Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Coordination Chemistry Reviews 251 (2007) 577–583

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Ligand-to-ligand and intraligand charge transfer and their relation to charge transfer interactions in organic zwitterions

Arnd Vogler*, Horst Kunkely

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

Received 15 December 2005; accepted 8 April 2006
Available online 25 April 2006

Contents

Abstract

Coordination compounds, which simultaneously contain a reducing and an oxidizing ligand are frequently characterized by low-energy LLCT transitions. In suitable cases, CT interactions between such donors and acceptors may also occur in purely organic molecules. In particular, certain zwitterions have been known for many decades to display CT bands in their absorption spectra. In the present review the close relationship between such zwitterions and metal complexes with low-energies LLCT transitions is illustrated by suitable examples. Moreover, in some cases the zwitterions themselves serve as ligands. The CT properties of these zwitterions are preserved but modified by coordination. Some examples of ILCT transitions of this type are discussed in the second part of our report.

Keywords: Electronic spectra; LLCT; ILCT

1. Introduction

In 1984 Barry Lever published the second edition of "Inorganic Electronic Spectroscopy" [1]. It is still the most important work on this subject. All types of electronic transitions, which occur in coordination compounds, have been discussed in much detail with one exception. Ligand-to-ligand charge transfer (LLCT) was more or less unknown at this time. In 1981 we drew attention to this transition type and introduced the term LLCT [2], but the credit for the first studies of LLCT goes to Coates and Green [3], Koester [4], Gouterman et al. (1976) [5], and Miller and Dance [6]. Their papers were somehow hidden in the literature but cited in our 1981 communication. In 1990 we wrote the first review about LLCT including ligand-based mixed-valence compounds [7]. Now, LLCT is as common as other electronic transitions of metal complexes.

The reason for ignoring LLCT prior to 1981 is not quite clear, but was probably based on the fact that LLCT involves two ligands, which do not interact directly but via a metal center (Scheme 1).

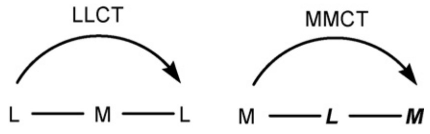
However, this remote CT had precedence. For many decades it was well known that two metal centers which are coupled by bridging ligands can show metal-to-metal charge transfer (MMCT) absorptions. So it was not really difficult to recognize this analogy.

In the present account we wish to emphasize another relationship. CT interactions between reducing and oxidizing ligands are not restricted to coordination chemistry. Also in the absence of an intervening metal, CT interactions can be observed provided the donor and acceptor ligand are electronically coupled by electrostatic attraction or covalent bonding. In fact, a close relationship exists between LLCT (and ILCT, intraligand charge transfer) in metal complexes and donor–acceptor interactions in analogous

---

* Corresponding author. Tel.: +49 941 943 4716.
E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

0010-8545/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2006.04.015



Scheme 1.

organic zwitterions [8]. The resemblance of both types of compounds is not only interesting in its own right, but represents another bridge between inorganic and organic spectroscopy.

The present report is not intended to comprehensively cover this subject. We rather try to illustrate this analogy by a few selected examples. Organic zwitterions (or betains) are neutral molecules which carry opposite charges at spatially separated parts of the same molecule. Frequently, the negative charge is associated with the HOMO while the positive charge is linked to the LUMO. As a consequence a low-energy CT transition occurs which leads to a charge recombination [8]. However, for many such compounds the zwitterionic structure is a limiting description. In these cases a partial charge compensation, which is represented by a non-polar valence formula takes place in the ground state. It follows that HOMO and LUMO are spatially not strictly separated but partially delocalized over the entire molecule. The HOMO–LUMO transition is then associated with a charge shift, but not with a complete transfer of one electron from one part of the molecule to another. Since zwitterionic structures are stabilized in polar solvents, such compounds are characterized by a negative solvatochromism [8]. Accordingly, the corresponding absorptions undergo a blue shift with increasing solvent polarity.

2. Charge transfer in organic zwitterions versus LLCT

When both benzene rings of biphenyl are replaced by the isoelectronic cyclopentadienyl anion (Cp^-) and cycloheptatrienyl cation (Ch^+), a redox asymmetry is introduced since Cp^- is a CT donor while Ch^+ is a CT acceptor. The resulting sesquifulvalene (Structure 1), which is an isomer of biphenyl is characterized by a low-energy CT transition [9] ($\lambda_{max} = 395$ nm) [10]. Electronic excitation reduces the polarity, which prevails in the ground state.

Such a CT should also occur when two benzene rings of $[M(C_6H_6)_2]$ are replaced by the isomeric combination Cp^- and Ch^+. Indeed, various sandwich-type complexes with the general composition $[M(Cp^-)(Ch^+)]$ have been described [11]. Moreover, MO calculations have shown that these complexes should have available $Cp^- \rightarrow Ch^+$ CT transitions at relatively low energies [11,12] (Fig. 1).

