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SPECTROSCOPIC PROPERTIES OF $(nd)^{10}$ TRANSITION METAL COMPLEXES

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ABSTRACT

Photoluminescence has been observed from a series of Zn(II) and Cd(II) complexes containing both N-heterocyclic and aromatic thiol ligands. The emission consists of overlapping bands, a structured phosphorescence that arises from the lowest $^3\pi\pi^*$ state of the heterocycle and a broad band luminescence that maximizes at still lower energies and decays on the order of 10-50 μs. This new band is assigned to an interligand charge-transfer excited configuration in which electronic charge has been transferred from the coordinated thiol ligand(s) to the N-heterocycle via the metal ion. A superexchange mechanism is proposed to account for the disposition of singlet and triplet states.

INTRODUCTION

Inorganic complexes exhibiting charge-transfer excited states have become a focus for numerous photochemical studies (1-3). For solar energy applications the complexes of ruthenium(II) have captured especial attention because of their rich visible absorption spectra and their capacity to retain excitation energy for relatively long times in fluid solution. The tris(bipyridine) ruthenium(II) ion, $Ru(bpy)_3^{2+}$, has become the prototype species because of its remarkable thermal and photochemical stability and its potential capacity, when excited, to split water into its elemental constituents (4). Recently, some attention has been directed toward complexes of copper(I) with heterocyclic ligands since chemically stable species can be synthesized that are deeply colored, possess excited states that live long enough to effect chemistry in fluid solution (5,6), and have the potential to be solar activated redox reagents.

The capacity of $Ru(bpy)_3^{2+}$ to effect chemistry from its lowest charge-transfer excited configuration is directly related to the fact that this d^6 system possesses no ligand field (LF) excited states that lie between the ground state and the lowest charge-transfer-to-ligand triplet ^{3}(CTTL) excited states. These latter easily accessible excited states are potential agents for solar driven redox chemistry.

During our search for metal complexes that exhibit low-lying charge-transfer excited states our curiosity was aroused by the magnificent variability of the colors of complexes containing the zinc(II) ion coordinated with both an N-heterocyclic bidentate ligand and a bidentate benzenethiol anion or two

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monodentate aromatic thiol ligands (7). The colors of these metal complexes can be changed from white to deep red or almost black by employing a judicious choice of substituents for the N-heterocycle, the thiophenol, or both. In this study we report spectroscopic investigations of complexes of the type $M(II)(BS)_2(NN)$ [M = Zn, Cd; BS = substituted benzenethiol; NN = N,N-dinitrogen heterocycle] particularly their luminescence properties. Evidence for the existence of a class of chemically tunable and potentially photoactive interligand charge-transfer excited states is presented.

EXPERIMENTAL

The molecules listed in Table 1 were synthesized and studied spectroscopically.

TABLE 1

Compound names and abbreviations

Compound	Abbreviation
bis(triphenylmethylthiolato)(1,10-phenanthroline)zinc(II)	$Zn(Ph_3CS)_2(phen)$
bis(4-chlorobenzenethiolato)(ethylenediamine)zinc(II)	$Zn(4\text{-}Cl\text{-}PhS)_2(en)$
bis(4-chlorobenzenethiolato)(1,10-phenanthroline)zinc(II)	$Zn(4\text{-}Cl\text{-}PhS)_2(phen)$
bis(4-methylbenzenethiolato)(1,10-phenanthroline)zinc(II)	$Zn(4\text{-}Me\text{-}PhS)_2(phen)$
bis(4-methoxybenzenethiolato)(1,10-phenanthroline)zinc(II)	$Zn(4\text{-}MeO\text{-}PhS)_2(phen)$
bis(4-methylbenzenethiolato)(2,2'-biquinoline)zinc(II)	$Zn(4\text{-}Me\text{-}PhS)_2(biq)$
bis(benzenethiolato)(1,10-phenanthroline)zinc(II)	$Zn(PhS)_2(phen)$
bis(pentafluorobenzenethiolato)(1,10-phenanthroline)zinc(II)	$Zn(F_5PhS)_2(phen)$
bis(benzenethiolato)(1,10-phenanthroline)cadmium(II)	$Cd(PhS)_2(phen)$
bis(4-methylbenzenethiolato)(1,10-phenanthroline)cadmium(II)	$Cd(4\text{-}Me\text{-}PhS)_2(phen)$
bis(4-chlorobenzenethiolato)(1,10-phenanthroline)cadmium(II)	$Cd(4\text{-}Cl\text{-}PhS)_2(phen)$
bis(triphenylphosphino)(2,9-dimethyl-1,10-phenanthroline)copper(I) tetrafluoroborate	$[Cu(I)(Ph_3P)_2(2,9\text{-}Me_2\text{-}phen)](BF_4)$
bis(triphenylarsino)(2,9-dimethyl-1,10-phenanthroline)copper(I) tetrafluoroborate	$[Cu(I)(Ph_3As)_2(2,9\text{-}Me_2\text{-}phen)](BF_4)$

