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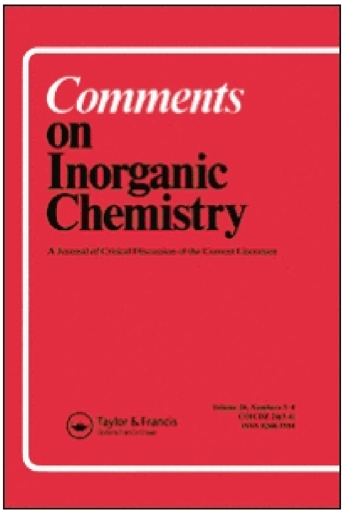

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Ion Pair Charge Transfer as a Particular Effect of Second-Sphere Coordination

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The interest in dealing with the classical phenomenon of second-sphere coordination has developed again during the past few years. This is due to some unusual chemical and physical properties caused by outer-sphere effects. Ion pair associates consisting of ionic Werner-type complexes and appropriate counter-ions are diverse representatives of second-sphere coordination. Such ion-pair compounds are of particular interest which are distinguished by spectroscopic ion pair charge transfer (IPCT) transitions. The spectroscopic and photochemical behavior of IPCT compounds, as well as a novel increment system for the prediction of the energy of optical IPCT transitions, are discussed in this Comment.

Key Words: *second-sphere coordination, ion pair associates, ion pair charge transfer, low-energy photo redox reactions, photocatalysis*

1. INTRODUCTION

Although coordination compounds, formed by central metal ions and ligands which are capable of separate existence, are already rather complex systems, they can interact with further molecules

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or ions and thus lead to higher associated species. This type of coordination, which is called second-sphere coordination,[1] has attracted considerable interest during the past few years,[2,3] since, depending on the strength of the interaction, second-sphere coordination may give rise to the formation of chemical species having molecular properties different from those of the isolated coordination compounds.

By the proper choice of solvent it is possible to observe novel electronic transitions corresponding to a charge transfer from (SMCT) or to the solvent (MSCT), respectively, or one can shift the relative order of excited state energies and thus tune the photoreactivity of a given coordination compound.[4]

Interactions of charged coordination compounds with counterions may lead to ion pair associates which sometimes exhibit additional electronic absorption bands known as ion pair charge transfer (IPCT) transitions.

In addition, the formation of complexes with cage-type ligands[5] or macrocyclic receptors[6] provides other possibilities of designing coordination compounds characterized by second-sphere phenomena.[2]

As concerns ion pair associates of coordination compounds, two types may be distinguished depending on whether the counter-ion of the coordination compound is a non-metal ion and a charged metal complex or metal ion, respectively. In the latter case the charge transfer interactions may be best described as metal-to-metal or intervalence charge transfer (IT).[7,8] However, recent results require that ligand-centered orbitals[9,10] also be taken into account.

Changes in the electronic spectra, due to charge transfer interactions with solvent molecules or ions in the second coordination sphere, are of considerable interest, particularly with respect to the spectral sensitization of photocatalytic reactions.[11]

In this Comment we will limit our discussion to ion pair interactions between charged coordination compounds and non-metal ions which give rise to ion pair charge transfer transitions. For the discussion of interactions between charged coordination compounds and metal ions or complexes, the reader is referred to other reviews.[7,8,11,12]

2. IPCT COMPOUNDS AND THEIR SPECTROSCOPIC BEHAVIOR

Ion pairing is a common phenomenon in coordination chemistry[13,14] and has been known for a long time. Generally, solvents with low dielectric constants and highly charged ions favor the formation of ion pair associates. An estimate of the formation constant of ion pairs may be made by using the theory derived by Eigen and Fuoss.[15,16]

Despite the numerous examples of ion pairing, only little is known about the spectroscopic changes sometimes associated with this phenomenon, the so-called ion pair charge transfer (IPCT).

IPCT compounds are characterized by spectroscopic transitions in the ultraviolet up to the near infrared spectral region, which can not be explained as the sum of the spectra of the components forming the ion pair associate. IPCT compounds of ionic complexes had been described for the first time by Linhard[17] in 1944. Linhard investigated the spectroscopic properties of various cobalt(III)ammines, and he was able to show new spectroscopic transitions in investigating $\{[Co(NH_3)_6]^{3+};\ I^-\}$ ion pair associates. These new transitions are due to electronic interactions between the iodide ion in the second coordination sphere and the central metal and the complex unit, respectively.

