

Optical ligand-to-ligand charge transfer of Zn(2,2'-bipyridyl)(3,4-toluenedithiolate)

R. Benedix, H. Hennig

Sektion Chemie, Karl-Marx-Universität, Talstrasse 35, O-7010 Leipzig, Germany

H. Kunkely and A. Vogler

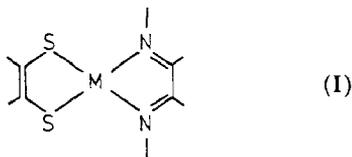
Institut für Anorganische Chemie, Universität Regensburg, Universitätsstrasse 31, W-8400 Regensburg, Germany

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The electronic structure and the optical ligand-to-ligand charge transfer (LLCT) of the pseudotetrahedral complex Zn(2,2'-bipyridyl)(3,4-toluenedithiolate) is interpreted on the basis of EHT calculations. By comparison with square-planar complexes, it is shown that the extent of electron delocalization between donor and acceptor ligand and charge separation by LLCT excitation depends on the mutual orientation of both ligands.

1. Introduction

In recent years, optical ligand-to-ligand charge transfer (LLCT) of metal complexes of the type $L_{red}-M-L_{ox}$, which contain a reducing or donor ligand and an oxidizing or acceptor ligand, has been studied extensively [1]. Compounds of the general formula I are of particular interest since the dithiolate donor and diimine acceptor ligand have basically the same electronic structure but differ in their redox states by two electrons. In a more general sense, such complexes can be viewed as ligand-based mixed-valence compounds [1]. Their electronic spectra are characterized by low-energy absorptions which are assigned to LLCT transitions from the dithiolate to the diimine ligand.



The majority of studies have been carried out with square-planar d^8 complexes of Ni^{II} , Pd^{II} , and Pt^{II} [1]. In these cases the planar structure is imposed by ligand-field effects. In one of the first publications on

optical LLCT, Koester reported preliminary results on Zn(diimine)(dithiolate) complexes [2] which may adopt a pseudo-tetrahedral geometry since ligand-field effects are not important. In the present work, we reexamined Koester's observations and interpret the results on the basis of EHT calculations. It was of great interest to compare the electronic structure and spectral properties of tetrahedral and square-planar M(diimine)(dithiolate) complexes, since the mutual orientation of donor and acceptor ligand is expected to have important consequences which can be evaluated theoretically and experimentally. Particularly, the extent of electron delocalization between both ligands, and hence the degree of charge separation which is associated with LLCT, should depend on the torsion angle which is formed by the planes of both ligands. In this context, it is remarkable that the LLCT state of Zn(diimine)(dithiolate) complexes seems to resemble the twisted-intramolecular charge-transfer (TICT) state of organic molecules [3].

2. Experimental

The compounds Zn(tdt) and Zn(bipy)(tdt) with

bipy=2,2'-bipyridyl and tdt^{2-} =3,4-toluenedithiolate were prepared according to published procedures [4]. Absorption spectra were measured in solution at room temperature on a Uvikon 860 absorption spectrometer. Emission spectra of the complex in the solid state, in solutions of CH_2Cl_2 or in ethanol/ CH_2Cl_2 (1:1) at room temperature or 77 K, were obtained on a Hitachi 850 spectrofluorimeter equipped with a Hamamatsu R 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency.

For MO calculations, the extended Hückel method was used. Details of the procedure were published elsewhere [5,6]. The calculations were based on structural data of Zn^{2+} [7,8] and Ni^{2+} [9-11] complexes taken from the literature.

