

# Ligand to Ligand Charge Transfer in (Hydrotris(pyrazolyl)borato)(triphenylarsine)copper(I)

Ana Acosta and Jeffrey I. Zink\*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095

Jinwoo Cheon

Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology (KAIST), Taejeon, 305-701, Korea

Received July 26, 1999

Emission and UV–vis absorption spectra of (hydrotris(pyrazolyl)borato)(triphenylarsine)copper(I), (CuTpAsPh<sub>3</sub>), (hydrotris(pyrazolyl)borato)(triethylamine)copper(I), (CuTpNEt<sub>3</sub>), and (hydrotris(pyrazolyl)borato)(triphenylphosphine)copper(I), (CuTpPPh<sub>3</sub>), are reported. The spectra of the arsine complex contain low-energy bands (with a band maximum at 16 500 cm<sup>-1</sup> in emission and a weak shoulder centered at about 25 000 cm<sup>-1</sup> in absorption) that are not present in the corresponding spectra of the amine or phosphine complexes. The lowest energy electronic transition is assigned to ligand to ligand charge transfer (LLCT) with some contribution from the metal. This assignment is consistent with PM3(tm) molecular orbital calculations that show the HOMO to consist primarily of  $\pi$  orbitals on the Tp ligand (with some metal orbital character) and the LUMO to be primarily antibonding orbitals on the AsPh<sub>3</sub> ligand (also with some metal orbital character). The absorption shoulder shows a strong negative solvatochromism, indicative of a reversal or rotation of electric dipole upon excitation, and consistent with a LLCT. The trends in the energies of the electronic transitions and the role of the metal on the LLCT are discussed.

## Introduction

Charge transfer (or electron transfer) transitions in metal complexes have been well studied and documented. By far the best studied types are ligand to metal (LMCT) and metal to ligand (MLCT) charge-transfer transitions, and both types have been observed in absorption as well as luminescence spectroscopy. (In this paper, the convention of naming a charge-transfer band in terms of the direction of the electron transfer in absorption is used.) Some quantification of the energies of charge-transfer transitions, such as the concept of optical electronegativities, has been developed,<sup>1</sup> but the most common descriptions are based on HOMO–LUMO separations calculated by molecular orbital theory.

An uncommon type of charge-transfer transition is ligand to ligand (LLCT) or interligand charge transfer. In comparison to the vast literature on MLCT and LMCT, very little has been published on LLCT.<sup>2–7</sup> In many cases LLCT bands are difficult to detect in absorption spectra; reasons for this difficulty include the fact that these bands may be hidden under or obscured by absorption bands of different origins, or they may occur at energies very different from those ordinarily studied. The molar absorptivities of the LLCT bands may be low because of the

poor overlap between the orbitals involved. In complexes of transition metals, the energies of metal d orbitals often lie between the highest occupied and lowest unoccupied ligand orbitals giving rise to ligand field, LMCT, and/or MLCT transitions lower in energy than LLCT. Further complicating the interpretation is metal–ligand covalency. Molecular orbitals that are primarily ligand orbital in character may have some amount of metal character mixed in, and a transition that is described as ligand to ligand may in fact also involve the metal to some extent. A “pure” LLCT would have a transition energy that does not change significantly when the metal is varied.

The first LLCT that was assigned was a near-UV band in the absorption spectra of [Be(bipy)(X<sub>2</sub>)] complexes.<sup>8</sup> The LLCT bands red-shifted in the order of the increasing reducing strength of the halide, consistent with an assignment of a halide orbital to bipy  $\pi$  antibonding orbital charge transfer. LLCT has been assigned in biomolecules; the absorption spectrum of carboxy-cytochrome P450 containing an axial thiolate ligand contains a band in the UV region that arises from a transition from a lone pair on the thiolate sulfur atom to a  $\pi$  antibonding orbital on the porphyrin.<sup>9</sup> The transition energy in a zinc porphyrin thiolate complex<sup>10,11</sup> was similar to that of the iron-containing compound. Among the most comprehensively studied series of compounds are the Ni, Pd, and Pt diimine dithiolate com-

(1) Jorgensen, K. *Inorganic Complexes*, 1st ed.; Academic Press: London, 1963.

(2) Vogler, A.; Kunkely, H. *Comments Inorg. Chem.* **1990**, *9*, 201.

(3) Kunkely, H.; Vogler, A. *Eur. J. Inorg. Chem.* **1998**, 1863.

(4) Kunkely, H.; Vogler, A. *Inorg. Chim. Acta* **1997**, *264*, 305.

(5) Benedix, R.; Vogler, A. *Inorg. Chim. Acta* **1993**, *204*, 189.

(6) Benedix, R.; Hennig, H.; Kunkely, H.; Vogler, A. *Chem. Phys. Lett.* **1990**, *175*, 483.

(7) Stor, G. J.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1992**, *31*, 1318.

(8) Coates, Y. E.; Green, S. I. E. *J. Chem. Soc.* **1962**, 3340.

(9) Hanson, L. K.; Eaton, W. A.; Sliagar, S. G.; Gunsalus, I. C.; Gouterman, M.; Connell, C. R. *J. Am. Chem. Soc.* **1976**, *98*, 2672.

(10) Nappa, M.; Valentine, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 5075.

