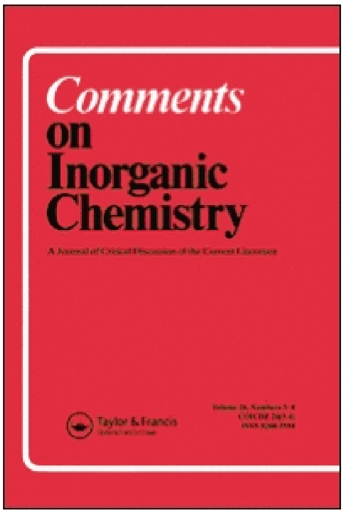

Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Inorganic Chromophores: Optical Charge Transfer in Coordination Compounds

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To cite this Article Vogler, Arnd and Kunkely, Horst(1997) 'Inorganic Chromophores: Optical Charge Transfer in Coordination Compounds', Comments on Inorganic Chemistry, 19: 5, 283 — 306

To link to this Article: DOI: 10.1080/02603599708032742

URL: http://dx.doi.org/10.1080/02603599708032742

Inorganic Chromophores: Optical Charge Transfer in Coordination Compounds

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Charge transfer (CT) transitions of coordination compounds of transition, main group, and f-block metals are classified according to the redox sites at the metals and ligands: ligand-to-metal (LMCT), metal-to-ligand (MLCT), metal-to-metal (MMCT), ligand-to-ligand (LLCT) and intraligand (ILCT). The energy of these CT transitions can be correlated with the reducing and oxidizing strength of the donor and acceptor, respectively. In many cases the colors of metal complexes are determined by CT absorption bands. A variety of examples demonstrate the importance of optical CT in coordination compounds.

INTRODUCTION

Electronic spectra of transition metal complexes have been studied extensively for many years.[1] Recently, coordination chemists have utilized electronic spectroscopy increasingly to characterize their compounds. In this context it seems timely to point out some important features of this subject as viewed by the inorganic chemist. For this purpose qualitative descriptions and simplified models are quite useful to facilitate the comprehension of this matter by the non-spectroscopist.

In organic compounds electronic transitions occur frequently in localized moieties (e.g., functional groups) which are termed chromophores.

Comments Inorg. Chem.
1997, Vol. 19, No. 5, pp. 283–306
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In another terminology the absorption bands of organic compounds are classified according to symmetry labels such as $\sigma\sigma^*$, $\pi\pi^*$, $\pi\sigma^*$, etc. While for metal complexes these assignments are also helpful as additional information, a different terminology has been developed to distinguish electronic transitions of coordination compounds.

In a metal complex the metal–ligand bonds are generally polar. The molecular orbitals are then not equally delocalized between metal and ligands but predominantely located at the metal or the ligands. The electronic transitions are categorized according to this localization. Three types of electronic excitations are possible. Electronic transitions are localized at the metals (metal-centered, MC), at the ligands (ligand-centered, LC or intraligand, IL) or they take place between MOs at the metals and the ligands. The latter transitions are associated with a spatial redistribution of electrons and therefore are termed charge transfer (CT) transitions. While the metal center or the ligands may be considered as chromophores in analogy to functional groups of organic compounds, CT transitions occur between metals and/or ligands. However, for organic compounds different types of electronic transitions are used as labels for chromophores. In this more general sense CT transitions of metal complexes can also be employed to characterize inorganic chromophores.

The present review deals with these CT transitions and the corresponding absorption bands. While the majority of studies have been restricted to coordination compounds of transition metals, our report also includes complexes of main-group and f-block metals.

It is appealing to inorganic chemists that the energy of CT transitions and the wavelength of CT bands, respectively, can be correlated with the redox properties of the metals and ligands since the CT transition is a redox process by definition. C. K. Jørgensen, who made pioneering contributions to this subject, introduced the concept of optical electronegativity[2] which can be used to estimate the energy of CT transitions. In addition to redox potentials other features are also important. Owing to the elctronic coupling between metals and ligands the molecular orbitals are generally delocalized to a certain extent. A CT transition involves, then, only transfer of a fraction of an electron between the redox sites at the metals and the ligands. In extreme cases MOs are completely delocalized and CT does not take place anymore. Nevertheless, a CT assignment may still be useful in order to indicate the origin of an absorption band.

CT transitions are classified according to the redox sites at the metals and ligands.[3] Their energy depends roughly on the reducing and oxidizing strength of the donor and acceptor, respectively. Accordingly, the labels M_{ox}, M_{red}, L_{ox} and L_{red} are used to stress the possibility of a low-energy transition:

M_{ox}-L_{red}	ligand-to-metal,	LMCT
M_{red}-L_{ox}	metal-to-ligand,	MLCT
M_{red}-L-M_{ox}	metal-to-metal,	MMCT
M_{red}-M_{ox}	metal-to-metal,	MMCT
L_{red}-M-L_{ox}	ligand-to-ligand,	LLCT
M-L (L = A_{ox}-D_{red})	intraligand,	ILCT

If these transitions occur at relatively low energies the corresponding CT absorptions may appear in the visible region and determine the color of the metal complexes. Occasionally, we mention the colors. It is then implied that the chromophoric transition is of the CT type.

In the following discussion the specific CT transitions are first illustrated by some classical examples, but more recent developments are emphasized later on. The choice of suitable examples was guided by the authors' interest. In many cases our own observations are included in order to provide competent comments. For a comprehensive treatise the reader is refered to Lever's book.[1] However, this monograph does not cover several topics such as LLCT and electronic spectra of complexes of the main group metals. These subjects are partially included in a recent book which, however, deals with the photochemistry associated with CT excitation.[4] Finally, it should be noted that in the present article we do not discuss outer-sphere CT transitions.[5,6]

LMCT

The most common CT transition of coordination compounds is of the LMCT type. The colors of many metal complexes are determined by LMCT absorptions. LMCT transitions are so widespread because every ligand is rather electron-rich by its nature and can serve as electron donor for optical CT. With increasing oxidizing strength of the metal and reducing power of the ligand LMCT absorptions undergo a red shift. Generally, metals in higher oxidation states are better acceptors. LMCT bands can be classified according to the electron configuration at the metal. The most important configurations are included in our report.

