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Charge Transfer Spectra of Octahedral Transition Metal Complexes

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The charge transfer (CTLM) spectra of octahedral transition metal compounds can be analyzed by using a simple model involving crystal field theory. It is shown that the metal and the ligand environment may be considered as two essentially separate, but weakly interacting entities. The charge transfer spectra of a d^n system can be treated by using crystal field theory of the corresponding d^{n+1} systems.

The method described here was used in the analysis of tetrahedral transition metal complexes in a previous paper. It seems therefore to be of rather wide applicability in the field of transition metal chemistry.

Introduction

The absorption spectra of octahedral transition metal complexes provided the experimental basis for Jørgensen's pioneering studies on charge transfer spectra [1]. By means of the concept of optical electronegativity, it was possible to rationalize the position of the lowest energy charge transfer bands within a given series of compounds.

In a previous paper on tetrahedral complexes [2], we developed a general scheme, allowing the description not only of the lowest charge transfer states, but also of the relative position of the higher excited states. The central idea is as follows: a ligand-to-metal charge transfer (LMCT) state of a d^n system can be considered as a state where one electron has been promoted from a ligand orbital to a vacant metal orbital. Therefore this particular type of excited state might be looked upon as arising from a d^{n+1} configuration. The interelectronic repulsion energy within the d-shell is probably much larger than the repulsion between an electron predominantly centered on the metal and another one, predominantly on the ligands. Therefore a simplified energy level diagram can be constructed as follows: for each relevant ligand field configuration $t_2^x e^y$ ($x + y = n + 1$) the interelectronic repulsion gives rise to a number of different states, whose energy separation can be described by the Racah parameters B and C. Each of these states is then coupled to the ligand hole; thereby the symmetry and spin labels are changed, but since the coupling is assumed to be comparatively small, the resulting energy splittings will be far less important than the splittings caused by the "intra-metal" repulsion. As a consequence, the charge transfer spectrum of a d^n system can be expected to be related to the ligand field spectrum of the corresponding d^{n+1} system.

This model has been worked out in detail for a number of tetrahedral complexes [2] such as VCl_4, MnO_4^{2-}, MnO_4^{3-}, FeO_4^{2-}, $Fe(NCS)_4^{2-}$ and $Fe(NCSe)_4^{2-}$. It is the purpose of this communication to apply the same general ideal to the charge transfer spectra of octahedral transition metal compounds.

Choice of the Complexes

In an absorption spectrum, the observability of the different charge transfer states depends on their accessibility from the ground state. Considering only the electric dipole transition mechanism, the spin and spatial selection rules are immediately obvious in all cases. Table I shows the results of such an analysis for all d^n systems in an octahedral environment. In general, both e_g and t_{2g} can be the acceptor orbitals. This gives rise to two different excited configurations per ligand hole; hence the two middle columns in Table I. For certain systems – designated "a" in the Table – a given excited configuration gives rise to only *one* charge transfer state, which is accessible from the ground state by the electric dipole mechanism. In these cases, the relative position of the different CT states will be determined primarily by orbital energy differences. In the other cases – designated "b" – more than one accessible state corresponds to a given configuration. The category "b1" contains systems where the different states belong to the *same* parent metal term; therefore, the resulting energy splittings are expected to be small. In the category "b2" on the other hand, the different accessible states belong to *different* parent metal terms. Therefore, the energy splittings are much larger and

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TABLE I. Group Theoretical Analysis of the CT Excited States in All d^n Systems with O_h Symmetry; the Class to Which a Given Complex Belongs is Given for the Two Possible Acceptor Levels.

System	e_g = Acceptor	t_{2g} = Acceptor	Examples
d^1	b2	b2	TiF_6^{3-} ReF_6
d^2	b2	b2	$V(H_2O)_6^{3+}$ $Mo(NCS)_6^{2-}$
d^3	b2	a	TcX_6^{2-} (X = Cl, Br or I) ReX_6^{2-} (X = Cl, Br or I)
d^4 high spin	b2	b2	$Mn(H_2O)_6^{3+}$ $Cr(H_2O)_6^{2+}$
low spin	b2	b1	OsX_6^{2-} (X = Cl or Br)
d^5 high spin	b1	b1	$Mn(H_2O)_6^{2+}$ $Mn(en)_3^{2+}$ ***
low spin	b2	b1	IrX_6^{2-} (X = Cl or Br)
d^6 high spin	b2	b1	CoF_6^{3-}
low spin	a	– *	IrX_6^{3-} (X = Cl or Br)
d^7 high spin	b2	a	$Co(NH_3)_6^{2+}$ $Co(en)_3^{2+}$
low spin	b2	–	
d^8	a	–	$Ni(H_2O)_6^{2+}$ $Ni(en)_3^{2+}$
d^9	a	–	$Cu(H_2O)_6^{2+}$ **

*t_{2g} cannot be the acceptor level (fully occupied). **Distorted octahedron. ***en = ethylenediamine.

connected to the crystal field spectrum of the corresponding d^{n+1} systems. The applicability of the present model is obviously limited to the "b2" cases. Table I contains a number of examples. We selected the 4d^3 Tc(IV)- and 5d^3 Re(IV)-hexahalides for further study. Indeed, these complexes allow at the same time to evaluate the role of increasing spin–orbit coupling and to assess the relative importance of spin–orbit coupling and electron repulsion effects.

Spectral Data

The absorption spectra of the Tc(IV)-hexahalides were studied by a number of authors [3–5]. Figure 1 shows the charge transfer region as given by Jørgensen and Schwochau [3].