A general formula of IPCT compounds (1) shows that obviously the redox asymmetry between cation and anion influences the

$$\{\overset{\text{et}}{\overleftrightarrow{[ML_x]^{n+/n-};\ X^{m-/m+}}}\} \qquad (1)$$

optical IPCT transitions. Balzani[2] has classified IPCT compounds into three groups depending on the position of the IPCT level relative to the other spectroscopic levels of the coordination compound. However, detailed theoretical investigations with respect to the IPCT phenomenon are not known at present.

Table I summarizes some examples of ion pair charge transfer compounds, their spectroscopic data as well as ion pair formation constants. Figure 1 shows the UV/Vis spectrum of the ion pair

TABLE I

Spectroscopic and photochemical behavior of selected IPCT compounds: (a) in 10^3 cm^{-1}; (b) calculated using the increment system (vide infra); (c) in M^{-1} cm^{-1}; (d) in M^{-1}; (e) quantum yield upon irradiation in the IPCT region; (f) concerning the photoinduced catalytic reaction; for further examples see, e.g., Refs. 2, 12, 28, 30, 33–35 and references cited therein

Cation	Anion	Solvent	ΔG_{CT}^{obs} [(a)]	ΔG_{CT}^{calc} [(a),(b)]	ϵ_{max} [(c)]	K_{IP} [(d)]	Φ_{IPCT} [(e)]	Ref.
$[Co(NH_3)_6]^{3+}$	I^-	H_2O	37.3		2300	3.6	0.77	17–19
	BPh_4^-	CH_2Cl_2/CH_3OH	>31		1400		0.44	20,21
$[Co(en)_3]^{3+}$	I^-	H_2O	35.0	33.6				12,17,22
	Hox^-	H_2O (pH 3)					0.13	23,24
	htc	H_2O	>25				<1.2^f	
$[Co(sep)]^{3+}$	I^-	H_2O (pH 5.5)	34.6	34.2			<10^{-6}	25
	Hox	H_2O (pH 3)	36.4				0.13	23
	BPh_4^-	THF	31.3		900			26
$[Co_2(fulvalen)_2]^{2+}$	BPh_4^-	CH_3CN	>24		240	26	0.12	27
$[Ru(NH_3)_5py]^{3+}$	I^-	H_2O (pH 2)	24.4	21.9		10		28
	Hox^-	H_2O (pH 2)	24.4				0.35	28
MV^{2+}	$[Mo(CN)_8]^{4-}$	H_2O	19.8	19.5	200	150	<10^{-6}	29
	$[Zn(mnt)_2]^{2-}$	DMSO	21.7		404	683		30
Hpy^+	$[Co(CO)_4]$	butan-2-one	24.1					31
Ph_2I^+	$[Mo(CN)_8]^{4-}$	CH_3OH	27.0	26.0	1050		0.5/>10^f	32

