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Spectroscopic and Magnetic Studies of Complexes of d^{10} Closed Shell Ions.

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ABSTRACT

Fluorescence, phosphorescence, and the triplet spin sublevel properties (zero-field splitting, total decay rate constants, and relative radiative decay rate constants for individual sublevels) are investigated for a series of complexes of the type MX_2(phen), where M is Zn(II) or Cd(II), and X is Cl, Br, or I. The fluorescence and the phosphorescence are almost identical to those of free phen indicating that the emission is from the phen localized $\pi\pi^*$ state. The rate constants for spin forbidden transitions increase as the atomic number of halogen increases. All the kinetic data as well as the zero-field splitting parameters are satisfactorily interpreted by a configurational mixing between the phen localized $\pi\pi^*$ state and the halogen p to phen π^* ligand-ligand charge-transfer state.

A. INTRODUCTION

In this paper we would like to raise a question as to what determines the excited state properties of complexes of d^{10} closed shell metal ions such as Zn(II) and Cd(II). In view of high ionization potentials of the closed shell metal ions (40 eV for Zn(II) and 38 eV for Cd(II)), any states involving the excitation of d electron should have quite high energies. Further, there exist no dd transitions. Therefore, a low-lying excited state should mainly be composed of ligand-localized and/or ligand-ligand charge-transfer states. Thus d orbital does not appear to be important in determining low-lying excited state properties. However, participation of d orbitals is frequently mentioned in the literature, especially in connection with the heavy atom effect. Even though the heavy atom effect due to such a "heavy" atom as Zn or Cd is frequently discussed, there do not appear to exist any experimental or theoretical studies trying to find out whether or not such heavy atom effect due to closed shell metal ions really exists.

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In an attempt to solve this question, we have chosen a series of complexes of the type MX_2(phen), where M is either Zn(II) or Cd(II), X is either Cl, Br, or I, and phen is 1,10-phenanthroline. For a series of this type of complexes, we study the fluorescence, phosphorescence, and the triplet spin sublevel properties. (For Zn complexes see [1].)

B. EXPERIMENTAL

Difficulty in working with this type of complex is that the complexes are insoluble to most of solvents. The Zn complexes are insoluble to any solvents except nitromethane. For the Cd complexes, we were unable to find any solvent which can dissolve the complexes. Therefore, all the spectra were taken for crystalline states.

C. RESULTS

The fluorescence and the phosphorescence of the series of complexes are shown in Figure 1. For the purpose of comparison, the spectra for free phen are also shown. (Here and in the following free phen means the phen coordinated by water; this choice is mainly due to our supposition that proper comparison is better made for coordinated phen because in the complexes phen is anyway coordinated.) As is evident from Figure 1, the fluorescence and the phosphorescence are almost identical to those of free phen. The similarity of the spectra indicates that both fluorescence and the phosphorescence of these complexes are phen localized $\pi\pi^*$ states.

The phosphorescence to fluorescence intensity ratio is greatly dependent on halogen. That is, the heavier the halogen, the more intense the phosphorescence. However, Zn and Cd complexes having the same halogens are not different in the intensity ratio. The halogen dependence of the intensity ratio is in accord with the notion of the heavy atom effect due to halogen. However, it is not at all clear why the phen localized $\pi\pi^*$ state should be affected by heavy atom. The observation that the intensity ratio is almost identical for the Zn and the Cd complexes seems to indicate that there is no heavy atom effect due to the central metal ion. This is in accord with the above prediction that d orbital participation should be very small for the complexes of closed shell metals.

