Structure and Assignment of the Luminescence of a New Mixed-Ligand Copper(I) Polymer

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Received August 29, 1996⊗

The synthesis and crystal structure of a new copper(I) polymer, $[\{(Ph_3P)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-pyrazine})\}_\infty]$, are reported. The polymer is photoluminescent with its emission maximum at 16 340 cm^{-1} at a temperature of 20 K. The emitting state is assigned with the assistance of excited state distortions determined by using resonance Raman intensities. The polymer consists of $(PPh_3)(pyz)Cu(\mu\text{-}Cl_2)Cu(pyz)(PPh_3)$ units in which pyrazine ligands bridge copper pairs to form a chain of dimers. The packing arrangement contains two inversion centers. Each dimer has an inversion center between the two coppers and the bridging chlorine atoms. A second inversion center is located in the center of the pyrazine ligand, which links the dimers in an infinite linear chain. The nitrogen atom of the pyrazine, the phosphorus atom of one triphenylphosphine, and the two chlorine atoms form a slightly distorted tetrahedron about the copper. The largest distortions in the lowest excited electronic state, determined from the resonance Raman intensities, occur along totally symmetric modes of the pyrazine ligand. The emission is assigned to copper(I) to pyrazine charge transfer.

Introduction

Luminescence spectroscopy of copper(I) complexes continues to attract attention because of the unusually large number of assignments of the emitting excited state and because of the challenges in identifying the nature of the emitting state.[1] Metal to ligand charge transfer is probably the most common assignment,[2−6] but in mixed-ligand complexes the identity of the ligand involved is sometimes difficult to ascertain. Ligand-centered emission is frequently concurrent with charge transfer, and dual emissions have been observed.[7−10] Copper-centered emissions ($d^{10} \rightarrow d^9s^1$) often have energies similar to those of the charge transfers,[11] and copper pair emission has also been identified.[12] Because the above types of emissions can occur in the visible region of the spectrum, assigning an emission from a new compound by comparing it with the assignments of emissions from similar compounds is risky.

Compounding the problems of assigning emitting states and increasing the interest in copper(I) compounds are the large numbers of stoichiometries that have been identified.[13] The coordination around the copper is frequently, but not always, based on a four-coordinate tetrahedral geometry. Species ranging from monomers, dimers, and tetranuclear cubic clusters to polymers have been identified. In addition, the multinuclear compounds exhibit a large variety of bridging ligand types ranging from a single bridging group (e.g. pyrazine) through multiple bridging ions (e.g. halides) to the multiple ligation in the cubic structures.[14−20]

Our interest in the luminescence spectroscopy of copper(I) complexes has centered around the assignments of emitting states assisted by resonance Raman-determined distortions in those states. For example, when large excited state distortions occur between atoms on a specific ligand, that ligand is implicated in the charge transfer transition. In the case of the photoluminescence of a cubic tetrameric copper(I) cluster containing a phosphole ligand, identification of large C═C bond length changes on that ligand assisted in assigning the emitting state as a metal-to-ligand charge transfer to the phosphole ligand.[20] During the course of our studies of emission from bridged copper(I) complexes, we obtained a unique mixed-ligand copper(I) polymer which contains a pair of copper(I) atoms bridged by two chlorides that in turn are bridged by pyrazine. The coordination shell around a given copper contains chloride, pyrazine, and triphenylphosphine ligands.

In this paper, we report the synthesis, crystal structure, and luminescence of the polymer *catena*-poly[(triphenylphosphinecopper)(μ-pyrazine)(triphenylphosphinecopper)bis(μ-chloro)], $[\{(Ph_3P)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-pyrazine})\}_\infty]$. The luminescence is compared to that of related copper complexes. Resonance Raman intensities are used to calculate the distortions along normal coordinates that occur in the emitting excited electronic state. The distortions are used to assign the emission to a copper to pyrazine charge transfer transition.

Experimental Section

Materials. Acetonitrile was dried by refluxing with P_2O_5, followed by distillation. Pyridine (py) was dried over potassium hydroxide for several days, followed by refluxing with barium oxide and fractional

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⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1997.

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S0020-1669(96)01059-2 CCC: $14.00

distillation. Benzene was dried by distilling slowly until the distillate was no longer cloudy. Methylene chloride was washed with concentrated sulfuric acid, dried over anhydrous sodium carbonate, refluxed over P_2O_5, and then distilled. Pyrazine (pyz) and triphenylphosphine (Aldrich) were used as received. Copper(I) chloride[21] and tetrakis[chloro(triphenylphosphine)copper(I)][22] were prepared according to literature methods.

