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The preparation and optical charge transfer spectrum of the hexachlororhenium(V) anion

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Abstract

A convenient synthesis of the relatively poorly studied pentavalent complex anion $[RCl_6]^{1-}$ as the tetra-butyl ammonium salt is reported. The complex has been characterised by electrochemical and spectroscopic measurements. The electrode potentials of $[ReCl_6]^{1-}$ ($Re^{V/IV}$ and $Re^{IV/III}$) in CH_2Cl_2 correspond with those of the $[ReCl_6]^{2-}$ ion. The solution electronic absorption spectrum is dominated by two intense Cl to Re^V charge transfer manifolds which are readily assigned to Laporte-allowed transitions. These features are more accessible than in other d^2 chlorides studied previously.

Introduction

The hexahalide complexes of the 2nd and 3rd row transition series provide an ideal family of isostructural compounds within which the electronic properties of simply coordinated heavy transition metals can be systematically explored. In addition to their availability for all pertinent metals, the obvious advantages of the hexahalometallates include their high symmetry, structural simplicity and the 'innocence' (in valence terms) of the halide ligands. Historically they have contributed strongly to our general understanding of the electronic structure and charge transfer processes in metal complexes [1].

The electronic spectra of hexahalogeno complexes of the 2nd and 3rd row transition elements have been extensively studied in their common valencies, and for d^4 and d^5 ions the ligand to metal charge transfer, LMCT, spectra are now well understood using a simple j–j coupling scheme [1–4]. For d^2 and d^3 ions there are relatively few detailed studies and the LMCT spectra are generally more complex in appearance [5, 6]. The preparation of suitable MX_6 complexes, however, requires considerable care; these highly oxidised materials are typically very reactive and samples prepared using aqueous solvents are often contaminated by variable amounts of mixed oxy/halide species making full analysis of the spectral features difficult. This is especially true for the early transition metal complexes; for example the d^2 ions $[WCl_6]^{2-}$ and $[MoCl_6]^{2-}$ are invariably contaminated when prepared from aqueous acid solutions. The preparation and manipulation of the hexahalides as organosoluble salts and the use of anhydrous non-coordinating solvents is one approach to overcoming these problems [7–9].

Unfortunately for the readily prepared d^2 hexachloride complexes such as $[WCL_6]^{2-}$ the LMCT transitions occur at relatively high energies, sometimes beyond the limit of accurate detection. Experimentally this limitation to the study of Cl → M CT processes in d^2 ions could be overcome by the oxidation of suitable $MCl_6{}^{n-}$ complexes, either chemically or electrochemically. Since oxidation results in a lowering of the metal d orbital energies the LMCT transitions are predicted to occur at lower energies, thus facilitating a detailed study of the CT processes [8, 9]. Spectroelectrochemical generation of the new species in non-coordinating solvents has a number of advantages: the species are prepared *in situ* from less reactive precursors, the integrity of the product is immediately evident and the spectral quality is high (equal to that reported for the less convenient molten salt media).

The synthesis of $ReCl_6{}^{1-}$ as the $(PCl_4)^+$ salt was first reported in 1970 [10] however no details about

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its electronic spectrum have subsequently been published. In part this may be due to experimental difficulties in replacing the $(PCl_4)^+$ cation with other cations which are more amenable to spectroscopic characterisation. $ReCl_6{}^{1-}$ provides only the second example of a $5d^2$ MCl_6 ion. It is isoelectronic with $WCl_6{}^{2-}$, and as shown below, the pentavalent rhenium complex is particularly well suited to extend our knowledge of the charge transfer spectra of such systems. As d^2 ions, $Ta^{III}Cl_6{}^{3-}$ ($E^\circ_{IV\rightarrow III} = -2.05$ V) and $Os^{VI}Cl_6$ ($E^\circ_{V\rightarrow VI} = +3.1$ V) are impracticable alternatives. Likewise for the 4d series, the electronic spectrum is only known for $MoCl_6{}^{2-}$, albeit for an impure sample. The $4d^n$ and $5d^n$ series are not interchangeable in this context because of the critical role of the metal spin orbit coupling.