Fluorescence lifetimes are summarized in Table 1. For both the Zn and Cd complexes, as the atomic number of halogen increases the lifetime significantly decreases. Thus, the fluorescence lifetime further supports the above observation that the rate constants for $S_1 \rightarrow T_1$ intersystem crossing increase as the atomic number of halogen increases. The Zn and Cd complexes have somewhat different

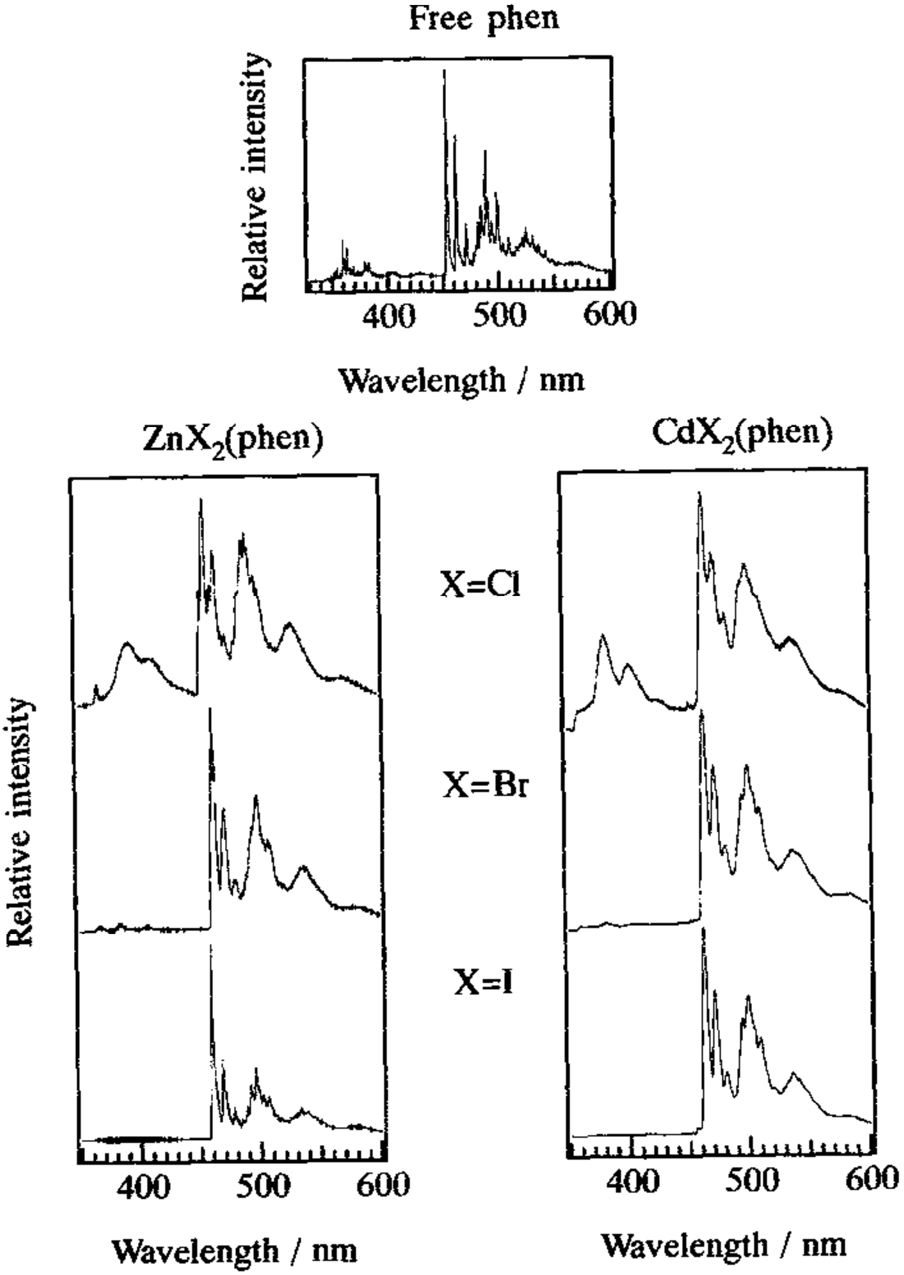

Fig. 1 Fluorescence and Phosphorescence of free phen, ZnX_2(phen) and CdX_2(phen) in the crystalline states at 4.2 K.

fluorescence lifetime. However, it is difficult to conclude anything from these data alone.

