	5559	3.55
193	8157	3.55	293	5331	3.53

Table V. Magnetic data over a temperature range for $[ReCl_4(PPh_3)_2]$.

T(°K)	$\chi_M^{corr}10^6$	μ_{eff}	T(°K)	$\chi_M^{corr}10^6$	μ_{eff}
103	13240	3.30	173	8533	3.44
113	12438	3.35	183	8073	3.44
123	11628	3.38	193	7646	3.43
133	10869	3.40	203	7263	3.43
143	10170	3.41	213	6922	3.43
153	9573	3.42	291	5148	3.46
163	9002	3.43			

Table VI. Magnetic susceptibility over a temperature range for $[ReCl_2(DPE)_2]Cl$.

T(°K)	$\chi_M^{corr}10^6$
112.8	1611
121.8	1649
138.6	1823
203	1996
300	1861

This equation is the correct one, while the analogous one reported in the literature[10] suggests dependence of $\bar{\chi}_M$ on the sign of δ. To determine the magnetic ground state, analysis of anisotropy in magnetic susceptibility down to liquid helium temperature or single crystal e.s.r. spectra would be necessary.

The d^4 compounds show low values of paramagnetic susceptibility, which increase on increase in temperature, as shown for $[ReCl_2(DPE)_2]Cl$ in Table VI. The paramagnetism of these compounds may be attributed to magnetic interaction between the ground state, itself non-magnetic (A_1, J = O), with the first excited state, which is magnetic (E, J = 1). Temperature variations may be explained using the energy level values of Table I. In fact, the A_1 and E states are c. 1000 cm^{-1} apart. This difference would suggest only a small magnetic variation on the basis of simple electronic excitations, within the temperature range studied. However, it is possible that several vibrational levels of the ground state, for example the linear X–Re–X bands (which should lie ~150 cm^{-1} from the ground state) may provoke a decrease in the ground-excited distance, thus favouring electronic modifications when the temperature is varied. The similar behoviour of $[OsCl_4L_2]$,[12] for which the distance between ground state (A_1, J = 0) and first excited state (A_2, J = 1) is c. 2500 cm^{-1}, by our calculations, supports the above mechanism. Elaboration of the magnetic data according to Griffith's method,[13] would predict a sensible magnetic anisotropy, which could be confirmed by single crystal measurements on $[ReCl_2(DPE)_2]Cl$.

Charge Transfer

Spectra in chloroform in the charge-transfer region are reported in Figure 6. The bands at energy less than 25 kK are due to mainly $\sigma(P)-\pi_d(Re)$ transfer, while those with $\nu > 25$ kK may be assigned to essentially $\pi(X)-\pi_d(Re)$ transfer. This is supported both by the spectra of the corresponding halogenorhenates-(IV),[2] and by the values of optical electronegativity of the phosphines[14] and of rhenium(IV),[2] from which the transfer $\sigma(P)-\pi_d(Re)$ is calculated to be ~20 kK. The optical electronegativities of triphenylphosphine from the spectra of Re^{IV} compounds of D_{4h} symmetry have been calculated. These were chosen instead of the C_{4h} symmetry ones because as predicted, and confirmed by experimental data (Figures 6), the D_{4h} symmetry presents spectra, near 20 kK, which are more

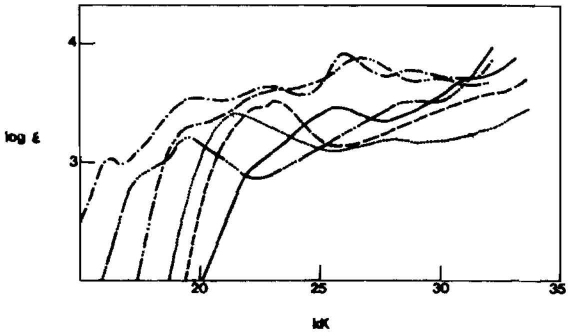

Figure 6. Absorption spectra in $CHCl_3$. —— $[ReCl_5(PPh_3)][PPh_3H]$; —··— $[ReBr_5(PPh_3)][PP_3H]$; —·····— $[ReCl_4(PPh_3)_2]$; —·— $[ReBr_4(PPh_3)_2]$; ---- $[ReCl_2(DPE)_2]Cl$; ···· $[ReBr_2(DPE)_2]Br$.

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similar within the series examined and thus more surely assigned (since there is less mixing between the two types of charge transfer). From the band at 19.4 kK for $[ReBr_4(PPh_3)_2]$ a value of $\chi_{op}=2.5$ is calculated for triphenylphosphine, which is close to that reported in the literature.[14] From this value and the band at 21.5 kK a value of the optical electronegativity for Re^{III} of 1.9 is calculated. Experimental frequencies have been modified by calculating the SPE using values of B and C shown in Table II.

Experimental Part

Compounds were prepared according to literature methods.[15-17] IR spectra were recorded on a Perkin Elmer mod. 621 and electronic spectra on a Beckmann DK 2A.

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