ELSEVIER

Coordination Chemistry Reviews
171 (1998) 399–406

COORDINATION CHEMISTRY REVIEWS

A new type of MLCT transition relevant to oxidative additions: d→σ* excitation

Arnd Vogler *, Horst Kunkely

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

Received 7 July 1997; accepted 19 November 1997

Contents

Abstract

Oxidative additions take place by a reductive cleavage of a σ bond: $M^{n+} + X_2 \rightarrow M^{n+2}(X^-)_2$. At intermediate stages, X_2 is assumed to be coordinated as a ligand: M^{n+}–X_2. Complexes of this type are characterized by $M^{n+} \rightarrow \sigma^*(X_2)$ MLCT transitions which represent the spectroscopic counterpart of the most important step of an oxidative addition. This new type of MLCT transition was detected in the electronic spectra of complexes such as $Re^{I}_2Br_2(CO)_6(Se_2Ph_2)$ and $Cr^{IV}(O_2)_2(NH_3)_3$. In contrast to d→π* MLCT states, d→σ* MLCT states are not luminescent but reactive. $Cr^{IV} \rightarrow \sigma^*(O_2^{2-})$ MLCT excitation of $Cr^{IV}(O_2)_2(NH_3)_3$ induces an intramolecular oxidative addition $[Cr^{IV}(O_2^{2-}) \rightarrow Cr^{VI}(O^{2-})_2]$ which finally leads to the formation of CrO_4^{2-} as stable photoproduct. © 1998 Elsevier Science S.A.

Keywords: Photochemistry; Charge transfer; Oxidative addition

---

1. Introduction

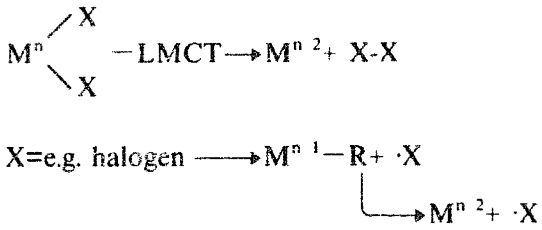
Oxidative additions and reductive eliminations are important reactions of transition metal complexes. They take place not only as thermal but also as photochemical

---

* Corresponding author. Fax: +49 941 943 4488.

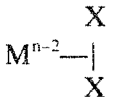
PII S0010-8545(98)00044-7

reactions [1–5]. Light-induced reductive eliminations are initiated by ligand-to-metal charge transfer (LMCT) excitation. They may proceed by a concerted mechanism or two consecutive one-electron transfer steps:

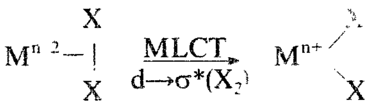


Generally, oxidative additions occur as intermolecular processes as the reversal of reductive eliminations:

However, at an intermediate stage X_2 should be coordinated as a ligand:

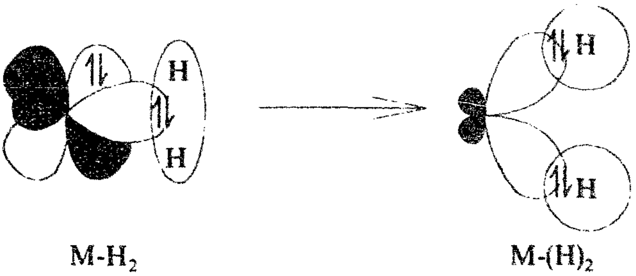


From this point product formation takes place by a shift of electron density from the metal to X_2. Electrons are accepted by the σ* orbital of X_2 which is subsequently transformed to two X^- ligands. In terms of electronic spectroscopy and photochemistry, this process should be induced by a d→σ* metal-to-ligand charge transfer (MLCT) transition:



We explored this possibility and searched for suitable complexes which contain a reducing metal and a ligand X–X. If X–X can be easily reduced to $2X^-$ it should possess a low-energy σ* orbital. Accordingly, the complex $M(X_2)$ is expected to display a low-energy d→σ* MLCT transition. The prototype of such a compound is represented by dihydrogen complexes such as $M^0(CO)_5H_2$ with M=Cr, Mo, W

[6–8]. The bonding interaction [9] and a simplified MO scheme [10] (Fig. 1) illustrate this situation. MLCT excitation may finally lead to the oxidative addition:



Unfortunately, dihydrogen complexes may not be the best choice for an initial study for various reasons. The σ* orbital of H_2 occurs at rather high energies.