d^0

Complexes with a d^0 configuration contain a transition metal in the highest possible oxidation state. Since no valence electrons are left at the metal, only LMCT transitions may occur (with the exception of IL bands of complexes such as metalloporphyrins). Typical examples are the tetrahedral oxo anions MO_4^{n-} and their thio analogues MS_4^{n-} (Table I). General trends in the periodic table can be nicely compared with these data. The stability of the highest oxidation state increases within a transition group from the top to the bottom (e.g., Cr^{VI}, Mo^{VI}, W^{VI}) and decreases in a period from left to right (e.g., Cr^{VI}, Mn^{VII}). The shift of the LMCT bands is completely consistent with these redox properties. For the same oxidation state the sulfide complexes absorb at longer wavelength than the oxo anions since sulfide is stronger reducing. CrS_4^{2-} and MnS_4^- do not exist because Cr^{VI} and Mn^{VII} oxidize sulfide thermally. Owing to these high oxidation states, metal–ligand bonds are rather covalent. Accordingly, most MOs are quite delocalized and the extent of charge transfer redistribution which is associated with a LMCT transition can be quite small. The lowest-energy LMCT transition of MO_4^{n-} and MS_4^{n-} does not terminate at pure metal orbitals but at a molecular orbital which is M-L π-antibonding. This is nicely illustrated by the vibrational structure of the absorption bands of d^0 oxometalates[1,8–10] (e.g., MnO_4^-, Fig. 1). In the LMCT state the metal–ligand bonds are weakened as indicated by the spacing of these vibrational features.

TABLE I

LMCT absorptions of d^0 complexes (Refs. 1 and 7).

Complexes	λ (nm)
CrO_4^{2-}	373
—	
MoO_4^{2-}	234
MoS_4^{2}	469
WO_4^{2-}	199
WS_4^{2-}	395
MnO_4	529
—	
ReO_4^-	233
ReS_4^-	505

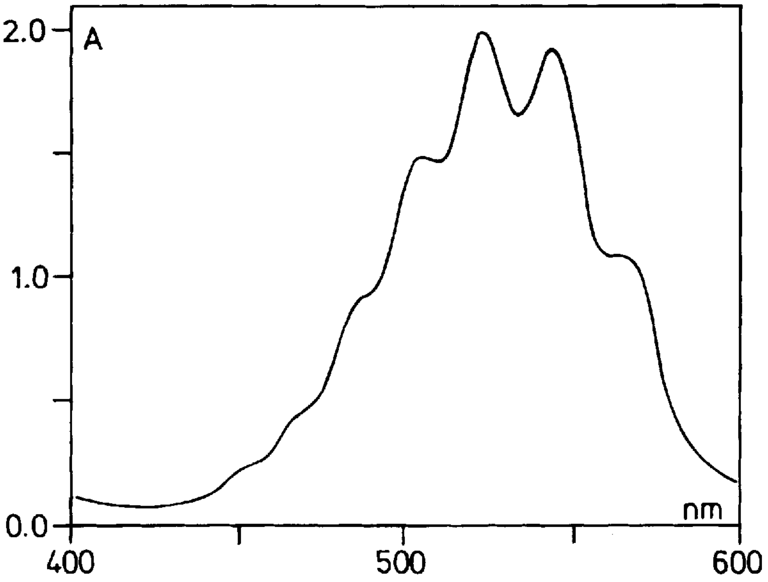


FIGURE 1 Electronic absorption spectrum of 8.32 × 10^{-4} M $KMnO_4$ in water at r.t., 1-cm cell.

Recently, organometallic oxides which contain transition metals in high oxidation states have attracted much attention.[11] A particularly interesting group of compounds with the general formula $RRe^{VII}O_3$ has been studied in detail.[12] Owing to the reducing strength of R^- the longest-wavelength bands of these neutral compounds can be safely assigned to $R^- \rightarrow Re^{VII}$ LMCT bands[13,14] (Table II).

A most intriguing but unresolved question concerns the participation of the hydride ligand in CT transitions which should not require too

TABLE II

LMCT absorptions of $RReO_3$ complexes (Refs. 13 and 14).

Complex	λ (nm)
CH_3ReO_3	260
$C_5H_5ReO_3$	377
$MeC_5H_4ReO_3$	380
$Me_5C_5ReO_3$[a]	402

[a] Me_5C_5 = pentamethylcyclopentadienyl.

much energy since H^- is a strong reductant. However, this expectation has not yet been confirmed. On the contrary, such a LMCT absorption was reported to appear at very short wavelength:

$$[\mathrm{Re}^{\mathrm{VII}}\mathrm{H}_9]^{2-}\ \mathrm{LMCT}\ \lambda_{\mathrm{max}} = 217\ \mathrm{nm},\ \epsilon = 1800.^{15}$$

However, recent evidence supports the assumption that LMCT transitions involving H^- as donor can occur at reasonably low energies.[16]

d^5

Octahedral low-spin d^5 complexes are characterized by a hole in the lower-energy t_{2g} subshell. Moreover, these π_d orbitals have only a small effect on the metal–ligand bonding. The reorganizational energy is then quite small and hardly contributes to the energy of the LMCT transition. It follows that such d^5 complexes are frequently colored since intense LMCT absorptions appear in the visible region. However, the appearance of low-energy LMCT bands is not limited to octahedral low-spin complexes. Irrespective of the particular complex, Fe(III) compounds generally display long-wavelength LMCT absorptions due to the oxidizing nature of the metal. The transition energies and the colors, respectively, depend strongly on the reducing strength of the ligands (Table III). Even organometallic compounds such as $Cr(CO)_5I$ ($\lambda_{max} = 638$ nm) which contain the metal in a low oxidation state show LMCT bands at rather long wavelength.[17]

d^6

Octahedral low-spin d^6 complexes show LMCT bands at relatively short wavelength since the transition terminates at a σ-antibonding e_g orbital which occurs at rather high energies and has a large influence on the

TABLE III

Colors and LMCT absorptions of Fe(III) complexes.

