Spectroscopic and magnetic studies of mixed-ligand complexes of zinc(II)

S YAMAMOTO¹, S IKEDA¹, T AZUMI^{1*} and G A CROSBY^{2*}

¹Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

²Department of Chemistry, Washington State University, Pullman, WA 99164-4630, USA

Abstract. Zero-field splittings and the kinetic parameters associated with the triplet spin sublevels of both the triplet $\pi\pi^*$ and the triplet ligand–ligand charge-transfer states were measured by the optically-detected magnetic-resonance method for a series of complexes with a d^{10} closed-shell metal ion of the type, $\text{Zn}(\text{X-PhS})_2(\text{phen})$, where $\text{X} = \text{F}$, 4-Cl, H, 4- CH_3 , or 4- CH_3O . Both the zero-field splittings and the kinetic decay parameters are satisfactorily interpreted in terms of mixing between the lowest phen-localized $^3\pi\pi^*$ and ligand–ligand charge-transfer states.

Keywords. Zero-field splittings; zinc(II) mixed-ligand complexes; ligand–ligand charge-transfer state; optically-detected magnetic-resonance method; closed-shell metal ion; phosphorescence.

1. Introduction

Complexes of closed-shell metal ions, such as zinc(II) and cadmium(II) are usually colorless. This is easily understood in view of their d^{10} closed-shell structures. First of all, no ligand-field $d-d$ transitions exist. Further, since the energy required to remove an electron from the d^{10} configuration is quite high (for example, the ionization energy of a free Zn^{2+} ion is ~ 40 eV), the contribution of metal-to-ligand charge-transfer (MLCT) states to the low-lying excited manifolds in complexes should be very small. Nonetheless some zinc complexes are deeply colored (Crosby *et al* 1985). These colored materials are of the type, $\text{Zn}(\text{NN})(\text{SS})$, where NN represents an aromatic diimine ligand, such as 1,10-phenanthroline or 2,2'-bipyridine and SS represents either a dithiol or two monothiol ligands. Previous studies (Highland *et al* 1986; Yamamoto *et al* 1990) have assigned the lowest energy excited state(s) responsible for the color to those involving charge transfer from the SS to the NN ligand. These types of excited states are commonly designated as ligand-to-ligand charge-transfer (LLCT) states.

In order to quantify the nature of these low-lying (LLCT) excited states in the present paper, we examine the phosphorescence spectra of a series of complexes of the general formula, $\text{Zn}(\text{X-PhS})_2(\text{phen})$, where $\text{X} = \text{F}$, 4-Cl, H, 4- CH_3 , 4- CH_3O ; PhS = thiophenol; phen = 1,10-phenanthroline. With the single exception of $\text{Zn}(4\text{-CH}_3\text{O-PhS})_2(\text{phen})$, all these complexes display phosphorescence in both the phen-localized $^3\pi\pi^*$ and $^3\text{LLCT}$ excited states. In the current investigation we report

*For correspondence

Figure 1. Schematic diagram for measurement of ODMR spectra. Spectra were measured with a Spex 1702 monochromator equipped with a Hamamatsu R3896 photomultiplier. Excitation source was a 500-W Xe lamp combined with a Nikon G250 monochromator and water filter. Microwave power was supplied from a HP8690B sweep oscillator with an appropriate plug-in module. Its frequency was swept in an external FM mode. The signal from the photomultiplier, amplified by an ORTEC 4660 bandpass amplifier, was fed into a Kawasaki Electronica TMR-10 transient memory.

data on the zero-field levels of the phen-localized $^3\pi\pi^*$ excited states as obtained from the optically-detected magnetic-resonance (ODMR) method.

2. Experimental

The spectroscopic properties reported in this paper are (a) phosphorescence spectra, (b) magnitudes of the zero-field splittings, (c) total decay-rate constants associated with the individual spin sublevels of the phen-localized $^3\pi\pi^*$ state, and (d) relative radiative decay-rate constants (at the 0,0-band of the phen-localized $^3\pi\pi^*$ phosphorescence) of the spin sublevels.

