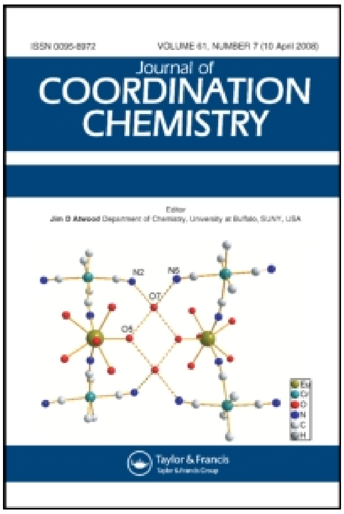

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND OPTICAL LIGAND-TO-LIGAND CHARGE TRANSFER OF Zn(2,6-BIS(BENZIMIDAZOLYL)PYRIDINE)-(3,4-TOLUENEDITHIOLATE)

Markus Leirer[a]; Günther Knör[a]; Arnd Vogler[a]
[a] Institut für Anorganische Chemie, Universität Regensburg, Regensburg, Germany

To cite this Article Leirer, Markus , Knör, Günther and Vogler, Arnd(2000) 'SYNTHESIS AND OPTICAL LIGAND-TO-LIGAND CHARGE TRANSFER OF Zn(2,6-BIS(BENZIMIDAZOLYL)PYRIDINE)-(3,4-TOLUENEDITHIOLATE)', Journal of Coordination Chemistry, 50: 1, 141 — 144

To link to this Article: DOI: 10.1080/00958970008054932

URL: http://dx.doi.org/10.1080/00958970008054932

J. Coord. Chem., 2000, Vol. 50, pp. 141–144
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Printed in Malaysia.

Note

SYNTHESIS AND OPTICAL LIGAND-TO-LIGAND CHARGE TRANSFER OF Zn(2,6-BIS(BENZIMIDAZOLYL)PYRIDINE)-(3,4-TOLUENEDITHIOLATE)

MARKUS LEIRER, GÜNTHER KNÖR* and ARND VOGLER*

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

(Received 19 May 1999)

The complex Zn[(BzImH)$_2$Py](TDT) with (BzImH)$_2$Py = 2,6-bis(benzimidazolyl)pyridine and TDT^{2-} = 3,4-toluenedithiolate was prepared and characterized spectroscopically. The yellow colour of this compound is caused by an absorption band (λ_{max} = 369 nm in ethanol), which is assigned to a ligand-to-ligand charge transfer transition from TDT^{2-} to the (BzImH)$_2$Py ligand.

Keywords: Charge transfer; imidazole complexes; thiolate complexes; zinc

INTRODUCTION

Coordination compounds, which simultaneously contain reducing and oxidizing ligands, are frequently characterized by long-wavelength ligand-to-ligand charge transfer (LLCT) absorptions in their electronic spectra.[1,2] This type of optical electron transfer has attracted much attention in recent years. Appropriate acceptor ligands include 1,2-diimines such as 2,2′-bipyridine, while anions such as thiolates or carbanions can serve as donor ligands. The electronic interaction between donor and acceptor ligands is mediated by typical transition metals (*e.g.*, Ni^{2+}, Pd^{2+}, Pt^{2+}), but also by closed-shell metals such as Zn^{2+}. Owing to the rather stable d^{10} electronic

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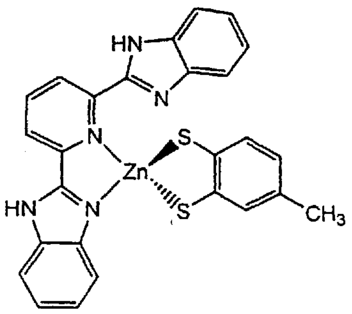
* Corresponding authors.

configuration, Zn^{2+} complexes are not accessible to many traditional spectroscopic methods. In biological environments, zinc(II) may be coordinated by thiolates (*e.g.*, cysteinate) as well as imidazole derivatives,[3] with zinc-finger proteins being an important example. Accordingly, in biological samples, Zn^{2+} could be identified by LLCT absorptions, which are caused by an electronic transition from the thiolate to the imidazole ligand. We have explored this possibility and selected the complex $Zn[(BzImH)_2Py](TDT)$ with $(BzImH)_2Py$ = 2,6-bis(benzimidazolyl)pyridine and TDT^{2-} = 3,4-toluenedithiolate for an initial study. This choice was guided by the following considerations. The stability of zinc complexes is considerably increased if bidentate ligands are employed. Toluenedithiolate has previously been shown to be a suitable bidentate donor ligand for LLCT.[1,2,4,5]