These transitions are now of the LLCT type. Unfortunately, in most cases such LLCT transitions are obscured by other low-energy transitions of different origin (e.g. LF, LMCT, MLCT). However, these complications may be avoided by an appropriate choice of the central metal and a suitable modification of the ligands. The cation $[Rh^{III}(Cp^*)Ch]^{3+}$ (Structure 2) seems to meet these requirements [13].

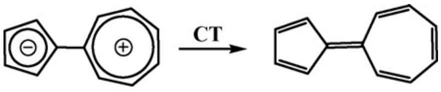


Plate 1.

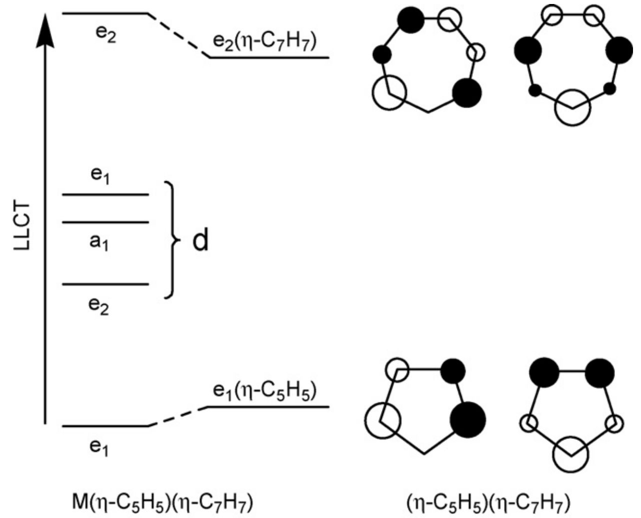


Fig. 1. Qualitative MO diagram for the frontier orbitals of $[M(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ in $C_{\infty v}$ symmetry adapted from Ref. [11,12].

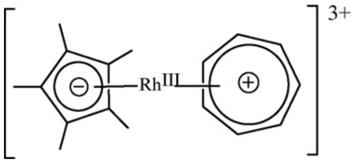


Plate 2.

Cp^{*-} is a much stronger CT donor than Cp^-. In addition, since Rh(III) is rather redox inert it does not participate in low-energy CT transitions. Moreover, LF excitation of Rh(III) occurs only at high energies.

The electronic spectrum of $[Rh^{III}(Cp^*)Ch]^{3+}$ (Fig. 2) shows a longest-wavelength absorption at $\lambda_{max} = 340$ nm which is assigned to the spin-allowed $Cp^{*-} \rightarrow Ch^+$ LLCT transition [13].

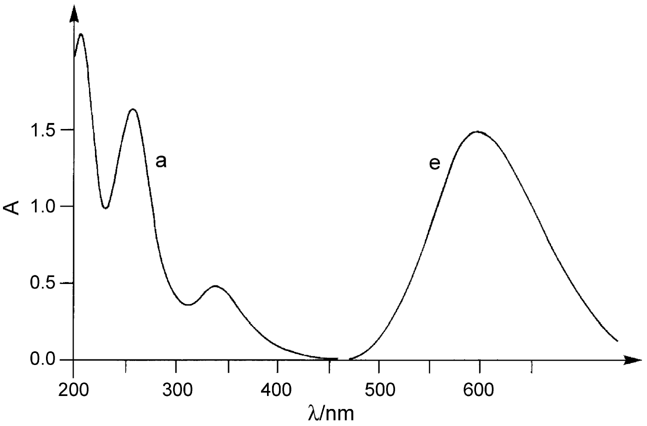


Fig. 2. Electronic absorption (a) and emission (e) spectra of 1.51×10^{-4} M $[Rh(Cp^*)(C_7H_7)](PF_6)_3$ under argon. Absorption: in MeCN at r.t., 1 cm cell; emission: in EtOH at 77 K, $\lambda_{exc} = 340$ nm, intensity in arbitrary units.

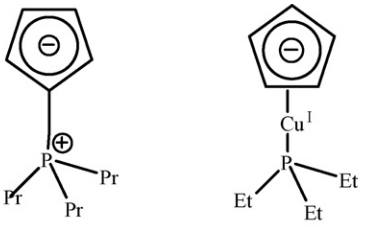


Plate 3.

The lowest-energy excited state of the complex is apparently a LLCT triplet which emits at $\lambda_{max} = 596$ nm.

The compound Cp^-–P^+Pr_3 (Pr = *n*-propyl) (Structure 3) is another example for CT interaction in zwitterions.

This ylide displays a negative solvatochromism [14]. The longest-wavelength band appears at 267 nm in *n*-hexane and 254 nm in methanol. This absorption had been assigned to the CT transition from the Cp anion to the phosphonium cation. While the ground state of this zwitterion is very polar and stabilized in polar solvents this polarity is reduced or even disappears in the CT state.