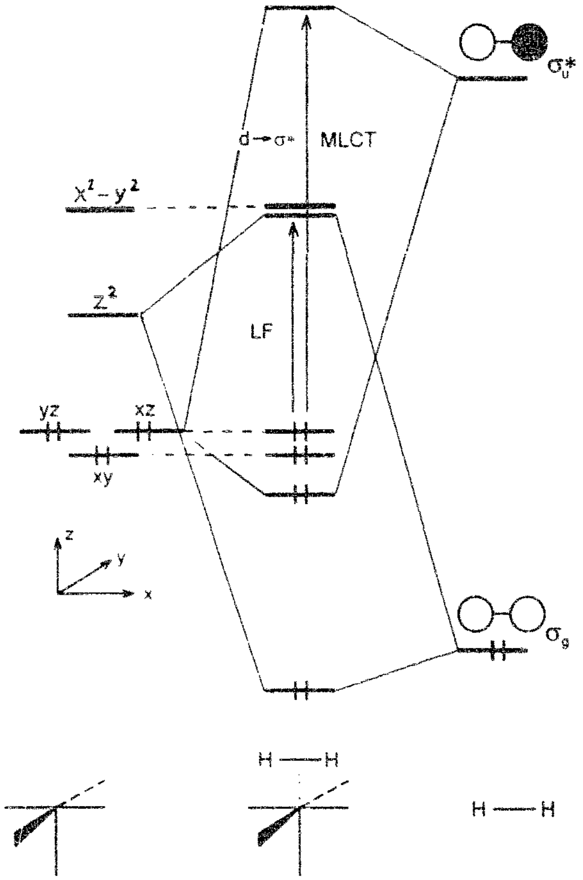


Fig. 1. Qualitative MO diagram for the interaction of a square-pyramidal $M(CO)_5$ fragment and H_2, adopted from ref. [10].

Moreover, the dihydrogen and the corresponding dihydride complexes are easily interconverted. Both facts would hamper the identification of MLCT states and elucidation of photochemical oxidative additions. Other ligands such as iodine, peroxide, hydrazine, disulfides, and diselenides are better candidates for this purpose. Complexes with these ligands are well-known but often not easily accessible (e.g. I_2 complexes [11]).

For the study of d→σ* MLCT excitation, we have finally chosen three complexes:

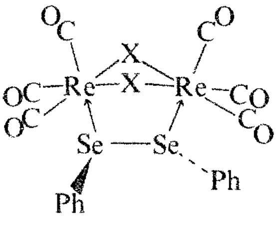
$Re^{I}_2Br_2(CO)_6(Se_2Ph_2)$ [12]
$Cr^{IV}(O_2^{2-})_2(NH_3)_3$ [13]
$Re^{I}Cl(CO)_3(PhNH{-}NH_2)_2$ [14]

These compounds are well-characterized and reasonably stable. They contain reducing metals and oxidizing ligands (Se_2Ph_2, O_2^{2-}, PhN–NH_2) which provide low-energy σ* orbitals. Unfortunately, the latter complex does not show a low-energy d→σ* MLCT absorption and does not undergo an oxidative addition.