(11) Nardo, J. V.; Sono, M.; Dawson, J. H. *Inorg. Chim. Acta* **1988**, *151*, 173.

plexes.<sup>12</sup> The LLCT absorption band energy is almost insensitive to the metal, suggesting that the LLCT is pure. Molecular orbital calculations<sup>13,14</sup> support and resonance Raman studies verify the LLCT assignment.<sup>15</sup> The Raman spectra were instrumental in the assignment of the LLCT transition because they proved that both ligands are distorted upon excitation, indicating that both ligands are involved in the electron-transfer process. If the band of interest overlaps other bands, interference effects can be observed that require careful interpretation.<sup>16,17</sup>

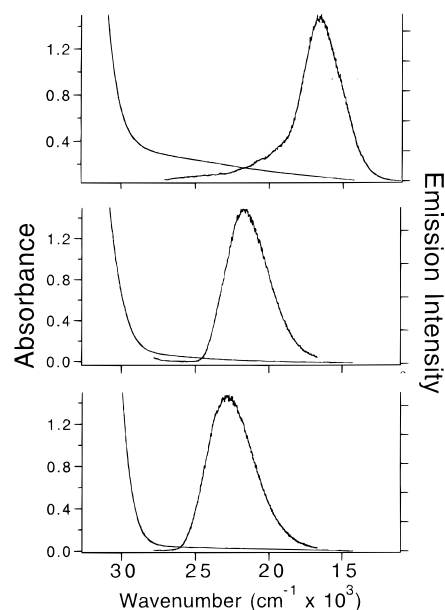
Very few emission spectra have been assigned to a LLCT. (Pyridine)(3,4-toluenedithiolato)platinum(II) in an ethanol glass at 77 K shows a strong red emission that was assigned to a LLCT transition from the dithiolate to the bipyridine.<sup>18</sup> Closed-shell zinc(II) complexes containing both N-heterocyclic and aromatic thiol ligands also show an emission band assigned to a LLCT transition,<sup>19</sup> and optical ligand-to-ligand charge transfer of Zn(2,2'-bipyridyl)(3,4-toluenedithiolate) has been reported.<sup>6</sup> In (2,2'-biquinoline)bis(cyclopentadienyl)zirconium(IV) a ligand to ligand charge transfer was reported and both absorption and emission spectra were presented.<sup>3</sup> In Cu(I) tetrameric clusters such as Cu<sub>4</sub>I<sub>4</sub>(2-(diphenylmethyl)pyridine)<sub>4</sub>, the emission was assigned as a highly mixed transition with significant halide to ligand charge transfer.<sup>20,21</sup>

In this paper the results of a study of complexes of the hydrotris(pyrazolyl)borato ligand with copper(I) are reported. The tridentate hydrotris (pyrazolyl)borato ligand is chosen because it forms complexes of the form TpML, where L can be systematically varied, and because the filled  $\pi$  bonding or empty  $\pi$  antibonding orbitals could participate in LLCT. The filled d-shell metal copper(I) is chosen because ligand field transitions are eliminated, because the coordination geometry results in high-symmetry ( $C_{3v}$ ) complexes, and because the neutral ligands L that are chosen for study produce stable neutral complexes. The lowest energy excited state of (hydrotris(pyrazolyl)borato)(triphenylarsine)copper(I), [CuTpAsPh<sub>3</sub>], contains a large ligand to ligand charge-transfer component. The complex is luminescent, a rare example of LLCT luminescence. Replacing the arsine ligand by triethylamine raises the LLCT energy and the lowest excited state changes. The assignment of the transition as LLCT in the arsine complex is assisted by the dependence of this transition on the medium, i.e., its strong negative solvatochromism, by resonance Raman spectroscopy, and by molecular orbital calculations.

## Experimental Section

**Materials.** The sodium salt of the hydrotris(pyrazolyl)borato ligand (NaTp), triphenylarsine (AsPh<sub>3</sub>), triphenylphosphine (PPh<sub>3</sub>), and triethylamine (NEt<sub>3</sub>) were purchased from Aldrich. NEt<sub>3</sub> was purified by distillation.

All of the TpCuL compounds (L = AsPh<sub>3</sub>, PPh<sub>3</sub>, or NEt<sub>3</sub>) were prepared by methods similar to that for CuTpPMe<sub>3</sub> and characterized by <sup>1</sup>H NMR.<sup>22</sup> A representative synthesis proceeded as follows: 0.64 g of CuCl (6.5 mmol) and 1.55 g of NaTp (6.5 mmol) were added to



**Figure 1.** Top panel: Room-temperature absorption spectrum in THF (left) and 20 K emission spectrum (right) of CuTpAsPh<sub>3</sub>. Middle panel: Room-temperature absorption spectrum in diethyl ether (left) and 20 K emission spectrum (right) of CuTpNEt<sub>3</sub>. Bottom panel: Room-temperature absorption spectrum in diethyl ether (left) and 20 K emission spectrum (right) of CuTpPPh<sub>3</sub>.

2 g of AsPh<sub>3</sub> in 30 mL of THF under nitrogen. All the solvents were distilled and degassed before utilization. The solution was stirred for 2 h at room temperature, and the solvent was removed in vacuo. A white microcrystalline solid, CuTpAsPh<sub>3</sub>, was obtained. This solid was further purified by recrystallization from THF/CHCl<sub>3</sub> or by sublimation in a vacuum (125 °C). The yield was approximately 60%. CuTpPPh<sub>3</sub> and CuTpNEt<sub>3</sub> were similarly prepared and characterized.

**Spectroscopy.** The room-temperature absorption spectra were recorded on Shimadzu-UV 260 and Shimadzu-UV 2501 spectrophotometers. The spectra after baseline subtraction are shown in Figure 1.