The complex $[Cu^ICp(PEt_3)]$ contains both components of the ylide as ligands [15]. Accordingly, the complex is expected to show a $Cp^- \rightarrow PEt_3$ CT absorption. This assumption is also derived from the general properties of both ligands. Cp^- has been observed to function as donor ligand for ligand-to-metal charge transfer (LMCT) and LLCT transitions [16]. On the contrary, phosphines are well known acceptor ligands. A variety of phosphine complexes with reducing metals display metal-to-ligand charge transfer bands in their electronic spectra [17]. In agreement with these properties the longest-wavelength absorption of $[Cu^ICp(PEt_3)]$ in *n*-hexane at $\lambda_{max} = 350$ nm is assigned to a $Cp^- \rightarrow PEt_3$ LLCT transition [15]. In analogy to the ylide this absorption apparently undergoes a blue shift in polar solvents such as methanol and acetonitrile. The emission of $[CuCp(PEt_3)]$ at $\lambda_{max} = 525$ nm is assumed to originate from the LLCT triplet [15].

While this LLCT assignment is certainly plausible, interferences by other electronic transitions are conceivable. Since Cu(I) is reducing as well as oxidizing, Cu(I) → PEt_3 MLCT and $Cp^- \rightarrow$ Cu(I) LMCT transitions may also occur at relatively low energies. While $Cp^- \rightarrow$ Cu(I) LMCT absorptions are yet unknown, Cu(I) → PR_3 MLCT transitions are expected to appear at shorter-wavelength than the LLCT band of $[CuCp(PEt_3)]$. Although other Cu^IPR_3 complexes display absorption bands in the near UV region these bands have been only observed when R is an aromatic substituent [18]. In this case these substituents participate in low-energy electronic transitions. Such IL or ILCT absorptions are not expected to appear when R is an alkyl substituent.

While these considerations are consistent with the LLCT assignment of the longest-wavelength absorption of $[CuCp(PEt_3)]$ this LLCT transition may be strongly mixed with $Cp^- \rightarrow Cu^I$ LMCT and Cu(I) → $P(Et_3)$ MLCT transitions in analogy to certain Cu(I) clusters such as $[Cu(pyridine)I]_4$ [19,20], In this case an iodide to pyridine LLCT transition has been identified but again, contributions by other CT transitions involving Cu(I) seem to be important.

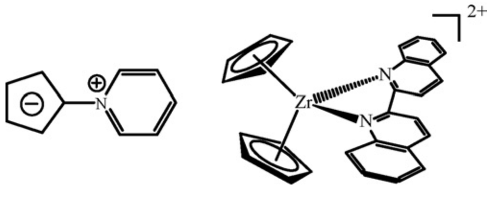


Plate 4.

The zwitterion *N*-cyclopentadienylpyridinium [8,21] is a further example, which finds its counterpart in coordination chemistry. The complex $[Zr^{IV}Cp_2(biq)]^{2+}$ [22] with biq = 2,2′-biquinoline as well as the zwitterion are characterized by cyclopentadienyl-pyridin donor–acceptor interactions (Structure 4).

The zwitterion in $CHCl_3$ shows a ($Cp^- \rightarrow$ pyridinium$^+$) CT band at $\lambda_{max} = 511$ nm [8,21]. The electronic spectrum of $[ZrCp_2(biq)]^{2+}$ (Fig. 3) shows absorptions at $\lambda_{max} = 360$ (ε/dm^3 mol^{-1} cm^{-1} 7700), 341 (8800), 329 (7400), 315 (5300), 304 (sh, 4300), 262 nm (20400) [22]. The bands at 341, 329, 315, 304 and 262 nm appear at almost the same wavelength as those of free biq and are thus attributed to intraligand (IL) transitions. However, while $[Zr(IV)Cp_2]$ compounds such as $[ZrCp_2Cl_2]$ and related complexes are colourless, $[ZrCp_2(biq)]^{2+}$ is bright yellow owing to a new absorption at $\lambda_{max} = 360$ nm which extends into the visible spectral region. The complex is solvatochromic. The longest-wavelength absorption undergoes a blue shift with increasing solvent polarity. This band is logically assigned to a LLCT transition from the $(Cp^-)_2$ donor ligands to the biq acceptor [22]. The intensity of this band is consistent with this assignment. Complexes of the type $[M^{IV}Cp_2L_2]$ with M = Ti, Zr and Hf are pseudotetrahedral (C_{2v}). The highest occupied orbitals of such $[MCp_2L_2]$ compounds are derived from the Cp^- ligands and are of the b_2, b_1, a_2 and a_1 symmetry in close energetic proximity [23]. The LUMO is a π^* orbital (b_1) at the diimine ligand. While the $b_2 \rightarrow b_1$ transition is forbidden the other $Cp^- \rightarrow$ biq LLCT transitions ($b_1 \rightarrow b_1$, $a_2 \rightarrow b_1$ and $a_1 \rightarrow b_1$) are allowed [22].

