Structure of the Rhenium *X*-Ray L_{III} Absorption Edge in Caesium Hexachlororhenate(IV) †

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The *X*-ray L_{III} absorption-edge structure of rhenium in $Cs_2[ReCl_6]$ has been measured with a bent-crystal *X*-ray spectrograph. An analysis in terms of molecular-orbital (m.o.) theory has been attempted. The energies of the m.o. levels, crystal-field splitting parameter, effective magnetic moment, magnetic susceptibility, and Landé *g* parameter have been determined from this analysis. An estimate of the Re–Cl bond length has also been made.

THE fine structures in the immediate neighbourhood of *X*-ray absorption discontinuities in crystalline solids have attracted considerable attention in recent years, particularly due to the success of molecular-orbital (m.o.) theory in interpreting their important features. Thus, Seka and Hanson [1] have studied the *K* absorption discontinuities in complexes of the first transition-metal series, and Fischer [2] has applied m.o. theory to the shapes of the *K* and L_{III} absorption edges in some compounds of vanadium, titanium, and chromium. Also, Bhide and Kaicker [3] and Sarode [4] have attempted to analyse the fine structure of the *K* absorption edges of the complexes of the second transition-metal series in terms of m.o. theory, and Sarode and Pendharkar [5] have reported the general features of the L_{III} absorption discontinuities in a number of covalent octahedral complexes of platinum and given m.o. interpretations of the observed spectral features.

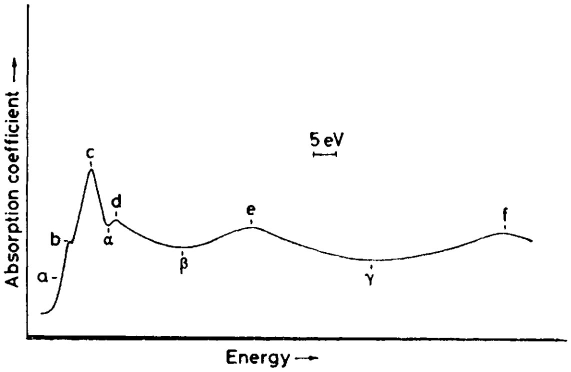
In the present paper, the structure of the rhenium L_{III} absorption edge in caesium hexachlororhenate(IV) ($Cs_2[ReCl_6]$) has been examined in order to study whether m.o. concepts can be used to explain such structure.

EXPERIMENTAL

The *X*-ray absorption spectrum of rhenium in caesium hexachlororhenate(IV) was recorded photographically on a 40-cm diameter curved-crystal spectrometer. The spectrometer was equipped with a mica crystal orientated to reflect from its ($\bar{2}01$) planes. A Machlett sealed *X*-ray tube having a tungsten target was used to supply continuous radiation at 16 kV and 10 mA. The absorption screens were made by mixing a small amount of grease with the finely powdered specimen and coating the mixture on thin paper to the required amount of *ca.* 10 mg cm^{-2}. The uniformity of the absorber was checked visually in white light as well as by moving the absorber across the *X*-ray beam. Traces of the recorded spectra were taken on a Moll microphotometer with magnification ×50. The shape of the discontinuity in the complex was determined from a number of microphotometer traces recorded in turn from three absorption spectra. The microphotometer curve which represents the transmitted intensity as a function of energy was converted into a plot of the absorption coefficient against energy by adopting the usual procedure [6] of determining the photodensities. Tungsten L_{β_5} and L_{γ_1} emission lines were used as reference lines for the measurement of wavelengths. The values of the wavelengths of these emission lines were taken from Bearden's tables.[7] The errors in the measurements close to the absorption edge (*ca.* 30 eV) ‡ were found to lie, statistically, within ±1 eV and those for the more distant peaks within ±2 eV. Other experimental details are described elsewhere.[8]

RESULTS AND DISCUSSION

The shape of the main absorption discontinuity and the fine structure associated with it are shown in the Figure. This curve represents the variation of absorption coefficient as a function of energy. It is observed that the main discontinuity splits into two components, $L_{III}{}^1$ and $L_{III}{}^2$. The inflexion point on $L_{III}{}^1$ component (labelled a) is considered as zero on the energy scale. The Figure also shows the first maximum in the main discontinuity (b), the pronounced maximum or the so-called white line [9] (c), and the other maxima (d, e, and f). The absorption minima (α, β, and γ) are also shown. The energy differences between ' a ' and the various labelled features of the curve for the rhenium complex are given in Table 1.