Luminescence spectra of powder samples in sealed capillaries were acquired. For the 20 K emission the samples were mounted in a Displex closed-cycle helium refrigerator. The emitted light was passed through a 0.75 m single monochromator (Spex). A cooled RCA C31034 photomultiplier tube was used to detect the signal, which was then fed into a Stanford Research Systems SR 400 photon counter and stored in a computer. The samples were excited with wavelengths of 351.1 and 488.0 nm from an argon ion laser.

Raman spectra were recorded at room temperature using argon ion (514.5 nm) excitation, and resonance Raman spectra were obtained at room temperature using the 457.9 nm line of the same laser. The laser beam was focused on the samples with a 150 mm focal length lens. The scattered light was collected and passed through a 0.85 m double monochromator (Spex 1401). A cooled RCA C31034 photomultiplier tube was used to detect the signal, which was then fed into a Stanford Research Systems SR 400 photon counter and stored in a computer. The computer program used to work up the data and to obtain the areas under the peaks and the peak maxima in emission and in Raman was IGOR Pro by WaveMetrics, Version 3.0.

**Computational Methodology.** Computations, including geometry optimization and molecular orbital calculations, were carried out using the standard PM3(tm) method with Spartan Version 5.0.3.<sup>23</sup>

## Results

**Emission Spectroscopy.** All of the compounds luminesce at both room temperature and low temperatures when powders or microcrystals are excited at 351.1 nm. The luminescence

(12) Miller, T. R.; Dance, I. G. *J. Am. Chem. Soc.* **1973**, *95*, 6970.

(13) Benedix, R.; Hennig, H. *Inorg. Chim. Acta* **1988**, *141*, 21.

(14) Benedix, R.; Pitsch, D.; Schöne, K.; Hennig, H. *Z. Anorg. Allg. Chem.* **1986**, *542*, 102.

(15) Wootton, J. L.; Zink, J. I. *J. Phys. Chem.* **1995**, *99*, 7251.

(16) Shin, K. S. K.; Zink, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 7148.

(17) Wootton, J. L.; Zink, J. I. *J. Am. Chem. Soc.* **1997**, *119*, 1895.

(18) Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1981**, *103*, 1559.

(19) Truesdell, K. A.; Crosby, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 1787.

(20) Vitale, M.; Ryu, C. K.; Palke, W. E.; Ford, P. C. *Inorg. Chem.* **1994**, *33*, 561.

(21) Vitale, M.; Palke, W. E.; Ford, P. C. *J. Phys. Chem.* **1992**, *96*, 8329.

(22) Plappert, E. C.; Stumm, T.; vandenBergh, H.; Hauert, R.; Dahmen, K. H. *Chem. Vap. Deposition* **1997**, *3*, 37.

(23) SPARTAN SGI Version 5.0.3, Wave function Inc., 18401 Von Karman Ave, #370, Irvine, CA 92612.

intensity increases and the bands sharpen as the temperature is decreased. Even at the lowest temperatures (20 K) the bands are smooth with no resolved vibronic structure.

**CuTpAsPh<sub>3</sub>.** The emission spectrum of CuTpAsPh<sub>3</sub> at 20 K as a powder in a sealed capillary excited at 351.1 nm is shown in top panel of Figure 1. The bright red luminescence has its maximum at 16 530 cm<sup>-1</sup> with a width at half-height of 3190 cm<sup>-1</sup>. The weak features in the high energy region between 20 000 and 25 000 cm<sup>-1</sup> are very low in intensity compared to the peak maximum but are always present even after repeated recrystallization.

The emission spectrum of CuTpAsPh<sub>3</sub> at room temperature is much lower in intensity and broader than the emission taken at 20 K, with the maximum at 20 425 cm<sup>-1</sup> and a width at half-height of 7280 cm<sup>-1</sup>.

**CuTpNET<sub>3</sub>.** The 20 K emission spectrum of CuTpNET<sub>3</sub> as a powder in a sealed capillary excited at 351.1 nm is shown in the middle panel of Figure 1. The luminescence shows a maximum at 21 680 cm<sup>-1</sup> with a width at half-height of 3420 cm<sup>-1</sup>. The band is smooth and featureless.

**CuTpPPh<sub>3</sub>.** The 20 K emission spectrum of CuTpPPh<sub>3</sub> as a powder in a sealed capillary excited at 351.1 nm is shown in the bottom panel of Figure 1. The luminescence has its maximum at 22 860 cm<sup>-1</sup> with a width at half-height of 3730 cm<sup>-1</sup> and has an intensity comparable to that of CuTpNET<sub>3</sub>.

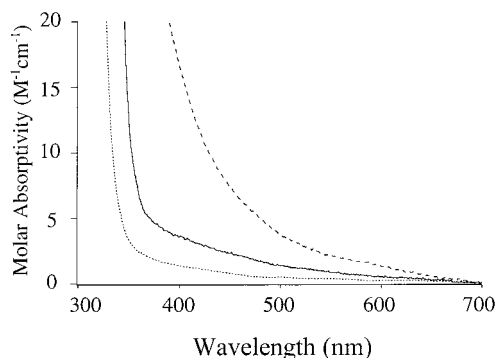
**CuTpPMe<sub>3</sub>.** The 20 K emission spectrum of CuTpPMe<sub>3</sub> as a powder in a sealed capillary excited with 351.1 nm has its maximum at 20 150 cm<sup>-1</sup> with a width at half-height of 4960 cm<sup>-1</sup>. It is the least intense of all of the emission spectra from CuTp complexes.