In 1985, Heath and Sharp and their co-workers [9] reported a comprehensive voltammetric study of fourteen 4d and 5d hexachlorometallates dissolved in very dry CH_2Cl_2. This revealed an extensive periodic pattern of stepwise reversible electrode potentials for the redox couples $[MCl_6]^{z/z-1}$ ($z = 0, -1, -2$; $M = Zr \rightarrow Pd$ and $Ta \rightarrow Pt$), related to orderly trends in central ion core charge and inter-electronic correlation terms. Since many of these redox couples span highly reactive entities which are otherwise unknown or unconfirmed, it is highly desirable to undertake spectroelectrochemical studies of the integrity of the various electrode couples, whereby each species implicit in a given couple is reversibly electrosynthesised and authenticated under the conditions prevailing in the original experiment. In accord with the Heath–Sharp progression the potential for the oxidation of $[Re^{IV}Cl_6]^{2-}$ is higher, *c.* 1.4 V than either the oxidation of $[WCl_6]^{2-}$ or $[OsCl_6]^{2-}$. Nevertheless, given proper precautions, this potential suggests the $[ReCl_6]^{1-}$ species is obtainable. In the current paper we show that the oxidation of $(TBA)_2[ReCl_6]$ in CH_2Cl_2 solution yields pure solutions of $[Re^VCl_6]^{1-}$ in a spectroelectrochemical cell. Subsequently we utilised the chemical oxidation of $ReCl_6{}^{2-}$ by PbO_2 to isolate pentavalent $(TBA)ReCl_6$ as a analytically pure and manageable organo-soluble solid.

Experimental

Materials

All operations were performed under a dry nitrogen atmosphere. Unless otherwise stated solvents were dried and deoxygenated prior to use. K_2ReCl_6 was synthesised from $KReO_4$ according to the method of Watt and Thompson [11]. The tetra n-butyl ammonium $(TBA)^+$ salt $(TBA)_2ReCl_6$ was prepared by precipitation from a saturated solution of K_2ReCl_6 in 0.5 M HCl with (TBA)Cl. *Anal.* Calc. for $C_{32}H_{72}N_2ReCl_6$: C, 43.49; H, 8.21; N, 3.17; Cl, 24.07. Found: C, 43.39; H, 8.93; N, 3.17; Cl, 25.16%.

Tetra n-butyl ammonium hexachlororhenate(V), $[(C_4H_9)_4N]ReCl_6$

0.66 g of $(TBA)_2ReCl_6$ was added to a stirred slurry of 0.18 g PbO_2 in 25 ml of dry deoxygenated CH_2Cl_2 and 0.2 ml of trifluoracetic acid (TFAA) was added. The solution rapidly turned red and stirring was continued for 2 h or until the UV–Vis spectra showed the absence of all bands indicative of unreacted $[Re^{IV}Cl_6]^{2-}$. The solution was then filtered through a fine sintered glass frit and an equal volume of n-pentane slowly added to the filtrate. The orange–red crystals which separated on cooling to 0 °C were collected, washed with a small amount of n-pentane and dried in a stream of nitrogen. Yield 0.32 g, 65%. *Anal.* Calc. for $C_{16}H_{36}NReCl_6$: C, 29.96; H, 5.66; N, 2.18; Cl, 33.17. Found: C, 30.29; H, 5.71; N, 2.13; Cl, 32.16%. The isolated solid, which decomposes if heated above 50 °C, may be stored at room temperature for short periods (weeks) with no apparent decomposition. Solutions rapidly decompose unless care is taken to exclude all traces of water.

Apparatus and procedures

Electronic absorption spectra in dichloromethane were recorded using a Perkin-Elmer Lambda 9 spectrometer. IR spectra were obtained using polythene discs on a Perkin-Elmer FT1800 spectrometer. Cyclic voltammograms were obtained with a BAS-100 potentiostat with Pt button working, Pt wire counter and Ag/Ag^+ reference electrodes. Measurements were performed in deoxygenated CH_2Cl_2 solutions with 0.1 M $(TBA)BF_4$ as supporting electrolyte. Thin layer electrolyses were performed in an OTTLE cell with a PAR 273 potentiostat/galvanostat, using 0.5 M $(TBA)BF_4$ as supporting electrolyte [12].

Results and discussion

Pure $[ReCl_6]^{1-}$ has been prepared and isolated as the $(TBA)^+$ salt by the PbO_2 oxidation of $[ReCl_6]^{2-}$ in $TFAA/CH_2Cl_2$. The far-IR spectra of $(TBA)ReCl_6$ shows strong bands at 346 and 321 cm^{-1}, assigned to the Re–Cl stretching mode ν_3 and at 162 cm^{-1} due to the ν_4 bending mode. These values compare with 318 and 161 cm^{-1} reported [10] for $(PCl_4)ReCl_6$ and as expected are shifted to lower frequencies than observed in $(TBA)_2ReCl_6$; ν_3 298 cm^{-1}, ν_4 163 cm^{-1}. The band positions in $[ReCl_6]^{2-}$ salts are reported [13] to be very sensitive to the cation and it appears that a similar effect may be present in the $[ReCl_6]^{1-}$ salts. The splitting of the ν_3 band in

(TBA)ReCl$_6$ is suggestive of a lowering of the site symmetry of the ReCl$_6$ core from O_h which removes the degeneracy of this mode. It is unclear if this is a result of a solid state crystal packing effect or if it reflects an intrinsic distortion, a point which will be returned to later.