For the Re(IV) compounds, most studies are concerned with the ligand field transitions [6–9]. Here again, the most complete set of data is given by Jørgensen and Schwochau [3], as shown in Figure 2. The spectra were taken in aqueous solution, to at least 42 kK. The symmetry in solution can be taken to be octahedral [8]. The more detailed polarized absorption spectra of Schenk and Schwochau [10] were not considered because they cover only a range up to 36 kK, and they do not report any data on the iodide complexes.

As a result of the Gaussian analysis of Figures 1 and 2 the values and intensity of certain transitions may be slightly different from the data in the literature.

Theoretical Analysis

One-electron Energy Levels

Figure 3 shows a qualitative orbital energy level diagram for an octahedral complex. The metal orbitals $e_g(\sigma^*)$ and $t_{2g}(\pi^*)$ are only accessible from ungerade ligand orbitals. The $t_{2u}(\pi)$ functions are pure ligand orbitals, while $t_{1u}(\pi^b)$ and $t_{1u}(\sigma^b)$ are predominantly localized on the ligands. Both sets of t_{1u} orbitals are at the same time π- and σ-bonding, but in parentheses, the principal bonding mode is designated. The notation of the LCAO–MO coefficients is given in Table II. As for the order of magnitude of these coefficients, c_1, c_1'', c_3' and c_2''' will probably vary between about 0.8 and 0.95 in absolute value; the absolute value of the other coefficients will be situated between 0.3 and 0.6. If the metal coefficients are taken to be positive, c_3' , c_2''' and c_3''' will also be positive, while c_2, c_2' and c_2'' will be nega-

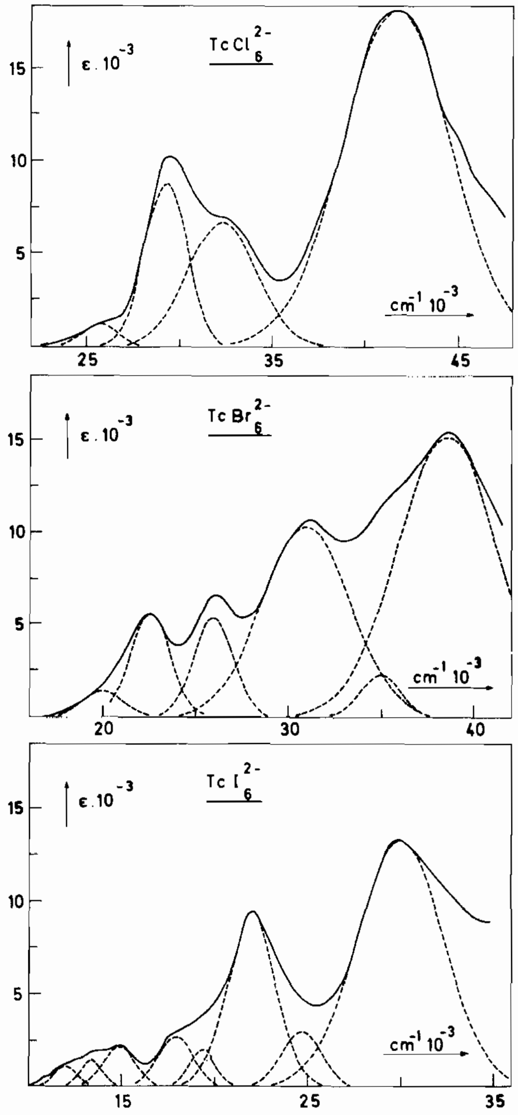

Figure 1. Gaussian analysis of the absorption spectra of the Tc(IV) hexahalides, as given in reference 3.

TABLE II. LCAO Coefficients of the Octahedral Molecular Orbitals.

MO	Metal d	Metal p	Ligand σ	Ligand π
$t_{2g}(\pi^*)$	c_1	–	–	c_2
$e_g(\sigma^*)$	c_1''	–	c_2''	–
$t_{1u}(\pi^b)$	–	c_1'	c_2'	c_3'
$t_{1u}(\sigma^b)$	–	c_1'''	c_2'''	c_3'''

tive. Since c_2' and c_3' have opposite signs, the relative position of $t_{1u}(\pi^b)$ and $t_{2u}(\pi)$ will depend on the balance of the σ-antibonding and the π-bonding interactions.

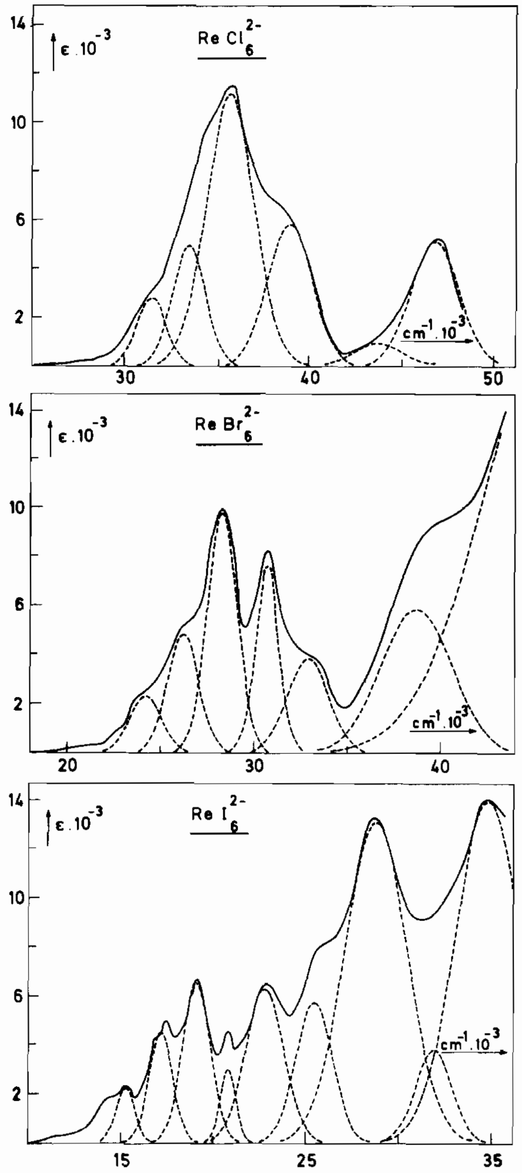

Figure 2. Gaussian analysis of the absorption spectra of the Re(IV) hexahalides, as given in reference 3.