The experimental apparatus for the ODMR measurements is schematically shown in figure 1. The microcrystalline sample was cooled to 1.3 K and irradiated by light from a 500-W xenon lamp. The phosphorescence was dispersed by a Spex 1702 monochromator and detected by a Hamamatsu R 3896 photomultiplier tube coupled to an appropriate amplifier and a transient digitizer. Microwaves were applied from a HP 8690B sweep oscillator operated in the FM mode, and the resultant signal was fed to a computer for accumulation and further data processing.

3. Results and discussion

3.1 Phosphorescence spectra

As a typical example of the luminescence displayed by these complexes, the phosphorescence spectrum of $\text{Zn(4-Cl-PhS)}_2(\text{phen})$ is shown in figure 2. The spectrum

Figure 2. Phosphorescence spectrum observed from a microcrystalline sample of $\text{Zn}(\text{4-Cl-PhS})_2(\text{phen})$ at 4.2 K.

consists of two components. The short-wavelength part is structured, and the spectrum almost coincides with that of the uncoordinated phen; therefore, this component has been assigned to emission from the $^3\pi\pi^*$ level of the phen ligand. The long-wavelength component, which is observed only from mixed-ligand complexes, is broad and structureless and was originally assigned to emission from the $^3\text{LLCT}$ state because of its millisecond lifetime at 77 K. This $^3\text{LLCT}$ assignment was corroborated later by the ODMR action spectrum (Nozaki *et al* 1992).

3.2 Zero-field splittings of the phen-localized $^3\pi\pi^*$ level

Zero-field energies can easily be obtained from the frequencies of the observed microwave transitions. Direct comparison of these zero-field energies from various complexes is meaningless, however, because the directions of the spin axes may not be identical. Therefore, we discuss the zero-field splittings in terms of the spin-axis-independent quantity, D^* , which is defined as follows (McGlynn *et al* 1969):

$$D^* = [(3/2)(X^2 + Y^2 + Z^2)]^{1/2}, \quad (1)$$

where X , Y , and Z are the energies of the triplet sublevels measured from the center of gravity, i.e., $X + Y + Z = 0$. The D^* values obtained are summarized in table 1. For comparison, we also include the data from $\text{ZnCl}_2(\text{phen})$, which has no LLCT low-lying triplet state.

As table 1 reveals, the D^* value of the phen-localized $^3\pi\pi^*$ level varies as the X substituent on the thiol ligand changes. This experimental evidence clearly indicates

Table 1. Zero-field splitting parameter D^* , and the $^3\pi\pi^* \rightarrow ^3\text{LLCT}$ mixing coefficients.

	$D^*(\text{GHz})$	$\cos^2 \alpha$	$\sin^2 \alpha$
$\text{ZnCl}_2(\text{phen})$	3.92	1.00	0
$\text{Zn}(\text{F}_5\text{-PhS})_2(\text{phen})$	3.88	0.99	0.01
$\text{Zn}(\text{4-Cl-PhS})_2(\text{phen})$	3.83	0.98	0.02
$\text{Zn}(\text{4-CH}_3\text{-PhS})_2(\text{phen})$	3.76	0.96	0.04

that the excitation energy of the so-called "phen-localized" state is really delocalized over the whole complex and that the degree of delocalization depends on the X substituent on the thiol ligand. In table 1 the complexes are listed in increasing order of the electron-donating ability of the X substituent. The data show that the D^* value decreases as the electron-donating ability of the substituent increases. We interpret this to mean that the degree of delocalization in the excited state also increases in the same way.

It is convenient to describe the delocalization of excitation in terms of a valence-bond-type mixing of a pure $^3\text{LLCT}$ state with a pure $^3\pi\pi^*$ state. In this framework the wavefunction Ψ for the low-lying (emitting) state is expressed as follows:

$$\Psi = \cos \alpha \psi(^3\pi\pi^*) + \sin \alpha \psi(^3\text{LLCT}). \quad (2)$$