**NaTp.** The Tp ligand is luminescent at low temperature, but its intensity is very weak compared to those of the copper complexes. The emission spectrum of sodium hydrotris(pyrazolyl)borate as a powder at 20 K excited with 351.1 nm has its maximum at 23 640 cm<sup>-1</sup> and a width at half-height of 6890 cm<sup>-1</sup>. This emission is in the same region as the high-energy, low-intensity features in the top panel of Figure 1. The photoluminescence intensity is comparable to the Raman scattering intensity; Raman peaks are readily distinguished at 25 045, 25 600, 26 288, 26 645, and 27 010 cm<sup>-1</sup> (corresponding to vibrations between 1470 and 3500 cm<sup>-1</sup> *vide infra*).

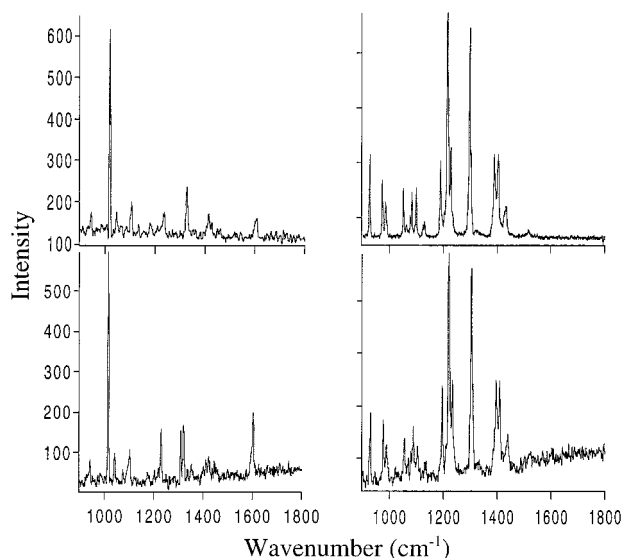
**[ZnTpAsPh<sub>3</sub>]NO<sub>3</sub>.** The ZnTpAsPh<sub>3</sub><sup>+</sup> ion, which will play a role in the discussion, was studied for comparison purposes. Its emission, if any, is very weak. Under highly sensitive detection conditions emission bands from the Tp and the AsPh<sub>3</sub> ligands (that were present as trace impurities) are observed. The absorption spectrum of this compound taken at room temperature in a THF solution starts around 33 330 cm<sup>-1</sup> and is smooth and featureless.

**Absorption Spectroscopy. CuTpAsPh<sub>3</sub>.** The room-temperature solution absorption spectrum of CuTpAsPh<sub>3</sub> taken in THF contains a weak broad band between about 17 000 and 30 000 cm<sup>-1</sup>. The extinction coefficient at 25 000 is 3.6 cm<sup>-1</sup> M<sup>-1</sup>. The extinction coefficient at 25 000 cm<sup>-1</sup> in toluene is 16.5 cm<sup>-1</sup> M<sup>-1</sup>, and in dimethyl sulfoxide it is 1.4 cm<sup>-1</sup> M<sup>-1</sup>. The absorbance rises toward high energy peaks at wavenumbers higher than 30 000 cm<sup>-1</sup>. The weak broad absorption band is absent in the spectra of the remaining compounds discussed below.

The low-energy shoulder present in the absorption spectrum of CuTpAsPh<sub>3</sub> shifts as a function of solvent. The solvent-dependent frequency shift is illustrated in Figure 2. This shoulder changes its extinction coefficient from 16.5 in toluene to 1.5 in dimethyl sulfoxide (DMSO) when measured at 400 nm.



**Figure 2.** Solvent dependence of the absorption spectra of CuTpAsPh<sub>3</sub>. The spectra are in toluene (dashed (top) line), THF (solid (middle) line), and DMSO (dotted (bottom) line) solutions.



**Figure 3.** Left panels: Raman spectra of solid CuTpAsPh<sub>3</sub> with 514.5 nm (top) and 457.9 nm (bottom) irradiation. Right panels: Raman spectra of solid CuTpNET<sub>3</sub> with 514.5 nm (top) and 457.9 nm (bottom) irradiation.

**CuTpNET<sub>3</sub>.** The room-temperature absorption spectrum in a diethyl ether solution is dominated by a peak at 33 110 cm<sup>-1</sup> with an extinction coefficient of 363 cm<sup>-1</sup> M<sup>-1</sup>. The absorption spectrum of CuTpNET<sub>3</sub> does not have a shoulder in the region between 25 000 and 28 000 cm<sup>-1</sup>.

**CuTpPPh<sub>3</sub>.** The absorption taken at room temperature in a diethyl ether solution does not contain any peaks or shoulders at energies lower than 28 000 cm<sup>-1</sup>.

**Raman Spectroscopy.** Raman data were obtained for CuTpAsPh<sub>3</sub> with 514.5 nm excitation, and resonance Raman spectra were obtained with 457.9 nm excitation, in resonance with the lowest energy absorption shoulder. The left panels of Figure 3 show these Raman spectra. The same excitation wavelengths were used to obtain Raman spectra for CuTpNET<sub>3</sub> and are shown in the right panels of Figure 3. All of the spectra are normalized relative to the intensity of the CH peaks of the Tp ligand. The frequencies, relative intensities, and assignments for each frequency for the arsine and amine compounds are given in Table 1. The assignments were made by comparison with similar compounds.<sup>24–27</sup>

In the case of CuTpNET<sub>3</sub> the relative intensities of the different peaks do not change when the laser line is changed from 514.5

(24) Durig, J. R.; Bergana, M. M.; Zunic, W. M. *J. Raman Spectrosc.* **1992**, *23*, 357.