Synthesis of $(PPh_3)_2Cu_2Cl_2(py)_2$. The mixed-ligand copper(I) dimer of chloro(pyridine)(triphenylphosphine)copper(I) was prepared by dissolving 5 mmol of $(PPh_3)_4Cu_4Cl_4$[22] in benzene and adding 10 mmol of pyridine. The solution was heated under reflux for 2 h. The white precipitate was collected by filtration and then washed with diethyl ether and dried in vacuo. Anal. Calcd for $CuClC_{23}H_{20}PN$: C, 61.00; H, 4.52; N, 3.41. Found: C, 60.85; H, 4.42; N, 3.43.

Synthesis of the Mixed-Ligand Copper(I) Polymer $[\{(Ph_3P)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-pyrazine})\}_\infty]$. Pyrazine (5 mmol) and triphenylphosphine (5 mmol) were added to deoxygenated acetonitrile (30 mL). The mixture was heated with stirring at 40 °C under N_2. Solid copper(I) chloride (5 mmol) was added to the boiling solution under dinitrogen. The reaction mixture was heated for 5 min and stirred with a stream of nitrogen until all the solid had dissolved. After the reaction mixture was cooled to room temperature, it was exposed to air and the product was collected by filtration as a red crystalline solid. Yield: 75%. The crystalline product was characterized by elemental analysis. Anal. Calcd for $C_{20}H_{17}ClCuNP$: C, 59.80; H, 4.27; N, 3.49. Found: C, 59.73; H, 4.24; N, 3.43.

Spectroscopy. Absorption spectra were recorded on a Shimatshu UV-260 spectrophotometer. The spectrum of the Cu(I) polymer was obtained for a finely ground Nujol mull, while that of the dimer was recorded in CH_2Cl_2 solution.

Luminescence spectra were acquired for powder samples of the dimer and for crystals of the polymer. The samples were mounted in a Displex closed-cycle helium refrigerator (Air Products) equipped with a thermocouple and cooled to 20 K. The emitted light was passed through a 0.75-m single monochromator (Spex). A cooled C31034 photomultiplier tube was used to detect the signal which was processed and stored in a computer. The samples were excited with wavelengths of 351.1, 488.0, and 515.5 nm from an argon ion laser.

Resonance Raman and Raman spectra were recorded using argon ion (457.9, 488.0, and 514.5 nm) or krypton ion (647.1 nm) excitation at room temperature. The laser beam was focused on the samples with a 150 mm focal length lens. The scattered light was collected and passed through a triple monochromator (Instruments SA, Inc., Models DHR320 and HR640) and detected by a charge-coupled device, CCD (Princeton Research). The wavelength was calibrated with the emission lines of a neon bulb. The resonance Raman intensities were measured by taking the integrated area of each peak.

X-ray Structure Determination. A suitable red parallelepiped of approximate dimensions 0.2 × 0.2 × 0.35 mm was mounted on the tip of a glass fiber and transferred to the 156 K nitrogen coldstream of a modified four-circle Picker diffractometer (Crystal Logic) for data collection and characterization. Accurate unit cell dimensions and the crystal orientation matrix were determined by a least-squares fit of the setting angles of 54 reflections with 2θ in the range 9−20° and are listed in Table 1 together with the experimental details. Data were collected by the $\theta/2\theta$ method using a scan speed of 6°/min up to a maximum 2θ of 50°. All data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ scans was applied.

The structure was solved in the monoclinic space group of $P2_1/n$ by conventional heavy-atom methods and Fourier techniques. All the hydrogen atoms were included in the calculated positions and were constrained to ride upon the appropriate carbon atoms. Of the total 2910 reflections measured, 2029 unique reflections with $I > 3\sigma(I)$ were used in the full-matrix least-squares refinement of 218 parameters, including positional and anisotropic thermal parameters of all nonhydrogen atoms. Refinement converged at $R = 0.026$ and $R_w = 0.034$ with GOF = 1.235. The final difference Fourier map was flat with a maximum residual of 0.59 e/Å^3.

Table 1. Crystallographic Data and Data Collection Parameters for the Cu(I) Polymer

empirical formula	$C_{20}H_{17}ClCuNP$
fw	401.33
crystal system	monoclinic
space group	$P2_1/n$
a, Å	13.090(7)
b, Å	8.831(4)
c, Å	16.273(9)
β, deg	94.35(2)
V, Å^3	1876(2)
Z	4
ρ(calcd), g cm^{-3}	1.421
T, °C	−142
radiation; λ, Å	Mo Kα; 0.710 73
μ, cm^{-1}	13.95
no. of unique reflcns	2910
no. of obsd reflcns ($I > 3\sigma(I)$)	2029
no. of params refined	218
$2\theta_{max}$, deg	50
R, R_w, GOF[a]	0.026, 0.034, 1.235

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$.