2. Discussion

2.1. $Re_2Br_2(CO)_6Se_2Ph_2$

Diphenyl diselenide is characterized by an empty low-energy σ* (Se–Se) orbital [15–17]. Moreover, Re^I of the $ReBr(CO)_3$ moiety is an excellent donor as indicated by the appearance of long-wavelength MLCT absorptions in the spectra of complexes of the type $ReX(CO)_3$(1,2-diimine) [3,18]. Accordingly, we expected to identify a low-energy dσ* MLCT transition from Re^I to Se_2Ph_2 in the absorption spectrum of $Re_2X_2(CO)_6Se_2Ph_2$ with X = Br and diphenyl diselenide as bridging ligands [12]:



The binuclear complex is composed of two nearly octahedral moieties which contain Re^I as d^6 metal centers.

The absorption spectrum of Se_2Ph_2 shows a longest-wavelength band at $\lambda_{max} = 331$ nm which is assigned to the π→σ* transition from the lone pairs at selenium to the σ* (Se–Se) orbital [15–17]. In the electronic spectrum of $Re_2Br_2(CO)_6Se_2Ph_2$ in CH_2Cl_2, this πσ* transition appears as intraligand (IL) absorption at $\lambda_{max} = 324$ nm [19].

The longest-wavelength band of the complex in CH_2Cl_2 ($\lambda_{max}=434$ nm) which causes the striking orange–red color of the substance is assigned to MLCT transition from filled d-orbitals of Re^I to the σ^* (Se–Se) orbitals of the ligand. This assignment is supported by the solvatochromism of the binuclear complex [19].

In contrast to $ReX(CO)_3$(diimine) complexes, $Re_2Br_2(CO)_6Se_2Ph_2$ is not luminescent but photoreactive [19]. These observations are consistent with the MLCT assignment of the lowest-energy transition. The $\pi\sigma^*$ excitation of free Se_2Ph_2 leads to the homolytic splitting of the Se–Se bond and the concomitant generation of SePh radicals. Since the MLCT transition of the complex terminates also at the σ^* (Se–Se) orbital, an analogous behavior is expected. Owing to the oxidation of the metal and reduction of the ligand in the MLCT excited state, an oxidative addition could take place: $Re^I_2(Se_2Ph_2)\rightarrow 2Re^{II}(SePh)$. As a thermal reaction, such an oxidative addition of Se_2Ph_2 to $[MoC_5H_5(CO)_3]_2$ was observed [20]. Unfortunately, such an intramolecular oxidative addition in $Re_2Br_2(CO)_6Se_2Ph_2$ could not yet be verified since its photolysis is associated with a decomposition to unidentified products.

2.2. $Cr(O_2)_2(NH_3)_3$

The complex $Cr(O_2)_2(NH_3)_3$ contains Cr(IV) and two peroxide ligands which are coordinated side-on [13]. The longest-wavelength absorption at $\lambda_{max}=390$ nm is assigned to a LF transition while a more intense band at shorter-wavelength ($\lambda_{max}=257$ nm) is of the CT type [21]. It may be either a LMCT or MLCT transition. Both alternatives are feasible since Cr(IV) and peroxide are reducing as well as oxidizing. In fact, LMCT transitions involving peroxide as electron donor have been detected for a variety of peroxo complexes [22,23]. However, LMCT excitation of these complexes leads to a reduction of the metal and oxidation of the peroxo ligand [23]. In the case of $Cr(O_2)_2(NH_3)_3$ there is no indication that the photolysis yields Cr(III) as stable product [21]. On the contrary, the photochemical generation of CrO_4^{2-} (see below) is consistent with MLCT excitation involving the promotion of a d-electron to the σ^* orbital of peroxide. This LUMO of O_2^{2-} ($3\sigma_u$) [24] should be accessible at relatively low energies in agreement with the oxidizing character of peroxide.