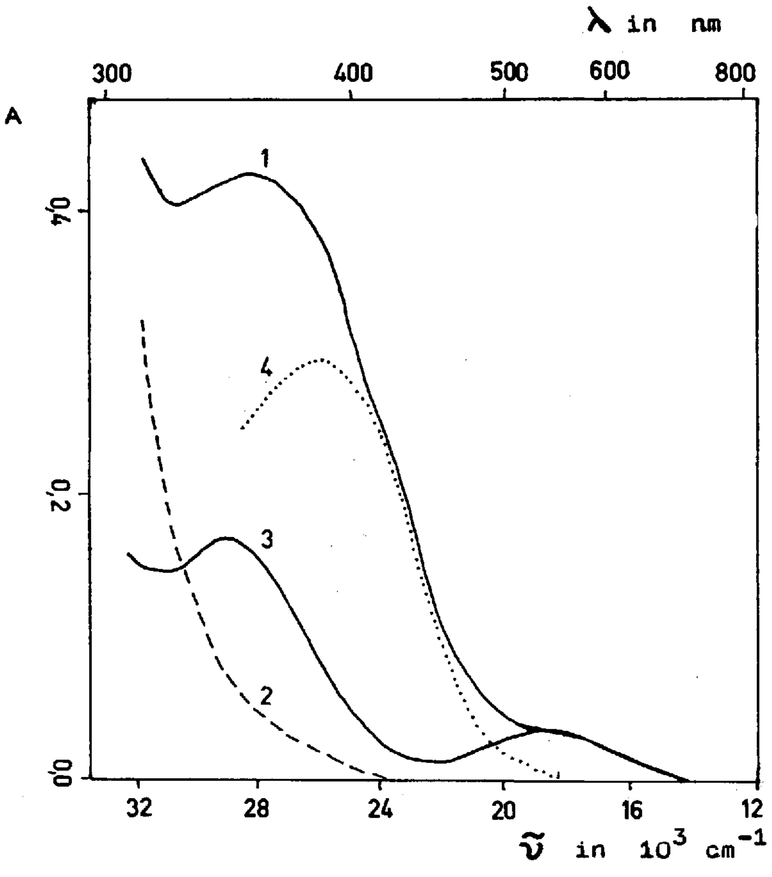


FIGURE 1 Absorption spectra of: (1) {Ph_2I^+; $[Mn(CN)_5NO]^{3-}$}; (2) Ph_2ICl; (3) $(Bu_4N)_3$ $[Mn(CN)_5NO]$, in appropriate concentrations. solvent: methanol; (4) additional IPCT absorption.

associate diphenyliodonium pentacyanonitrosylmanganate(I) as a typical representative of IPCT spectra.

The following examples of IPCT compounds have been investigated with respect to their thermal, thermomagnetic, spectroscopic and photochemical properties: {$[Cu(phen/bpy)_2]^{2+}$; Ph_4B^-},[36]

$\{[Co(NH_3)_5RCOO]^{2+}; RCOO^-\}$,[37] $\{[Co(phen/bpy)_2ox]^+; X^-\}$,[38-43] $\{[Co(NH_3)_6]^{3+}; Ph_4B^-\}$,[20,21] $\{Ph_2I^+: [M(CN)_m]^{n-}\}$.[27,44-46] Unusual thermal, magnetochemical, spectroscopic and also photochemical properties of these compounds may be explained unambiguously by second-sphere effects. However, there are considerable problems in designing ion pair associates with distinguished IPCT behavior, because of the general difficulties in the theoretical treatment of the IPCT phenomenon. Therefore, very recently we have proposed[47,48] an increment system for the prediction of the energy of optical IPCT transitions.

3. THE PREDICTION OF THE ENERGY OF OPTICAL IPCT TRANSITIONS—A NOVEL INCREMENT SYSTEM

The energetic interactions between cations and anions forming an ion pair associate distinguished by IPCT properties can be described by using an energy cycle as proposed by Cannon in describing usual CT transitions[49] and by considering the following assumptions:

—The charge delocalization between A^+ and D^- within the ion pair $(A^+;D^-)$ can be neglected;
—the Franck–Condon excited state of the successor $(A;D)$ is considered as a thermodynamic state, and
—entropy changes during the absorption of light can be neglected.

Based on these assumptions the energy of optical IPCT transitions can be described by the following equation:

$$\Delta G_{CT}(A^+;D^-) = \Delta G_E + \Delta G_{W'} - \Delta G_W + \Delta G_{FC} \qquad (2)$$

Neglecting the work terms ΔG_W and $\Delta G_{W'}$ connected with the association of the precursor and the successor, respectively, and thus considering ΔG_E as the difference of the redox potentials of the ions forming the ion pair $(A^+;D^-)$, the Franck–Condon or reorganization energy ΔG_{FC} may be obtained as proposed by Marcus[50]: The reorganization energy corresponds to the arithmetic mean of the reorganization energy of the self-exchange reactions of A^+/A and D/D^-. Thus, $\Delta G_{CT}(A^+;D^-)$ may be expressed as:

$$\Delta G_{CT}(A^+;D^-) = F[E^0(D/D^-) - E^0(A^+/A)] \\ + \tfrac{1}{2}[\Delta G_{FC}(A^+/A) + \Delta G_{FC}(D/D^-)] \quad (3)$$

It may easily be seen that $\Delta G_{CT}(A^+;D^-)$ consists of separate energy contributions of both ions forming the ion pair, independently of any partner. Therefore, there is no need for the experimental estimation of E^0 and ΔG_{FC}, respectively, because the absolute values of the energy contributions can be replaced by increments of each ion.