Cyclic voltammetry on either (TBA)ReCl$_6$ or (TBA)$_2$ReCl$_6$ in 0.1 M (TBA)BF$_4$ in CH$_2$Cl$_2$ showed a fully reversible couple at 1.36 V versus SCE which can be attributed to the Re^{V}Cl$_6$$^{1-}$/Re^{IV}Cl$_6$$^{2-}$ couple, and a second couple, that only became fully reversible upon cooling to *c.* −40 °C due to the Re^{IV}Cl$_6$$^{2-}$/Re^{III}Cl$_6$$^{3-}$ couple [9, 14, 15]. The spectrum of a freshly prepared solution of analytically pure (TBA)ReCl$_6$ is presented in Fig. 1, and coincides exactly with that derived by the electrolysis of ReCl$_6$$^{2-}$. Upon progressive oxidation of ReCl$_6$$^{2-}$ at 1.45 V in the OTTLE cell the single complex absorption manifold centred at $\nu_{max} = 35\,000$ cm^{-1} collapses smoothly, with the retention of strict isosbestic points at 32 000 and 40 000 cm^{-1}. The emergent spectrum characterising ReCl$_6$$^{1-}$ is dominated by the two intense bands at longer wavelengths. The electronic spectrum obtained by the re-reduction of resulting red CH$_2$Cl$_2$ solution of [ReCl$_6$]$^{1-}$ at +1.2 V in the OTTLE is identical with that of the starting spectrum. Careful examination confirms that the weaker Re(V) features between 30 000 and 45 000 cm^{-1} are authentic despite their proximity to intense Re(IV) absorptions. These observations, together with the IR spectral data offer conclusive evidence for the formation of monomeric [ReCl$_6$]$^{1-}$.

The intensities and relative positions of the two dominant manifolds at 22 000 and 30 000 cm^{-1} readily identify them as Laporte-allowed chloride to metal charge transfer bands connected with the widely separated terms of the resultant d^3 ion (see below). In general LMCT transitions in hexahalogeno TM ions can be explained by considering Laporte-allowed transitions from filled ligand based molecular orbitals of π symmetry to unfilled d orbitals at the metal centre. For d^5 ions such as [IrCl$_6$]$^{2-}$ the LMCT transition leads to a single state at the metal corresponding to (t$_{2g}$)^6, and so the absorption spectra simply reflects the ligand orbital energies [1]. The highest occupied MO is a t$_{1g}$(π) which gives rise to a weak Laporte-forbidden transition, whilst ≃6000 cm^{-1} below this is the t$_{1u}$($\pi+\sigma$) level and the t$_{2u}$(π) MO is a further 3000 cm^{-1} lower in energy. This results in the observed spectral pattern of a weak band and two much stronger bands separated by ≃3500 cm^{-1}. A similarly simple spectra is found for the d^4 complex [OsCl$_6$]$^{2-}$ as a consequence of nearly pure j–j coupling in the charge transfer state, which results in some transitions becoming forbidden as two electron jumps [1].

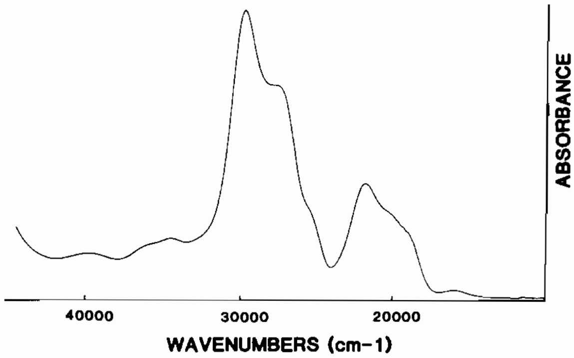

Fig. 1. Electronic absorption spectrum of (TBA)ReCl$_6$ in CH$_2$Cl$_2$.