Thus, D^* associated with the emitting state can be expressed as

$$D^* = \cos^2 \alpha D^*(^3\pi\pi^*) + \sin^2 \alpha D^*(^3\text{LLCT}), \quad (3)$$

where $D^*(^3\pi\pi^*)$ is the D^* value of a pure $^3\pi\pi^*$ state and can be approximated from the experimental value for $\text{ZnCl}_2(\text{phen})$, which is 3.92 GHz (see table 1). Further, $D^*(^3\text{LLCT})$ is the D^* value of a pure $^3\text{LLCT}$ state. The D^* value for the charge-transfer state should be extremely small since the electrons are spread over two different ligands. The required D^* value for a pure $^3\text{LLCT}$ state is, however, not available because any experimentally accessible $^3\text{LLCT}$ state has considerable contribution from a nearby $^3\pi\pi^*$ state. Therefore, as a first approximation, we set the value $D^*(^3\text{LLCT})$ to zero. The mixing coefficients in (2) calculated in this manner are also tabulated in table 1. The calculation shows that the degree of mixing of the $^3\text{LLCT}$ state with the $^3\pi\pi^*$ level increases as the electron-donating ability of the substituent X increases.

3.3 Kinetic parameters for triplet sublevels of the $^3\pi\pi^*$ term

The total decay rate constants, $k_u(u = x, y, z)$, and the relative radiative rate constants $k'_u(\text{rel})$ were determined for the $^3\pi\pi^*$ sublevels. The results are summarized in table 2.

First, we consider the total decay-rate constant (that is, the sum of the radiative and radiationless decay-rate constants) for the individual sublevels. A detailed treatment of the data for the individual levels will be presented elsewhere (Yamamoto *et al* 1993). Here we discuss the general behavior in terms of the average rate constant,

Table 2. Total decay rate constants, $k_u(u = x, y, z)$, and the relative radiative decay rate constants, $k'_u(\text{rel})$ ($u = x, y, z$) associated with the individual spin sublevels.

	$k_u(\text{s}^{-1})$				$k'_u(\text{rel})$		
	x	y	z	Average	x	y	z
Phen	1.36	0.49	1.51	1.12	0.09	0.06	1.00
$\text{Zn}(\text{F}_5\text{-PhS})_2(\text{phen})$	0.68	3.87	4.87	3.15	0.44	1.00	0.03
$\text{Zn}(4\text{-Cl-PhS})_2(\text{phen})$	7.62	3.52	1.48	4.21	0.24	1.00	0.05
$\text{Zn}(\text{PhS})_2(\text{phen})$	8.62	4.07	1.59	4.76	0.36	1.00	0.14

$k[k = (k_x + k_y + k_z)/3]$. Table 2 shows that the average decay-rate constant of the $^3\pi\pi^*$ level of uncoordinated phen generally increases with complexation. This experimental evidence is again interpretable in terms of (2). The decay-rate constant for a pure $^3\text{LLCT}$ is $\approx 50 \text{ s}^{-1}$, significantly larger than that of the pure $^3\pi\pi^*$ state. Thus, the finding that as the electron-donating ability of the substituent X on the thiol ligand increases the decay rate also increases is well accounted for in terms of the mixing of the pure $^3\text{LLCT}$ state with the pure $^3\pi\pi^*$ state (Nozaki *et al* 1992).

We next focus attention on the relative radiative rate constants of individual sublevels. As table 2 indicates, for uncoordinated phen the z-sublevel is the most effective for the radiative transition to the ground state. On the other hand, for all the $\text{Zn}(\text{X-PhS})_2(\text{phen})$ complexes we have studied to date, the y-sublevel is by far the most active in the radiative transition.

Mechanisms for radiative transitions from the triplet spin states of the $^3B_2(\pi\pi^*)$ level of uncoordinated phen are schematically expressed in the conventional way (Yamauchi and Azumi 1978) as follows:

The spin-orbit-coupling matrix elements associated with the T_y and the T_z sublevels are one-center type. However, the dipole transition associated with the radiative transition from the T_y sublevel is group-theoretically forbidden. Thus, the T_z sublevel is expected to be the most radiative. This theoretical expectation is indeed confirmed experimentally (Ikeda *et al* 1992).

In complexes the situation is different. These complexes do not have C_{2v} symmetry. Therefore, the forbiddenness of the radiative transition from the T_y sublevel is formally lifted; that is, none of the sublevels in the complex is group-theoretically forbidden. Thus, to rationalize the experimental results we must examine the coupling mechanisms a little more quantitatively.