(25) Diaz, G.; Campos, M.; Klahn, A. H. *Vibr. Spec.* **1995**, *9*, 257.

(26) Whiffen, D. H. *J. Chem. Soc.* **1956**, 1350.

**Table 1.** Raman Data for CuTpAsPh<sub>3</sub> and CuTpNEt<sub>3</sub> with the Intensities of the Peaks Relative to That of the 3140 cm<sup>-1</sup> CH Stretching Mode<sup>a</sup>

| frequency | $I_k/I_{k'}$          |           |                      |           | assignt                                  |
|-----------|-----------------------|-----------|----------------------|-----------|--|
|           | CuTpAsPh <sub>3</sub> |           | CuTpNEt <sub>3</sub> |           |  |
|           | 457.9 nm              | 514.5 nm  | 457.9 nm             | 514.5 nm  |  |
| 930       | 0.48                  | 0.35      | 0.58                 | 0.55      | $\delta(\text{C-H})_{\text{oop of Tp}}$  |
| 1001      | 3.40                  | 3.15      |                      |           | phenyl ring breathing p mode             |
| 1032      | 0.51                  | 0.40      | 0.39                 | 0.38      | $\delta(\text{C-H})$ of Tp               |
| 1090      | 0.65                  | 0.55      |                      |           | phenyl ring breathing x-sens. q-mode     |
| 1215      | 0.85                  | 0.37      | 2.06                 | 1.76      | $\nu(\text{N-N})$ of Tp                  |
| 1297      | 1.04                  | 0.11      | 1.88                 | 1.62      | $\nu(\text{C-C})$ of Tp                  |
| 1306      | 0.66                  | 0.77      |                      |           | $\nu(\text{C-C})$ of phenyl rings o-mode |
| 1395      | 0.54                  | 0.38      | 0.87                 | 0.64      | pyrazolyl ring stretch                   |
| 1585      | 0.85                  | 0.40      |                      |           | $\nu(\text{C-C})$ of phenyl k mode       |
| 3140      | 1.0 (ref)             | 1.0 (ref) | 1.0 (ref)            | 1.0 (ref) | $\nu(\text{C-H})$ from Tp                |

<sup>a</sup> The experimental uncertainty in the  $I_k/I_{k'}$  values is 20%.

to 457.9 nm. In contrast, in the spectrum of the CuTpAsPh<sub>3</sub> complex the peaks corresponding to vibrations of both the pyrazolyl rings on the Tp ligand and the phenyl rings on the AsPh<sub>3</sub> ligand exhibit resonance enhancement when compared to the peaks corresponding to the CH stretches on the Tp ligand.

## Discussion

**1. General Considerations.** The intent of this study is to determine if the Tp ligand can be used in conjunction with a second ligand to design new low-energy luminescent ligand to ligand charge-transfer complexes. A filled d-shell metal was chosen in order to eliminate ligand field transitions. The Cu(I) complexes reported in this study are luminescent, but the assignment of the luminescence to a ligand to ligand electron transfer is not straightforward.

The luminescence properties of the triphenylarsine complex provide the first suggestion that the ligand to ligand charge-transfer assignment is valid. The luminescence from this complex is in the red to near-IR region of the spectrum. In addition, the absorption spectrum contains a broad weak band extending well into the visible region of the spectrum. In contrast, the spectroscopic properties of the triethylamine complex, which would not be expected to exhibit low-energy ligand to ligand charge transfer, are very different. This complex emits in the blue region of the spectrum and does not have an absorption band in the visible. The triphenylphosphine complex also emits in the blue region of the spectrum and also does not have an absorption band in the visible region. The large red shift of the arsine complex is not inconsistent with a LLCT assignment.

An alternative assignment that must be considered is a metal to ligand charge transfer. The charge-transfer luminescence of copper(I) to  $\pi^*$  orbitals in phenanthroline rings occurs in the red section of the visible region extending into the near-IR.<sup>28</sup> Cu(I) to phosphine charge transfer (also called  $\sigma\text{-a}_\pi$  or M-P  $\sigma$  to  $\pi$  antibonding charge transfer) occurs in the blue-green region of the spectrum.<sup>29,30</sup> In the case of the charge transfer from Cu(I) to  $\pi^*$  orbitals in the pyrazolyl rings, the lowest energy transition would be from a  $t_2$  d orbital (in tetrahedral symmetry) to the  $\pi^*$  orbital on the pyrazolyl ring. Because the Tp ligand is not considered to be a good acceptor, copper to Tp charge

transfer might be expected to occur at higher energies.<sup>31</sup> As the ligand field strength of the unique ligand increases (As < P < N), the energy of the filled d orbital increases and the energy of the transition from that orbital to the ligand  $\pi^*$  orbital decreases. This trend is observed for the amine and phosphine complexes, but the arsine complex is out of order. These results are not inconsistent with a LLCT assignment for the arsine complex but a MLCT assignment for the others.