It is not easy to determine the 10Dq values directly from the ligand field spectra. One can, however, use a general approximation [11], where 10Dq – in kK units – is written as a product of a ligand factor (f) and a metal factor (g). The ligand factors are f = 0.78, 0.72 and 0.68 for Cl^-, Br^- and I^- respectively. The metal factors are [12] g = 30 for Tc(IV) and 34 for Re(IV); the latter g-value was interpolated between g = 32 for Ir(III) and g = 36 for Pt(IV) on the basis of the spectrochemical series [11]. The resulting 10Dq values (in cm^{-1}) are listed in Table V.

TABLE III. Energy Matrices for the Relevant d^3 and d^4 Configurations.

$(t_{2g})^3$	$^4A_{2g}$	3A – 15B	
	^2E_g	3A – 6B + 3C	
	$^2T_{1g}$	3A – 6B + 3C	
	$^2T_{2g}$	3A + 5C	
$(t_{2g})^4$	$^3T_{1g}$	6A – 15B + 5C	
$(t_{2g})^3(^4A_{2g})e_g$	^5E_g	6A – 21B	
$(t_{2g})^3(^4A_{2g})e_g$	^3E_g	6A – 13B + 4C	–4B
$(t_{2g})^3(^2E_g)e_g$	^3E_g	–4B	6A – 10B + 4C
$(t_{2g})^3(^2E_g)e_g$	$^3A_{1g}$	6A – 12B + 4C	
$(t_{2g})^3(^2E_g)e_g$	$^3A_{2g}$	6A – 8B + 4C	
$(t_{2g})^3(^2T_{1g})e_g$	$^3T_{1g}$	6A – 11B + 4C	$5B\sqrt{3}$
$(t_{2g})^3(^2T_{2g})e_g$	$^3T_{1g}$	$5B\sqrt{3}$	6A – 3B + 6C
$(t_{2g})^3(^2T_{1g})e_g$	$^3T_{2g}$	6A – 9B + 4C	$5B\sqrt{3}$
$(t_{2g})^3(^2T_{2g})e_g$	$^3T_{2g}$	$5B\sqrt{3}$	6A – 5B + 6C

Electron Repulsion

The lowest energy configuration consists of a number of closed shells, and $[t_{2g}(\pi^*)]^3$, yielding a $^4A_2$ ground state. An LMCT (ligand-to-metal charge

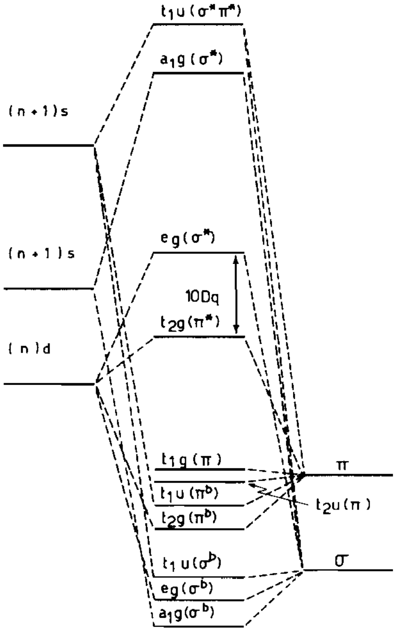

Figure 3. Partial and qualitative molecular orbital energy level diagram for an octahedral transition metal complex.