Complex	λ (nm)	Color	Ref.
$[FeF_6]^{3-}$	<190	colorless	16
$[FeCl_4]^-$	364	yellow	18
$[Fe(CN)_6]^{3-}$	425	red[a]	19
$[Fe(SCN)(H_2O)_5]^{2+}$	448	red	20
$[Fe(C_5H_5)_2]^+$	617	blue	21

[a] In the solid state.

metal–ligand bonding. The reorganizational energy is then quite large and contributes considerably to the LMCT transition. So it is not surprising that LMCT absorptions of low-spin d^6 complexes of metals such as Fe(II) and Co(III) appear frequently in the UV region.[1]

d^{10}

Since metals such as Au(I) and Hg(II) have completely filled d shells, LMCT transitions must terminate at the next higher s orbital of the metal. Generally, d^{10} complexes are colorless because their LMCT absorptions appear in the UV region. Au(I) complexes of the formula $[AuX_2]^-$ show such LMCT bands at energies comparable to those of metal-centered ds transitions.[22] The d^{10} orbitals of mercury are much more stable and do not participate in low-energy electronic transitions. Consequently, the absorption spectra of simple Hg(II) complexes contain only LMCT bands (Table IV). Since Zn^{2+} is not oxidizing, LMCT absorptions are not expected to be observed. However, in the cluster complex Zn_4O (acetate)$_6$ a LMCT band appears at $\lambda_{max} = 216$ nm.[24] It has been suggested that this observation can be attributed to the electronic interaction in the cluster. If this is extended to bulk ZnO, LMCT occurs as a band gap transition at $\lambda = 365$ nm.[25] While the valence band is composed of occupied orbitals of oxide, the conduction band consists of empty 3s orbitals of the Zn^{2+} ions. Analogous considerations apply to ZnS[26] and CdS.[27] The cluster $[Cu(PPh_3)H]_6$ is red and shows its longest-wavelength absorption at $\lambda_{max} = 530$ nm. This band has been assigned to a mixed ds/LMCT transition red-shifted by cluster interaction.[16] This is a rare case of LMCT which involves hydride as the donor ligand.

TABLE IV

LMCT absorptions of various Hg(II) complexes (Ref. 23).

Complex	λ (nm)
$HgCl_2$	~200
$HgCl_3^-$	240
$HgCl_4^{2-}$	234
HgI_2	266
HgI_3^-	301
HgI_4^{2-}	329
$Hg(N_3)_3^-$	246

s^0

Au(I) and Hg(II) may also be classified as s^0 metals. However, in order to distinguish between d-block and main group metals the designation s^0 is reserved for main group elements in their highest oxidation state. Owing to the absence of valence electrons at the metal, s^0 complexes show only LMCT bands (Table V). As expected the energy of the LMCT transition decreases from colorless $SnCl_6^{2-}$ to yellow $PbCl_6^{2-}$ since Pb(IV) is more oxidizing than Sn(IV) in accord with the general trend in the main groups. Contrary to the transition metal groups the stability of the highest oxidation state decreases within a main group from the top to the bottom owing to relativistic effects.[28]

While much attention has been paid to LMCT spectra of thio complexes of d^0 metals (see above), corresponding complexes of s^0 metals have hardly been studied. The anion $[SbS_4]^{3-}$ shows a LMCT band (Fig. 2) at $\lambda_{max} = 285$ nm.[34]

s^2

LMCT transitions of s^2 complexes terminate at the empty p orbitals of the metal. Generally, such LMCT bands (Table VI) appear at much shorter wavelengths than those of comparable s^0 complexes.

f^n

Compounds of oxidizing f^n metals such as Ce(IV), U(VI) with f^0 or Eu(III) with f^6 are characterized by low-energy LMCT transitions which terminate at the empty or partially filled f shell of the metal. The yellow-green uranyl ion $[UO_2]^{2+}$ ($\lambda_{max} = 415$ nm)[37,38] and $[Eu(H_2O)_n]^{3+}$ ($\lambda_{max} = 190$ nm)[39] are well documented examples.

TABLE V

LMCT absorptions of halide complexes of s^0 metals.

Complex	λ (nm)	Ref.
$TlCl_4^-$	247	29
$PbCl_6^{2-}$	307	29
$SbCl_6$	272	30
$SnCl_6^{2-}$	278	31
$SnBr_6^{2-}$	285	32
$Sn(N_3)_6^{2-}$	264	33

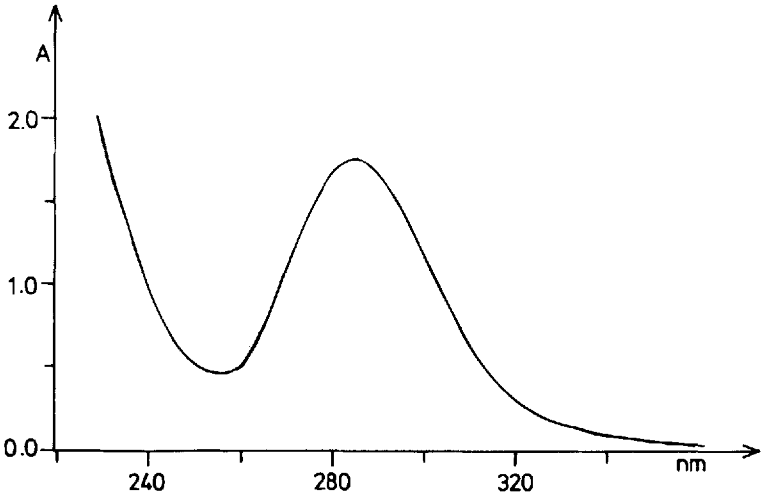


FIGURE 2 Electronic absorption spectrum of 1.28×10^{-4} M $[SbS_4]^{3-}$ in 10^{-3} M NaOH at r.t., 1-cm cell.

MLCT

MLCT absorptions appear at long wavelength if the metal is reducing and the ligands (e.g., CO, CN^-, olefins, 2,2′-bipyridyl) provide rather stable empty orbitals which are generally of the π^* type.[1] The position of MLCT bands may depend on the solvent polarity. Many complexes with MLCT bands, in particular cyano complexes, also display charge transfer to solvent (CTTS) bands.[40–42] The distinction between MLCT

TABLE VI

LMCT absorptions of bromide (Ref. 35) and iodide (Ref. 36) complexes of s^2 metals.