Synthesis of complexes

The zinc and cadmium molecules were synthesized according to a single general procedure. One millimole of zinc acetate dihydrate (Baker and Adamson) was dissolved in 20 mL of hot absolute ethanol. Two millimoles of the appropriate benzenethiol (Eastman Kodak) dissolved in 10 mL of hot absolute ethanol was added slowly to the hot zinc acetate solution. No precipitate formed.

Immediately, 1 mL of the N-heterocycle (Aldrich), dissolved in 10 mL of hot absolute ethanol was slowly added to the zinc solution. A color change occurred. The solution was heated for a minute or two and then set aside to cool. Within an hour crystals formed. The crystals were collected by vacuum filtration, redissolved, and recrystallized from absolute ethanol. The final crop was washed with ether and dried in vacuo at room temperature overnight. Elemental analyses were performed on all products and were found to yield the calculated values within normal experimental limits. When a compound was resynthesized, its purity was subsequently verified by comparison of its optical parameters (absorption, fluorescence, decay time) with those of an analyzed sample. The copper complexes were prepared by the method described by Rader et al. (6).

Spectroscopic Measurements

Absorption spectra were taken at room temperature in a chloroform-ethanol solvent (1:19; v/v). The chloroform (Fisher uv spectrophotometric grade) and absolute ethanol (USI-USP) were used without further purification. Spectra were collected on a Perkin-Elmer 330 spectrophotometer interfaced to a DEC PDP 11/23 computer.

For all the zinc and cadmium complexes the emission spectra were taken from rigid glass solutions at 77 K composed of one part $CHCl_3$ to nineteen parts absolute ethanol. The complexes were first dissolved in $CHCl_3$, then diluted to volume with ethanol, and quickly frozen to a homogeneous, but cracked, glass. For the copper(I) spectra an ethanol-methanol (4:1; v/v) clear glass was employed. Spectra for Fig. 1 were recorded on an Hitachi MPF-2A fluorescence spectrometer. The remaining spectra were taken on a spectrometer consisting of a 150-W Hg-Xe light source, a Spex Minimate monochromator, and a cooled RCA 7102 photomultiplier tube. Excitation was limited to the range of 300-400 nm by a filter train consisting of $CuSO_4$ solution and a Corning 7-60 glass filter. Emitted light was filtered through a KNO_2 blocking filter (transmitted light > 420 nm) and collected at right angles to the excitation beam.

Time-resolved spectra were taken on the same setup as that used for the steady state emission spectra except that the uv source was replaced by a Molectron UV22 laser and the output of the detector was fed to a PAR 164 gated integrator coupled with a PAR Model 162 mainframe boxcar integrator. The boxcar output was interfaced to the PDP 11/23 computer. For recording submicrosecond emission spectra the PAR 164 integrator was replaced with a PAR 163 sampling integrator equipped with a Tektronix Type S-1 sampling head.