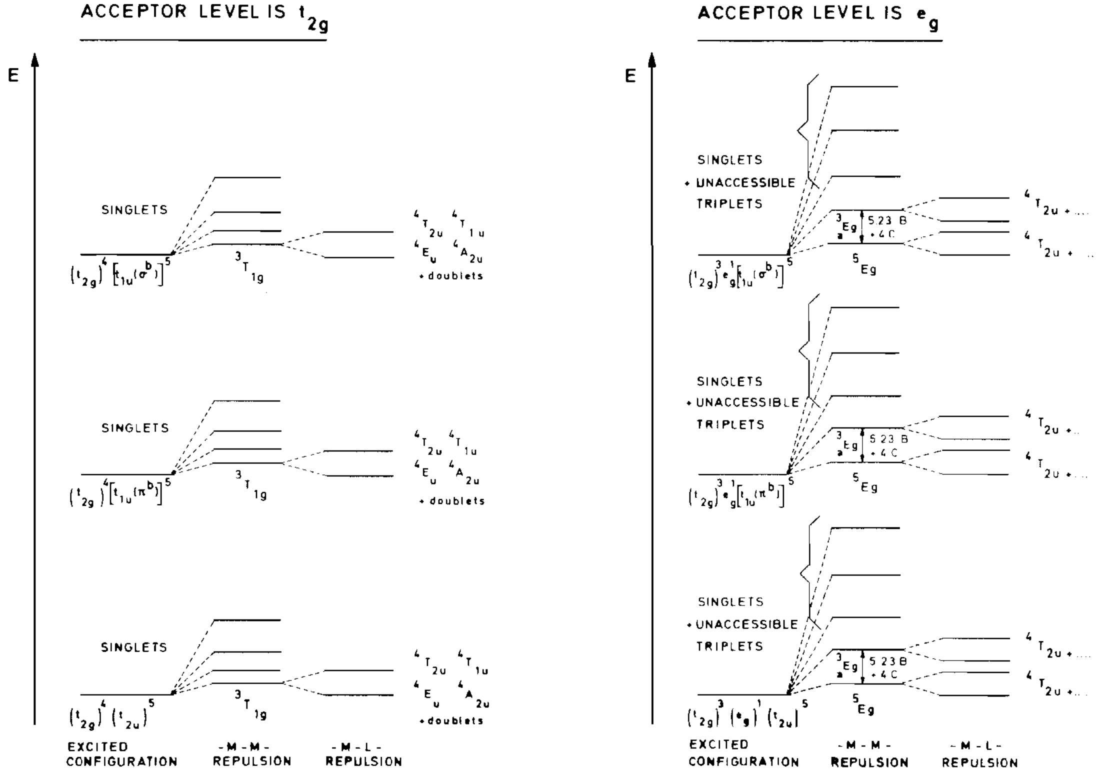

Figure 4. Qualitative energy level diagram of the charge transfer excited states in octahedral d^3 systems. The ground state is ^4A_g; the accessible excited states are $^4T_{2u}$.

TABLE IV. Theoretical Crystal Field Splittings in the Excited CT States of O_h d^3 Complexes; Racah Parameters and Nephelauxetic Parameters for d^4 Ions (in kK).

Complex	B_0	β	10Dq	$B = \beta B_0$	$^3_aE_g - {}^5E_g =$ 5.23 B + 4C	−6 − 5C + 10Dq
$TcCl_6^{2-}$	0.66	0.81	23.4	0.53	11.25	9.62
$TcBr_6^{2-}$	0.66	0.78	21.6	0.51	10.83	8.34
TcI_6^{2-}	0.66	0.75	20.4	0.49	10.40	7.66
$ReCl_6^{2-}$	0.60	0.83	26.5	0.50	10.62	13.50
$ReBr_6^{2-}$	0.60	0.79	24.5	0.47	9.98	12.28
ReI_6^{2-}	0.60	0.77	23.1	0.46	9.77	11.14

transfer) excitation gives rise to a number of configurations, as shown in Figure 4.

In this energy level diagram, each configuration is split into a number of states, primarily due to the repulsion between electrons, mainly localized on the central metal ion (middle part of the diagrams). The smaller energy splittings at the right hand side of Figure 4 are due to the coupling of the different d^4 states with the ligand hole.

The $(t_{2g})^3(e_g)^1$ states can be considered to be built from $(t_{2g})^3$ and one e_g electron. The ensuing singlets may be omitted, since only quintets or triplets can combine with the ligand hole to yield the required (accessible) quartet states. The relevant energy expressions were taken from Griffith's standard work [13] and are given in Table III (see also Figure 4).

The energy difference between $^5E_g[t_{2g}(\pi^*)]^3[e_g(\sigma^*)]^1$ and $^3T_{1g}[t_{2g}(\pi^*)]^4$ equals 10Dq − 6B − 5C.

The free ion Racah parameters B_0 and C_0 cannot be derived directly from Moore's tables [14] for $4d^4$ and $5d^4$ ions. The extrapolated values [11] for B_0 are ~660 cm^{-1} for Tc(III) and 600 cm^{-1} for Re(III). The nefelauxetic parameters are not known for the d^4 ions, but Jørgensen and Schwochau [3] give the β_{55} values compatible with the crystal field spectra of the six d^3 complexes under consideration. In what follows, we put $C_0 = 4B_0$ and $C = 4B$; moreover, the nefelauxetic effect will be described by one parameter in each case: $\beta_{55} \sim \beta$. It will further be assumed that the difference in β between three- and four-valent metal ions varies as a function of the principal quantum number n, in the same way as B_0 itself, *i.e.* in the ratio 15:10:9 for n = 3, 4, 5. The difference between β for 3d-MF_6^{3-} and β for 3d-MF_6^{4-} complexes is about 0.2–0.25 units [15]. From these data and assumptions, the *in situ* Racah parameters B and C are as shown in Table IV.

Spin–Orbit Coupling

In Griffith's double group notation [16], the $^4A_{2g}$ ground state becomes a U'_g spinor state, and $^4T_{2u}$ gives rise to four spinor terms, E'_u E''_u, $3/2U'_u$ and $5/2U'_u$. The transitions between U'_g and any one of these four spinor components are electric dipole allowed.

In order to evaluate the matrix elements of the matrix elements of the spin–orbit coupling hamiltonian, we use Griffith's irreducible tensor method [16]. The equations have been extended so as to include the matrix elements between spinor states, resulting from three open shells.

In working out the one electron matrix elements, the one-center approximation was used [17–19]. The energies are expressed as a function of the MO coefficients and the spin–orbit constants of the different atoms in the complex. The groundstate is unaffected by spin-orbit coupling. As for the $^4T_{2u}$ excited states the sign and magnitude of the reduced element will vary from case to case, but the factor multiplying this element will be the same, irrespective of the parentage of the state in question. The factors are $-1/2\sqrt{10}$ for E'_u and $5/2$ U'_u, $5/6\sqrt{10}$ for E'_u and $1/3\sqrt{10}$ for $3/2U'_u$. The splitting pattern, shown in Figure 5, therefore shows an accidental degeneracy, which will of course be lifted if second order effects are included. Table V shows the analytical expression of the reduced matrix elements for the relevant states.In evaluating these elements LCAOMO's were used, in which the constituent ligand AO's refer to local coordinate systems parallel to the central coordinate system. A semi-quantitive estimate of the spin–orbit splittings can be obtained

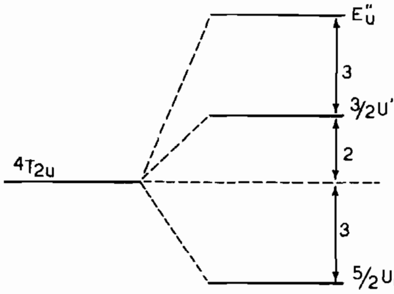

Figure 5. Spin–orbit splitting of the $^4T_{2u}$ CT states in O_h d^3 systems.