3. Results

3.1. Electronic spectra

The absorption spectrum of $\text{Zn}(\text{bipy})(\text{tdt})$ in CH_2Cl_2 (fig. 1) shows absorption maxima at $\lambda_{\text{max}}=276$ nm ($\epsilon=14000$), 296 nm ($\epsilon=16760$), 307 nm ($\epsilon=19200$), 323 nm (shoulder, $\epsilon=5200$), and 445 nm ($\epsilon=72$). The latter absorption band which causes the orange color of the compound was also

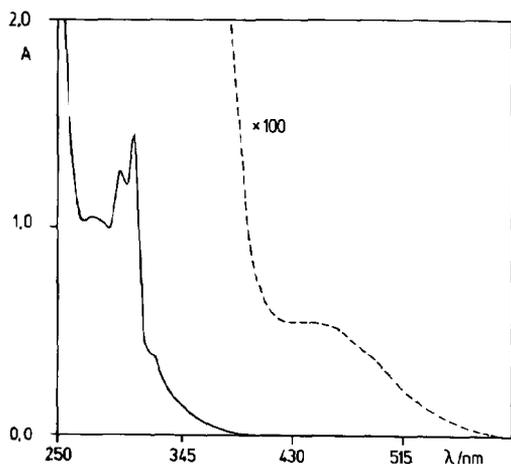


Fig. 1. Electronic absorption spectrum of 7.54×10^{-5} M $\text{Zn}(\text{bipy})(\text{tdt})$ at room temperature in CH_2Cl_2 ; 1 cm cell.

identified by Koester ($\lambda_{\text{max}}=465$ nm, $\epsilon=65$ in ethanol).

At room temperature or 77 K, we did not detect any luminescence which could be assigned unambiguously to $\text{Zn}(\text{bipy})(\text{tdt})$. In the solid state or in $\text{CH}_2\text{Cl}_2/\text{ethanol}$ glasses at 77 K, we identified two extremely weak emissions. A blue luminescence appeared at $\lambda_{\text{max}}=432$ and 462 nm and a red emission at $\lambda_{\text{max}}=620$ nm. These emissions were identical with the blue bipy intraligand phosphorescence of $\text{Zn}(\text{bipy})_3^{2+}$ and $\text{Zn}(\text{bipy})^{2+}$ [12] and the red luminescence of $\text{Zn}(\text{tdt})$. The excitation spectra of these compounds matched also that of $\text{Zn}(\text{bipy})(\text{tdt})$. Accordingly, we ascribe the very weak emission of $\text{Zn}(\text{bipy})(\text{tdt})$ to impurities by $\text{Zn}(\text{bipy})^{2+}$ and $\text{Zn}(\text{tdt})$ species. The presence of such impurities is certainly not surprising since Zn^{2+} complexes are kinetically not very stable. The high quantum yield of the intraligand phosphorescence of $\text{Zn}(\text{bipy})^{2+}$ complexes [12] would account for the detection of very small concentrations of such impurities.

Koester observed three emissions of $\text{Zn}(\text{phen})(\text{tdt})$ (phen=1,10-phenanthroline) which he assigned to the phen-intraligand fluorescence, phosphorescence and the LLCT emission at longer wavelengths [2]. On the basis of our results, we believe that these emissions originate also from impurities. This assumption is supported by the fact that Koester measured a phen-intraligand-phosphorescence lifetime of about 2 s. While this lifetime agrees with that of $\text{Zn}(\text{phen})_3^{2+}$ and $\text{Zn}(\text{phen})^{2+}$ [12], it seems to be much too long for an phen-intraligand phosphorescence of $\text{Zn}(\text{phen})(\text{tdt})$. Since the intraligand triplet is located at energies above the LLCT state (see below), a rapid radiationless transition to this state should quench the phen phosphorescence.

3.2. Calculations

The model calculations were carried out for $\text{Zn}(\text{edt})(\text{dim})$ with edt^{2-} =1,2-ethylenedithiolate dianion and dim=1,2-ethanediiimine. The MO diagram of the pseudo-tetrahedral (C_{2v} -symmetry) complex is shown in fig. 2. The frontier orbitals are located at the dithiolate (HOMO: $7b_2$) and the diimine (LUMO: $7b_1$). The dependence of the total EHT energy and the energies of the one-electron mo-