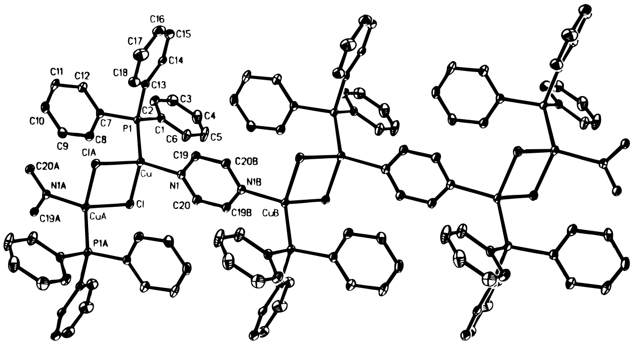

Figure 1. ORTEP plot of the Cu(I) polymer showing three repeating units.

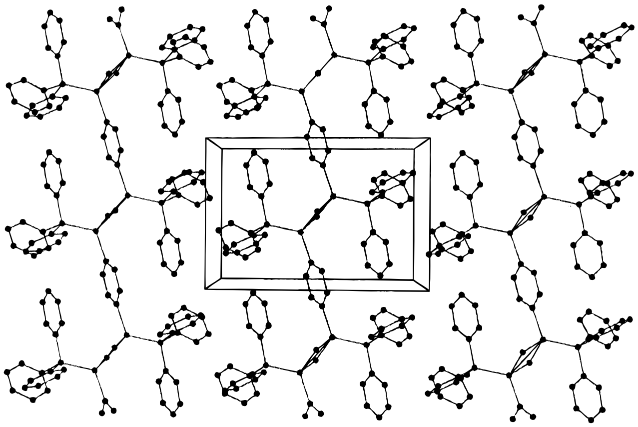

Figure 2. Packing diagram of the Cu(I) polymer.

Results

Structure of the Polymer. An ORTEP plot of the polymer is shown in Figure 1, and the packing arrangement is shown in Figure 2. Tables 1 and 2 give the selected fractional coordinates and bond lengths and angles. The dimer has an inversion center between the two coppers and in the center of the bridging pyrazine ligand that links the chloride-bridged copper pairs in an infinite chain. The geometry around each copper is a distorted tetrahedron. The Cu−Cu distance is 3.059(1) Å.

Optical Properties of the Polymer. The absorption and luminescence spectra of the Cu(I) polymer are shown in Figure 3. The Nujol mull absorption spectrum of the Cu(I) polymer at room temperature has a maximum at 20 200 cm^{-1} (495 nm)

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Table 2. Selected Distances (Å) and Angles (deg) for the Cu(I) Polymer

Distances (Å)			
Cu−N	2.044(3)	P−C(7)	1.824(3)
Cu−P	2.197(1)	P−C(13)	1.825(3)
Cu−Cl′	2.378(1)	N−C(19)	1.336(4)
Cu−Cl	2.381(1)	N−C(20)	1.341(4)
P−C(1)	1.822(3)		
Angles (deg)			
N−Cu−P	120.97(7)	C(1)-P−C(13)	105.6(1)
N−Cu−Cl	112.77(7)	C(1)-P-Cu	116.1(1)
N−Cu−Cl	103.49(8)	C(7)-P−Cu	113.2(1)
P−Cu−Cl	107.22(4)	C(13)-P−Cu	114.3(1)
P−Cu−Cl	110.32(4)	C(19)−N−Cu	122.2(2)
Cl−Cu−Cl	100.00(4)	C(20)−N−Cu	121.3(2)
Cu−Cl−Cu	80.00(4)		
C(1)−P−C(7)	101.8(1)		

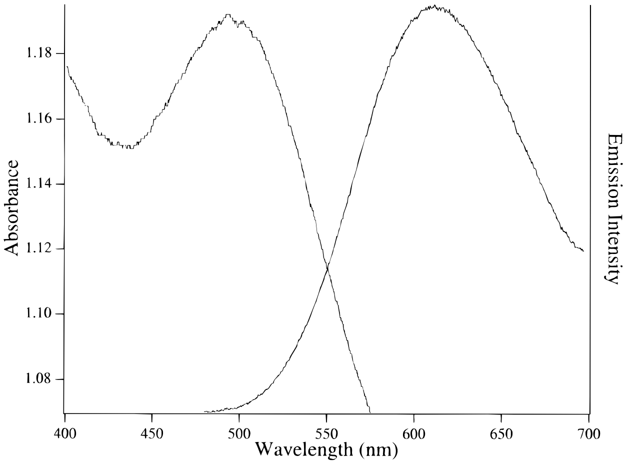

Figure 3. Absorption and luminescence spectra of the Cu(I) polymer. The absorption spectrum was acquired for a finely ground Nujol mull at 298 K. The emission spectrum of the solid Cu(I) polymer at 20 K, excited with 351.1 nm light, was recorded in the range 450−700 nm.