TABLE V. Analytical Expresssion of the Reduced Matrix Elements of the Spin–Orbit Coupling Operator in the CT Excited States of Octahedral d^3 Systems.

Orbital Transition	Metal Term		Reduced Matrix Elements
$t_{2u}(\pi) \rightarrow t_{2g}$	$(t_{2g})^4\ {}^3T_{1g}$	${}^3T_{1g}$	$\frac{-5}{\sqrt{10}}\{(c_1)^2\zeta_{nd} + [(c_2)^2/2 + 1/2]\zeta^L_{np}\}^a$
$t_{1u}(\pi^b) \rightarrow t_{2g}$	$(t_{2g})^4\ {}^3T_{1g}$	${}^3T_{1g}$	$\frac{5}{\sqrt{10}}\{(c_1)^2\zeta_{nd} + [(c_2)^2/2 - (c'_3)^2/2 + \sqrt{2}\sqrt{1-\delta^2}\ c'_3c'_2]\zeta^L_{np} - (c'_1)^2\zeta^M_{np}\}$
$t_{1u}(\sigma^b) \rightarrow t_{2g}$	$(t_{2g})^4\ {}^3T_{1g}$	${}^3T_{1g}$	$\frac{5}{\sqrt{10}}\{(c_1)^2\zeta_{nd} + [(c_2)^2/2 - (c'''_3)^2/2 + \sqrt{2}\sqrt{1-\delta^2}\ c'''_3c'''_2]\zeta^L_{np} - (c'''_1)^2\zeta^M_{np}\}$
$t_{2u}(\pi) \rightarrow e_g$	$(t_{2g})^3\ {}^4A_{2g}(e_g)^1$	${}^5E_g$	$\frac{-3}{2\sqrt{10}}\zeta^L_{np}$
$t_{1u}(\pi^b) \rightarrow e_g$	$(t_{2g})^3\ {}^4A_{2g}(e_g)^1$	${}^5E_g$	$\frac{3}{\sqrt{10}}\{(c'_1)^2\zeta^M_{np} + \zeta^L_{np}[(c'_3)^2/2 - \sqrt{2}\sqrt{1-\delta^2}\ c'_3c'_2]\}$
$t_{1u}(\sigma^b) \rightarrow e_g$	$(t_{2g})^3\ {}^4A_{2g}(e_g)^1$	${}^5E_g$	$\frac{3}{\sqrt{10}}\{(c'''_1)^2\zeta^M_{np} + \zeta^L_{np}[(c'''_3)^2/2 - \sqrt{2}\sqrt{1-\delta^2}\ c'''_3c'''_2]\}$
$t_{2u}(\pi) \rightarrow e_g$	$(t_{2g})^3\ {}^4A_{2g}(e_g)^1$	${}^3_aE_g$	$\frac{5}{2\sqrt{10}}\zeta^L_{np}$
$t_{1u}(\pi^b) \rightarrow e_g$	$(t_{2g})^3\ {}^4A_{2g}(e_g)^1$	${}^3_aE_g$	$\frac{-5}{\sqrt{10}}\{(c'_1)^2\zeta^M_{np} + \zeta^L_{np}[(c'_3)^2/2 - \sqrt{2}\sqrt{1-\delta^2}\ c'_3c'_2]\}$
$t_{1u}(\sigma^b) \rightarrow e_g$	$(t_{2g})^3\ {}^4A_{2g}(e_g)^1$	${}^3_aE_g$	$\frac{-5}{\sqrt{10}}\{(c'''_1)^2\zeta^M_{np} + \zeta^L_{np}[(c'''_3)^2/2 - \sqrt{2}\sqrt{1-\delta^2}\ c'''_3c'''_2]\}$

[a] The superscripts M and L refer to metal and ligand respectively.

TABLE VI. Approximate Numerical Values of the Reduced Matrix Elements of the Spin–Orbit Coupling Operator in the CT Excited States of O_h d^3 Systems. Energies are in kK.

Orbital Transition	Metal Term	$TcCl_6^{2-}$	$TcBr_6^{2-}$	TcI_6^{2-}	$ReCl_6^{2-}$	$ReBr_6^{2-}$	ReI_6^{2-}
$t_{2u}(\pi) \rightarrow t_{2g}$	${}^3T_{1g}$	−1.9	−3.6	−5.7	−4.8	−6.4	−8.6
$t_{1u}(\pi^b) \rightarrow t_{2g}$	${}^3T_{1g}$	0.5	−1.7	−4.5	1.6	−0.6	−3.4
$t_{1u}(\sigma^b) \rightarrow t_{2g}$	${}^3T_{1g}$	1.5	2.5	4.0	2.6	3.7	5.1
$t_{2u}(\pi) \rightarrow e_g$	${}^5E_g$	−0.3	−1.2	−2.4	−0.3	−1.2	−2.4
$t_{1u}(\pi^b) \rightarrow e_g$	${}^5E_g$	0.6	2.0	3.8	1.2	2.6	4.4
$t_{1u}(\sigma^b) \rightarrow e_g$	${}^5E_g$	−0.01	−0.6	−1.3	0.6	0.02	−0.7
$t_{2u}(\pi) \rightarrow e_g$	${}^3_aE_g$	0.5	2.0	3.9	0.5	2.0	3.9
$t_{1u}(\pi^b) \rightarrow e_g$	${}^3_aE_g$	−1.0	−3.3	−6.3	−2.0	−4.3	−7.3
$t_{1u}(\sigma^b) \rightarrow e_g$	${}^3_aE_g$	0.02	1.0	2.2	−1.0	−0.03	1.2

by incorporating a set of reasonable parameter values in the expressions of Table V. With