TABLE 1
Fluorescence lifetime (ns)

	Zn	Cd
free phen	1.90	
Cl	6.59	5.34
Br	0.22	0.79
I	< 0.01	~ 0.02

The $T_1 \rightarrow S_0$ decay rate constants (the reciprocals of the triplet lifetimes) are summarized in Table 2. The data again exhibit the heavy atom effect due to halogen. As for the Zn and Cd complexes, the heavier Cd complexes have smaller rate constants; this is in a opposite direction to the heavy atom effect.

TABLE 2
$T_1 \rightarrow S_0$ decay rate constant (s^{-1})

	Zn	Cd
free phen	1.12	
Cl	1.37	--
Br	44.8	7.41
I	558	137

The behavior discussed above is not necessarily easy to understand. In order to get better understanding, we have investigated the triplet spin sublevel properties by means of the optical detection of magnetic resonance (ODMR) method.

The zero-field energies of individual sublevels are summarized in Table 3. Unfortunately, for $CdCl_2$(phen) we were unable to detect any ODMR signals. Here X, Y, and Z are the energies of the sublevels measured from the center of gravity (i.e. X+Y+Z=0), for the sublevels x, y, and z. Here z axis is along the short axis of the phen ligand, and at the same time the principal axis of the C_{2v} point group; y axis is along the long axis of phen and x axis is perpendicular to the phen plane [2].

TABLE 3
Zero-field energies (in GHz) of sublevels

	Y	Z	X
free phen	2.48	−0.42	−2.07
$ZnCl_2$(phen)	2.46	−0.45	−2.02
$ZnBr_2$(phen)	2.36	−0.51	−1.86
ZnI_2(phen)	2.17	−0.55	−1.62
$CdCl_2$(phen)	–	–	–
$CdBr_2$(phen)	2.35	−0.42	−1.92
CdI_2(phen)	2.33	−0.41	−1.91

The zero-field splitting parameter D^* defined by $D^* = \sqrt{\frac{3}{2}(X^2+Y^2+Z^2)}$ are summarized in Table 4. As the atomic number of halogen increases the D^* value decreases. Further, Zn complexes have smaller D^* values than Cd complexes.

TABLE 4
Zero-field splitting parameter D^* (GHz)

	Zn	Cd
free phen	3.99	
Cl	3.94	––
Br	3.73	3.75
I	3.38	3.72

Relative radiative rate constants for sublevels are summarized in Table 5. The most remarkable observation is that the most radiative sublevel for the Zn complexes is the x out-of-plane sublevel, whereas for the Cd complexes the z in-plane short axis sublevel is the most radiative.

TABLE 5
Relative radiative rate constants for sublevels

	Y	Z	X
free phen	0.09	1	0.06
$ZnCl_2$(phen)	0.38	0.91	1
$ZnBr_2$(phen)	0.08	0.06	1
ZnI_2(phen)	<0.01	<0.01	1
$CdBr_2$(phen)	<0.01	1	0.32
CdI_2(phen)	<0.01	1	0.05

D. DISCUSSION

We now try to theoretically understand the above experimental results. We approach by valence bond picture. The emitting state is best described by the configurational mixture of pure phen localized $\pi\pi^*$ state and the halogen p to phen π^* ligand-ligand charge-transfer state. Namely, the lowest triplet state T_1 is expressed as follows

$$T_1 = c_1{}^3(\pi\pi^*) + c_2{}^3(p\pi^*) \qquad |c_1| >> |c_2| \qquad (1)$$

In the comparison of the Zn and Cd complexes, due to the difference in electronegativity, electron polarization is larger for the Zn-halogen bond than the Cd-halogen bond. Therefore, the ionization potential of the halogen is higher for Cd complexes than Zn complexes. Therefore, the $p\pi^*$ state energy should be higher for Cd complexes than Zn complexes.

In view of this difference in the energy of $p\pi^*$ state, contribution of $p\pi^*$ in T_1 should be expected in the order: I>Br>Cl for the halogen and Zn>Cd for the metal ion. Therefore, the spin density on phen ligand and hence the zero-field splitting of the T_1 state should be in the order: I<Br<Cl for the halogen and Zn<Cd for the metal. This expectation is exactly what we have observed in Table 4.