Variation of absorption coefficient with energy in the region of the L_{III} absorption discontinuity of rhenium in $Cs_2[ReCl_6]$

TABLE 1

Energy differences (eV) measured from the inflexion point ' a '

System	b	c	α	d	β	e	γ	f
$Cs_2[ReCl_6]$	2.00	6.43	10.20	11.81	26.26	41.45	67.65	96.54

b: $2p_{\frac{3}{2}} \rightarrow 2t_{2g}$ $E(2t_{2g} - 3e_g) = 4.43 \text{ eV} = \Delta = 10Dq$

c: $2p_{\frac{3}{2}} \rightarrow 3e_g$ $E(2t_g - 3a_{1g}) = 9.81 \text{ eV}$

d: $2p_{\frac{3}{2}} \rightarrow 3a_{1g}$

$\Delta E_{e-\gamma} = 26.20 \text{ eV}$ $E(3e_g - 3a_{1g}) = 5.38 \text{ eV}$

(*i*) *Molecular-orbital* (*m.o.*) *Theory and Spectral*

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‡ Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 B.M. ≈ 9.27×10^{-24} A m^2.

Features of the Absorption Discontinuity.—It is generally recognised[10] that the fine structure within the discontinuity and that in its close vicinity corresponds to the transitions of electrons from the core levels of the absorbing atom to unoccupied levels of appropriate symmetry situated beyond the Fermi level in the conduction band, and also to any such hybrid levels which have an admixture of suitable symmetries. It has been shown[1,11-14] recently that in transition-metal complexes the fine structure within a 20 eV range of energies is characteristic of the chemical bonding in the material and that it originates from the distribution and availability of the appropriate molecular orbitals formed by the metal atoms and the ligands' orbitals. Accordingly, I begin my analysis with a brief discussion of the various m.o.s of the metal and ligand.

The $[ReCl_6]^{2-}$ ion has O_h symmetry with the central Re atom surrounded by six Cl ligands (Re–Cl 2.32 Å). Its ground-state configuration is $^4A_{2g}$ ($t_{2g}^3e_g^0$) and the bonding orbitals are $5d^26s6p^3$ hybrid (high-spin type). Cotton and Harris[15] have shown that for $[MCl_6]^{2-}$ ions (M = Re, Os, Ir, or Pt), the highest unoccupied m.o., $4t_{1u}$, lies at *ca.* 25 eV from the ground-state m.o., $2t_{2g}$. The absorption maxima in the fine structure asssociated with the L_{III} edge within this 25 eV range can, thus, be attributed to these empty m.o. levels of suitable symmetry.

Schematic m.o. diagrams for octahedral ions are available in the literature.[16-18] For $[ReCl_6]^{2-}$ one finds that the highest (partially) occupied orbital is the $2t_{2g}$ antibonding orbital of d symmetry and has three electrons. The higher energy levels, *viz.* $3e_g$, $3a_{1g}$, and $4t_{1u}$, are empty; these have d, s, and p symmetries respectively. Thus, employing the dipole selection rules, $\Delta l = \pm 1$, the absorption peaks b, c, and d can be attributed to the electron transitions $2p_{\frac{3}{2}}\rightarrow 2t_{2g}$, $2p_{\frac{3}{2}}\rightarrow 3e_g$, and $2p_{\frac{3}{2}}\rightarrow 3a_{1g}$, the initial level involved in the X-ray absorption process being $2p_{\frac{3}{2}}$ (or L_{III}). Although the m.o.s $2t_{2g}$ and $3e_g$ and $3a_{1g}$ have $5d$ and $6s$ character respectively, they are also expected to have some p character due to rhenium–chlorine orbital overlap. No absorption peak within 20 eV of the edge in the absorption curve was observed corresponding to the $4t_{1u}$ orbital, probably because the $2p_{\frac{3}{2}}\rightarrow 4t_{1u}$ transition is dipole forbidden ($\Delta l \neq \pm 1$) and the next absorption peak is at 41.45 eV, *i.e.* beyond the 'chemical region' ($\leqslant$20 eV) of the absorption edge.

(*ii*) *Determination of Ligand-field Splitting Parameter.*—An estimate of the crystal-field splitting parameter ($10Dq$) can be made from the spectral features of the discontinuity. Fischer[19] has determined this parameter in the case of the tetrahedral $[CrO_4]^{2-}$ ion from the $2e$ and $4t_2$ antibonding m.o.s, to which have been attributed the first two absorption maxima in the fine structure associated with the L_{III} discontinuity of chromium in $Na_2[CrO_4]$. In the present investigation the crystal-field splitting for $[ReCl_6]^{2-}$ corresponds to the energy difference between the two absorption maxima b and c in the Figure. These peaks arise from the $2p_{\frac{3}{2}}$ electron transition to the $2t_{2g}$ and $3e_g$ levels respectively. The value of Δ for $[ReCl_6]^{2-}$ ion was thus obtained as 4.43 eV. Figgis[20] and Jørgensen[21] obtained a corresponding value of 4.09 eV from electronic-absorption spectra, while the recent m.o. calculations by Cotton and Harris[15] yielded a value of 4.91 eV. Thus there is good agreement between the value of Δ determined from X-ray absorption spectra and the earlier values obtained by alternative methods.