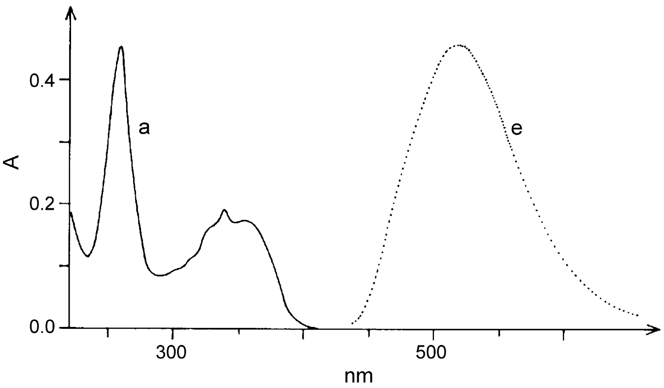


Fig. 3. Electronic absorption (a) and emission (e) spectra of 2.18×10^{-4} M $[ZrCp_2(biq)]^{2+}$ at r.t. under argon in THF, 1-cm cell; emission: $\lambda_{exc} = 380$ nm, intensity in arbitrary units.

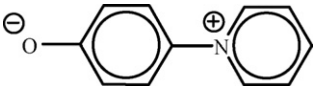


Plate 5.

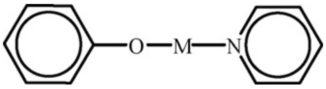


Plate 6.

The cation $[ZrCp_2(biq)]^{2+}$ shows a bright yellow-green luminescence at $\lambda_{max} = 518$ nm in solution (Fig. 3) and 524 nm in the solid state at r.t. [22]. The quantum yield of the emission is $\phi = 0.01$. The excitation spectrum matches the absorption spectrum. It is concluded that the luminescence originates from the lowest-energy LLCT excited state which is most likely of triplet multiplicity in agreement with the general behavior of diamagnetic complexes with metals of the second transition row [24].

The zwitterion 4-(pyridinium-1-yl)-phenolate (Structure 5) shows a long-wavelength (phenolate → pyridinium) CT absorption which is strongly solvatochromic ($\lambda_{max} = 615$ nm, in $CHCl_3$) [8,25]. The substituted derivative 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)-phenolate is commercially available as Reichardt's or Dimroth-Reichardt's dye. Its solvatochromism serves as a standard for the determination of solvent polarities [26,27].

When pyridine is attached to a metal its electronic structure resembles that of pyridinium cations, which carry a substituent (e.g. alkyl groups) at the nitrogen atom. Accordingly, complexes of the type phenolate-M-pyridine (Structure 6) are expected to display phenolate-to-pyridine LLCT absorptions. Simple complexes with this ligand combination have not yet examined with regard to the existence of such CT transitions. Moreover, other electronic absorptions of different origin (e.g. LF, MLCT, LMCT) may obscure LLCT bands. However, complexes of the type $[Cu^{II}(catecholate)(1,2\text{-diimine})]$ have been shown to display such (catecholate → 1,2-diimine) LLCT absorptions [28]. The complex $[Cu^{II}(catecholate)(bipy)]$ illustrates this ligand combination (Structure 7).

The LLCT band of this complex (Fig. 4) appears at $\lambda_{max} = 480$ nm (in DMSO). It undergoes a red shift when bipy is replaced by 1,10-phenanthroline (490 nm), pyridine-2-aldehyde-*N*-phenylimine (510 nm), *N*,*N*′-diphenyldiacetyl diimine (555 nm) and *N*,*N*′-diphenylbenzil diimine (612 nm).

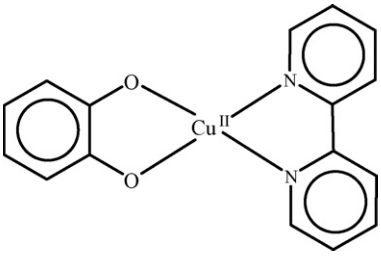


Plate 7.

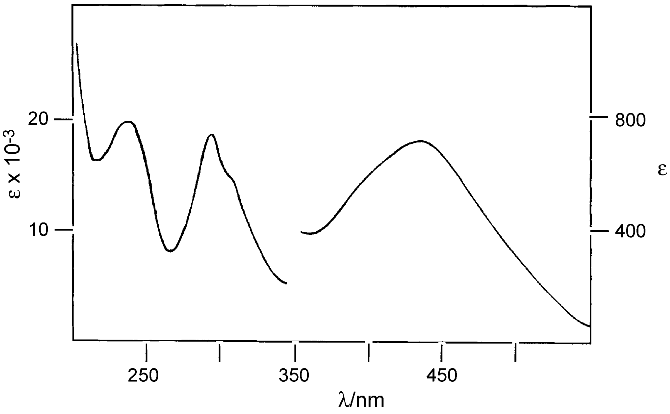


Fig. 4. Electronic absorption spectrum of [Cu(catecholate)bipy] at r.t. in MeOH.

The LLCT band should shift to longer-wavelength when the π-acceptor ability of the diimine ligand is increased. Indeed, the measurements agree with independent experimental and theoretical data on diimine ligands. In particular, the lower energy of the π^* LUMO of aliphatic diimines compared to that of aromatic diimines is in accord with the LLCT energies.