Decay times in the range of 0.1 μs to 0.1 s were recorded on a Biomation Model 6500 waveform recorder. The signal from the 7102 PMT (wired for fast response) was terminated by a resistor, picked up by a Tektronix P6202 FET probe, amplified, and fed to the Biomation recorder. The output from the waveform recorder was collected by the PDP 11/23 and subsequently analyzed.

For lifetimes greater than 0.1 s a mechanical chopper interrupted the exciting light from a Hg-Xe lamp. The decaying signal, detected by the 7102 PMT, was fed to a Keithley 610 CR electrometer whose output was connected to a Tektronix Type 549 storage oscilloscope. The signal was photographed, digitized, and fit by a least-squares method. All the long phosphorescence decay times were exponential over 3 to 5 lifetimes.

DISCUSSION OF RESULTS

Structural Prerequisites

When the $Zn(Ph_3CS)_2(phen)$ complex, a white solid, is dissolved in an organic glass at 77 K, both fluorescence and phosphorescence occur (Fig. 1a). Both bands are highly structured and exhibit the known characteristics of the spectra of the uncoordinated phen ligand, although slight shifts in the band energies and a lengthening of the lifetime of the phosphorescence (see below) due to coordination are manifest (7,8). Relative to the uncoordinated ligand, there is also a noticeable increase in the fluorescence to phosphorescence ratio. These

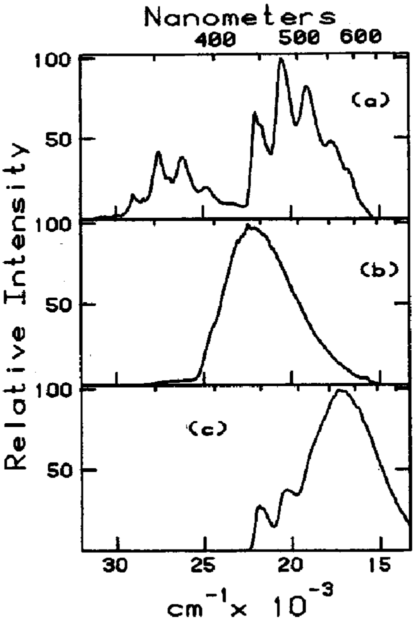

Fig. 1. Steady state emission spectra of Zn(II) complexes at 77 K. (a) $Zn(Ph_3CS)_2(phen)$, 6.0×10^{-5} M, excited at 310 nm. (b) $Zn(4\text{-}Cl\text{-}PhS)_2(en)$, 1.1×10^{-4} M, excited at 310 nm. (c) $Zn(4\text{-}Cl\text{-}PhS)_2(phen)$, 1.1×10^{-4} M, excited at 350 nm.

visible luminescence bands are confidently assigned to the lowest $^1\pi\pi^*$ and $^3\pi\pi^*$ states of the phen ligand. In the spectrum no trace of a third transition occurs below 30 000 cm^{-1}. We conclude that, in the $Zn(Ph_3CS)_2(phen)$ molecule, the Zn(II) ion plays an unimportant role in determining the nature of the low-lying excited state manifold of the system. Although two coordinated sulfur atoms are present, they, too, appear to play no essential role in defining the excited state structure. We note that the carbon atom is tetrahedral in this ligand.

In Fig. 1b we have reproduced the emission spectrum of $Zn(4\text{-}Cl\text{-}PhS)_2(en)$ in an organic glass. The broad band maximizing at approximately 22 500 cm^{-1} is a phosphorescence since it appears at essentially the same energy as the phosphorescence from the uncoordinated thiol ligand in the same solvent. The role of the Zn(II) ion appears to be to increase somewhat the ratio of phosphorescence to fluorescence from the thiol ligand. There is no evidence for a third transition in the region below 30 000 cm^{-1}. The ethylenediamine moiety, as expected, is spectroscopically transparent in this region. This saturated ligand also plays no essential role in defining the low-lying excited-state structure of the complex.