The contribution of A^+ and D^- to $\Delta G_{CT}(A^+;D^-)$ may be defined as the sum of the increments of these ions in a certain solvent (H_2O, for example). Using the increments I_{A^+} and I_{D^-} estimated for the solvent, $\Delta G_{CT}(A^+;D^-)$ is given by:

$$\Delta G_{CT}(A^+;D^-) = I_{A^+} + I_D \quad (4)$$

Reference increment values have been defined for any solvent. The tropylium cation has been applied as reference cation in aqueous solution and its increment value has been defined to be nought:

$$I_{TROP^+} \overset{\text{Def.}}{=} 0 \quad (5)$$

Thus, for any donor anions D^- the increment I_{D^-} is given by:

$$I_{D^-} = \Delta G_{CT}(TROP^+;D\ ) \quad (6)$$

Analogously, for any acceptor cations A^+, expression (7) may be used:

$$I_{A^+} = \Delta G_{CT}(A^+;D'^-) - I_{D'^-} \quad (7)$$

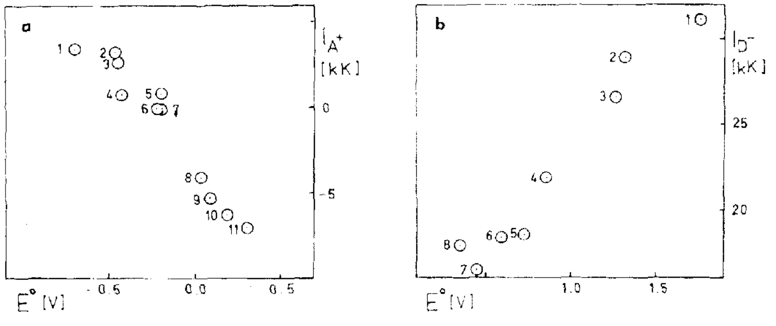
where D′ represents a reference anion with known increment value, such as hexacyanoferrate(II) in aqueous solution.

Thus, ΔG_{CT} of any ion pair combinations may be estimated spectroscopically by using the proposed increment system. ΔG_{CT} values obtained by applying the increment system are in good agreement with the experimental results (Table I).

In some cases ion pair associates of tropylium cations and hexacyanoferrate(II), respectively, give rise to thermal redox reactions, and therefore, I_{D^+} or I_{A^-} cannot be obtained by UV/Vis spectroscopy. The same is true if IPCT bands are covered by absorption bands of reference ions and counter-ions, respectively. However, because of the linear relationship between I_{A^-} and I_{D^+} increment values and the standard electrode potentials of A^+ and D^- (Fig. 2), I_{A^-} and I_{D^+} can be obtained by using the appropriate redox potentials and regression calculations.

The reliability of the increment system has been strengthened by comparing calculated and experimentally estimated ΔG_{CT} values of a number of ion pair associates. It has been shown that there is no deviation greater than 2500 cm^{-1} (cf. Table I, for example). Some exceptions may be explained by diverse electronic configurations of certain central metals and by changes of the spin state, respectively. Furthermore, it has been shown that the increment system can be applied to non-aqueous solvents, too.[47,48]

However, it may be considered that the proposed increment system cannot answer the general questions with respect to the



(1) 1-Ethyl-4-carboxymethylpyridinium
(2) 1-Methylpyrazinium (3) $[Rh(bpy)_3]^{3+}$
(4) 1,1′-Dimethyl-4,4′-bipyridinium
(5) $[Eu\ 2.2.1]^{3+}$ (6) 1-Methylquinoxalinium
(7) Tropylium (8)–(11) $[Ru(NH_3)_5L]^{3+}$ with
L = NH_3, imidazole, pyrazole, pyridine

(1) SCN^- (2) I^- (3) $SeCN^-$
(4) $[Ru(CN)_6]^{4-}$ (5) $[Mo(CN)_8]^{4-}$
(6) $[Mn(CN)_5NO]^{3-}$ (7) $[W(CN)_8]$
(8) $[Fe(CN)_6]^{4-}$

FIGURE 2 Dependence of increment values of selected cations (a) and anions (b) on their standard redox potentials E^0 in aqueous solution.

kind of electronic interactions between ionic complexes and appropriate counter-ions leading to the IPCT phenomenon. Furthermore, there is also no sufficient explanation of why "reverse IPCT compounds" consisting of donor cations (D^+) and acceptor anions (A^-) have not been detected experimentally until now.