The position of the LLCT band should also correlate with the energy of the donor level. This expectation is confirmed. While $[Cu^{II}(3,5\text{-di-tert-butylcatecholate})(bipy)]$ absorbs at $\lambda_{max} = 530$ nm, $[Cu^{II}(catecholate)(bipy)]$ and $[Cu^{II}(tetrachlorocatecholate)(bipy)]$ exhibit their LLCT bands at 480 and 420 nm, respectively. In this order the hypsochromic shift arises from a stepwise stabilization of the donor HOMO. These copper complexes also show a negative solvatochromism [28]. The blue shift of the LLCT band with increasing solvent polarity suggests a polarized ground state that can be stabilized by polar solvents. In the excited state the dipole moment is apparently reduced and polar solvents do not stabilize the excited state to the same extent. The application of Reichardt's E_T parameter [26,27] for solvent polarities yields a linear correlation between the energy of the LLCT band and the E_T values. Owing to the low solubility of the complexes only a limited number of solvents could be used. It is quite interesting that this solvatochromism is rather independent of the donor ligand. When the ligand catecholate is replaced by 3,5-di-tert-butylcatecholate the red shift of the LLCT band of about 50–80 nm is preserved in different solvents, e.g. from 480 to 530 nm in DMSO, 433–501 nm in *n*-propanol and 435–501 nm in DMF. The observations of LLCT transitions in these copper(II) complexes are supported by MO calculations [28].

3. Charge transfer in organic zwitterions versus ILCT

A ligand itself may simultaneously contain a donor and an acceptor site. If they are coupled the free ligand displays a CT absorption. In some cases this coupling is mediated by a metal. As a result an ILCT band appears. We reported a first example in 1981 [29]. A special type of ILCT interaction is observed when organic zwitterions serve as ligands. In most cases it is the donor site of the zwitterion which is attached to the metal. Of course,

Plate 8.

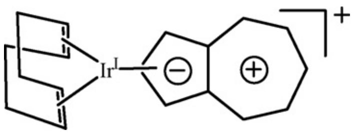


Plate 9.

the CT interaction in the zwitterion must then be modified by coordination.

As discussed above sesquifulvalene can be described as a zwitterions, which contains the cyclopentadienyl anion and the cycloheptatrienyl cation connected by a carbon–carbon bond. As an alternative this combination can be also achieved by incorporating both ions in a common ring system. The resulting molecule is azulene, which is characterized by striking electronic properties (Structure 8).

The HOMO of azulene is to a larger extent localized at the five-membered ring while the LUMO is dominated by the seven-membered ring [30–32]. However, since HOMO and LUMO extend to a certain degree also to the seven-membered and five-membered ring, respectively, the real electron distribution is not only described by the zwitter ionic resonance formula but also by a non-polar valence structure with conjugated double bonds. In summary, the HOMO–LUMO transition of azulene which, determines the blue colour of this compound ($\lambda_{max} = 580$ nm) is associated with a charge shift from the five-membered to the seven-membered ring. Does this CT transition also appear as an ILCT band in the absorption spectrum of azulene complexes? The complex [Ir^{I}(COD)(azulene)]$^+$ [33] (Structure 9) with COD = 1,5-cyclooctadiene was recently selected in order to explore this possibility.

It is suggested that the longest-wavelength absorptions of [Ir(azulene)(COD)]$^+$ Fig. 5 should be assigned to mixed (Ir^{I} → azulene) MLCT and azulene ILCT transitions [34]. This assignment is based on the following considerations. The HOMO of [Ir(Cp)(CO)$_2$] has been calculated to be composed of iridium d-orbitals and Cp$^-$ π-orbitals [35]. Since the IrCp fragment is also part of the [Ir(azulene)(COD)]$^+$ structure we assume that it is also the HOMO of our target complex. In contrast, [IrCp(COD)] is colourless while [Ir(azulene)(COD)]$^+$ is intensely purple owing to long-wavelength absorptions extending to 800 nm. This leads to the conclusion that the LUMO of [Ir(azulene)(COD)]$^+$ is also associated with the azulene ligand. Since the LUMO of azulene is largely associated with the seven-membered ring, which is not attached to the metal, it should be essentially preserved by coordination. It follows that the lowest-energy transition from HOMO to LUMO is a mixed MLCT/ILCT transition. The absorption of [Ir(azulene)(COD)]$^+$ at $\lambda_{max} = 536$ nm is assigned to the spin-allowed MLCT/ILCT transition while the weaker band at $\lambda_{max} = 675$ nm (shoulder) is assumed to belong to the corresponding spin-forbidden transition. The singlet–triplet separation of approximately 3800 cm^{-1} is comparable to that of the MLCT transition of [Ir(en)(COD)] and related complexes ($\Delta E \sim 3500$ cm^{-1}) [36]. The emission of [Ir(azulene)(COD)]$^+$ at $\lambda_{max} = 816$ nm is assumed to originate from the MLCT/ILCT triplet. The overlap of the emission and the longest-wavelength absorption ($\lambda_{max} = 675$ nm) supports this assignment. However, this phosphorescence appears only in the solid state at 77 K. Under these conditions the rigidity apparently prevents any ligand displacement. In contrast, at r.t. in solution this emission is absent and the complex undergoes a photosubstitution of the azulene ligand.