RESULTS AND DISCUSSION

The commercially available bidentate 1,2-diimines 2,2′-bis(4,5-dimethylimidazolyl) and $(BzImH)_2Py$ were chosen as imidazole-containing acceptor ligands. However, only the latter ligand yielded a stable and analytically pure compound, which was obtained according to the following procedure. A solution of 125 mg (0.4 mmol) of 2,6-bis(benzimidazolyl)pyridine in ethanol (10 cm^3) was added to a stoichiometric amount of Zn(TDT),[6] dissolved in 0.9 cm^3 of dimethylformamide. The resulting yellow precipitate (103 mg, 49%) was filtered and dried under vacuum (*Anal.* Calcd. for $C_{26}H_{19}N_5S_2Zn$ (%): C, 58.8; H, 3.6; N, 13.2. Found: C, 58.1; H, 3.7; N, 13.0).

The $(BzImH)_2Py$ molecule may coordinate as a bi- or tridentate ligand,[7] utilizing the nitrogen atoms at the pyridine and imidazole rings. As a bidentate ligand, it is assumed to build up a five-membered chelate ring with two neighbouring nitrogen atoms forming a 1,2-diimine function. Since a variety of tetrahedral 1,2-diimine complexes of zinc(II) are known, there is little doubt that $Zn[(BzImH)_2Py](TDT)$ also belongs to this category.



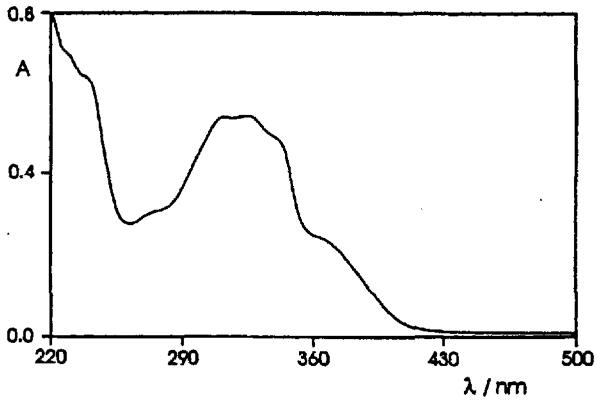


FIGURE 1 Absorption spectrum of 2.5×10^{-5} M Zn[(BzImH)$_2$Py](TDT) in ethanol (1 cm cell).

The electronic spectrum of Zn[(BzImH)$_2$Py](TDT) in ethanol (Figure 1) shows absorptions at $\lambda_{max} = 273$ nm ($\varepsilon = 13200$ M^{-1} cm^{-1}), 310 nm (19500 M^{-1} cm^{-1}), 326 nm (20700 M^{-1} cm^{-1}), 340 nm (19300 M^{-1} cm^{-1}), and $\lambda_{max} = 369$ nm ($\varepsilon = 5300$ M^{-1} cm^{-1}). The bands below 350 nm essentially are intraligand (IL) absorptions of the (BzIMH)$_2$Py ligand.[7] The band at 369 nm, which causes the yellow colour of the complex, must arise from a new electronic transition. A LLCT assignment involving TDT^{2-} as the donor and (BzImH)$_2$Py as the acceptor is the only reasonable explanation. However, in comparison with the complex Zn(bpy)(TDT), where bpy = 2,2′-bipyridine, the LLCT absorption of Zn[(BzImH)$_2$Py](TDT) is quite intense. The low extinction coefficient ($\varepsilon = 65$ M^{-1} cm^{-1}) of Zn(bpy)(TDT) is related to the high symmetry (C_{2V}) of this complex.[8] In the case of Zn[(BzImH)$_2$Py](TDT), the diimine ligand itself is rather unsymmetrical. Moreover, the non-coordinating imidazole substituent may impose further distortions from a pseudotetrahedral structure. Accordingly, the symmetry-forbidden $b_2 \rightarrow b_1$ LLCT transition of Zn(bpy)(TDT) should become much more allowed for Zn[(BzImH)$_2$Py](TDT).

In conclusion, our expectation to detect a LLCT absorption in the electronic spectrum of Zn[(BzImH)$_2$Py](TDT) has been confirmed. In this context it must be emphasized that the imidazole of (BzImH)$_2$Py is part of a 1,2-diimine ligand, which generally is a strong acceptor ligand for CT transitions. However, isolated imidazoles are characterized by π^* orbitals at rather high energies.[9] Therefore, zinc(II) complexes which contain simple imidazole and thiolate ligands, as they occur in biological environments, are not expected to show LLCT absorptions at long wavelengths.

Acknowledgements

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

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