The geometrical structure determined by X-ray analysis for the $\text{Zn}(\text{4-Cl-PhS})_2(\text{phen})$ complex is schematically shown in figure 3 (Gamble G R and Crosby G A, unpublished work). As seen from the figure, one of the thiol ligands is located directly over the phen ligand. Therefore the LLCT state can be ascribed essentially to charge transfer from this adjacent thiol moiety to the phen ligand with a substantial contribution from the coordinated sulfur of the distant ligand. This supposition is supported by our extended Hückel calculation. We further note that the in-plane short axis of this thiol molecule is almost parallel to the y axis (as seen in figure 3, the phen is almost in the yz plane). In view of this geometrical structure, mechanisms for radiative transitions from the $^3\text{LLCT}$ sublevels can be schematically expressed as

Figure 3. Geometrical structure of $\text{Zn}(\text{4-Cl-PhS})_2(\text{phen})$ and principal spin axes. Spin axes (that is, axes that diagonalize the spin–spin coupling tensor) were determined by an extended Hückel calculation. In this axis system the molecular plane of the phen molecule is almost in the yz plane. Note that the in-plane short axis of one of the benzenethiol molecules is nearly parallel to the y axis.

where π_{th} is the π orbital on the benzenethiol ligand, π^* refers to an orbital on the phen ligand, and n_s is the non-bonding orbital centered on the S-atom of the thiol.

In the above scheme, spin-orbit coupling between the $^1\text{LLCT}$ and $^3\text{LLCT}$ states contains a one-center spin-orbit term on the S atom and should have a significant value. Closer examination of the spin-orbit-coupling terms reveals, however, that there is little difference among the three routes described above; that is, from a consideration of the spin-orbit coupling alone, any sublevel selectivity observed experimentally cannot be understood. Therefore we must examine the magnitudes of the dipole-transition moments.

For the transition between the $^1\text{LLCT}$ state and the ground state, theoretical evaluation of the transition dipole moment is difficult because no one-center term exists. We, therefore, appeal to a simple approximation. We assume that the transition dipole moment is proportional to the overlap between the component orbitals of the combining states. As can be seen from the geometrical structure in figure 3, the overlap between the π_{th} and π^* orbitals is much larger than the overlap between the n_s and π^* orbitals. Hence we predict that the y -sublevel should be more radiative than the other two sublevels. This is indeed what we observed experimentally for all the complexes.

4. Conclusions

The zero-field splitting parameter, D^* of $\text{Zn}(\text{X-PhS})_2(\text{phen})$ complexes decreases as the electron-donating ability of the X substituent on the benzene thiol ligand increases. This trend is satisfactorily interpreted in terms of a valence-bond type mixing of the $^3\text{LLCT}$ state with the phen-localized $^3\pi\pi^*$ state. The radiative properties of the phen-localized $^3\pi\pi^*$ state were also determined for the individual sublevels. For uncoordinated phen the z -sublevel is the most active, whereas for all the complexes the y -sublevel dominates. This experimental observation is rationalized in terms of the magnitudes of the dipole transition moments between the mixing $^1\text{LLCT}$ state and the ground state.

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References

- Crosby G A, Highland R G and Truesdell K A 1985 *Coord. Chem. Rev.* **64** 41
Highland R G, Brummer J G and Crosby G A 1986 *J. Phys. Chem.* **90** 1593
Ikeda S, Yamamoto S, Azumi T and Crosby G A 1992 *J. Phys. Chem.* **96** 6593
McGlynn S P, Azumi T and Kinoshita M 1969 *Molecular spectroscopy of the triplet state* (Englewood Cliffs, NJ: Prentice Hall)
Nozaki K, Ikeda S, Yamamoto S, Ikeyama T, Azumi T, Burt J A and Crosby G A 1992 *Proc. Ind. Acad. Sci. (Chem. Sci.)* **104** 241
Yamamoto S, Ikeda S, Ikeyama T, Azumi T and Crosby G A 1990 *Chem. Phys. Lett.* **174** 176
Yamamoto S, Ikeda S and Azumi T 1993 (to be published)
Yamauchi S and Azumi T 1978 *J. Chem. Phys.* **68** 4138