When the $Zn(4\text{-}Cl\text{-}PhS)_2(phen)$ complex is synthesized, a yellow solid is obtained. Upon irradiation with uv light of approximately 330 nm in a glass at 77 K a strong emission occurs that is comprised of two easily recognizable components (Fig. 1c). There is a prominent structured blue-green emission that decays in 0.76 s and obviously originates from a perturbed $^3\pi\pi^*$ state of the phen ligand. This structured long-lived emission band is overlapped by a new broad transition maximizing at $\sim$17 000 cm^{-1}. This broad band decays on the order of 10 μs (there is also a short nanosecond spike on this decay) and is demonstrably not related to the $^3\pi\pi^*$ state of either the phen or thiol ligands. The appearance of this band signals the existence of a new low-lying excited state (or states) in the complex that is not present in either of the coordinated ligands.

Extensive spectroscopic studies of a host of complexes of Zn(II) of the type $Zn(BS)_2(NN)$ and Zn(SS)(NN) [SS = aromatic dithiol] confirm the existence of this novel low-lying excited configuration. Moreover, it is present only when both N-heterocyclic and aromatic thiol ligands are coordinated to the Zn(II) ion.

Tunability

The energy of the novel low-lying excited configuration can be tuned in several ways. Modification of the thiol portion of the complex produces substantial shifts in the emission wavelength. This is clearly seen in Fig. 2 where the time-resolved photoluminescence bands from $Zn(4\text{-}Me\text{-}PhS)_2(phen)$ and $Zn(4\text{-}MeO\text{-}PhS)_2(phen)$ are compared. A decided red shift occurs when the methyl group on

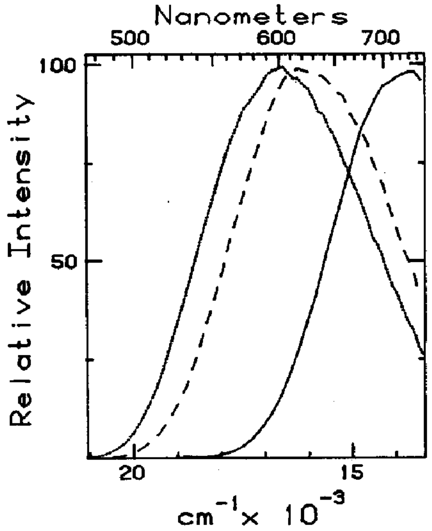

Fig. 2. Time-resolved emission spectra of Zn(II) complexes at 77 K. The boxcar parameters were 0.5 µs aperture duration at 1 µs delay after the laser pulse. (·······) $Zn(4\text{-}Me\text{-}PhS)_2(phen)$; (- - - -) $Zn(4\text{-}MeO\text{-}PhS)_2(phen)$; (———) $Zn(4\text{-}Me\text{-}PhS)_2(biq)$.

the thiol ligand is replaced by the methoxy substituent. More dramatic shifts in this low-lying emission band can be imposed by introducing substituents on the N-heterocycle or by switching to a different heterocycle altogether. In Fig. 2 we have included the time-resolved emission band from $Zn(4\text{-}Me\text{-}PhS)_2(biq)$. One sees that replacing the 1,10-phenanthroline with 2,2′-biquinoline, while retaining the identity of the sulfur moiety, causes an $\sim$3000 cm^{-1} red shift in the band energy. For the corresponding $Zn(4\text{-}MeO\text{-}PhS)_2(biq)$ complex the band falls even farther in the red. Thus, it is apparent that the energy of the excited state(s) responsible for the broad new luminescence can be tuned chemically by careful selection of the ligands. In general, both electron donating groups on the thiol ligand and electron withdrawing groups on the N-heterocycle decrease the band energy. Significant, but smaller, shifts of the band maximum can be induced via solvent perturbations. These are discussed below.