The photolysis of $Cr(O_2)_2(NH_3)_3$ induced by MLCT excitation ($\phi=0.35$ at $\lambda_{irr}=254$ nm) proceeds according to the equation [21]:

$$Cr^{IV}(O_2)_2(NH_3)_3+2H_2O\rightarrow(NH_4)_2[Cr^{VI}O_4]+H_2O_2+NH_3$$

In this context it should be noted that photochemical oxidative additions of transition metal complexes have been observed before, e.g. [thpy$^-$ = 2-(2-thienyl)pyridine anion]:

$$Pt^{II}(bipy)Cl_2+CHCl_3\rightarrow Pt^{IV}(bipy)Cl_4+CHCl \quad [25]$$
$$Pt^{II}(thpy)_2+CHCl_3\rightarrow Pt^{IV}(thpy)_2Cl(CHCl_2) \quad [26,27]$$

However, these reactions are apparently induced by intermolecular excited-state electron transfer processes. In contrast to these reactions the $d\sigma^*$ MLCT excitation represents the initial step of an intramolecular oxidative addition which proceeds as a two-electron redox reaction: $Cr^{IV}(O_2^{2-}) \rightarrow Cr^{VI}(O^{2-})_2$.

2.3. $ReCl(CO)_3(PhNH\text{–}NH_2)_2$

Hydrazine and its derivatives play an important role as ligands in coordination chemistry [28]. Hydrazine complexes may occur as intermediates in nitrogen fixation and related processes [29]. Although a variety of hydrazine complexes are known, the electronic spectra and photoreactivity of such compounds have not yet been studied. Owing to its peculiar electronic structure and redox behavior, hydrazine may participate in diverse electronic transitions. In agreement with its ability to disproportionate ($3N_2H_4 \rightarrow 4NH_3 + N_2$; $\Delta H = -336.5$ kJ) [30], it is reducing and oxidizing [31]. It follows that low-energy LMCT and MLCT transitions involving coordinated hydrazines are feasible.

The complex $ReCl(CO)_3(PhNH\text{–}NH_2)_2$ is pseudo-octahedral and contains a reducing d^6 metal center. The longest-wavelength absorption at $\lambda_{max} = 332$ nm is assigned to a LF transition while shorter-wavelength bands at $\lambda_{max} = 272$ and 235 nm belong to IL transitions of phenylhydrazine [32]. In analogy to complexes of the type $Re^{I}X(CO)_3$(1,2-diimine) which are characterized by long-wavelength dπ* MLCT absorptions, the complex $ReCl(CO)_3(PhNH\text{–}NH_2)_2$ may also have available low-energy MLCT transitions which terminate at the σ* orbital of phenyl hydrazine. However, only IL bands were detected.

The complex $ReCl(CO)_3(PhNH\text{–}NH_2)_2$ is light sensitive [32]. The photoreactive excited state is apparently of the IL type. The photoreaction of the complex corresponds to that of the free ligand:

$$2PhNH\text{–}NH_2 \rightarrow C_6H_6 + N_2 + PhNH_2 + NH_3$$

The identification of d→σ* (hydrazine) MLCT transitions of $ReCl(CO)_3(PhNH\text{–}NH_2)_2$ was obviously hampered by the interference of IL absorptions of coordinated phenylhydrazine. Unsubstituted hydrazine which is transparent above 220 nm may be a better candidate for the detection of a dσ* MLCT band.

3. Conclusion

MLCT states play an important role in the photophysics and photochemistry of transition metal complexes [1–5,33–36]. Generally, MLCT transitions terminate at π* orbitals of suitable acceptor ligands such as polypyridyls, cyanide, carbon monoxide, alkenes, carbenes and carbynes. Usually, saturated ligands with σ bonds do not provide low-energy acceptor orbitals for MLCT transitions. However, in some cases σ* orbitals might be low enough to serve as acceptor orbitals in optical CT transitions. Appropriate candidates are reducible ligands which possess weak σ bonds. Accordingly, the complexes $Re_2Br_2(CO)_6(Se_2Ph_2)$ [19] and $Cr(O_2)_2(NH_3)_2$ [21] are characterized by low-energy MLCT transitions from Re(I) and Cr(IV) to the σ* orbitals of Se_2Ph_2 and O_2^{2-}, respectively. MLCT excitation of this type should represent a well-defined first step of an oxidative addition. Both complexes are indeed photoreactive upon dσ* MLCT excitation. $Cr^{IV}(O_2)_2(NH_3)_3$ undergoes a clean intramolecular oxidative photoaddition yielding $Cr^{VI}O_4^{2-}$ as final product [21].