$c_1 \cong 0.95$
$c'_3 \cong c'''_2 \cong 1 - \delta^2 \cong 0.9$ (δ is the coefficient of the ligand s-orbital in the ligand σ-basis combination)
$c_2 \cong c'_2 \cong -c'_1 \cong -c'''_1 \cong -c'''_3 \cong -0.3$
$\zeta_{4d} \cong 1000\ cm^{-1}$, $\zeta_{5p} \cong 2000\ cm^{-1}$ for Tc(III)
$\zeta_{5d} \cong 3000\ cm^{-1}$; $\zeta_{6p} \cong 9000\ cm^{-1}$ for Re(III)
$\zeta_{3p} \cong 600\ cm^{-1}$; $\zeta_{4p} \cong 2500\ cm^{-1}$ and
$\zeta_{5p} \cong 5000\ cm^{-1}$ for the halogens

one obtains the numerical values of Table VI. The values of the different spin–orbit coupling constants were taken or extrapolated from Dunn [20, 21] or Jϕrgensen [22].

Intensities

In the absence of spin–orbit coupling, the intensities can be calculated from Griffith's irreducible tensor method, as applied in a previous paper [2]. In the evaluation of the one-electron transition integrals,

TABLE VII. Intensity Calculations in Octahedral d^3 Systems. The dipole strength is expressed in units of R^2 (R is the metal–ligand distance); all the CT excited states have $^4T_{2u}$ symmetry.

Acceptor Orbital	Metal Term		Dipole Strength for Different Ligand Donor Orbitals		
	Composition	Term	$t_{2u}(\pi)$	$t_{1u}(\pi^b)$	$t_{1u}(\sigma^b)$
t_{2g}	$(t_{2g})^4\ {}^3T_{1g}$	$^3T_{1g}$	$1.5(c_2)^2$	$1.5(c_3')^2(c_2)^2$	$1.5(c_3''')^2(c_2)^2$
e_g	$(t_{2g})^3\ {}^4A_{2g}(e_g)^1$	^5E_g	~0	$2.5(c_2')^2(c_2'')^2$	$2.5(c_2''')^2(c_2'')^2$
e_g	$(t_{2g})^3\ {}^4A_{2g}(e_g)^1$	$^3_aE_g$	~0	$1.5(c_2')(c_2'')^2$	$1.5(c_2''')^2(c_2'')^2$

TABLE VIII. Identification of the CT Spectra of TcX_6^{2-} (X = Cl, Br, I) by Previous Authors. Band positions are given in kK and shoulders are in parentheses.

Complex	Jørgensen–Schwochau		Schenk–Schwochau		
	Position	Transition	Position	Polarization	Transition
$TcCl_6^{2-}$	(25.97)	$t_{1g}(\pi^b) \rightarrow t_{2g}$	(26.30)	π, σ	$t_{1g}(\pi^b) \rightarrow t_{2g}$
	29.58	$t_{1u}(\pi^b) \rightarrow t_{2g}$	(28.17)	π, σ	$t_{1u}(\pi^b) \rightarrow t_{2g}$
	(32.47)	$\pi \rightarrow t_{2g}$	28.82	σ	
	41.67	$t_{1u}(\pi^b) \rightarrow e_g$	28.94	π	
			32.15	π	$t_{2u} \rightarrow t_{2g}$
			32.19	σ	
$TcBr_6^{2-}$	22.55	$\pi \rightarrow t_{2g}$	(20.30)	$\pi < \sigma$	$t_{1u}(\pi^b) \rightarrow t_{2g}$
	26.00	$\pi \rightarrow t_{2g}$	20.83	$\pi < \sigma$	
	30.79		22.15	σ	
	34.84		22.29	π	
	38.29	$t_{1u}(\pi^b) \rightarrow e_g$	(23.00)	$\pi < \sigma$	
			(24.10)	σ	$t_{2u} \rightarrow t_{2g}$
			(24.54)	π	
TcI_6^{2-}	14.03	$\pi \rightarrow t_{2g}$			
	14.90				
	(17.96)				
	22.08	$\pi \rightarrow e_g$?			
	30.20	$\pi \rightarrow e_g$			

only the diagonal elements on the ligand atoms are important [17, 23, 24]. A certain number of excited states, corresponding to the $(t_{2g})^3(e_g)^1$ configurations are inaccessible since they differ in more than one spin-orbital from the ground state. The only transitions that are to be considered are shown in Table VII. The two entries ~0 indicate that the diagonal elements on the ligands lead to a zero transition probability. Incorporation of the other contributions in the transition integrals would lead to a finite, but small intensity.

The first-order effect of spin–orbit coupling is simply to distribute the total dipole strength, as shown in Table VII, over the four spinor components. Harnung's equations [25] show that the fractions to be attributed to $U_g' \rightarrow E_u', E_u'', 3/2U_u', 5/2U_u'$ are 0.16, 0.16, 0.33 and 0.33 respectively. Considering the approximate degeneracy of E_u' and 2.5 U_u', the intensity ratio is 3:2:1 for an energetic order as shown in Figure 5.

Interpretation of the Spectra

The TcX_6^{2-} Complexes

The charge transfer spectra of these compounds have been analyzed by Jørgensen and Schwochau [3] and by Schenk and Schwochau [10]. The latter authors studied the complexes in monocrystals of $(C_2H_5NH_3)_2[SnX_6]$ having a local D_{3d} symmetry. Their interpretation is shown in Table VIII.