Complexes	λ (nm)
$SbBr_4^-$	216
$BiBr_4^-$	232
$BiBr_6^-$	241
SnI_3^-	208
PbI_3^-	223
SbI_4^-	246
BiI_4^-	279

and CTTS transitions is not always clear since the MLCT acceptor orbital is also exposed to and influenced by the solvent. Even other transitions of quite different origin can be considered to have some MLCT contribution. Rydberg (or inter-configurational) MC transitions of the $nd^{10} \rightarrow nd^{9}(n+1)s^{1}$ type (e.g., Cu(I)) should contain some MLCT[43] or CTTS[44] character due to the diffuseness of the (n + 1)s orbitals. The majority of complexes which display typical MLCT spectra include those of reducing d^6, d^8, d^{10}, and s^2 metals. Especially, organometallic compounds with metals in low oxidation states and π-acceptor ligands are often characterized by long-wavelength MLCT absorptions.[1,40] Generally colors of coordination compounds are determined less frequently by MLCT compared to LMCT absorptions since the appearance of MLCT bands in the visible region requires the presence of special ligands such as polypyridyls.

A rather new type of MLCT transition terminates at ligand σ* instead of π* orbitals. Suitable ligands (e.g., Se_2Ph_2, O_2^{2} , I_2) are oxidizing due to the presence of low-energy σ* orbitals. The binuclear complex $Re^{I}_{2}Br_2(CO)_6(Se_2Ph_2)$ shows such a d → σ* MLCT absorption (Fig. 3) at $\lambda_{max} = 434$ nm.[45] This type of MLCT transition has also been suggested to occur in dihydride complexes of Ir(III) and Mo(IV).[40] However, while a d → σ* (H_2) MLCT assignment may be

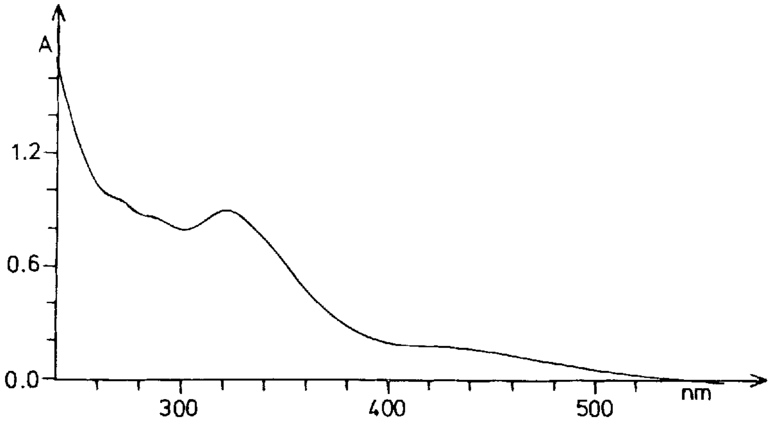


FIGURE 3 Electronic absorption spectrum of 1.34×10^{-4} M $Re_2Br_2(CO)_6(Se_2Ph_2)$ in CH_2Cl_2 at r.t., 1-cm cell.

appropriate for real dihydrogen complexes, it hardly applies to dihydride complexes.

d^6

Octahedral low-spin d^6 complexes with a reducing metal center (e.g., Cr(0), Mo(0), W(0), Mn(I), Re(I), Fe(II), Ru(II), and Os(II)) and polypyridyl (or 1,2-diimine) ligands (e.g., 2,2′-bipyridyl, 1,10-phenanthroline) represent the largest family of compounds with low-energy MLCT transitions.[1,40,46,47] These compounds are frequently colored since their MLCT bands appear in the visible region. A typical spectrum is that of $[Ru(bipy)_3]^{2+}$ (Fig. 4) which shows the MLCT band at λ_{max} = 452 nm. It is remarkable that M → bipy MLCT bands are not only shown by $[M(bipy)_3]^{2+}$ with M = Fe, Ru and Os but also by the polynuclear complexes $(bipy)(H_2O)Pt\text{-}\mu NC\text{-}M(CN)_4\text{-}\mu CN\text{-}Pt(H_2O)(bipy)$. In the latter case the M → bipy MLCT transitions involve remote redox centers which are separated by the Pt-NC moiety.[48]

Another large family of d^6 complexes with MLCT absorptions which, however, appear in the UV region comprises cyano complexes[1] (e.g., $[M(CN)_6]^{4-}$ with M = Fe, Ru and Os) and metal carbonyls (e.g., $M(CO)_6$ with M = Cr, Mo, W).[40] These MLCT bands may obscure less intense

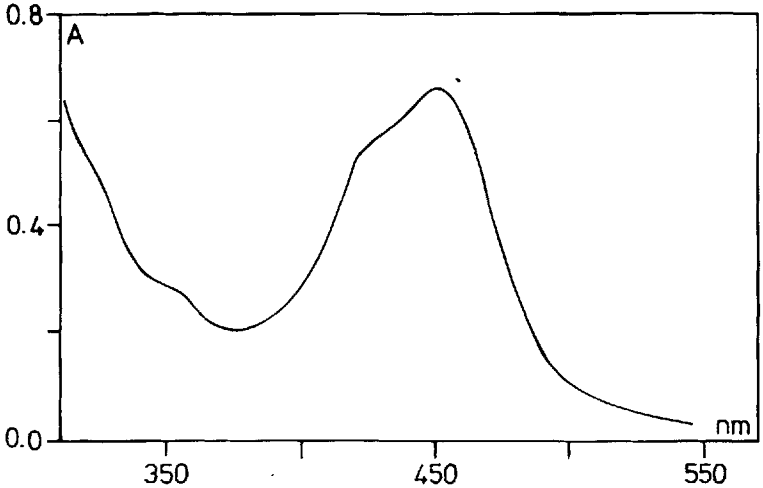


FIGURE 4 Electronic absorption spectrum of 1.0×10^{-4} M $[Ru(bipy)_3]Cl_2$ in CH_3CN at r.t., 1-cm cell.