Excited State Properties

The novel low-lying emitting state(s) has a unique set of spectroscopic properties. The spectrum is generally unstructured, even at very low temperatures (10 K), and spans a broad spectral range. It also has a characteristic decay time. For most of the species the measured decay curve is approximately bimodal, consisting of an extremely fast component (ns) and a longer-lived tail in the range of 10-50 µs. This latter component is somewhat non-exponential (Table 2). Both the short (ns) and the long (10 μs) bands span the same spectral region.

TABLE 2

Luminescence decay data for Zn(II), Cd(II), and Cu(I) complexes

Compound[a]	Phen LL[b]	ITCT
phen	F[c]; 1.4 s	-
$ZnCl_2$(phen)	F; 2.3 s	-
Zn(Ph_3-CS)$_2$(phen)	F; 1.9 s	-
Zn(F_5-PhS)$_2$(phen)	1.3 s	FP[d]
Zn(4-Cl-PhS)$_2$(phen)	0.76 s	FP
Zn(PhS)$_2$(phen)	0.79 s	FP
Zn(4-Me-PhS)$_2$(phen)	0.83 s	FP
Zn(4-MeO-PhS)$_2$(phen)	-	FP
Cd(PhS)$_2$(phen)	0.74 s	FP
Cd(4-Me-PhS)$_2$(phen)	0.79 s	FP
Cd(4-Cl-PhS)$_2$(phen)	0.82 s	FP
[Cu(Ph_3P)$_2$(2,9-Me_2-phen)](BF_4)	9.0 ms	220 μs[e]
[Cu(Ph_3As)$_2$(2,9-Me_2-phen)](BF_4)	8.1 ms	210 μs

[a] All measurements on zinc and cadmium complexes were made on samples dissolved in 77 K rigid glasses composed of $CHCl_3$-ethanol (1:19; v/v). For copper(I) species an ethanol-methanol (4:1; v/v) glass was employed.

[b] Ligand-localized transition.

[c] Fluorescence (<15 ns).

[d] Decay consisting of a prompt fluorescence (<15 ns) and a non-exponential tail of 5-50 μs mean life.

[e] Tentative assignment; see text.

The solvent medium affects the emission spectrum in two ways (Fig. 3). For Zn(PhS)$_2$(phen) increasing the alcoholic content of the glass both decreases the relative amount of $^3\pi\pi^*$ contribution from the N-heterocycle and also shifts the new broad band to the red. This behavior is representative of most of the complexes investigated. Solvent effects on the decay times of the spectral components are minor.

Influence of the Metal Ion

Although subtle differences between the chemical properties of corresponding Zn(II) and Cd(II) complexes exist, as revealed during their syntheses, their absorption and photoemission spectra are remarkably similar. In Fig. 4 we

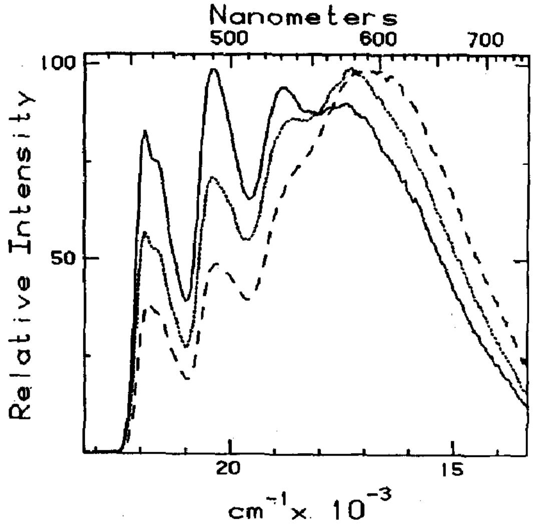

Fig. 3. Solvent dependence of the emission spectrum of $Zn(PhS)_2(phen)$ at 77 K. (———) $CHCl_3$-EtOH (1:9; v/v), 6.5 x 10^{-5} M; (·········) $CHCl_3$-EtOH (1:19; v/v), 5.6 x 10^{-5} M; (- - - -) MeOH-EtOH (4:1; v/v), 8.6 x 10^{-5} M.