Pure LLCT, i.e., a transition where the HOMO is almost entirely donor ligand in character and the LUMO is almost entirely acceptor ligand in character, is relatively insensitive to the metal. Metal diimine dithiolate complexes are among the most extensively studied compounds that show a pure LLCT transition, where changing the metal does not affect the LLCT band.<sup>12</sup> A variety of these types of complexes were synthesized and characterized by UV-vis absorption and electrochemical measurements.<sup>12</sup>

If the lowest energy transition of the Tp-arsine complex were pure LLCT, then changing the metal from copper(I) to another filled shell metal such as zinc(II) should not dramatically change the transition energy. To test this idea, the zinc complex was synthesized and studied. [TpZnAsPh<sub>3</sub>]NO<sub>3</sub> does not luminesce in the red region of the spectrum and does not have a low-energy absorption band in the visible region of the spectrum. The absence of luminescence is not particularly diagnostic; many sources of luminescence quenching exist. However, the absence of an absorption band in the visible that is comparable to that of the analogous copper(I) complex suggests that the Tp-AsPh<sub>3</sub> pair of ligands does not provide a pure LLCT in these first-row transition metal complexes.

The optical emission and absorption properties of the complexes alone do not provide enough evidence to allow assignments to be made. The trends in the energies of the transitions support the LLCT hypothesis, but they are insufficient to allow definitive conclusions to be drawn.

**2. Solvatochromism.** A characteristic of LLCT absorption is the presence of a large solvatochromatic shift in the absorption band. In a LLCT there is a large electric dipole associated with the transition. The negative solvatochromism is a result of reversing, reducing, or rotating the dipole moment of the molecule, and the large transition dipole moment change causes a large solvatochromatic shift to exist.

The effect of increasing the polarity or dielectric constant of the solvent is to increase the contribution of the polar structure of the molecule in the ground state. Once the transition occurs, the dipole associated with this molecule is reversed or rotated,

(27) Wootton, J. L.; Zink, J. I.; Díaz, G.; Campos, M. *Inorg. Chem.* **1997**, *36*, 789.  
 (28) Everly, R. M.; Ziessel, R.; Suffert, J.; McMillin, D. R. *Inorg. Chem.* **1991**, *30*, 559.  
 (29) Kutal, C. *Coord. Chem. Rev.* **1990**, *99*, 213.  
 (30) Seters, D. P.; DeArmond, M. K.; Grutsch, P. A.; Kutal, C. *Inorg. Chem.* **1984**, *23*, 3, 2874.

(31) Kunkely, H.; Vogler, A. *J. Photochem. Photobiol.* **1998**, *119*, 187.

and this big change leads to a hypsochromic shift (negative solvatochromism). This same idea can be explained by the model that considers the interaction between the solvent and the molecule as the interaction between polarizable point dipoles in a homogeneous dielectric continuum.<sup>32</sup>

Absorption spectra were obtained for CuTpAsPh<sub>3</sub> in different solvents to test for any dependence on the medium. The low-energy shoulder present in the absorption spectrum blue shifts as the solvent's dielectric constant increases. If it is assumed that only the position of the band maximum changes as a function of the solvent (and not the extinction coefficient), then the apparent change in the extinction coefficient is caused by the shift of the absorption band to higher energy as the polarity of the solvent increases.<sup>32–35</sup> In an attempt to be more quantitative, the wavenumber of the shoulder at a constant extinction coefficient (chosen as 20 M<sup>-1</sup> cm<sup>-1</sup>) was measured. This part of the shoulder was located at 26 900 cm<sup>-1</sup> in toluene, at 29 000 cm<sup>-1</sup> in THF, and at 30 500 cm<sup>-1</sup> in DMSO.

The broad band corresponding to the lowest energy absorption shifts by approximately 3600 cm<sup>-1</sup>. This shift indicates that there is a large electric dipole change, and the negative solvatochromism indicates that the dipole is reversed or rotated as a result of the transition. The molecular orbital calculations show that this is the case for the CuTp compounds. The Tp ligand is the negative part of the molecule in the ground state. The HOMO to LUMO one-electron transition involves removing an electron from the Tp ligand and placing it on the AsPh<sub>3</sub> ligand, decreasing or reversing the dipole.

The solvatochromic shift is of similar magnitude to that observed in the LLCT band of Ni(tfd)(phen) (where tfd is a dithiolenic ligand and phen is 1,10-phenanthroline).<sup>12</sup> As the dielectric constant increases, this band shifts from 17 850 to 20 600 cm<sup>-1</sup>, a total shift of 2750 cm<sup>-1</sup>.

**3. Resonance Raman Spectroscopy.** Resonance Raman intensities can be used to determine excited-state distortions, i.e., bond length and bond angle changes, in excited electronic states.<sup>36,37</sup> The distortions along specific normal coordinates are related to the orbitals that are involved in the electronic transitions because removal of an electron from a filled orbital or population of an unoccupied orbital will cause changes in the bond strengths.

The locations of the biggest distortions in a molecule can assist in the assignment of an electronic transition. In ligand to ligand charge transfer, the electron is transferred from an occupied orbital on one ligand to an unoccupied orbital on a different ligand. Removal of the electron from the donor ligand will cause changes in the bond strengths on that ligand, and populating a previously empty orbital on the acceptor ligand will result in bond length changes on it. Thus, the resonance Raman spectrum taken in resonance with the LLCT will reveal enhancements of normal modes corresponding to bond length and angle changes on both of the ligands involved.<sup>15</sup> In contrast, for metal to ligand charge transfer, orbitals on the acceptor ligand will be populated, and significant bond length changes will only occur on that ligand.<sup>38–40</sup> The resonance Raman

signature for MLCT will be enhancement of the intensities of the acceptor ligand.

