Optical d$_{\sigma*}$ metal-to-ligand charge transfer of [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)]

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The binuclear complex [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)] shows an absorption at λ_{max} = 434 nm (in CH$_2$Cl$_2$) which is assigned to a MLCT (metal-to-ligand charge transfer) transition from Re^I to the σ*(Se–Se) orbital of the bridging diphenyl diselenide ligand.

Metal-to-ligand charge transfer (MLCT) states play an important role in the photophysics and photochemistry of transition-metal complexes.[1-8] MLCT transitions terminate at π* orbitals of suitable acceptor ligands such as polypyridyls, cyanide, carbon monoxide, alkenes, carbenes and carbynes. Generally, 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 such as hydrazines or disulfides. We explored this possibility and selected the complex [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)][9] for the present study. Diphenyl diselenide is characterized by a low-energy σ* (Se–Se) orbital.[10-12] Moreover, Re^I of the ReBr(CO)$_3$ moiety which is present in the binuclear complex is an excellent donor. Complexes of the type [ReX(CO)$_3$(1,2-diimine)] (e.g. diimine = bipy) display long-wavelength Re^I-to-diimine MLCT absorptions.[3,13] Accordingly, we expected to identify a low-energy d$_{\sigma*}$ MLCT transition from Re^I to Se$_2$Ph$_2$ in the absorption spectrum of [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)].
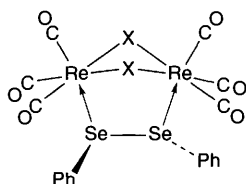
The detection of a d$_{\sigma*}$ MLCT transition is not only interesting in its own right but is also of importance with regard to oxidative additions which are key steps in many catalytic reactions.[14,15] In these reactions simple molecules with σ bonds are reductively broken by a metal which undergoes a simultaneous two-electron oxidation and subsequently adds both reduced anions as new ligands. In the case of [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)] the d$_{\sigma*}$ MLCT excitation should represent a well defined first step of an oxidative addition. Although it was not a goal of the present study it is anticipated that time-resolved spectroscopy of this or related complexes will yield valuable information on the molecular mechanism of oxidative additions.

[Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)] is reasonably stable in non-coordinating solvents. The electronic spectrum of this complex in CH$_2$Cl$_2$ (Fig. 1) shows absorption bands at λ_{max} = 434 nm (ε/dm^3 mol^{-1} cm^{-1} = 1400), 324 (6900), 290 (6600), 272 (7400) and 250 (sh, 10 000). While the 324 nm band is not solvent dependent, the longest wavelength band undergoes a blue shift with increasing solvent polarity (Table 1). [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)] does not emit at room temp. or 77 K, but is light-sensitive. Upon irradiation of [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)] in CH$_2$Cl$_2$ (λ_{irr} = 436 nm) a decomposition takes place as indicated by concomitant spectral changes. However,

the photoreaction was obscured by competing and subsequent thermal reactions. In coordinating solvents the complex undergoes a substitution of the Se$_2$Ph$_2$ ligand by solvent molecules such as thf or MeCN.

The structure of Se$_2$Ph$_2$ is characterized by a torsion around the Se–Se single bond.[9] The C–Se–Se–C dihedral angle is 98°. In addition, both selenium atoms carry a lone pair in p orbitals† which are in an orthogonal orientation to each other.[10-12] These lone pairs are available for σ-bonding to metals. Accordingly, a binuclear complex which contains a bridging Se$_2$R$_2$ ligand should contain an M–Se–Se–M moiety with a rectangular dihedral arrangement. In the binuclear complex [(Me$_2$PhP)Cl$_2$Pt–Se(CH$_2$Ph)–Se(CH$_2$Ph)–PtCl$_2$(PMe$_2$Ph)][16] the torsional angles are approximately 60 and 90° for the Pt–Se–Se–Pt and C–Se–Se–C fragments, respectively. The deviation from the expected 90° angle for the Pt–Se–Se–Pt group might be caused by steric hindrance. In the case of [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)] a planar Re–Se–Se–Re arrangement is imposed and the C–Se–Se–C torsional angle opens up to ca. 120° while 180° would provide the optimal Re–Se σ interaction. Consequently, Re–Se bonding should be relatively weak.