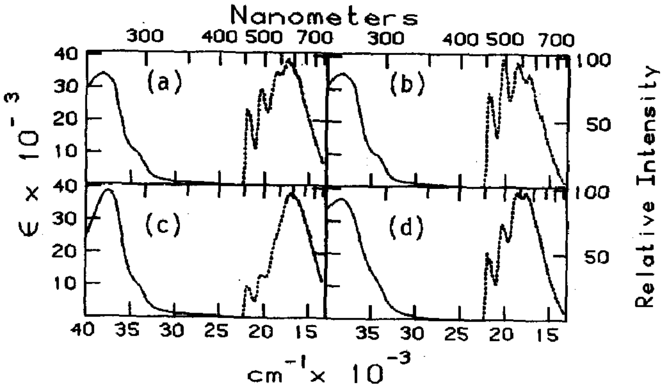

Fig. 4. Comparison of spectra of M(II)$(BS)_2$(NN) complexes [M = Zn; Cd]. (———) absorption, RT; (- - -) emission, 77 K.

compare two sets of analogous complexes, M(II)$(PhS)_2$(phen) and M(II)(4-Me-PhS)$_2$(phen) [M = Zn; Cd]. The corresponding absorption spectra are virtually identical [compare (a) with (b) and (c) with (d)], but subtle differences in the emission spectra are apparent. Relative to that of the Zn(II) complex, the $^3\pi\pi^*$ (phen) component is enhanced in the spectrum of the Cd(II) complex. In addition, replacing Zn(II) by Cd(II) shifts the broad new emission band blue by $\sim$500 cm^{-1}.

PROPOSED MODEL FOR EXCITED STATES

To rationalize the existence of the low-lying excited state(s) giving rise to the novel broad emission band observed from these closed shell compounds, we adopt the model first proposed by Koester (7) to rationalize the visible absorption spectra of analogous Zn(II) complexes containing phen and a single dithiol ligand. In this view a new low-lying excited state(s) is introduced into the molecule whenever a good pi-acceptor (phen) is coordinated to a d^{10} metal ion that is also coordinated to a pi-donor such as an aromatic thiol. Excitation of the complex to this state(s) can be viewed as a transfer of electronic charge from the thiol moiety to the N-heterocycle. Thus, the broad emission can be viewed as arising from a ligand-ligand charge-transfer excited configuration in which incipient oxidation and reduction have occurred at the thiol and N-heterocyclic ligands, respectively. Koester labelled the corresponding absorption band as an interligand transmetallic charge-transfer band (ITCT), thus implying a transfer of charge across the metal. A schematic orbital diagram and consequent energy level scheme are depicted in Fig. 5.

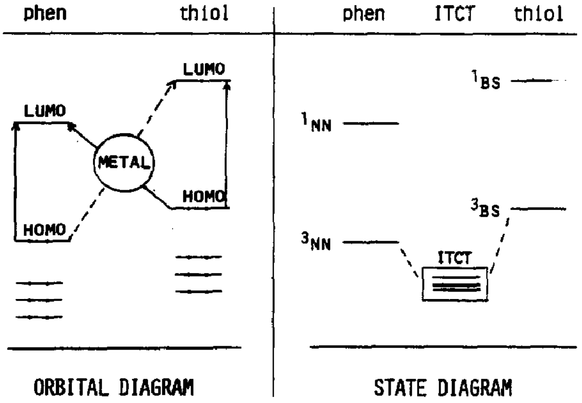

Fig. 5. Schematic energy-level and orbital schemes for closed-shell metal complexes displaying ligand-ligand CT excited states.