Of course, saturated hydrocarbons would be the most interesting ligands in order to study optical MLCT and subsequent photochemical oxidative additions. Unfortunately, there is not much known about such complexes. However, complexes with alkyl halide ligands such as $CpMn(CO)_2(n\text{-}BuX)$ with X = Cl, Br have been described [37]. Since alkyl halides are characterized by low-energy σ* orbitals, these complexes may show long-wavelength dσ* MLCT absorptions. There is an indication for the presence of such MLCT transitions. The complexes $CpMn(CO)_2(R\text{–}X)$ display band maxima near 500 and 400 nm [37] which are probably of the LF type. However, with X = Br the 400 nm absorption is much more intense compared to that with X = Cl. It seems that the 400 nm band of $CpMn(CO)_2(R\text{–}Br)$ is superimposed on a more intense band at shorter-wavelength. This absorption may indeed be of the $Mn^I \rightarrow R\text{–}X$ MLCT type. MLCT absorptions with alkyl bromides are expected to appear at shorter-wavelength since alkyl bromides are stronger oxidants than alkyl chlorides. In this context it is of considerable interest that alkyl halides function as acceptors of outer-sphere CT transitions. They are well-known as charge-transfer-to-solvent (CTTS) when reducing complexes such as ferrocene are dissolved in alkyl halides as solvents [1–5,33–36]. Moreover, CTTS excitation leads to the photo-oxidation of the complex and reduction of the alkyl halide. There is little doubt that these photo-oxidations are initiated by the population of the σ* orbital of the R–X bond which is subsequently irreversibly split ($R\text{–}X + e^- \rightarrow {}^{\cdot}R + X^-$).

A further intriguing acceptor ligand for dσ* MLCT is molecular iodine. Although I_2 as a ligand is known [11], coordinated iodine has not yet been characterized by electronic spectroscopy. This is in contrast to countless studies of CT spectra involving I_2 as an acceptor and organic compounds such as aromatic molecules, amines, alcohols, and ethers as donors [38,39]. While the CT bands appear in the UV, the brown color of these solutions originates from the internal π*σ* (I_2) transition which is modified by the CT interaction. In non-donating solvents the violet color of I_2 is caused by the absorption at $\lambda_{max} = 560$ nm which is assigned to the unperturbed π*σ* transition of I_2. It should be quite interesting to characterize the CT spectra of $M(I_2)$ complexes in comparison to those of organic donor–iodine acceptor systems.

Acknowledgements

Support of this research by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

[1] A. Vogler, H. Kunkely, in: K. Kalyanasundaram, M. Grätzel (Eds.), Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, Kluwer Academic, Dordrecht, 1993, p. 71.

[2] J. Sykora, J. Sima, Coord. Chem. Rev. 107 (1990) 1.

[3] G.L. Geoffroy, M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979.

[4] D.M. Roundhill, Photochemistry and Photophysics of Metal Complexes, Plenum Press, New York, 1994.

[5] O. Horváth, K.L. Stevenson, Charge Transfer Photochemistry of Coordination Compounds, VCH, New York, 1993.

[6] R.K. Upmacis, G.E. Gadd, M. Poliakoff, M.B. Simpson, J.J. Turner, R. Whyman, A.F. Simpson, J. Chem. Soc., Chem. Commun. (1985) 27.

[7] R.K. Upmacis, M. Poliakoff, J.J. Turner, J. Am. Chem. Soc. 108 (1986) 3645.