Raman spectra were obtained for CuTpNET<sub>3</sub> and for CuTpAsPh<sub>3</sub> using 457.9 and 514.5 nm excitation. The 457.9 nm excitation is in resonance with the state giving rise to the shoulder in the absorption spectra of the arsine complex but is out of resonance with the amine complex. The relative intensities of the peaks in the spectra of CuTpNET<sub>3</sub> change by an average of about 15% when going from 514.5 to 457.9 nm. In contrast, the relative intensities of some of the peaks in the spectrum of CuTpAsPh<sub>3</sub> significantly increase. The frequencies that more than double their intensities when compared to the reference peak (3140 cm<sup>-1</sup>, CH stretching mode) correspond to vibrations due to the phenyl k-mode at 1585 cm<sup>-1</sup> in the AsPh<sub>3</sub> ligand, a nitrogen–nitrogen stretch at 1215 cm<sup>-1</sup> in the Tp ligand, and a carbon–carbon stretch at 1297 cm<sup>-1</sup> in the Tp ligand. These enhancements involve distortions on both of the ligands.

The LLCT band is a shoulder on a more intense charge-transfer band, and when two bands overlap, interference effects can occur.<sup>16,17</sup> The comparison between the resonance and out of resonance spectra of CuTpAsPh<sub>3</sub> and CuTpNET<sub>3</sub> suggests that there is a resonance effect on the intensities in the spectra of CuTpAsPh<sub>3</sub> from the LLCT (with both ligands being involved) that is absent in the spectra of CuTpNET<sub>3</sub>. The trends observed are qualitatively consistent with LLCT, but the presence of the overlapping MLCT band at higher energy complicates a more detailed analysis.

**4. Molecular Orbital Calculations.** The presence of low-energy emission and absorption bands in the electronic spectra, the dependence of the low-energy absorption shoulder on the solvent polarity, and the enhancement of normal mode intensities involving both of the ligands in resonance with the lowest excited state support the assignment of the state as ligand–ligand charge transfer. To gain insight into the nature of the orbitals on the ligands and the relative trends in orbital energies as the ligands are varied, semiempirical molecular orbital calculations were carried out using the PM3(tm) program in Spartan.

The calculated HOMO and LUMO of CuTpAsPh<sub>3</sub> are shown in Figure 4. The HOMO is degenerate and consists mainly of orbitals on the Tp ligand and some copper metal participation. There is almost no contribution from the arsine ligand. The primary Tp ligand orbitals in the HOMO are p orbitals of nitrogen and carbon that comprise the  $\pi$  system of the pyrazolyl rings. The copper metal orbitals mainly involved in the degenerate HOMO are the pairs  $d_{x^2-y^2}$  and  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ , and  $p_x$  and  $p_y$ .

The LUMO consists mainly of orbitals on the AsPh<sub>3</sub> ligand and the copper metal with almost no contribution from the Tp ligand. On the triphenylarsine ligand the biggest contributions are from the s and  $p_z$  orbitals of arsenic with moderate contributions from the carbons of the phenyl rings adjacent to the arsenic. This interpretation bears some similarity to results from ab initio calculations on trimethylphosphine complexes that suggest the acceptor orbitals primarily involve P–C antibonding orbitals.<sup>41</sup> The atomic orbitals of the metal involved in the LUMO are mainly s,  $p_z$ , and  $d_{z^2}$ .

The HOMO to LUMO transition, on the basis of these calculations, is a ligand to ligand, Tp to arsine charge transfer, but at the same time there is a large participation of the metal orbitals. Because the coefficients of the metal orbitals in the

(32) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29.

(33) Liptay, W. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 177.

(34) Kosower, E. M. *Part Two, Medium Effects*; Wiley: New York, 1968; p 259.

(35) Paw, W.; Cummings, S. D.; Mansour, M. A.; Connick, W. B.; Geiger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, *171*, 125.

(36) Meyers, A. B. *Laser Techniques in Chemistry*; Meyers, A. B., Rizzo, T. R., Eds.; John Wiley & Sons, Inc.: New York, 1995; Vol. XXIII, p 325.

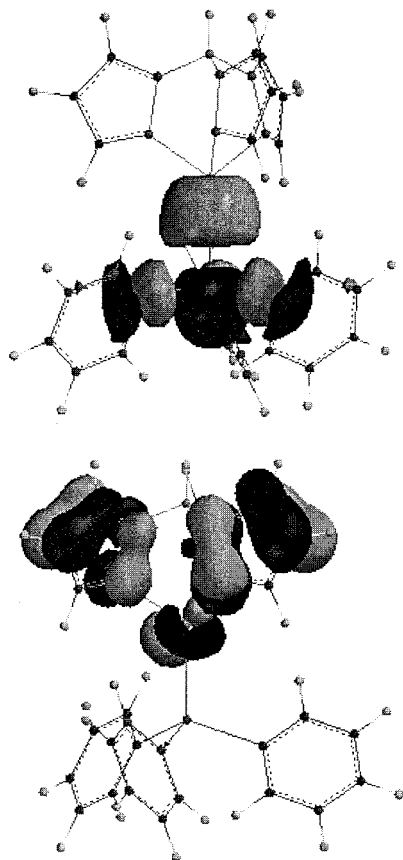
(37) Zink, J. I.; Shin, K. S. K. *Adv. Photochem.* **1991**, *16*, 119.