A consideration of Fig. 5 reveals that several modes of excitation and deactivation of these complexes are possible. Excitation of the thiol moiety could produce characteristic thiol fluorescence or phosphorescence or conversion to the ITCT state(s) followed by quenching or ITCT luminescence. Alternatively the N-heterocycle could be excited leading to fluorescence or phosphorescence from that ligand or conversion to the ITCT manifold. Conceivably, direct energy transfer from thiol to N-heterocycle, or vice versa, could occur, although this appears to be unlikely. What emission spectrum would arise experimentally would depend upon the wavelength of excitation and the relative magnitudes of the various rate constants associated with the several possible paths of radiative and radiationless degradations.

Spin Signature of the ITCT Excited States

Since the lifetime of the ITCT state(s) is ~10 μs, it is tempting to label it as a triplet. The decay curves are bimodal, however, and clearly contain fast (ns) and slow (μs) components. Lowering the temperature to ~10 K increases the length of the long decay; the nanosecond component remains. We speculate that the ITCT excited manifold is really best described as the consequence of superexchange coupling between the promoted electron residing on the heterocycle and the unpaired electron left on the thiol. In this view the metal ion mediates the coupling between the two separated electrons in the excited CT configuration. Superexchange leads to small singlet-triplet splittings (9,10), and one would predict the presence of almost isoenergetic fast (singlet) and slow (triplet) decaying states. Virtually identical spectra, only slightly shifted in energy, should arise, and this is precisely what we observe. In this view the closed metal ion d-shell remains closed in the excited configuration. The presence of the metal ion and its d-electrons are, however, fundamental determinants for the existence of the ligand-ligand CT excited states, since they provide the mechanism for the superexchange coupling.

Since we have ascribed the low-lying excited states for both Zn(II) and Cd(II) closed-shell d^{10} complexes as interligand charge-transfer states, it is interesting to apply this same model to rationalize the spectra of isoelectronic Cu(I) complexes containing both potential pi-donors and N-heterocyclic acceptors. Recently, Rader et al. (6) have reported the emissions of several Cu(I) complexes at 77 K including $[Cu(I)(Ph_3P)_2(2,9\text{-}Me_2\text{-phen})]^+$. We have measured the luminescence of this ion and that of the corresponding triphenylarsine derivative (Fig. 6). Both complexes are strong emitters and display features reminiscent of the $Zn(II)(BS)_2(NN)$ molecules (Fig. 1c). In fact, the emission consists of two luminescence bands, a relatively weak structured component that can be assigned to the perturbed $^3\pi\pi^*$ state of the heterocycle and a broad emission maximizing at lower energies that resembles the ITCT bands of the Zn(II) and Cd(II) compounds discussed above. Subtle differences between the $Zn(II)(BS)_2(NN)$ and $[Cu(I)(Ph_3P)_2(2,9\text{-}Me_2\text{-phen})]^+$ spectra do exist, however, for the measured lifetime of the $^3\pi\pi^*$ (phen) becomes ~10^2 shorter in the Cu(I) compound than in the Zn(II) or Cd(II) species (Table 2). Furthermore, the measured life of the broad band of the Cu(II) complex is considerably longer (~0.2 ms) than those of the Zn(II) and Cd(II) species (~10 μs). We conjecture that the broad luminescence band in the $[Cu(I)(Ph_3P)_2(2,9\text{-}Me_2\text{-phen})]^+$ is best associated with a ligand-ligand (ITCT) state and not a $d\pi^*$ state derived from a simple charge-transfer from Cu(I) to the N-heterocyclic ligand. In our view the coordinated triphenylphosphine ligands are incipiently oxidized in this excited configuration and the N-heterocycle is partially reduced. The Ph_3P does not