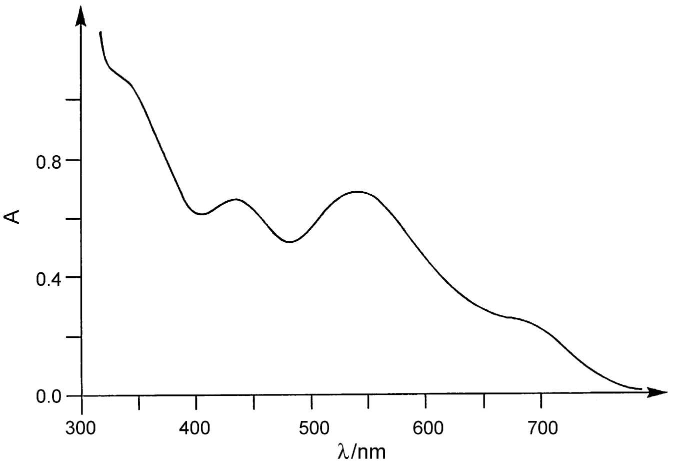


Fig. 5. Electronic absorption spectrum of 1.73 × 10^{-4} M [Ir(azulene)(COD)]$^+$ in CH$_2$Cl$_2$ under argon at room temperature, 1 cm cell.

What is the origin of the photosubstitution of [Ir(azulene)(COD)]$^+$? In principle, MLCT excitation can initiate the release of a ligand when the CT transition leads to the population of M–L antibonding orbitals [37]. However, in the case of [Ir(azulene)(COD)]$^+$ the MLCT transition largely terminates at the seven-membered ring which is less involved in coordination. On the other hand, azulene IL excitation is associated with the depopulation of the azulene HOMO, which is engaged in Ir-azulene bonding. Accordingly, it seems reasonable to attribute the photorelease of azulene from the iridium complex to the electron distribution in the azulene ILCT state. There is precedent for substitutions initiated by IL (or ILCT) excitation. The complex Pt(naphthylamine)$_2$Cl$_2$ liberates an amine ligand upon irradiation which is associated with a charge shift from the amine nitrogen to the naphthyl moiety [38]. As a consequence the ligand looses its coordination ability.

At this point it should be mentioned that generally the deep colours are a striking feature of azulene complexes [39] In a few cases some spectral measurements have been reported but without any further discussion [40,41]. Since azulene as a ligand is stabilized by metals in low oxidation states [39] an assignment of long-wavelength absorptions to mixed MLCT/ILCT transitions may also apply to many other complexes of this type.

The zwitterion *N*-cyclopentadienylpyridinium has been discussed above. When a carbon–carbon double bond is inserted between the cycopentadienyl donor and pyridinium acceptor (Structure 10) the CT interaction should be preserved.

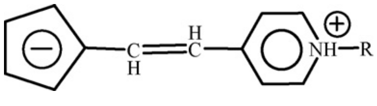


Plate 10.

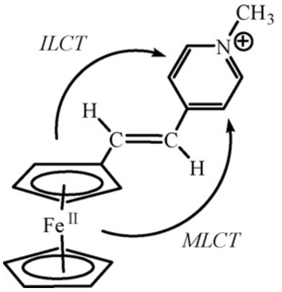


Plate 11.

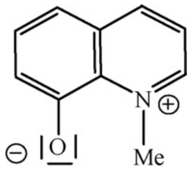


Plate 12.

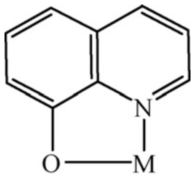


Plate 13.

Unfortunately, this zwitterion is unknown. However, it exists as a ligand in the coordinated state. The complex (E)-1-ferrocenyl-2-(1-methyl-4-pyridiniumyl)ethylene cation [42] (Structure 11) (E-fmpe$^+$) shows two long-wavelength absorptions [42,43] (Fig. 6).

The longest-wavelength absorption of [E-fmpe]$^+$ near 570 nm is assigned to a Fe^{II} → pyridinium metal-to-ligand charge transfer (MLCT) transition. As expected the MLCT absorption of E-fmpe$^+$ is shifted to shorter-wavelength when Fe^{II} is replaced by the less reducing Ru^{II} metal center [42]. The MLCT transition certainly terminates at the pyridinium moiety, which is a strong electron acceptor. The MLCT assignment is consistent with the negative solvatochromism of [E-fmpe]$^+$ in analogy to MLCT transitions of many other complexes [1]. A linear correlation of $\bar{\nu}_{\max}$ (MLCT) versus E^*_{MLCT} is observed [43]. The slope is rather steep ($\Delta\bar{\nu}_{\max}/\Delta E^*_{\mathrm{MLCT}} = 3332 \pm 122\,\mathrm{cm}^{-1}$) indicating a considerable charge separation.

The shorter-wavelength absorption of [E-fmpe]$^+$ near 370 nm is assigned to an intraligand charge transfer (ILCT) transition from the cyclopentadienyl ring of the ferrocene moiety to the pyridinium substituent [43]. Since the ferrocene moiety of E-fmpe$^+$ provides Fe(II) and the Cp$^-$ ligand as donor sites for the MLCT and ILCT transitions, respectively, their solvatochromism is also comparable.