[8] D.M. Heinekey, W.J. Oldham Jr., Chem. Rev. 93 (1993) 913.

[9] Z. Lin, M.B. Hall, J. Am. Chem. Soc. 114 (1992) 6102.

[10] J.-Y. Saillard, R. Hoffmann, J. Am. Chem. Soc. 106 (1984) 2006.

[11] J.A.M. van Beek, G. van Koten, W.J.J. Smeets, A.L. Spek, J. Am. Chem. Soc. 108 (1986) 5010.

[12] J. Korp, I. Bernal, J.L. Atwood, F. Calderazzo, D. Vitali, J. Chem. Soc., Dalton Trans. (1979) 1492.

[13] R. Stromberg, Ark. Chem. 22 (1964) 49.

[14] H. Kunkely, A. Vogler, Z. Naturforsch. 52b (1997) 214.

[15] G. Bergson, G. Claeson, L. Schotte, Acta Chem. Scand. 16 (1962) 1159.

[16] G. Bergson, Ark. Kemi 13 (1958) 11.

[17] H. Kunkely, A. Vogler, J.K. Nagle, Inorg. Chem. 34 (1995) 4511.

[18] D.J. Stufkens, Comm. Inorg. Chem. 13 (1992) 359.

[19] H. Kunkely, A. Vogler, J. Chem. Soc., Chem. Commun. (1996) 2519.

[20] R. Franzi, M. Geoffroy, J. Organomet. Chem. 218 (1981) 321.

[21] H. Kunkely, A. Vogler, Inorg. Chim. Acta 256 (1997) 169.

[22] M.H. Gubelmann, A.F. Williams, Struct. Bond. 55 (1983) 1.

[23] H.R. Mäcke, A.F. Williams, in: M.A. Fox, M. Chanon (Eds.), Photoinduced Electron Transfer, Elsevier, Amsterdam, 1988, part D, p. 28.

[24] M.B. Hall, in: A.E. Martell, D.T. Sawyer (Eds.), Oxygen Complexes and Oxygen Activation by Transition Metal Complexes, Plenum Press, New York, 1987, p. 3.

[25] A. Vogler, H. Kunkely, Angew. Chem., Int. Ed. Engl. 21 (1982) 209.

[26] L. Chassot, A. von Zelewsky, D. Sandrini, M. Maestri, V. Balzani, J. Am. Chem. Soc. 108 (1986) 6084.

[27] D. Sandrini, M. Maestri, V. Balzani, L. Chassot, A. von Zelewsky, J. Am. Chem. Soc. 109 (1987) 7720.

[28] B.F.G. Johnson, B.L. Haymore, J.R. Dilworth, Comp. Coord. Chem. 2 (1987) 130.

[29] R.A. Henderson, G.J. Leigh, C.J. Pickett, Adv. Inorg. Chem. 27 (1983) 197.

[30] A.F. Hollemann, E. Wiberg, Lehrbuch der Anorganischen Chemie, de Gruyter, Berlin, 1995, p. 661.

[31] E.W. Schmidt, Hydrazine and its Derivates, Wiley, New York, 1984.

[32] H. Kunkely, A. Vogler, Z. Naturforsch. 52b (1997) 214.

[33] A.W. Adamson, P.D. Fleischauer, Concepts of Inorganic Photochemistry, Wiley-Interscience, New York, 1975.

[34] V. Balzani, V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, New York, 1970.

[35] G.J. Ferraudi, Elements of Inorganic Photochemistry, Wiley-Interscience, New York, 1988.

[36] K. Kalyanasundaram, M. Grätzel, Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, Kluwer, Dordrecht, 1993.

[37] P.-F. Yang, G.K. Yang, J. Am. Chem. Soc. 114 (1992) 6937.

[38] G. Briegleb, Elektronen-Donator-Acceptor-Komplexe, Springer, Berlin, 1961.

[39] R. Foster, Molecular Association, vol. 1, Academic Press, London, 1975.