From the present point of view, the analysis can be carried out as follows. For the first transition in each complex, there are essentially two possibilities as far as orbital transitions are concerned (Figure 3): either one has $t_{2u}(\pi) \rightarrow t_{2g}(\pi^*)$, or one has $t_{1u}(\pi^b) \rightarrow t_{2g}(\pi^*)$. The relative energy of $t_{2u}(\pi)$ and $t_{1u}(\pi^b)$ was discussed briefly in Section IV.A. The relevant $^4T_{2u}$ state exhibits a total spin–orbit splitting of approximately $4/3\sqrt{10} \cong 0.42$ times the reduced matrix element of Table VI. The first three transitions in TcI_6^{2-} satisfy the qualitative requirements of the

TABLE IX. Spectral Identification of the TcX_6^{2-} Complexes. Band positions are given in kK and molar extinction coefficients are in parentheses.

Complex	Positions	Orbital Transition	Metal Term	CT State (Spinor Component)
$TcCl_6^{2-}$	29.2 (8800)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
	32.2 (6700)	$t_{1u}(\pi^b) \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
	41.7(17200)	$t_{1u}(\pi^b) \rightarrow e_g$	^5E_g	$^4T_{2u}$
$TcBr_6^{2-}$	22.5 (5600)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
	25.9 (5400)	$t_{1u}(\pi^b) \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
	30.9(10300)	$t_{1u}(\pi^b) \rightarrow e_g$	^5E_g	$^4T_{2u}$
	34.9 (2300)	$t_{1u}(\sigma^b) \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
	38.5(15200)	$t_{1u}(\sigma^b) \rightarrow e_g$	^5E_g	$^4T_{2u}$
TcI_6^{2-}	12.0 (1100)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(E_u'')$
	13.4 (1400)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(3/2U_u')$
	14.9 (2100)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(5/2U_u'$ and $E_u')$
	17.9 (2700)	$t_{1u}(\pi^b) \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
	19.4			
	22.0 (9400)	$t_{1u}(\pi^b) \rightarrow e_g$	^5E_g	$^4T_{2u}$
	24.7 (3000)	$t_{1u}(\sigma^b) \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
	30.0 (13300)	$t_{1u}(\sigma^b) \rightarrow e_g$	^5E_g	$^4T_{2u}$

$t_{2u}(\pi) \rightarrow t_{2g}(\pi^*)$ transition: from the previous considerations one expects three transitions split by roughly 2.4 kK and with a relative intensity of 1:2:3. In the other two complexes, the spin-orbit splitting is smaller and cannot be observed; the total intensity of the first band is somewhat larger than the intensity of the second band. From Table VII, this is indeed to be expected if the first transition(s) correspond to $t_{2u}(\pi) \rightarrow t_{2g}(\pi^*)$ and the second transition(s) to $t_{1u}(\pi) \rightarrow t_{2g}(\pi^*)$. This identification is detailed in Table IX.

The shift of the first band from the chloride to the iodide complex (29.3 kK, 22.5 kK and ~14 kK) are in agreement with the difference in optical electronegativity between the halogen ligands. From Table VI the spin–orbit splitting of the second band is smaller and is not observed in $TcCl_6^{2-}$ or $TcBr_6^{2-}$. It might be observable in TcI_6^{2-}; if so, the splitting pattern and the intensity distribution should be similar to the first band. Since this is not verified experimentally, only the 17.9 kK band is assigned as $t_{1u}(\pi) \rightarrow t_{2g}(\pi^*)$.

If the metal–ligand two-center repulsion integrals are indeed small quantities, it should be concluded that $E[t_{2u}(\pi)] - E[t_{1u}(\pi^b)]$ is positive in all cases, being 3, 3.5 and ~4 kK in the chloride, bromide and iodide complexes respectively.

All $t_{2u}(\pi) \rightarrow e_g(\sigma^*)$ transitions are predicted to have negligible transition probabilities. Therefore the next orbital transitions to be considered are $t_{1u}(\sigma^b) \rightarrow t_{2g}(\pi^*)$ and $t_{1u}(\pi^b) \rightarrow e_g(\sigma^*)$. In the latter case the ^5E_g term lies approximately 10 kK lower than the $^3_aE_g$ term (Table V); so the CT excited state with ^5E_g parentage need not be considered at this moment. The relative position of the two remaining relevant states is not obvious. Indeed, $t_{1u}(\pi^b) \rightarrow e_g(\sigma^*)$ is 10Dq – 5B – 6C higher than $t_{1u}(\pi^b) \rightarrow t_{2g}(\pi^*)$. From Table V, the numerical values vary between 10 and 7 kK. On the other hand, the energy difference between $t_{1u}(\pi^b)$ and $t_{1u}(\sigma^b)$ is unknown, but it is estimated at 6 to 10 kK by Carrington and Jørgensen [26] and Jørgensen [27]. Therefore, a distinction can only be made on the basis of intensities. Table VII predicts the higher intensity for $t_{1u}(\pi^b) \rightarrow e_g(\sigma^*)$. Hence we assign the bands at 41.7 kK, 30.9 kK and 22 kK in the spectra of the chloride, bromide and iodide complexes respectively to $^4T_{2u}(^5E_g; t_{1u}(\pi^b) \rightarrow e_g(\sigma^*))$.

The 34.9 kK and 24.7 kK bands in the chloride and bromide compounds are assigned as $^4T_{2u}(t_{1u}(\sigma^b) \rightarrow t_{2g}(\pi^*))$. The fact that the first set of bands are particularly broad, is an additional indication that the $e_g(\sigma^*)$ orbital is involved, rather than $t_{2g}(\pi^*)$ [28].