with a full width at half-maximum of approximately 3700 cm^{-1}. There is a strong sloping background in the Nujol mull absorption spectrum which complicates the measurement of the absorption bandwidth. The reflectance spectrum shows the maximum absorbance at the same wavelength. The luminescence spectrum of the polymer at 20 K excited with 488 nm light has a maximum at 16 340 cm^{-1} (615 nm) and has a full width at half-maximum of 3050 cm^{-1}. The room-temperature luminescence is broader and much less intense with its band maximum near 14 500 cm^{-1}.

Raman Spectroscopy of the Polymer. A list of the observed frequencies and the assignments of the bands in the Raman spectrum of the Cu(I) polymer are given in Table 3. A resonance Raman spectrum of the polymer excited at 514.5 nm is shown in Figure 4. The most intense peaks are observed at 638, 1000, 1020, 1226, and 1586 cm^{-1}. The most intense peak observed in the nonresonance spectrum excited at 647.1 nm is the 638 cm^{-1} band, while the 1586 cm^{-1} peak is the most intense with resonant excitation. The resonance Raman intensities at 457.9, 488.0, and 514.5 nm with intensities down to 10% of that of the most intense peak at 1585 cm^{-1} are given in Table 4. The resonance Raman intensity ratios remain constant within experimental error with the different excitation wavelengths.

Optical Spectroscopy of the Dimer. The absorption and emission spectra of the copper dimer complex are shown in Figure 5. The maximum of the emission spectrum occurs at 19 605 cm^{-1} (510 nm) with a full width at half-maximum of 3065 cm^{-1}. The full width at half-maximum of the dimer's emission spectrum is comparable to that of the polymer.

Table 3. Raman Frequencies and Assignments

obsd freq, cm^{-1}	assignment
173	ν(Cu−Cl)
182	
205	
222	ν(Cu−Cl)
253	ν(Cu−P)
260	ν(Cu−P)
270	ν(Cu−P)
434	ν(Cu−N)
440	ν(Cu−N)
525	pyz ring, B_{2g} (ν_{6b})
620	PPh_3, s δ(C-C) ring
638	pyz ring, A_g (ν_{6a})
670	
685	PPh_3, r X-sens
741	PPh_3, γ(C−H) p-ring
745	pyz ring, B_{1g} (ν_{10a}) or f γ(C−H) p-ring
905	PPh_3, i γ(C−H) p-ring
1000	pyz ring
1012	
1019	pyz ring, $A_{g\,(\nu 1)}$
1025	PPh_3, b β(C−H)
1100	PPh_3, q X-sens
1105	PPh_3, q X-sens
1219	PPh_3, q X-sens
1228	pyz ring, A_g (ν_{9a})
1258	PPh_3, e β(C−H)
1570	
1577	$PPh_{3,\,1\,\nu(C-C)}$
1586	pyz ring, $A_{g\,(\nu 8a)}$
1605	
1654	

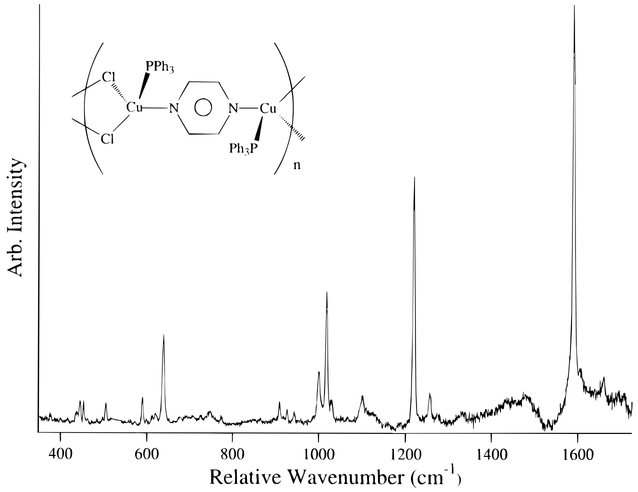

Figure 4. Resonance Raman spectrum of the solid Cu(I) polymer excited with 514.5 nm light.