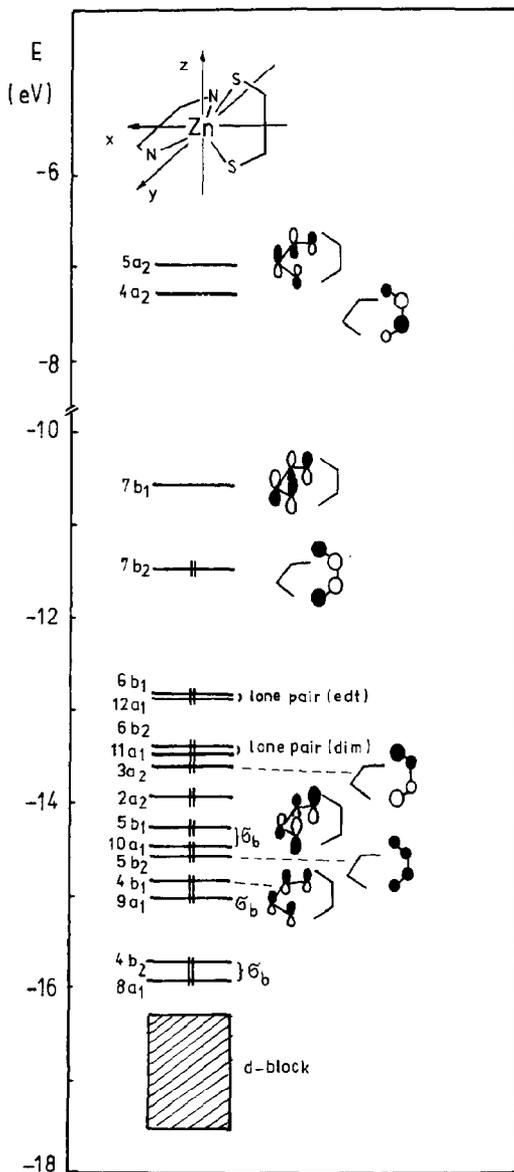


Fig. 2. MO diagram of Zn(edt)(dim) (C_{2v} symmetry).

lecular orbitals on the torsion angle θ is presented in fig. 3.

The lowest-energy transition ($7b_2$ to $7b_1$) of Zn(edt)(dim) that involves LLCT from the dithiolate to the diimine is forbidden. According to a model applied by Wepster to 4-aminonitrobenzene [13], the intensity of the LLCT transition was calculated as a function of the torsion angle. As an internal cal-

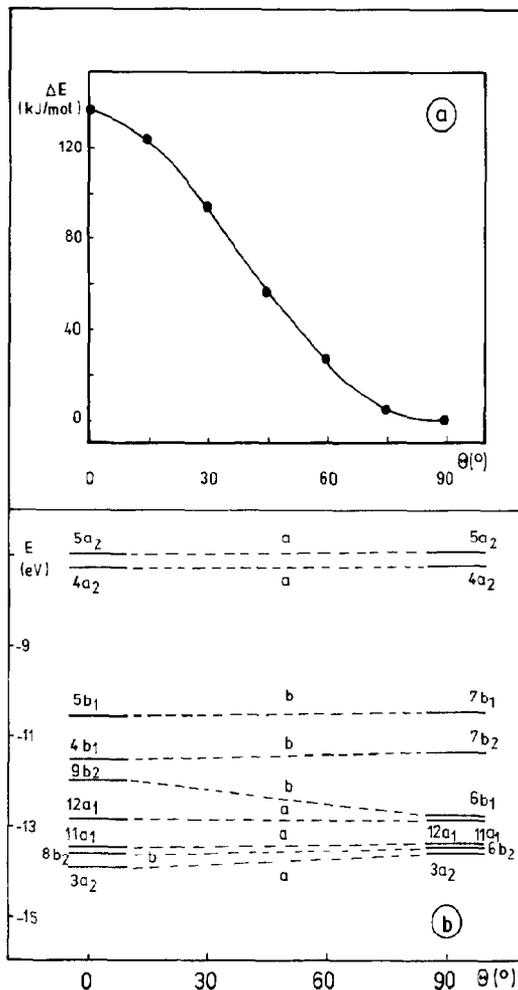


Fig. 3. (a) Total EHT energy of Zn(edt)(dim) as a function of the torsion angle θ . (b) Dependence of the MO energies on the torsion angle.

ibration, we used $\epsilon=2000$ for $\theta=0$. This is a lower limit of the extinction coefficients which were found for a variety of planar (C_{2v} -symmetry) Ni^{II} complexes of this type [1]. At $\epsilon=65$ as measured for the LLCT transition of Zn(bipy)(tdt), a torsion angle of 81° was obtained.