The absorption spectrum of Se$_2$Ph$_2$ shows a longest wavelength band at 331 nm which is assigned to the π→σ* transition from the lone pairs at the selenium atoms to the σ*(Se–Se) orbital.[10-12] The π$_{σ*}$ absorption undergoes a red shift if the torsional angle deviates from 90°.

The absorption of [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)] at λ_{max} = 324 nm (in CH$_2$Cl$_2$, Fig. 1) is assigned to the π$_{σ*}$ intraligand (IL)
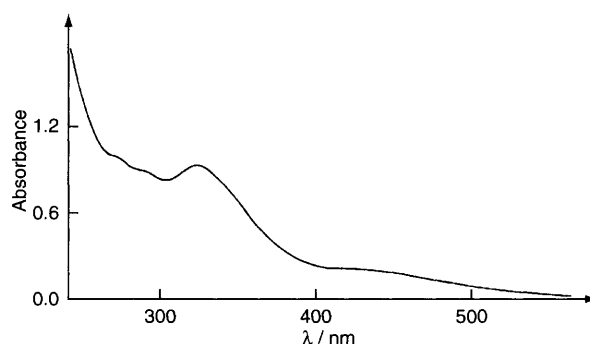
Fig. 1 Electronic absorption spectrum of [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)] (1.34 × 10^{-4} mol dm^{-3}) in CH$_2$Cl$_2$ at room temp. under argon; 1 cm cell

Table 1 Longest wavelength absorption maxima of [Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$)] in various solvents

	λ_{max}/nm	
Solvent	π → σ* (IL)	d(Re) → σ*(Se–Se) (MLCT)
Ethanol	324	402
Acetonitrile	323	408
Acetone	—	420
Dichloromethane	324	434
Toluene	324	440
Cyclohexane	324	446

transition of the coordinated Se_2Ph_2. Compared to the free ligand this band is slightly blue shifted. Since the lone pairs in these π orbitals are stabilized by a σ-interaction with the rhenium atoms a larger blue shift might be expected. However, the σ-interaction is relatively weak (see above). Moreover, the large C–Se–Se–C torsional angle ($120°$) in the complex would shift the $\pi_{\sigma*}$ absorption in the opposite direction. Consequently, owing to both compensating effects the $\pi_{\sigma*}$ transition of Se_2Ph_2 should not change very much upon coordination to both Re atoms.

The longest wavelength band of $[Re_2Br_2(CO)_6(Se_2Ph_2)]$ in CH_2Cl_2 at $\lambda_{max} = 434$ nm which causes the striking orange–red colour of the compound is assigned to a MLCT transition from filled d orbitals of Re^I to the $\sigma*(Se–Se)$ orbital of the ligand. This assignment is supported by the solvatochromism of the binuclear complex (Table 1). Analogous behaviour was observed for $d_{\pi*}$ MLCT transitions of $[ReX(CO)_3(\text{diimine})]$ complexes.[3,13] Other electronic transitions such as LMCT (ligand-to-metal charge transfer) or LF (ligand field) are less probable assignments for the visible absorption of $[Re_2Br_2(CO)_6(Se_2Ph_2)]$. Related complexes such as $[Re(CO)_5X]$ or $[Re_2(CO)_8X_2]$ do not show LMCT bands.[3] Since Se_2Ph_2 is not a strong reductant[17] LMCT transitions involving this ligand are not expected to occur at low energies. The LF absorptions of $[Re(CO)_5X]$ and $[Re_2(CO)_8X_2]$[3] are less intense than the 434 nm band of $[Re_2Br_2(CO)_6(Se_2Ph_2)]$ and are not solvatochromic.