It is noted that two types of halogen p orbitals can mix with π orbital. One denoted by p_{x+} is the plus combination of the two p_x orbitals, and the other denoted by p_{z-} is the minus combination of the two p_z atomic orbitals. From the comparison of the interaction energy, p_{z-} orbital should be located below the p_{x+} orbital.

Thus for Zn complexes, both $p_{x+}\pi^*$ and $p_{z-}\pi^*$ state can mix with $\pi\pi^*$ state. However, for Cd complexes, $p_{z-}\pi^*$ state is located at much higher energy, and thus only the $p_{x+}\pi^*$ state can mix effectively with $\pi\pi^*$ state. This difference is very important, and as will be described below, all the experimental results are satisfactorily interpreted in terms of this idea.

The radiative properties of the sublevels are examined based on the above model. The mechanism of the radiative transitions for Zn complexes is schematically shown in Table 6, in which essence regarding the perturbing singlet state, spin–orbit coupling, and the dipole transition moment in the singlet manifold is shown.

TABLE 6

$T_1 \rightarrow S_0$ radiative mechanism for ZnX_2(phen)

T_1	Sublevel	Perturbing Singlet	Spin–Orbit Coupling	Dipole Transition
$(\pi\pi^*)$ $+(p_{x+}\pi^*)$ $+(p_{z-}\pi^*)$	y			forbidden
	z	$(\sigma\pi^*)$ $+(p_{y+}\pi^*)$	$\langle p_{x+}\pi^* \| H_{so} \| p_{y+}\pi^* \rangle$ one center on halogen	$\langle \sigma\pi^* \| er \| S_0 \rangle$ small
	x	$(\pi\pi^*)$ $+(p_{y-}\pi^*)$	$\langle p_{z-}\pi^* \| H_{so} \| p_{y-}\pi^* \rangle$ one center on halogen	$\langle \pi\pi^* \| er \| S_0 \rangle$ large

The transition from the y sublevel is group theoretically forbidden. Both the z and x sublevels are associated with the one–center spin–orbit coupling on halogen. Therefore, the decay from the z and x sublevels are expected to increase by the heavy atom effect due to halogen. Of these two sublevels, the dipole transition moment should be larger for the x sublevel. Therefore, we expect that the x sublevel should be most radiative, and the z sublevel comes next, and the y sublevel is almost non–emissive. This is exactly what we observed experimentally in Table 5.

The radiative mechanism is similarly shown in Table 7 for the Cd complexes. As is discussed above, in this case, only $p_{x+}\pi^*$ state can mix with $\pi\pi^*$ state. As a result, only the z sublevel is associated with the one-center spin-orbit coupling on halogen. The transition from the y sublevel is still forbidden. Therefore we expect the radiative properties in the order z>>x>>y. This is exactly what we observed experimentally in Table 5.

TABLE 7

$T_1 \rightarrow S_0$ radiative mechanism for CdX_2(phen)

T_1	Sublevel	Perturbing Singlet	Spin-Orbit Coupling	Dipole Transition
$(\pi\pi^*)$ $+(p_{x+}\pi^*)$	y			forbidden
	z	$(\sigma\pi^*)$ $+(p_{y+}\pi^*)$	$\langle p_{x+}\pi^* \| H_{so} \| p_{y+}\pi^* \rangle$ one center on halogen	$\langle \sigma\pi^* \| er \| S_0 \rangle$ small
	x	$(\pi\pi^*)$ $+(p_{y-}\pi^*)$	no one center term on anything	

E. SUMMARY

Zero-field splitting and radiative properties of the triplet spin sublevels of the "ligand localized" state of the complexes of closed shell metal ions such as Zn(II) and Cd(II) are all interpreted satisfactorily in terms of the configurational mixing between phen localized $\pi\pi^*$ state and the halogen p to phen π^* ligand-ligand charge-transfer state. Metal d orbitals do not participate in determining excited state properties. Apparent difference experimentally observed is traced back to the difference of the electronegativity of Zn(II) and Cd(II).

F. ACKNOWLEDGMENTS

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G. REFERENCES

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