For Re(V) d^2 where there are several excited states, available to the charge transfer excited d^3 ion, it is possible to predict the order and relative energies of the first few charge transfer excited states by considering the electronic structure to be well represented by Re$^{(4+)}$Cl$_6$$^{(5-)}$. Noting that transitions from the t$_{1u}$($\sigma+\pi$) orbital are generally much weaker than those from either the t$_{1u}$($\pi+\sigma$) or t$_{2u}$(π) orbitals then the charge transfer states can be described as in Fig. 2. From this splitting diagram it is apparent

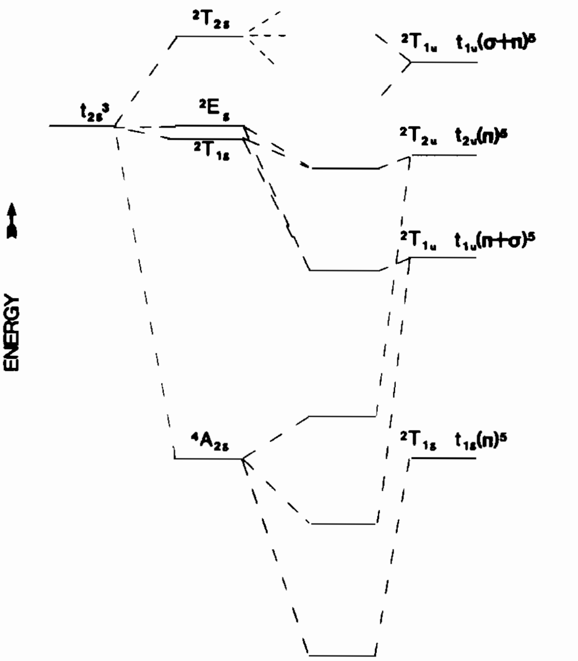

Fig. 2. Formation of charge transfer states of [ReCl$_6$]$^{1-}$ from the lowest lying states of Re^{4+} and [Cl$_6$]$^{5-}$. Diagram is not to scale. The influences of both the ligand spin–orbit coupling and electrostatic splitting between holes in the ligand MO and the metal states have been assumed to be small. There are a multitude of CT states originating from the ^2E_g and $^2T_{1g}$ states.

that the first two allowed transitions will both involve the lowest charge transfer state, the $^4A_{2g}$ of Re(IV), and thus their energy separation will reflect the ligand orbital energies.

The first band maximum, at 22 000 cm^{-1} is unambiguously assigned to the $^4A_{2g} \times {}^2T_{2u}$ CT state (Table 1). This is accompanied by an obvious shoulder at *c.* 19 500 cm^{-1} due to the $^4A_{2g} \times {}^2T_{1u}$ CT state and a substantially weaker feature at 16 000 cm^{-1} from the Laporte-forbidden $^4A_{2g} \times {}^2T_{1g}$ CT state. The spacing of these features is typical of the observed separation of the t_{2u}, t_{1u} and t_{1g} components of familiar systems, and reported for isoelectronic Cs_2MoCl_6 [6].

As anticipated above, the second manifold, near 30 000 cm^{-1} can be attributed to CT states arising from transitions to higher excited states on the d^3 metal, viz. the ^2E_g and $^2T_{1g}$ levels. However it is unlikely that the corresponding transitions to ^2E_g and $^2T_{1g}$ terms are truly superimposed. The near-IR solution spectrum of $(TBA)_2ReCl_6$ recorded in CH_2Cl_2 is in good agreement with that published by Maverick and co-workers [16, 17] and shows the ligand field transitions to Γ_8 of $^2T_{1g}$ and Γ_8 of ^2E_g are well resolved and lie 7500 and 9000 cm^{-1}, respectively, above $^4A_{2g}$, followed by Γ_6 of $^2T_{1g}$ at 9500 cm^{-1}. The possibility that the peak and prominent shoulder near 30 000 cm^{-1} in the spectra of $ReCl_6{}^{1-}$ represents $^2T_{1g} \times {}^2T_{2u}$ and $^2E_g \times {}^2T_{2u}$ CT states is unlikely because the separation between $^2T_{1g}$ and $^4A_{2g}$ terms would then be 5700 cm^{-1} which is much less than the well established value. Accordingly we prefer to ascribe the obvious maximum and shoulder to the $^2T_{1g}(\Gamma_8) \times {}^2T_{2u}$, $^2T_{1u}$ transitions in which case the corresponding $^2E_g \times {}^2T_{2u}$ transition lies in the blue edge of the manifold, together with the contribution from $^2T_{1g}(\Gamma_6)$. A more apparent splitting of the ^2E_g and $^2T_{1g}$ levels might have been expected, if the d^2 $[ReCl_6]^{1-}$ ion is distorted from octahedral symmetry as suggested by the distinct asymmetry of the ν_3 band in the solid state IR spectra. Since it is difficult to definitively characterise structural effects from solution spectra, an exact understanding of the nature and extent of any distortion of the $[ReCl_6]^{1-}$ core must wait until single crystal studies are undertaken.