bands of different origin such as LF absorptions. A characteristic long-wavelength MLCT band was also identified in the absorption spectrum of the carbene complex $Mn(C_5H_5)(CO)_2(CPh_2)$ ($\lambda_{max} = 380$ nm).[49]

d^8

Generally, d^8 complexes occur in square-planar or trigonal-bipyramidal structures. Reducing d^8 metals include Fe(0), Ru(0), Os(0), and Pt(II). Pt^{II} polypyridyl (e.g., $Pt(bipy)Cl_2$ in water, $\lambda_{max} = 340$ nm)[50] and olefin complexes (e.g., $[Pt(C_2H_4)Cl_3]^-$, $\lambda_{max} = 330$ nm)[51,52] display long-wavelength MLCT absorptions. MLCT bands also appear in the spectra of $Fe(CO)_5$ ($\lambda_{max} = 240$ nm)[53] and $[Os(CPh)(CO)_2(PPh_3)_2]^+$ ($\lambda_{max} = 318$ nm).[54] In the latter case the carbyne ligand provides π^* orbitals at rather low energies.

d^{10}

Complexes with d^{10} metals in low oxidation states such as Fe(-II), Pt(0), Cu(I), and Au(I) are generally reducing. Low-energy MLCT absorptions are expected to appear if the ligands are π-acceptors. Although MLCT bands cannot be obscured by LF bands the presence of long-wavelength ds and dp absorptions may interfere with the identification of MLCT bands. Nevertheless, various d^{10} complexes are known to display MLCT bands in their absorption spectra.[55] Examples are shown in Table VII. An interesting acceptor ligand is fullerene. Owing to its high electron affinity the MLCT absorption of $Pt[P(OPh)_3]_2C_{60}$ occurs at very long wavelength (Table VII, Fig. 5).

s^2

Main group metal ions with an s^2 configuration are frequently reducing (e.g., Tl^+, Sn^{2+}, Sb^{3+}). Accordingly, long-wavelength absorptions of the compounds $M(bipy)X_3$ with Sb, Bi and X = Cl, Br, I were assigned to MLCT transitions.[60] However, these compounds exist only as solids, and

TABLE VII

MLCT absorptions of complexes of d^{10} metals.

Complex	λ (nm)	Ref.
$Cu^I(o\text{-}phen)(PPh_3)_2^+$	365	56
$Fe(CO)_4^{2-}$	<400	57
$Pt[P(OPh)_3]_2C_{60}$	770	58
$Au(CN)_2^-$	240	59

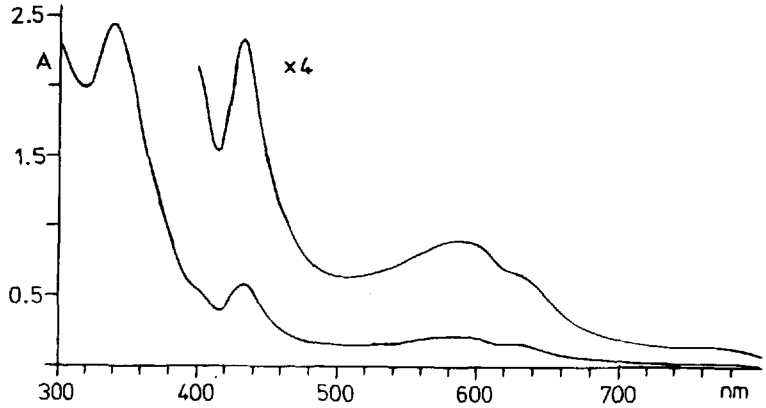


FIGURE 5 Electronic absorption spectrum of 5.97 × 10^{-5} M $Pt(PPh_3)_2C_{60}$ in toluene at r.t., 1-cm cell.

complications by solid state effects can presently not be excluded. MLCT assignments were also made for the organometallic cation $[Sn^{II}(C_5Me_5)bipy]^+$ [61] and metalloporphyrins of Sn(II), Sb(III) and Bi(III).[62,63] A few selected examples of s^2 complexes with MLCT absorptions are shown in Table VIII.

MMCT

Two different types of MMCT transitions can be distinguished. More familiar are those which occur in polynuclear complexes with bridging ligands between oxidizing and reducing metal centers (M_{red}-L-M_{ox}). In addition, MMCT bands also appear in the spectra of polynuclear complexes with direct but polar metal–metal bonds (M_{red}-M_{ox}).

TABLE VIII

MLCT absorptions of main group complexes of s^2 metals.

Complex	λ (nm)	Ref.
$Sb(bipy)Br_3$	435	60
$Bi(bipy)I_3$	485	60
$Sn(C_5Me_5)bipy^+$	(orange-red)	61
Sb(OEP)Cl[a]	376	63

[a] OEP = octaethylporphine.

M_{red}-L-M_{ox}

Our knowledge of MMCT spectra is largely based on observations on mixed-valence (MV) complexes[64-66] such as the Creutz–Taube ion $[(NH_3)_5Ru\text{-pyrazine-}Ru(NH_3)_5]^{5+}$ which formally contains Ru(II) and Ru(III). Since both metals are electronically coupled, an electron delocalization takes place. With increasing metal–metal interaction the individual metal ions Ru^{2+} and Ru^{3+} lose their identity. Finally, the valence orbitals of both metals are completely delocalized and the metals no longer exist in well-defined ("trapped") oxidation states. Both ruthenium atoms now have the intermediate oxidation state 2.5. While the localized MV complex is characterized by a $Ru^{2+} \rightarrow Ru^{3+}$ MMCT transition, little CT is associated with the "MMCT" transition of a delocalized MV complex. MMCT absorptions of symmetric MV complexes including many Ru(II)/Ru(III) compounds usually appear in the near IR region. If a redox asymmetry is introduced, MMCT bands are shifted to shorter wavelength and frequently determine the colors of MV compounds. Different ligands at the redoxactive metal centers lead to a slight redox asymmetry. For example, the ion $[(NH_3)_5Ru^{III}\text{-NC-}Ru^{II}(CN)_5]^-$ which is dark blue displays its MMCT absorption at $\lambda_{max} = 680$ nm[67] (Fig. 6). In this case the redox asymmetry is based on the larger stabilization of Ru(III) by NH_3 and Ru(II) by CN^-, respectively. In Prussian Blue $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$ ($\lambda_{max} \sim 665$ nm)[68] the redox asymmetry is also related to the different spin states of both iron ions (Fe^{II} low spin, Fe^{III} high spin).