Table 4. Resonance Raman Intensities and Bond Distortions (Δ) in the Cu(I) Polymer

freq, cm^{-1}	457.9 nm	488.0 nm	514.5 nm	av ratio	rel Δ	abs Δ
638	0.22 ± 0.08	0.19 ± 0.03	0.20 ± 0.05	0.20	1.12	1.43
1000	0.07 ± 0.03	0.09 ± 0.04	0.12 ± 0.05	0.09	0.48	0.62
1020	0.32 ± 0.12	0.23 ± 0.05	0.27 ± 0.07	0.27	0.81	1.04
1025	0.03 ± 0.01	0.05 ± 0.02	0.08 ± 0.02	0.05	0.36	0.46
1100	0.09 ± 0.03	0.13 ± 0.04	0.11 ± 0.03	0.11	0.48	0.61
1228	0.58 ± 0.21	0.50 ± 0.11	0.47 ± 0.10	0.52	0.93	1.19
1258	0.09 ± 0.04	0.08 ± 0.02	0.07 ± 0.03	0.08	0.36	0.46
1586	1.00	1.00	1.00	1.00	1.00	1.28

Conductivity of the Polymer. The conductivity of the polymer was measured with a standard four-point probe method with an EG&G Princeton Applied Research potentiostat/galvanostat, Model 273. The conductivity was less than 10^{-8} S cm^{-1}.

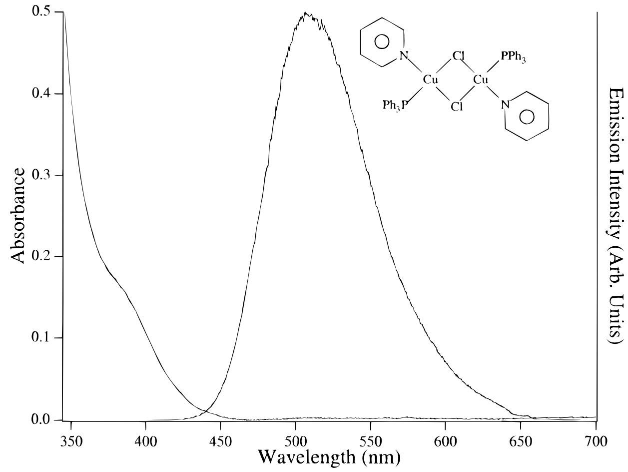

Figure 5. Absorption and luminescence spectra of $(PPh_3)Cu_2Cl_2(py)$.

Discussion

1. Structure. The polymer consists of $(PPh_3)_2Cu(\mu\text{-}Cl)_2Cu(pyz)$ units in which a bridging pyz ligand between two copper pairs forms a connecting polymeric chain of dimers. The packing arrangement contains two inversion centers. Each dimer has an inversion center between the two coppers and the bridging chlorine atoms. A second inversion center is located in the center of the pyz ligand, which links the dimers in an infinite linear chain.

The nitrogen atom of pyz, the phosphorus atom of one PPh_3, and the two chlorine atoms form a slightly distorted tetrahedron about the copper. The pyz−Cu−P angle is 120.97(7)° and pyz−Cu−Cl is 108.13° (average). The angles P−Cu−Cl, Cl−Cu−Cl, and Cu−Cl−Cu are 108.76, 100.00, and 80.00°, respectively.

The Cu−Cu distance in the polymer of 3.059(1) Å is typical of that in halide-bridged copper(I) complexes. It is longer than the sum of the van der Waals radii of copper(I) (2.8 Å) and suggests that there is no significant metal−metal bonding interaction. The distance is shorter than that in the polymers $[\{Cu_2(\mu\text{-}Cl)_2(\mu\text{-}phz)\}_\infty]$ (3.258(1) Å) and $[\{Cu_2(\mu\text{-}Br)_2(\mu\text{-}phz)\}_\infty]$ (3.391(2) Å) but longer than that in $[\{Cu_2(\mu\text{-}I)_2(\mu\text{-}phz)\}_\infty]$ (2.525(1) Å).[23] The metal−ligand distances are typical for copper(I) complexes. In comparison with distances in similar polymers, the Cu−N distance of 2.044(3) Å is longer than the 1.993(8) Å distance in $[\{Cu(\mu\text{-}Cl)(py)\}_\infty]$[23] and the Cu−Cl distance of 2.379(1) Å is shorter than the 2.419(4) Å distance in $[\{Cu(\mu\text{-}Cl)(py)\}_\infty]$.[23]

2. Optical Properties. A. Absorption Spectra. The absorption spectrum of the copper polymer complex shows a band at 495 nm. This transition could be interpreted as the promotion of an electron from the valence band to the conduction band. The energy of the band gap in the copper polymer is approximately 2.25 eV corresponding to an E_{00} of 550 nm. However, the width of the absorption band (0.46 eV) is small for a solid-state material, suggesting that the widths of the conduction and valence bands are narrow in energy. Thus the electronic transition can be approximately described in terms of molecular orbitals within a repeating unit.