4. PHOTOCHEMICAL BEHAVIOR OF IPCT COMPOUNDS

As already mentioned before, ion pair associates distinguished by low-energy IPCT transitions are of particular photochemical interest. Electronic excitation of IPCT states may be used to induce irreversible photo redox reactions by irradiation with visible light of energies comparable to the energy of optical IPCT transitions. Inducing photo redox reactions in the visible spectral region is of considerable interest with respect to the spectral sensitization of photocatalytic systems[11,51,52] to be used for solar energy conversion[53] and unconventional imaging processes.[4]

The following examples show irreversible redox reactions induced by electronic excitation of IPCT states with visible light:

$$\{[Co(NH_3)_6]^{3+}; I^-\} \xrightarrow{h\nu\ (IPCT)} [Co(NH_3)_6]^{2+} + I^{\cdot} \qquad (8)$$

$$\{[Co(NH_3)_6]^{3+}; Ph_4B^-\} \xrightarrow{h\nu\ (IPCT)} [Co(NH_3)_6]^{2+} + Ph_4B^{\cdot} \qquad (9)$$

$$\{Ph_2I^+; [Mo(CN)_8]^{4-}\} \xrightarrow{h\nu\ (IPCT)} [Mo(CN)_8]^{3-} + Ph_2I^{\cdot} \qquad (10)$$

Equations (8)–(10) illustrate the general scheme of irreversible photo-induced redox reactions due to electronic excitation of IPCT states lower in energy than the usual LMCT states of the complexes forming these ion pair associates. The irreversibility of the latter reactions is due to the very fast decomposition reactions of the radicals formed during the primary step of the photolysis and which compete very efficiently with the back electron transfer, one of the most decisive barriers in photocatalytic reactions. The other possibility of irreversible photo-redox reactions consists of spin state changes as described for the first time by Adamson[19] by investigating $\{[Co(NH_3)_6]^{3+}; I^-\}$ ion pair associates (10).

The importance of the irreversible decomposition of the photoproducts has been shown, also, by Balzani[23,25] in investigating the photoreactions of cobalt(III)sepulchrate with the counter-ions iodide and hydrogenoxalate, respectively (11),(12).

$$\{[\mathrm{Co(sep)}]^{3+}; \mathrm{I}^-\} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \{[\mathrm{Co(sep)}]^{2+}; \mathrm{I}^\cdot\} \tag{11}$$

$$\{[\mathrm{Co(sep)}]^{3+}; \mathrm{Hox}^-\} \xrightarrow{h\nu} [\mathrm{Co(sep)}]^{2+} + \mathrm{Hox}^\cdot \tag{12}$$

While IPCT excitation of the iodide ion pair did not lead to detectable amounts of Co(II), the fast decomposition of Hox$^\cdot$ radicals formed in reaction (12) leads to the irreversibility of the photoreaction of the hydrogenoxalate ion pair (cf. Table I).

In the case of diphenyliodonium ion pairs, a high Franck–Condon barrier has been assumed as the origin of the efficient photo redox reaction.[32] This is remarkable because organic compounds usually show negligibly low reorganization energies.