A much larger redox asymmetry can be achieved in heteronuclear complexes.[69] MMCT absorptions may then appear even in the UV region. Several examples are presented in Table IX. If the acceptor is a low-spin d^6 metal such as Co(III), the MMCT transition terminates at a σ^*_d orbital. The reorganizational energy contributes considerably to this MMCT transition.

While d^0 metals in high oxidation states are attractive candidates to serve as acceptors for MMCT transitions, corresponding absorptions have been identified only recently (Table X). The occurrence of MMCT bands is not restricted to typical transition metals. The moiety $Hg^{II}NCFe^{II}(CN)_5$ exhibits a $Fe^{II} \rightarrow Hg^{II}$ MMCT band at $\lambda_{max} = 265$ nm.[75] Even binuclear main group metal complexes have been observed to show MMCT absorptions. For example, the anion $[Sn_2Cl_{10}]^{4-}$ displays a $Sn^{II} \rightarrow Sn^{IV}$ CT absorption maximum near 340 nm.[76]

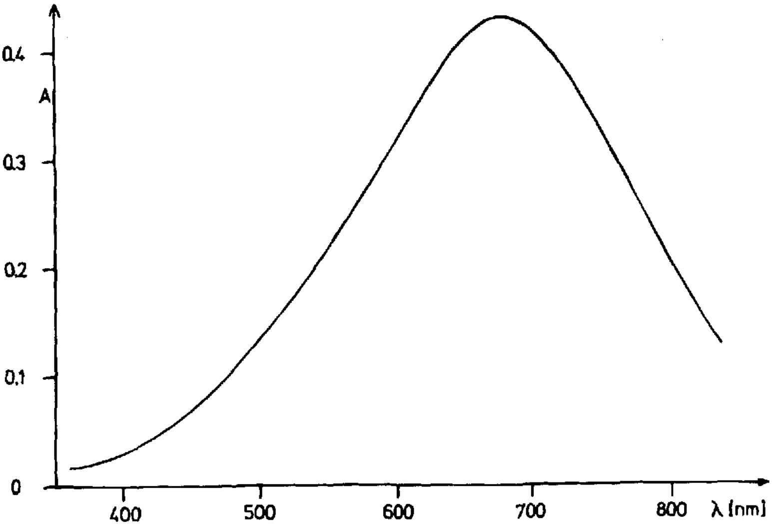


FIGURE 6 Electronic absorption spectrum of 1.77 × 10^{-4} M $[(NH_3)_5Ru^{III}\text{-}NC\text{-}Ru^{II}(CN)_5]^-$ in H_2O at r.t., 1-cm cell.

For all complexes discussed above it is quite obvious that the presence of a reducing and an oxidizing metal center leads to the appearance of a MMCT absorption. Does a MMCT band also appear if both metal centers are identical but are simultaneously reducing and oxidizing? As thermal reactions such redox processes are well known as disproportion-

TABLE IX

MMCT absorptions of heteronuclear complexes of the type $M_{ox}\text{-}L\text{-}M_{red}$.

Complex	λ (nm)	Ref.
$[(NH_3)_5Co^{III}NCRu^{II}(CN)_5]^-$	375	70
$[(NC)_5Co^{III}NCFe^{II}(CN)_5]^{6-}$	312	71
$[\text{cobalamin-}\mu NC\text{-}Fe^{II}(CN)_5]^{3-}$	~405	72
$[(NC)_5Co^{III}NCRu^{II}(CN)_5]^{6-}$	360	71
$[(NC)_5CO^{III}NCOs^{II}(CN)_5]^{6-}$	360	73
$[(NH_3)_5Os^{III}NCFe^{II}(CN)_5]^-$	628	73
$[(NH_3)_5Os^{III}NCRu^{II}(CN)_5]^-$	490	73
$[(NH_3)_5Os^{III}NCOs^{II}(CN)_5]^-$	559	73
$[(NH_3)_5Cr^{III}NCOs^{II}(CN)_5]^{6-}$	376	73
$Cl_3Fe^{III}ClCu^{I}(PPh_3)_3$	540	74

TABLE X

MMCT absorptions of polynuclear complexes with d^0 acceptor metals.

Complex	λ (nm)	Ref.
$\{(C_5H_5)_2Ti^{IV}[\mu\text{-}NCRu^{II}(CN)_5]_2\}^{6-}$	630	77
$\{(C_5H_5)_2Zr^{IV}[\mu\text{-}NCRu^{II}(CN)_5]_2\}^{6-}$	420	77
$\{(C_5H_5)_2Hf^{IV}[\mu\text{-}NCRu^{II}(CN)_5]_2\}^{6-}$	365	77
$[O_3MeRe^{VII}NCFe^{II}(CN)_5]^{4-}$	437	78
$S_2Re^{VII}(\mu\text{-}S)_2Re^{I}Cl(CO)_5$	500	79

ations. Although they are not yet common, such MMCT bands were recently identified:

$$[(NH_3)_5Os^{III}\text{-}NC\text{-}Os^{III}(NH_3)_5]^{5+}, \quad \lambda_{max} = 523 \text{ nm}^{80},$$

$$[(edta)Fe^{III}\text{-}O\text{-}Fe^{III}(edta)]^{4-}, \quad \lambda_{max} = 342 \text{ nm}^{81}.$$

In this context it is quite interesting that the dark color of solid $V(CO)_5$ has also been attributed to the occurence of a $V^0 \rightarrow V^0$ MMCT transition[82] which is, however, in this case of the outer-sphere type.

M_{red}-M_{ox}

If a reducing and an oxidizing metal are not bridged by a ligand but are connected by a direct but polar metal–metal bond, MMCT bands may be also observed. Generally, polar metal–metal bonds are found in heteronuclear complexes which contain metals of different electronegativity. Metal–metal coupling is strong in this case, and electron delocalization is only limited by the different energies of the overlapping metal orbitals. This type of polar metal–metal bond occurs in the complex $Ph_3PAu^{I}\text{-}Co^{-I}(CO)_4$.[83] The absorption spectrum exhibits a low-energy Co(-I) → Au(I) MMCT band. This MMCT transition involves the promotion of a metal–metal bonding electron to a σ^* (M-M) orbital. The complexes $[(NC)_5Co^{I}\text{-}Hg^{II}\text{-}Co^{I}(CN)_5]^{6-}$ (λ_{max} = 361 nm)[75] and $(OC)_4Co^{-I}\text{-}M^{II}\text{-}Co^{-I}(CO)_4$ with M = Zn, Cd and Hg (Fig. 7)[84] are further examples which are characterized by such MMCT absorptions. In the latter case the Co(-I) → M(II) MMCT bands undergo a blue shift from Hg (λ_{max} = 328 nm) to Cd (302 nm) and Zn (284 nm) since the energy of the ns acceptor orbitals of M(II) increases in this order.