In contrast to $[ReX(CO)_3(\text{diimine})]$ complexes $[Re_2Br_2(CO)_6(Se_2Ph_2)]$ is not luminescent but photoreactive. 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.[18,19] Since the MLCT transition of the complex terminates also at the $\sigma*(Se–Se)$ orbital, analogous behaviour 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: $Re^I_2Se_2Ph_2 \rightarrow Re^{II}_2(SePh)_2$. As a thermal reaction such an oxidative addition of Se_2Ph_2 to $[Mo(C_5H_5)(CO)_3]_2$ was observed.[20] Unfortunately, the photolysis of $[Re_2Br_2(CO)_6(Se_2Ph_2)]$ is accompanied and followed by other thermal reactions as indicated by the complicated pattern of spectral changes which are associated with the irradiation. While $[Re_2Br_2(CO)_6(Se_2Ph_2)]$ was an appropriate candidate to identify a $d_{\sigma*}$ MLCT transition it is apparently not suitable to study oxidative additions induced by MLCT excitation. Towards this end we are currently searching for other complexes with reducible ligands which are characterized by low-energy $\sigma*$ orbitals. Potential compounds include hydrazine[14,15] and iodine complexes.[21]

Footnote

† The corresponding molecular orbitals contain an s-orbital contribution. However, a simplified description as p orbitals is sufficient for most purposes.[10–12]

References

1 Concepts of Inorganic Photochemistry, ed. A. W. Adamson and P. D. Fleischauer, Wiley-Interscience, New York, 1975.
2 V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, New York, 1970.
3 G. L. Geoffroy and M. S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979.
4 G. J. Ferraudi, Elements of Inorganic Photochemistry, Wiley-Interscience, New York, 1988.
5 J. Sykora and J. Sima, Coord. Chem. Rev., 1990, 107, 1.
6 O. Horváth and K. L. Stevenson, Charge Transfer Photochemistry of Coordination Compounds, VCH, New York, 1993.
7 D. M. Roundhill, Photochemistry and Photophysics of Metal Complexes, Plenum, New York, 1994.
8 Photosensitization and Photocatalysis using Inorganic and Organometallic Compounds, ed. K. Kalyanasundaram and M. Grätzel, Kluwer, Dordrecht, 1993.
9 J. Korp, I. Bernal, J. L. Atwood, F. Calderazzo and D. Vitali, J. Chem. Soc., Dalton Trans., 1979, 1492.
10 G. Bergson, G. Claeson and L. Schotte, Acta Chem. Scand., 1962, 16, 1159.
11 G. Bergson, Ark. Kemi, 1958, 13, 11.
12 H. Kunkely, A. Vogler and J. K. Nagle, Inorg. Chem., 1995, 34, 4511.
13 D. J. Stufkens, Comments Inorg. Chem., 1992, 13, 359.
14 F. A. Cotton and G. Wilkinson, Inorganic Chemistry, Wiley, New York, 1988.
15 N. N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon, Oxford, 1984.
16 W. Baratta, P. S. Pregosin, A. Bacchi and G. Pelizzi, Inorg. Chem., 1994, 33, 4494.
17 A. Bewick, D. E. Coe, G. B. Fuller and J. M. Mellor, Tetrahedron Lett., 1980, 21, 3827.
18 U. Schmidt, A. Müller and K. Markan, Chem. Ber., 1964, 97, 405.
19 R. Franzi and M. Geoffroy, J. Organomet. Chem., 1981, 218, 321.
20 E. W. Tillay, E. D. Schermer and W. H. Baddley, Inorg. Chem., 1968, 7, 1925.
21 J. A. M. van Beek, G. van Koten, W. J. J. Smeets and A. L. Spek, J. Am. Chem. Soc., 1986, 108, 5010.