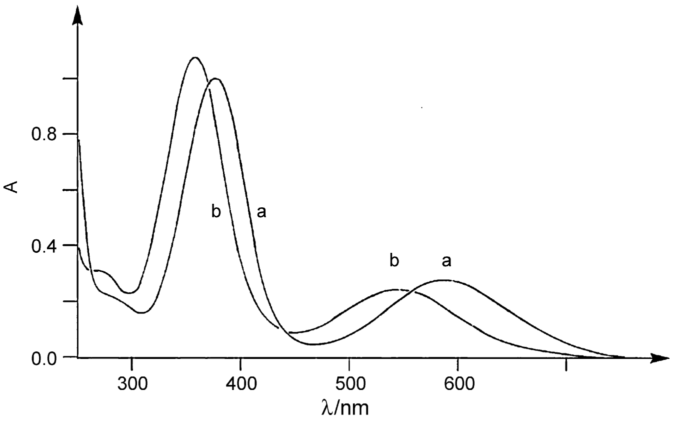


Fig. 6. Electronic absorption spectra of 4.32×10^{-5} M [E-fmpe$^+$I]I$^-$ in (a) CH_2Cl_2 and (b) H_2O at r.t., 1 cm cell.

A zwitterion consisting of a phenolate anion and a pyridinium cation cannot only be formed by connecting both ions by a carbon–carbon or carbon–nitrogen bond (see above). As an alternative they can be fused together in a common ring system (Structure 12).

This compound is solvatochromic and shows a long-wavelength absorption ($\lambda_{\max} = 568$ nm, in benzene and 443 nm in water), which is caused by a CT from the phenolate to the pyridinium function [8,44]. This CT transition appears also as an ILCT band in the spectrum of 8-quinolinolato (or oxinato) complexes, which are formed by a variety of main group and transition metals [45] (Structure 13).

Depending on the metal this ILCT absorption occurs between 360 and 480 nm. It is moderately solvatochromic. Frequently, such oxinate complexes are luminescent. With light metals they show only a fluorescence (e.g. [Al(oxinate)$_3$], $\lambda_{\max} = 540$ nm) [46] while oxinate complexes of metals beginning with the second transition row may display a fluorescence and a phosphorescence at r.t. They also originate from the oxinate ILCT excited state. A thorium oxinate complex illustrates this spectral behavior [47] (Structure 14).

Since Th(IV) does not participate in low-energy electronic transitions only those of the IL type are observed (Fig. 7). The spin-allowed ILCT (oxinate) absorption shows up at $\lambda_{\max} = 362$ nm while the fluorescence and phosphorescence appear at 510 and 775 nm, respectively. Owing to its larger lifetime the triplet emission is quenched by oxygen.

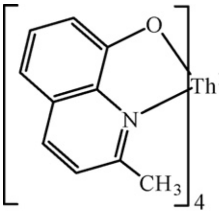


Plate 14.

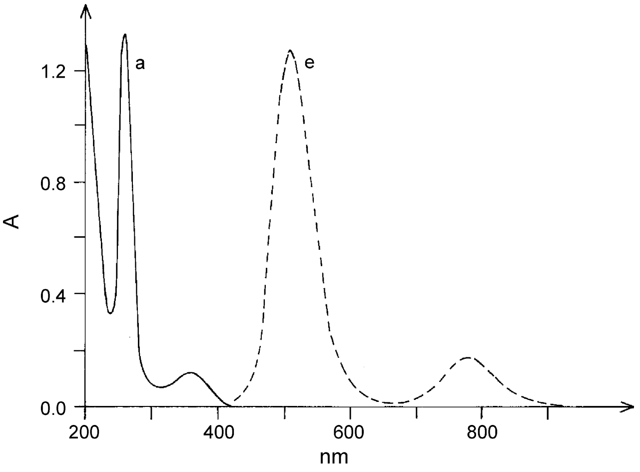


Fig. 7. Electronic absorption (a) and emission spectra (e) of 2.95×10^{-5} M [Th(Me-oxinate)$_4$] in MeCN under argon at r.t., 1 cm cell. Emission: $\lambda_{ecx} = 360$ nm, intensity in arbitrary units.

4. Conclusion

Optical CT transitions attract much recent attention owing to potential applications such as artificial photosynthesis and nonlinear optics (NLO). Luminescence from CT states is also useful in other areas including oleds (organic light emitting diodes) and optical sensors. In inorganic spectroscopy, CT transitions with participation of the metal (MLCT, LMCT) have been emphasized in the past. However, LLCT and ILCT become increasingly important. A very interesting aspect of these CT transitions is their close relationship to CT interactions in organic compounds. In particular, zwitterions represent a significant group of CT systems, which find their counterparts in suitable metal complexes. In these cases, LLCT and ILCT take place between or within ligands, which also provide the donor and acceptor sites in organic zwitterions [8]. It is anticipated that inorganic and organic chemists can mutually benefit from this analogy.