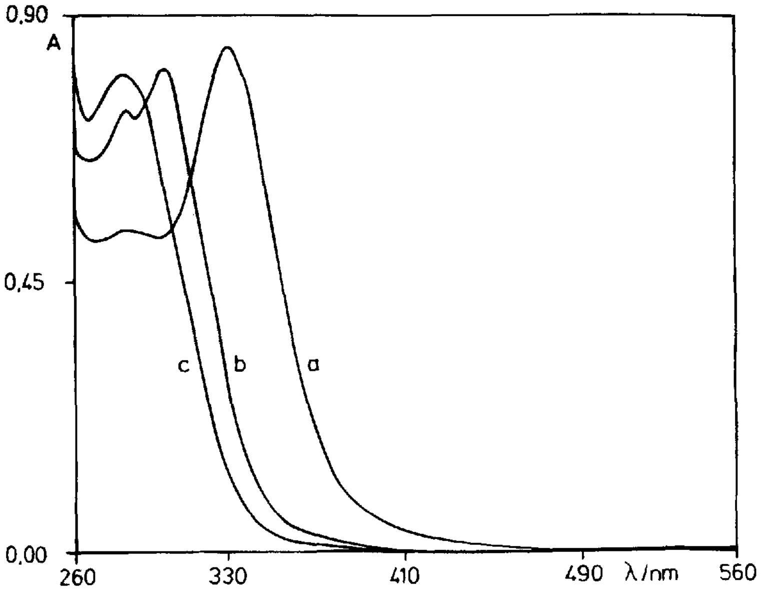


FIGURE 7 Electronic absorption spectra of (a) 3.39 × 10^{-5} M [$HgCo_2(CO)_8$], (b) 4.27 × 10^{-5} M [$CdCo_2(CO)_8$], and (c) 5.37 × 10^{-5} M [$ZnCo_2(CO)_8$] in THF under argon at r.t., 1-cm cell.

LLCT

Any mixed-ligand complex of the type L_{red}-M-L'_{ox} may display LLCT bands in its absorption spectrum.[85] In contrast to this expectation, surprisingly little is known about it. Nevertheless, during recent years an increasing number of observations on LLCT has been reported. LLCT bands were identified in the absorption spectra of complexes which contain the following donor and acceptor ligands: Donors: X^- (halides), RS^- (thiolates), R^- (carbanions); acceptors: polypyridyls (e.g., bipy), porphyrins. Some complexes which show LLCT absorptions are presented in Table XI. In most cases the band assignments are rather clear since other absorptions of different origin do not appear in the same energy region.

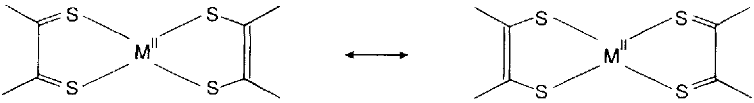
An interesting class of compounds which features long-wavelength LLCT absorptions comprises ligand-based MV complexes.[85] These compounds contain the same ligand in two different redox states in analogy to metal-based MV complexes. Generally, the ligands are derived

TABLE XI

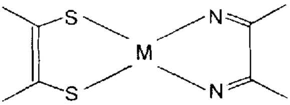
LLCT absorptions.

Complex	λ (nm)	Ref.
Be(bipy)Br_2	364	86
Zn(bipy)$(C_2H_5)_2$	420	87
Zn(1,4-diaza-1,3-butadiene)Et_2	490	88
(o-phen)Zn$(SC_6H_5)_2$	365	89
$[Tl(bipy)_2I_2]^+$	374	90
$Re(CO)_3$(p-tolyl-1,4-diaza-1,3-butadiene)Br	505	91
Re(bipy)O_3Me	360	92
methylcobalamin	317	93
carboxycytochrome P-450	360	94

from quinones and the corresponding hydroquinones. LLCT involves an electronic transition from the hydroquinone donor to the quinone acceptor ligand. However, the electronic coupling of both ligands introduces a serious complication. Since the intervening metal mediates a strong ligand–ligand interaction they may exist in intermediate redox states (e.g., as semiquinones). A "LLCT" transition occurs, then, in a delocalized ligand system and does not involve any CT. Intense long-wavelength absorptions of this type appear in the electronic spectra of square-planar dithiolene complexes such as $M^{II}(\text{dithiolene})_2$ with M = Ni, Pd, and Pt[95,96] represented by two equivalent resonance forms:



A chemical modification of the ligands leads to a redox asymmetry which reduces the delocalization and favors one resonance structure in the ground state[85,97]:



Such complexes which contain a 1,2,-diimine (e.g., bipy) and a 1,2-dithiolate ligand exhibit a long-wavelength absorption (e.g., Pt(bipy)tdt,[98] Fig. 8). It belongs to a real (dithiolate to diimine) LLCT transition. Since

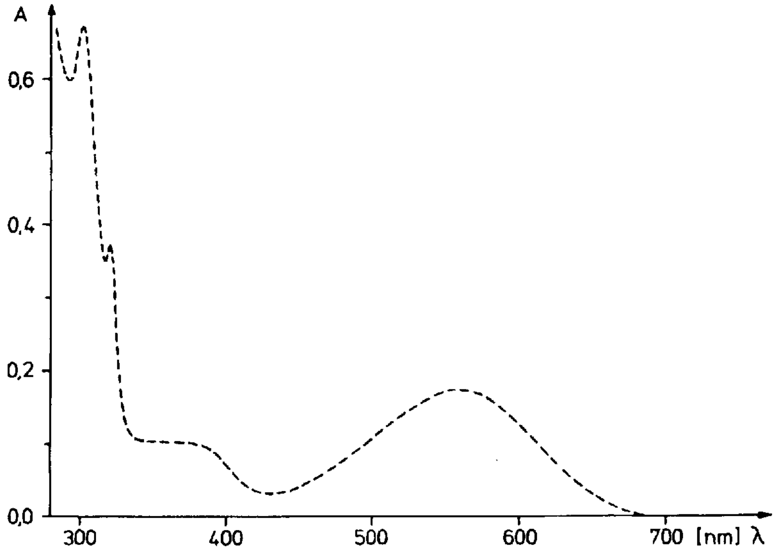


FIGURE 8 Electronic absorption spectrum of 4.9×10^{-5} M Pt(bipy)tdt in EtOH at r.t., 1-cm cell.