B. Emission Spectra. The emission spectrum of the copper polymer, shown in Figure 3, has its maximum at 16 340 cm^{-1}. The full width at half-maximum, 3050 cm^{-1}, is similar to that of the lowest energy absorption band, and the two electronic spectra overlap in the region 18 180 cm^{-1}. Both the overlap and the similarity of the bandwidths suggest that the emitting state is the same as that giving rise to the lowest energy absorption.

The assignment of the lowest electronic excited state in the copper polymer poses an interesting problem. The transition could be charge transfer in nature, most likely copper to ligand charge transfer because the oxidation state of the copper in the polymer is +1. There are two possibilities: copper to pyrazine or copper to triphenylphosphine charge transfer. Another strong possibility that has been proposed for many copper(I) complexes is a metal-centered d to s orbital transition. Still another possibility is ligand-centered emission; such assignments have been made for complexes with heterocyclic ligands containing nitrogen. Finally, an interligand charge transfer is possible, but this assignment is highly unlikely because of the relatively low energy of the observed emission. Many of the reported luminescent Cu(I) complexes show a large Stokes shift such that the emission and absorption bands do not overlap. The shift may be caused by Cu(I) pair formation.[1,12] Because the Stokes shift in the polymer is normal and because the copper−copper distance precludes strong interaction between the Cu(I) centers, it seems unlikely that the transition involves a Cu(I)−Cu(I) interaction.

Mixed-ligand complexes of the general formula $[Cu(PPh_3)_2\text{-}NN]^+$, where NN denotes a derivative of 1,10-phenanthroline or 2,2′-bipyridine, are closely related to the Cu(I) coordination site of the polymer.[2] In the complex $[Cu(PPh_3)_2(phen)]^+$ two emissions at 608 and 575 nm were observed and were tentatively assigned as $d-\pi^*$ charge transfer.[3,4] However, a metal-centered d−s orbital transition was not ruled out. The photophysical properties of a series of dinuclear complexes with the general formula $[\{Cu(PPh_3)_2\}_2L]^{2+}$ (where L is a diimine ligand) were recently studied.[5] The lowest energy absorption band was assigned as a $d(Cu) \rightarrow \pi^*(L)$ metal-to-ligand charge transfer and a higher energy emission between 400 and 500 nm was assigned as ligand centered.[5]

A structurally dependent luminescence was reported for the complex $[(\mu\text{-}bipyrimidine)\{Cu(PPh_3)_2\}_2](BF_4)_2$.[6] This complex displays a strong luminescence in the solid state which is not so intense in $CHCl_3$ solution, after anion exchange, and which is also not so intense when other monodentate phosphine ligands PR_3 are used.[6] The emission was assigned as copper to bipyrimidine charge transfer.

The photophysical properties of $[Cu(NN)_2]^+$ complexes have been extensively studied. The complex $[Cu(dmp)_2]^+$ (where dmp is 2,9-dimethyl-1,10-phenanthroline) has an emission maximum at 730 nm.[7] The complexes $[Cu(bcp)_2]^+$ (where bcp is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) and $[Cu(tmbp)_2]^+$ (where tmbp is 4,4′,6,6′-tetramethyl-2,2′-bipyridine) have emission maxima at 685 and 680 nm, respectively.[8,9] These emissions arise from multiple excited states in thermal communication because both the emission intensity and the energy increase with increasing temperature.[10] The emissions were proposed to involve ligand-centered $\pi-\pi^*$ transitions and metal to ligand charge transfer transitions.

There is extensive literature on the emission of polynuclear copper(I) complexes. In the trinuclear Cu(I) complex $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]^+$, where dpmp is bis(diphenylphosphinomethyl)methylphosphine, an emission at 560 nm was assigned as a metal-centered $3d^94s^1 \rightarrow 3d^{10}$ transtion.[11] The tetranuclear copper complex $Cu_4I_4(dmmp)_4$, where dmmp is 1-phenyl-3,4-dimethylphosphole, emits at 15 000 cm^{-1}.[20] The emission was assigned as copper to dimethylphosphole charge transfer. The copper cubic mixed-metal tetrameric cluster $(DENC)_3Cu_4(NS)Cl_4$ emits around 15 000 cm^{-1}.[19] $Cu_4I_4(py)_4$

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has an emission maximum of 580 nm at 294 K while its maximum is 619 nm at 77 K in the solid state.[14] Extensive experimental studies[14−16] and molecular orbital calculations[17,18] have been carried out on the cubic complexes, and the lowest state was defined as a triplet cluster-centered (^{3}CC) excited state with roughly equal contributions from halide-to-metal charge transfer (XMCT) and Cu d → s character to the excited states.