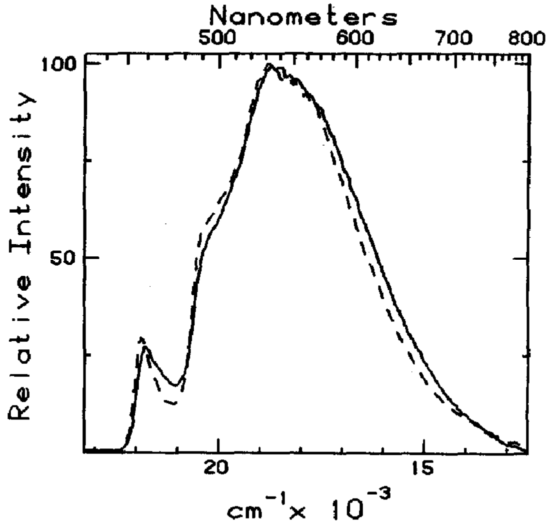

Fig. 6. Emission spectra of copper(I) complexes in ethanol-methanol at 77 K. (———) $[Cu(Ph_3P)_2(2,9\text{-}Me_2\text{-phen})](BF_4)$, 4.7 × 10^{-5} M; (- - - -) $[Cu(Ph_3As)_2(2,9\text{-}Me_2\text{-phen})](BF_4)$, 1.0 × 10^{-4} M.

act simply as a sigma-donor that lowers the ionization potential of the Cu(I) ion. This assertion about these Cu(I) transitions is quite tentative.

If the low-lying configuration responsible for the broad emission of the $[Cu(I)(Ph_3P)_2(2,9\text{-}Me_2\text{-phen})]^+$ ion is indeed an ITCT excited configuration and thus appropriately described as a superexchange coupled electronic system, then the coupling should be greater in the Cu(I) species than in those of Zn(II) and Cd(II). One would expect the electrons in d-orbitals of the monovalent Cu(I) to be more extended than in divalent Zn(II), and we infer that this d-orbital extension is responsible for the shortening of the $^3\pi\pi^*$ (phen) lifetime relative to its value in a Zn(II) complex. A greater extension of d-orbitals should also lead to greater superexchange coupling and hence a larger splitting of the ITCT singlet and triplet states in Cu(I) than in Zn(II) complexes. In both types of molecules, however, the excited ITCT configuration could be reasonably described as a biradical configuration with an unpaired electron residing on the N-heterocycle (reductant) and a hole on the pi-donor (oxidant).

Another example of a ligand-ligand excited state exhibiting broad band luminescence was reported by Vogler and Kunkely (11). The molecule, bis(3,4-toluenedithiolato)(2,2′-bipyridine)platinum(II), emits a red luminescence that resembles the ITCT bands reported here. The platinum molecule is an open-shell $(5d)^8$ system, but the empty d-orbital is evidently so high in energy that ligand-field states occur at much higher energy than the postulated ligand-ligand charge-transfer configuration, which lies lowest and is purported to be the origin of the reported emission. Because of the switch from tetrahedral

[Zn(II)] to square-planar [Pt(II)] geometry, there may be other subtle differences between the properties of the ITCT configurations of the two systems. Significantly, this platinum complex undergoes a photochemical oxidation when irradiated in $CHCl_3$ at room temperature or in a chloroform/toluene glass at 77 K.

SUMMARY

The broad range of colors that can be obtained by coordinating closed shell $(nd)^{10}$ ions with N-heterocyclic pi-acceptors and aromatic thiol donors is attributed to the incidence of a low-lying excited electronic configuration that involves ligand-to-ligand charge transfer. Photoluminescence measurements confirm the existence of a low-lying excited configuration with charge-transfer properties. The new configuration (a) arises only when both N-heterocyclic and aromatic thiol ligands are coordinated to the metal ion, (b) decays on the order of microseconds at 77 K, (c) is tunable in frequency by making judicious changes in either or both types of ligands, (d) influences the radiative and radiationless paths of energy degradation in the complexes, and (e) is fundamentally related to the pseudo noble gas structure of the metal ions. The excited configuration is described as a superexchange coupled electronic system in which the coupling of the promoted electron on the N-heterocycle with the one on the thiophenol ligand is mediated through the d^{10} shell of the metal ion. The spin signature of the lowest excited state arising from this ligand-ligand charge-transfer configuration is assigned to be a triplet but a corresponding singlet state is predicted to lie nearby.

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