Besides changes in the spin state, high Franck–Condon barriers, and fast unimolecular decomposition of the photoproducts, respectively, the irreversibility of photo redox reactions may be strengthened by a catalytic action of metal ions with respect to the decomposition of the primary photoproduct. Thus, the photolysis of the ion pair associate methylviologentetraphenylborate leads to biphenyl in relatively low yields[54]; however, in the presence of catalytic amounts of proper cobalt(III) and copper(II) complexes, respectively, phenyl radicals were observed and the quantum yields increased by an order of magnitude.[20,36]

Interesting photocatalytic reactions may be induced upon excitation of IPCT compounds. Thus, Kida *et al.*[24] have shown the following photo-induced catalytic cycle (Fig. 3) leading to the formation of $[\mathrm{Co(htc)_3}]$ complexes starting from $[\mathrm{Co(en)_3}]^{3+}$ in the presence of an excess of htc^-. Another example has been described very recently.[32] Ion pair associates consisting of octacyanomolybdate(IV) and diphenyliodonium cations give rise to the very efficient formation of aldehydes in the presence of the appropriate alcohols as solvents (Fig. 4).

These and other results (cf. Table I) illustrate the general importance of photochemical reactions of ion pair associates distinguished by IPCT properties.

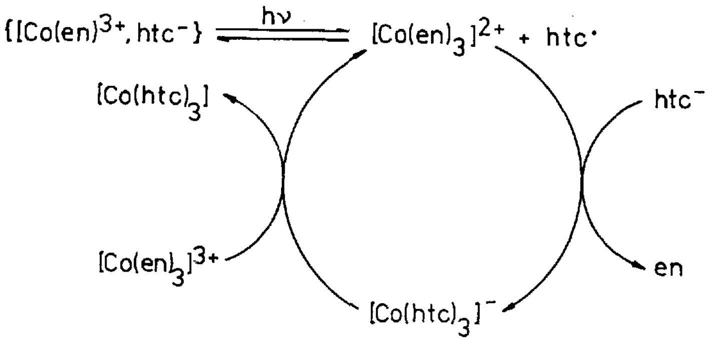


FIGURE 3 Photoinduced catalytic formation of aldehydes from alcohols.

5. CONCLUDING REMARKS

Second-sphere coordination plays an increasingly important role in various fields of inorganic chemistry, particularly in connection with long-range electron transfer and energy transfer processes. Second-sphere coordination and photochemistry may lead to in-

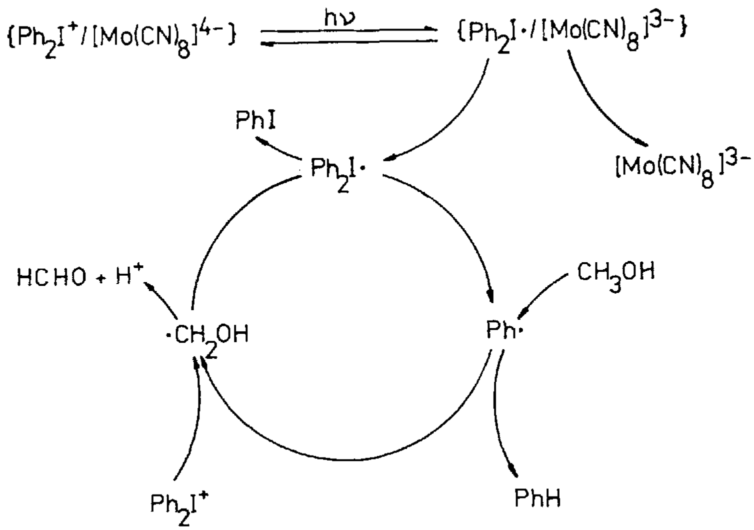


FIGURE 4 Photoinduced catalytic formation of $[Co(htc)_3]$ (htc^- = bis(2-hydroxymethyl)dithiocarbamate).

teresting results with respect to efficient charge separation induced by electronic excitation of such supramolecular devices.[55]

In second-sphere coordination, ion pair associates distinguished by low-energy IPCT states are of particular interest with respect to the static spectral sensitization of photo-induced catalytic or photoassisted reactions to be used for unconventional imaging processes and solar energy conversion, respectively.[4,11,56]

However, so far no systematic investigations of these classical inorganic compounds have been achieved, particularly with respect to the quantum-chemical or semi-empirical description of the electronic structure of IPCT compounds in the ground state and electronically excited states, as well. Therefore, there are no clear answers concerning the comparability of IPCT compounds with both organic donor–acceptor complexes and mixed-valence compounds distinguished by spectroscopic IT transitions. A number of further open questions, some of them discussed previously, may explain the further interest in investigating ion pair charge transfer compounds.

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