The assignment of the emission in the polymer cannot be made solely on the basis of comparisons of its transition energy with those of analogous compounds reported in the literature. The polymer's 19 600 cm^{-1} (510 nm) emission band falls well within the range of emissions that have been assigned to charge transfer transitions and to metal-centered transitions. Intraligand transitions and interligand transitions can probably be ruled out because they generally occur at higher energies. Likewise, transitions involving interactions between the coppers can probably be eliminated because of the distance between the metal atoms in the polymer. Resonance Raman data, discussed in the next section, are necessary to assign the transition.

3. Resonance Raman Spectra and Distortions. Vibrational modes which show a large resonance enhancement in a resonance Raman spectrum have large excited state distortions. The information about highly displaced vibrational modes can aid in the assignment of the resonant excited state. For example, if the enhancement is caused by a metal to ligand charge transfer transition, vibrational modes on the acceptor ligand will be enhanced because the bond length and bond order will be changed. If the electronic transition is ligand-to-ligand charge transfer then enhancement of vibrational modes on both ligands would be observed.[24]

A. Vibrational Assignments. The vibrational assignments for the Cu(I) polymer are based on the literature assignments for the free ligands pyz and PPh$_3$ and for coordination compounds containing these ligands. The vibrational modes in the Cu(I) polymer attributable to pyz were assigned in comparison to the enhanced pyz modes observed in the resonance Raman spectrum of the Creutz−Taube (CT) ion (where pyz bridges two Ru ions)[25] and in the infrared and Raman spectra of free pyz.[26,27] For the CT ion, resonantly enhanced vibrational modes corresponding to totally symmetric stretching motions of the bridging pyz ligand were observed at 697, 1004, 1232, and 1596 cm^{-1}. For the Cu(I) polymer, the 638 cm^{-1} mode was assigned as the A$_g$ (ν_{6a}) mode from the pyz ring. The ν_{6a} mode was assigned at 609 cm^{-1} for free pyz and 697 cm^{-1} for the CT ion. The 1020 cm^{-1} mode of the polymer was assigned as the A$_g$ (ν_1) mode; it was observed at 1015 cm^{-1} for free pyz and 1004 cm^{-1} for the CT ion. The 1228 cm^{-1} mode of the polymer was assigned as the A$_g$ (ν_{9a}) pyz ring mode, which was observed at 1232 cm^{-1} for free pyz and the CT ion. The 1586 cm^{-1} mode of the polymer was assigned as A$_g$ (ν_{8a}); it was observed at 1584 cm^{-1} for free pyz and 1596 cm^{-1} for the CT ion. Other vibrational modes attributable to pyz are given in Table 3.

The vibrational modes for the Cu(I) polymer that arise from the PPh$_3$ ligand are based on the Raman spectrum of PPh$_3$[28] and coordination compounds with PPh$_3$ such as (Ph$_3$P)$_3$CuCl.[29] The vibrational modes assigned to PPh$_3$ are given in Table 3 and are based on the nomenclature of Whiffen[30] for monosubstituted benzene molecules. The 1025, 1100, and 1258 cm^{-1} modes observed in the resonance Raman spectrum of the Cu(I) polymer were assigned as PPh$_3$ modes. The 1025 cm^{-1} mode was assigned as b β(C−H), the 1100 cm^{-1} mode was assigned as q X-sens, and the 1258 cm^{-1} mode was assigned as e β(C−H). The corresponding modes were observed at 1024, 1098, and 1269 cm^{-1} for free PPh$_3$.

In some cases the vibrational modes for the PPh$_3$ and pyz ligands have similar frequencies and the assignments are ambiguous. The most intense band observed in the Raman spectrum of the free PPh$_3$ ligand was observed at 1000 cm^{-1} and was assigned as a p-ring vibration. However, a band at 1004 cm^{-1} that was attributed to the pyz ring was observed in the resonance Raman spectrum of the CT ion. We assigned the 1000 cm^{-1} band in the resonance Raman spectrum of the Cu(I) polymer as a pyz ring vibration because it exhibits a large resonance enhancement.