A further point of interest was the extent of electronic coupling between the donor and acceptor ligand. The delocalization of HOMO and LUMO reflects the degree of charge separation which is achieved upon LLCT excitation. A population analysis for the pseudotetrahedral (C_{2v}) complex

Zn(edt)(dim) yields the following contributions: HOMO ($7b_2$): 0.6% Zn, 98.3% dithiolate, and 1.1% diimine; LUMO ($7b_1$): 0.3% Zn, 0.9% dithiolate, and 98.8% diimine. In a hypothetical planar (C_{2v}) complex the delocalization would increase: HOMO ($4b_1$): 2.7% Zn, 95.1% dithiolate, and 2.2% diimine; LUMO ($5b_1$): <1% Zn, 1.9% dithiolate, and 97.1% diimine. For comparison, we add also the corresponding numbers for the planar complex Ni(edt)(dim): HOMO ($4b_1$): 13% Ni, 81% dithiolate, and 6% diimine; LUMO ($5b_1$): 4% Ni, 3% dithiolate and 93% diimine. The differences between the planar Zn and Ni complexes is caused by the different d-orbital energies. The much larger stability of the 3d-orbitals of Zn reduces the metal contribution to the frontier orbitals.

4. Discussion

In the absence of particular packing effects in the solid state, four-coordinate Zn^{2+} complexes will certainly adopt a tetrahedral geometry. Although the molecular structure of Zn(bipy)(tdt) is yet unknown, there is little doubt that it is pseudotetrahedral (C_{2v}). The absorption spectrum (fig. 1) shows the characteristic $\pi\pi^*$ intraligand absorptions of the coordinated bipy ligand [12] at $\lambda_{max} = 307$ nm ($0-0'$ transition) and 296 nm. In agreement with Koester [2], we assign the band in the visible region ($\lambda_{max} = 445$ nm in CH_2Cl_2) to the LLCT transition from the HOMO ($7b_2$) at the dithiolate to the LUMO ($7b_1$) at the bipy ligand. If the orientation of both ligands would be exactly orthogonal (torsion angle $\theta = 90^\circ$) the LLCT transition is symmetry forbidden and the corresponding absorption should not appear. However, as can be seen from fig. 3, a small deviation from 90° does not require much energy. The experimental extinction coefficient of $\epsilon = 65$ for Zn(bipy)(tdt) yields an angle of $\theta = 81^\circ$. It is assumed that this is a statistical average which is obtained by the thermal excitation of torsional vibrations. In addition to the spin-allowed singlet-singlet LLCT transition, a corresponding singlet-triplet transition must occur at lower energies. Such a spin-forbidden LLCT band was not detected and may be too weak.

Owing to the orthogonal orientation of donor and

acceptor ligand, the weak electronic coupling leads to two important consequences for the charge separation upon LLCT excitation of Zn(dithiolate)-(diimine) complexes: The charge separation is rather complete since the delocalization of HOMO and LUMO is quite small. In addition, the charge-separated LLCT state should be long-lived because the return to the ground state is essentially symmetry-forbidden. If the lowest LLCT triplet would be populated by intersystem crossing, its life time may be extremely large since the transition to the singlet ground state is then overlap- and spin-forbidden. The missing luminescence of Zn(bipy)(tdt) is an indication for such a long life time. Other modes of deactivation can now easily quench the emission. This assumption is in agreement with the observation of a LLCT phosphorescence of the planar complex Pt(bipy)(tdt) [14]. In this case, the radiative life time of the LLCT triplet is certainly much shorter because the LLCT transition is not symmetry-forbidden and the spin-electron rule breaks down due to the heavy-atom effect of platinum.

In conclusion, we would like to emphasize that Zn(diimine)(dithiolate) complexes seem to be good models for an efficient light-induced charge-separation process. The LLCT state of these Zn^{2+} complexes has certainly much in common with the TICT state of organic molecules [3].

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