TABLE 1. Electronic spectral properties of $[ReCl_6]^{1-}$ in dichloromethane

Energy (cm^{-1})	ϵ (M^{-1} cm^{-1})	Assignment
16000	500	$^4A_{2g} \times {}^2T_{1g}$
19500^a	4000	$^4A_{2g} \times {}^2T_{1u}$
22000	5700	$^4A_{2g} \times {}^2T_{2u}$
25500^a	4500	$^4A_{2g} \times {}^2T_{1u}$ $^2T_{1g} \times {}^2T_{1g}$
27700^a	10800	$^2T_{1g} \times {}^2T_{1u}$
29800	14700	$^2T_{1g} \times {}^2T_{2u}$
34500	2950	$^2T_{2g} \times {}^2T_{1u}{}^b$
36500	2600	$^2T_{2g} \times {}^2T_{2u}{}^b$
40000	2140	$^2T_{2g} \times {}^2T_{1u}{}^b$

^{a}Shoulder. ^{b}See text for discussion of alternative assignments.

Assignment of the somewhat weaker high energy bands is more tenuous. In $ReCl_6{}^{2-}$, Γ_7 and Γ_8 from the highest energy $^2T_{2g}$ term lie 14 000 and 15 500 cm^{-1}, respectively, above the $^4A_{2g}$ ground state. Therefore it is certain that above 30 000 cm^{-1} is energetically the correct region for the charge transfer excitations connecting with these components, so that the Laporte-allowed symmetry allowed transitions are either represented by these relatively weak features, or absent altogether. The charge transfer excitation to Γ_8 (which contains two thirds of the total degeneracy of the $^2T_{2g}$ term) is uniquely electronically forbidden under j-j selection rules, since it requires two electrons to change their quantum numbers.

Consequently we locate $\Gamma_7(^2T_{2g}) \times {}^2T_{1u}$, $^2T_{2u}$ at 34 500 and 36 400 cm^{-1}, respectively, which gives the best agreement with the independently determined term separations. It should be stressed that whilst the features in this region are weak *relative* to the intense 30 000 cm^{-1} feature, their absolute intensity is relatively high $\epsilon_{max} \simeq 2$–3000 and comparable to that found for the analogous transition in $[IrBr_6]^{2-}$ and the estimated area under this region is a respectable proportion (0.5 to 0.7) of the first $^4A_{2g}$ manifold.

It is appealing to assign the shoulder at 25 500 cm^{-1} as part of the manifold of transitions to the ^2E_g, $^2T_{1g}$ based states; its intensity suggesting that it is due to transitions from the (Laporte-forbidden) $^2T_{1g}$ level. However an alternative possibility is to postulate a weak (^2E_g, $^2T_{1g} \times {}^2T_{1g}$) unresolved absorption near 24 000 cm^{-1}, thus maintaining a consistent separation between the $^2T_{2u}$ and $^2T_{1g}$ components. In this case the shoulder at 25 000 cm^{-1} may be the higher lying ligand $^2T_{1u}(\sigma+\pi)$ component of the $^4A_{2g}$ manifold, which is not often recognised. The broad shallow peak at 40 000 cm^{-1} is then correspondingly placed to be assigned as $^2T_{1u}(\sigma+\pi) \times {}^2T_{2g}$ rather than as an unexpectedly high energy (and j-j forbidden) $\Gamma_8(^2T_{2g})$ component. It must be stressed that since there are a multitude of CT states in this region other assignments of these weaker transitions are possible and more detailed measurements in this region are needed to confirm these assignments.

In conclusion the $5d^2$ case is particularly interesting since it is the only $5t_{2g}^n$ system which spans more than one electronically allowed Russell–Saunders term when excited, $5t_{2g}^n \rightarrow 5t_{2g}^{n+1}$. It is possible to describe the charge transfer spectrum of $ReCl_6^{1-}$ on the familiar premise that the charge transfer states are realistically described by coupling the accessible states of the d^3 ion with the appropriate electronic hole in the ligand shell. There is a remarkable energy match between the term separations prevailing in $ReCl_6^{2-}$ and the CT promoted $ReCl_6^{1-}$. The spectrum is largely determined by electronic interactions on the metal (d–d terms) and within the ligand array. It is crucial to take into account the pronounced spin–orbit coupling on the 5d metal ion in order to understand the detailed position of the charge transfer bands and the apparent absence of a $\Delta j = 2$ band. In comparison to these effects, chloride spin–orbit coupling ($\zeta = 600$ cm^{-1}) is unresolved and the influence of spin-pairing between the metal and ligand (the so called 'electrostatic' interaction) is relatively small.

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