(38) Hanna, S. D.; Khan, S. I.; Zink, J. I. *Inorg. Chem.* **1996**, *35*, 5813.

(39) Hanna, S. D.; Zink, J. I. *Inorg. Chem.* **1996**, *35*, 297.

(40) Henary, M.; Zink, J. I. *Inorg. Chem.* **1991**, *30*, 3111.

(41) Pacchioni, G.; Bagus, P. S. *Inorg. Chem.* **1992**, *31*, 4391.

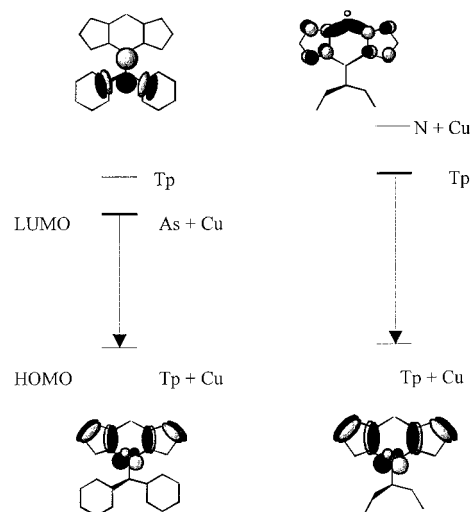


**Figure 4.** Contour diagrams of the calculated LUMO (top) and HOMO (bottom) of  $\text{CuTpAsPh}_3$ .

HOMO and LUMO are not small, the charge transfer is not “pure” ligand to ligand but instead is characterized as ligand to ligand with metal involvement. The  $\text{Cu } d \rightarrow s,p$  involvement is well-known for  $\text{Cu(I)}$  complexes. In a detailed study of tetramers, LLCT is highly mixed with intraligand and  $d \rightarrow s,p$  contributions.<sup>20,21</sup>

The importance of the involvement of the metal is found in the calculated HOMO and LUMO of the  $\text{ZnTpAsPh}_3^+$  complex. The HOMO of the zinc compound is similar to that of the copper complex except that it does not have any contribution from the metal atomic orbitals. The LUMO has a big contribution from the zinc with some participation from the arsine ligand. The HOMO–LUMO gap is bigger, shifting all the transitions to higher energy. If the LLCT were pure, changing from copper to zinc would not change the energy of this transition. As the absorption spectra confirm, the transition assigned to a LLCT moves to higher energy.

The  $\text{CuTp}$  complex containing the aliphatic amine ligand was chosen because the absence of  $\pi$  orbitals was expected to eliminate the possibility of low-lying ligand to ligand charge-transfer states. Calculations were carried out on  $\text{CuTpNEt}_3$  to provide insight into the lowest energy transition in this complex. The calculated HOMO (Figure 5) is mainly Tp ligand and copper metal in character, almost identical to that of the  $\text{CuTpAsPh}_3$  complex. In contrast, the LUMO (Figure 5) is almost entirely Tp in character, quite different from that of the arsine complex. In the case of the amine compound, the calculated HOMO to LUMO transition is metal to Tp ligand charge transfer with a contribution from a Tp-centered intraligand transition. This trend is similar to those reported for Tp complexes of  $\text{Ti(IV)}$  and  $\text{Re(I)}$ ; the Tp is a good donor, but MLCT to the  $\pi^*$  orbital is higher in energy.<sup>31</sup>



**Figure 5.** Calculated trends in orbital compositions and energies of  $\text{CuTpAsPh}_3$  (left) and  $\text{CuTpNEt}_3$  (right).

The interpretations of the transitions obtained from the MO calculations are consistent with those derived from the experimental results. The low-energy emission and absorption bands in the electronic spectra of  $\text{CuTpAsPh}_3$  are ligand to ligand charge transfer mediated strongly by the metal. Changing the metal from copper to zinc causes a large change in the transition energy because of the metal orbital participation. Changing the ligand from triphenylarsine to triethylamine removes the low-lying ligand orbital involved in the ligand–ligand charge transfer. The calculated direction of the electron transfer is consistent with the negative solvatochromism of  $\text{CuTpAsPh}_3$ .

## Summary

The electronic absorption and emission spectra of  $\text{CuTpAsPh}_3$  support the assignment of the lowest energy excited state as containing a large ligand to ligand charge-transfer component. A low-energy absorption band is observed in  $\text{CuTpAsPh}_3$  that is absent in comparison compounds. Negative solvatochromism is also observed. Resonance Raman experiments suggest that both the Tp and the  $\text{AsPh}_3$  ligands participate in the lowest energy transition. Changing the metal from copper to zinc causes a large increase in the transition energy, showing that the ligand to ligand charge transfer is not “pure” in the sense that metal orbitals are involved. Semiempirical MO calculations further support the interpretations and assignments.

The most important orbitals and a sketch of their energy changes as the ligand is varied from an arsine to amine are shown in Figure 5. The LLCT transition with copper participation is shown on the left. The transition is not “pure”; many orbital components are mixed, but the components from the two ligands are large. When the arsine is replaced with an amine ligand, the HOMO remains about the same but the amine-localized orbitals move higher in energy than the Tp-centered orbitals that become the LUMO. Thus the LLCT state is raised in energy.

**Acknowledgment.** This work was made possible by a grant from the National Science Foundation (CHE 9816552). J.C. acknowledges financial support from the Center of Molecular Science, and A.A. acknowledges support from the CONACYT of Mexico.