The bands at 38.5 kK (bromide) and 30.0 kK (iodide) have very large extinction coefficients and the assignment $t_{1u}(\sigma^b) \rightarrow e_g(\sigma^*)(^5E_g)$ seems indicated. Also on the basis of relative positions, one expects to find the $t_{1u}(\pi^b) \rightarrow e_g(\sigma^*)(^3_aE_g)$ transitions at higher energies.

If the present assignments are correct, a number of regularities are expected in the band positions. For the bromide and the iodide complexes, the energy difference 10Dq – 6B – 5C should be found twice. Indeed, for the bromide complex, it should be equal to (30.9 – 25.9) kK and also to (38.5 – 34.9) kK; for the iodide complex, it should be equal to (22 – 17.9) kK and also to (30 – 24.7) kK. Both equalities are

TABLE X. Identification of the CT Spectra of ReX_6^{2-} (X = Cl, Br, I) by Previous Authors. Band positions are in kK; shoulders are in parentheses.

Complex	Jørgensen–Schwochau		chenk–Schwochau		
	Position	Transition	Position	Polarization	Transition
$ReCl_6^{2-}$	(31.65)	$\pi \rightarrow t_{2g}$	30.89	$\pi < \sigma$	$t_{1g}(\pi^b) \rightarrow t_{2g}$
	(34.08)	$\pi \rightarrow t_{2g}$	33.06	σ	$t_{1u}(\pi^b) \rightarrow t_{2g}$
	35.65	$t_{1u}(\pi^b) \rightarrow t_{2g}$	33.33	π	
	(39.12)		34.48	σ	
	46.88		34.78	π	
$ReBr_6^{2-}$	(20.92)	$t_{1u}(\pi^b) \rightarrow t_{2g}$	(22.87)	$\pi < \sigma$	$t_{1g}(\pi^b) \rightarrow t_{2g}$
	(23.98)	$\pi \rightarrow t_{2g}$	23.10	$\pi < \sigma$	
	(26.39)	$\pi \rightarrow t_{2g}$	(23.56)	σ	
	28.38	$\pi \rightarrow t_{2g}$	(23.67)	π	
	30.38		(23.78)	σ	
	33.06				
	39.60				
ReI_6^{2-}	11.55	$\pi \rightarrow t_{2g}$			
	(12.44)				
	(14.50)	$\pi \rightarrow t_{2g}$			
	⋮				
	9 maxima				
	(23.64)				
	25.87	$\pi \rightarrow e_g$?			
	28.50	$\pi \rightarrow e_g$			
	34.46	$\pi \rightarrow e_g$			

TABLE XI. Interpretation of the CT Spectra of ReX_6^{2-} Complexes. Band positions are in kK; molar extinction coefficients are in parentheses.

Complex	Position	Orbital Transition	Metal Term	CT State (Spinor Component)
$ReCl_6^{2-}$	31.4 (2400)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(E_u'')$
	33.4 (4260)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(3/2U_u')$
	35.6 (9660)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(5/2U_u'$ and $E_u')$
	38.8 (5060)	$t_{1u}(\pi^b) \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
	43.5 (800)	?		
	46.6 (4400)	$t_{1u}(\sigma^b) \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
$ReBr_6^{2-}$	24.2 (2300)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(E_u'')$
	26.2 (4840)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(3/2U_u')$
	28.3 (9850)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(5/2U_u'$ and $E_u')$
	30.7 (7690)	$t_{1u}(\pi^b) \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
	32.9 (3850)	?		
	38.7 (5920)	$t_{1u}(\sigma^b) \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
ReI_6^{2-}	15.2 (2230)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(E_u'')$
	17.1 (4460)	$t_{2u} \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}(3/2U_u')$
	19.0 (6540)	$t_{2u} \rightarrow t_{2g}$?	$^3T_{1g}$	$^4T_{2u}(5/2U_u'$ and $E_u')$
	20.7 (3000)	$t_{2u}(\pi^b) \rightarrow t_{2g}$?	$^3T_{1g}$	$^4T_{2u}$
	22.65(6310)	?		
	25.2 (5770)	$t_{1u}(\sigma^b) \rightarrow t_{2g}$	$^3T_{1g}$	$^4T_{2u}$
	28.6 (13150)	$t_{1u}(\pi^b) \rightarrow e_g$	^5E_g	$^4T_{2u}$
	31.7 (3770)	?		
	34.6 (14000)	$t_{1u}(\sigma^b) \rightarrow e_g$	^5E_g	$^4T_{2u}$

approximately satisfied. Similar relationships might be anticipated for the energy difference $E(t_{1u}(\pi^b)) - E(t_{1u}(\sigma^b))$. For the bromide, it equals (34.9 – 25.9) kK and (38.5 – 30.9) kK; for the iodide, the numbers are (24.7 – 17.9) kK and (30 – 22) kK. The energy gap between the two t_{1u} orbitals is thus consistently found at about 8 kK in both complexes.

The ReX_6^{2-} Complexes

Exactly the same methodology has been applied to the Rheniumhalides. The identification was not always as unambiguous as in the case of the TcX_6^{2-} compounds. The inclusion of second order spin-orbit coupling effect might prove useful in this case. However, even without this refinement, it has been possible to propose a consistent set of assignments. The results in Table XI can be compared with the conclusions of previous authors (Table X).

Conclusion

The charge transfer spectra of both octahedral and tetrahedral [2] transition metal compounds can be analyzed by the here proposed method. It appears that the metal and the ligand can be considered as two essentially separate, but weakly interacting entities. The charge transfer spectra of a d^n system can be treated by using crystal field theory of the corresponding d^{n+1} systems.

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