References

[1] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.
[2] A. Vogler, H. Kunkely, J. Am. Chem. Soc. 103 (1981) 1559.
[3] G.E. Coates, S.I.E. Green, J. Chem. Soc. (1962) 3340.
[4] V.J. Koester, Chem. Phys. Lett. 32 (1975) 575.
[5] L.K. Hanson, W.A. Eaton, S.G. Sligar, I.C. Gunsalus, M. Gouterman, C.R. Connell, J. Am. Chem. Soc. 98 (1976) 2672.
[6] T.R. Miller, I.G. Dance, J. Am. Chem. Soc. 95 (1973) 6970.
[7] A. Vogler, H. Kunkely, Comments Inorg. Chem. 9 (1990) 201.
[8] J. Griffith, Colour and Constitition of Organic Molecules, Academic Press, 1976, p. 200.
[9] M. Yang, D. Jacquemin, B. Champagne, Phys. Chem. Chem. Phys. 4 (2002) 5566, and references cited therein.
[10] H. Prinzbach, L. Knothe, A. Dieffenbacher, Tetrahedron Lett. (1969) 2093.
[11] M.L.H. Green, D.K.P. Ng, Chem. Rev. 95 (1995) 439.
[12] J.C. Green, S.Y. Kaltsoyannis, K.H. Sze, M. McDonald, J. Am. Chem. Soc. 116 (1994) 1994.
[13] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 7 (2004) 650.
[14] K. Iwata, S. Yoneda, Z. Yoshida, J. Am. Chem. Soc. 93 (1971) 6745.
[15] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 5 (2002) 112.
[16] A. Vogler, H. Kunkely, Coord. Chem. Rev. 211 (2001) 223.
[17] A. Vogler, H. Kunkely, Coord. Chem. Rev. 230 (2002) 243.
[18] C. Kutal, Coord. Chem. Rev. 99 (1990) 213.
[19] P.C. Ford, A. Vogler, Acc. Chem. Res. 26 (1993) 220.
[20] P.C. Ford, E. Cariati, J. Bourassa, Chem. Rev. 99 (1999) 2625.
[21] E.M. Kosover, B.G. Ramsey, J. Am. Chem. Soc. 81 (1959) 856.
[22] H. Kunkely, A. Vogler, Eur. J. Inorg. Chem. (1998) 1863.
[23] M.R.M. Bruce, A. Kenter, D.R. Tyler, J. Am. Chem. Soc. 106 (1984) 639.
[24] A. Vogler, H. Kunkely, Top. Curr. Chem. 213 (2001) 143.
[25] K. Dimroth, C. Reichardt, T. Siepmann, F. Bohlmann, Liebigs Ann. Chem. 661 (1963) 1.
[26] C. Reichardt, Angew. Chem. Int. Ed. Engl. 4 (1965) 29.
[27] C. Reichardt, Solvent Effects in Organic Chemistry, Verlag Chemie, Weinheim, 1979.
[28] R. Benedix, A. Vogler, Inorg. Chim. Acta 204 (1993) 189.
[29] A. Vogler, H. Kunkely, Inorg. Chim. Acta 54 (1981) L273.
[30] R.S.H. Liu, J. Chem. Ed. 79 (2002) 183.
[31] R.S.H. Liu, A.E. Asato, J. Photochem. Photobiol. C: Photochem. Rev. 4 (2003) 179.
[32] T. Zieliński, M. Kędziorek, J. Jurczak, Tetrahedron Lett. 46 (2005) 6231.
[33] L.A. Oro, M.V.P. Cifuentes, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 276 (1984) 67.
[34] H. Kunkely, A. Vogler, Inorg. Chem. Commun., in press.
[35] Z. Hu, R.J. Boyd, H. Nakatsuji, J. Am. Chem. Soc. 124 (2002) 2664.
[36] W.A. Fordyce, G.A. Crosby, Inorg. Chem. 21 (1982) 1023.
[37] A. Vogler, H. Kunkely, Coord. Chem. Rev. 177 (1998) 81.
[38] A. Vogler, A. Kern, Angew. Chem. Int. Ed. Engl. 15 (1976) 625.
[39] M.R. Churchill, Prog. Inorg. Chem. 11 (1970) 53.
[40] A.M. McNair, K.R. Mann, Inorg. Chem. 25 (1986) 2519.
[41] A.J. Rippert, D.N. Laikov, H.-J. Hansen, Helv. Chim. Acta 85 (2002) 2469.
[42] S.R. Marder, J.W. Perry, B.G. Tiemann, W.P. Schaefer, Organometallics 10 (1991) 1896.
[43] H. Kunkely, A. Vogler, J. Organomet. Chem. 637–639 (2001) 777.
[44] J.P. Saxena, W.H. Stafford, W.L. Stafford, J. Chem. Soc. (1959) 1579.
[45] H. Kunkely, A. Vogler, J. Photochem. Photobiol. A: Chem. 144 (2001) 69, and references cited therein.
[46] R. Ballardini, G. Varani, M.T. Indelli, F. Scandola, Inorg. Chem. 25 (1986) 3858.
[47] H. Kunkely, A. Vogler, Chem. Phys. Lett. 304 (1999) 187.