the band position depends strongly on the polarity of the solvent, the complexes are extremely solvatochromic. If M(II) is Zn^{2+}, the complexes are tetrahedral. Due to the orthogonal orientation of the planes of both ligands, the electronic coupling of the ligands is weak and the LLCT absorption is of low intensity (e.g., λ_{max} = 445 nm, ϵ = 72 for [Zn(bipy)(3,4-toluenedithiolate)].[99,100] LLCT absorptions were also observed for square planar Cu^{II} diimine complexes which contain catecholates instead of dithiolates as donor ligands.[101] A selection of complexes which display LLCT absorptions of this type are presented in Table XII.

ILCT

A ligand itself may consist of a reducing and oxidizing part. The spectrum of the metal complex should then show an ILCT band which belongs to an electronic transition from the donor to the acceptor site of the same ligand. Such an ILCT absorption appears in the spectrum of [biacetyl-bis(mercaptoethylimine)-nickel(II)] (λ_{max} = 585 nm, Fig. 9).[107]

TABLE XII

LLCT absorptions of complexes related to the ligand-based mixed valence compounds.

Complex	Solvent	λ (nm)	Ref.
Ru(bipy)$_3^+$	dmso	222	102
Ni(o-phen)($S_2C_2Ph_2$)	CH_2Cl_2	608	97
Ni(phi)(mnt)	acetone	678	103
Pd(baba)(mnt)	CH_2Cl_2	600	104
Pt(bipy)(tdt)	$CHCl_3$	610	98
Pt(bipy)(cat)	$CHCl_3$	578	105
Pt(bipy)(dmit)	dmso	570	106
Cu(bipy)(cat)	dmso	480	101
Zn(bipy)(tdt)	CH_2Cl_2	445	99,100

Abbreviations: (baba) biacetylbisanil; (cat) catecholate; (dmit) 1,3-dithiole-2-thione-4,5-dithiolate; (mnt) maleonitriledithiolate; (phi) phenanthrenechinonediimine; (tdt) 3,4-toluenedithiolate.

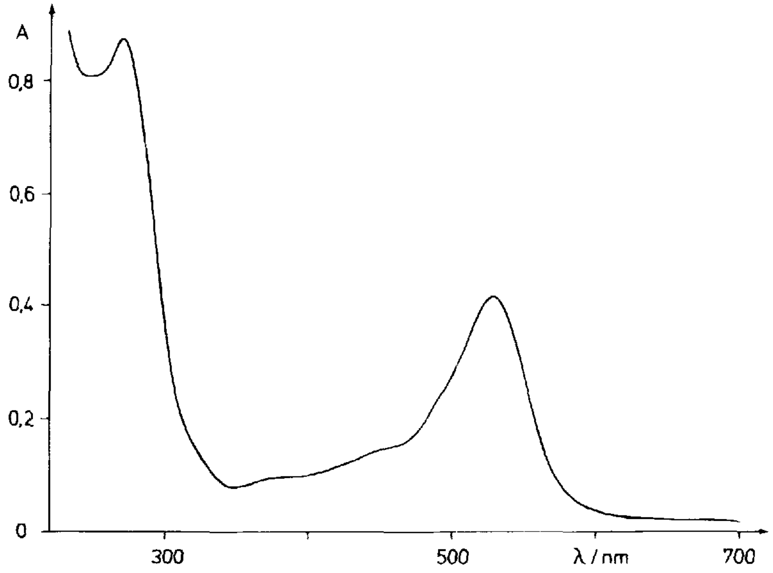
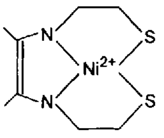
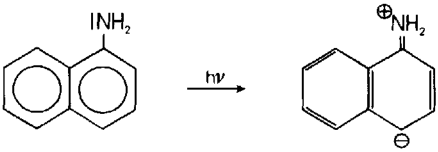


FIGURE 9 Electronic absorption spectrum of 6.75 × 10^{-5} M [biacetyl-bis(mercaptoethylimine)nickel(II)] in CCl_4 at r.t., 1-cm cell.



The donor site is the reducing thiolate moiety while the diimine is the accepting part of the chelate ligand. Such ILCT bands were also detected in the spectra of similar Zn(II) and Ni(II) complexes.[108]

An interesting case of ILCT occurs in the complex [Pt^{II}(1-naphthylamine)$_2Cl_2$]. Light absorption by the free naphthylamine leads to a shift of electron density from the nitrogen lone pair into the aromatic ring system.[109] Ground and excited state are described by two limiting resonance structures:



This electronic transition appears as an ILCT absorption of the platinum complex at $\lambda_{max} = 293$ nm.[109] The complexes

Ir^{III}(6-isopropyl-8-quinolydimenthylsilyl)$_3$, $\lambda_{max} \sim 385$ nm (SBLCT)[110]
SBLCT = σ-Bond-to-Ligand CT

$Cu(PPh_3)_2Cl$, $\lambda_{max} = 295$ nm $(\sigma \rightarrow a_\pi)$[55,111]

$Pt(qol)_2$, $\lambda_{max} = 480$ nm[112] (qol = 8-quinolinolato-O, N)

show analogous ILCT absorptions.

CONCLUSION

A variety of different CT transitions exists in coordination compounds of transition, maingroup, and f-block metals. The corresponding absorption bands may appear in the UV, visible, and near infrared spectral region. The colors of many metal complexes originate from CT transitions.

Acknowledgment

Support of this research by the DFG is gratefully acknowledged.

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