(*iii*) *Determination of Effective Magnetic Moment, Magnetic Susceptibility, and Landé* g *Parameter.*—It is well known[22-25] that the magnetic moments of transition-metal complexes having A ground terms are in most instances appreciably different from the spin-only value. The effect is most noticeable towards the right-hand side of the transition-metal series. It arises because, on account of spin–orbit coupling, the quenching of orbital angular momentum by the ligand field can never be complete. Taking spin–orbit coupling into account in systems with A ground terms, the effective magnetic moment is given by (1), where $\mu^{\text{s.o.}}$ is

$$\mu_{\text{eff.}} = \mu^{\text{s.o.}}[1 - (4\lambda/\Delta)], \text{ for } A_{2g} \text{ terms} \tag{1}$$

the spin-only magnetic moment and λ is a constant which can be obtained from the single-electron spin–orbit coupling constant ζ_{nd} for the set of d electrons [equation (2)]. In this expression n is the principal quantum

$$\lambda = \pm\zeta_{nd}/2S \tag{2}$$

number of the d shell concerned and S is the multiplicity of the term. The minus sign applies to a d shell which is more than half filled. The corresponding expressions for the magnetic susceptibility χ_A and the Landé splitting factor g, for an A_{2g} term, are given by (3) and (4).

$$\chi_A = \chi_A^{\text{s.o.}}[1 - (8\lambda/\Delta)] \tag{3}$$

$$g = 2[1 - (4\lambda/\Delta)] \tag{4}$$

The number of d electrons for a Re^{4+} ion is three. Therefore, the value of $\mu^{\text{s.o.}}$ {$= [n(n + 1)]^{\frac{1}{2}}$, n being the number of unpaired electrons} is 3.87 B.M. The magnetic susceptibility $\chi_A^{\text{s.o.}}$ has the value 6.250×10^{-6} c.g.s. units per mol, and the constant $\lambda (= \zeta/3 = 3\,300/3)$ is 1 100 cm^{-1}. Using the above expressions with the present value of Δ, I have calculated the values of $\mu_{\text{eff.}}$, χ_A, and g (Table 2). Agreement between my values and those obtained from magnetic-susceptibility measurements by Figgis *et al.*[26] is satisfactory.

TABLE 2

Comparison between the values of the magnetic quantities obtained by X-ray absorption and those obtained from magnetic-susceptibility measurements

Technique	Effective magnetic moment, $\mu_{\text{eff.}}$/B.M.	Magnetic susceptibility, $10^6\chi_A$/c.g.s. units per mol	Landé g factor
X-Ray absorption (this work)	3.39	4 710.6	1.75
Magnetic-susceptibility measurements (ref. 26)	3.35	4 670	1.80

(*iv*) *Determination of Bond Length.*—The absorption maxima b, c, and d (in Figure) in the fine structure of the Re L_{III} absorption edge in $Cs_2[ReCl_6]$ lie in the m.o. region. The fine structure peaks beyond this region can now be used to estimate the Re–Cl bond length.

Levy and his co-workers [27,28] have given a method for calculating the bond length in transition-metal compounds and complexes from *X*-ray absorption fine structure associated with the *K* edges of central metal ions. Their method is based on the spherical-wave theory of Kozlenkov [29] for extended *X*-ray absorption fine structure in which the absorption coefficient is expressed as a sine wavefunction of the wavenumber, the distance between the absorbing atom and the first co-ordination sphere of ligands, and the phase shift. Levy and his co-workers [27,28] showed that the mean radius r_1 of the first co-ordination sphere of ligands around the absorbing atom can be related to ΔE, the separation between the prominent second absorption maximum (the so-called escape or ionisation peak) and the subsequent minimum [equation (5)]. Assuming that

$$r_1 = (151/\Delta E)^{\frac{1}{2}} \qquad (5)$$

the fluctuations of the absorption coefficient are sinusoidal in nature in the region of the escape peak, equation (5) can be extended to the determination of bond lengths in compounds from the fine structure associated with L_{III} as well as other discontinuities. Thus, in the fine structure of the discontinuity I studied, the absorption maximum e corresponds to a kind of escape peak of the $2p_{\frac{3}{2}}$ electron from the molecule, because the peaks lying at lower energies belong to the m.o. region. The Re–Cl bond length calculated from the value of the energy separation $\Delta E_{e-\gamma}$ using equation (5) is 2.40 Å. The available *X*-ray diffraction data [30] give a value of 2.32 Å. The agreement between the two values is quite satisfactory.

Conclusions.—This work shows that it is possible to explain reasonably well the fine structure associated with the *X*-ray L_{III} absorption edge of rhenium in $Cs_2[ReCl_6]$ on the basis of a simple qualitative m.o. picture. This interpretation enables us to obtain the energies of the molecular levels, *viz.* $3e_g$, $3a_{1g}$, with respect to the ground-state level $2t_{2g}$, and the crystal-field splitting parameter Δ for $[ReCl_6]^{2-}$. The effective magnetic moment, magnetic susceptibility, and Landé splitting factor, all of which are, in general, affected by the crystal field of the ligands surrounding the central metal ion, have also been determined.

[8/1059 *Received, 6th June, 1978*]

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