Bowmaker has done extensive studies on the vibrational spectroscopy of chloride-bridged copper dimer complexes. For the copper complex [PPh$_3$Cu(μ-Cl$_2$)Cu(PPh$_3$)$_2$] bands at 220 and 179 cm^{-1} were assigned as ν(Cu−Cl).[31] In the complex (Ph$_3$P)$_3$CuCl bands at 283 cm^{-1} were assigned as ν(Cu−Cl), while bands at 233 and 226 cm^{-1} were assigned as ν(Cu−P).[29]

B. Excited State Distortions. The determination of excited state distortions from resonance Raman intensities is a method that has been applied to a wide variety of molecules with different types of electronic transitions.[32] A detailed description of the method has been presented in the literature[33,34] but it is briefly reviewed here. Relative bond distortions are determined from the relative resonance Raman intensities using Savin's formula[34−36]

$$\frac{I_k}{I_{k'}} = \left(\frac{\Delta_k \omega_k}{\Delta_{k'} \omega_{k'}}\right)^2 \qquad (1)$$

where I_k is the resonance Raman intensity, Δ_k is the dimensionless bond distortion, and ω_k is the vibrational frequency of the kth mode. The relative distortions are converted into absolute distortions using the absorption spectrum[33]

$$2\sigma^2 = \sum_k {\Delta_k}^2 {\omega_k}^2 \qquad (2)$$

where $2\sigma^2$ is the full width of the absorption spectrum at $1/e$ of its height. The relative resonance Raman intensities at 457.9, 488.0, and 514.5 nm, the relative bond distortions, and the dimensionless bond distortions are given in Table 4.

The ratios of the resonance Raman intensities remain constant within experimental error with all of the wavelengths in resonance with the lowest energy absorption band. Because the relative intensity ratios are constant, the ratios of the calculated distortions also remain constant. Therefore, measurement of the complete resonance Raman excitation profiles for the modes is not necessary.

The distortions determined from the resonance Raman intensities provide a quantitative measure of the bond length

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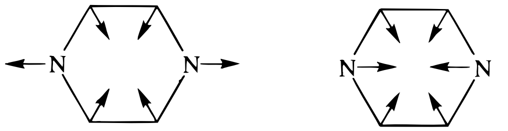
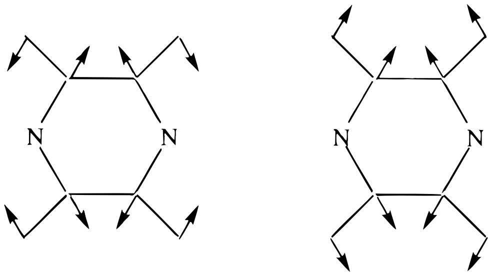
Chart 1



ν_{6a}, 638 cm^{-1} $\Delta = 1.43$ ν_1, 1020 cm^{-1} $\Delta = 1.04$



ν_{9a}, 1228 cm^{-1} $\Delta = 1.19$ ν_{8a}, 1586 cm^{-1} $\Delta = 1.28$

changes along the normal coordinates. The vibrational modes of the pyz ring have the largest distortions. The four largest distortions are calculated in the 638, 1020, 1228, and 1586 cm^{-1} modes, which correspond to pyz symmetric ring-stretching vibrations. The distortions and the atom vector displacements of the four modes having the largest displacements are given in Chart 1.

The calculated distortions assist in the assignment of the lowest excited state in the polymer. Vibrational modes that are involved in the electronic transition will be enhanced in the resonance Raman spectrum. Modes corresponding to totally symmetric pyz ring-stretching vibrations have the largest distortions. Therefore, the magnitudes of the distortions support the assignment of the lowest excited state as a charge transfer to the pyz ligand. The excited state is probably Cu(I) to pyrazine metal-to-ligand charge transfer, but halide to metal charge transfer (as proposed for tetrameric clusters) is not ruled out by the Raman data.

C. Assignment of the Lowest Excited State in the Polymer. There is a red shift of 3330 cm^{-1} in the emission maximum of the pyrazine-containing polymer compared with that of the pyridine-containing dimer. The shift can be explained in terms of an electronic effect involving the nature of the diimine ligand. For tungsten pentacarbonyl diimine complexes, when the diimine ligand is changed from py to pyz, there is a red shift of 4100 cm^{-1} in the emission maximum between the two ligands. For W(CO)$_5$pyz[37] the emission maximum is 645 nm, while for W(CO)$_5$py[38,39] the emission maximum is 510 nm. A major contributor to the red shift is the decrease in the energy of the acceptor ligand π^* orbital of pyz compared with py.

A similar trend was observed by Ford[40] in the MLCT energies of Ru(II) pentammine complexes with pyridine and pyrazine ligands. For the complex Ru(NH$_3$)$_5$(py) the MLCT absorption maximum was observed at 408 nm, while for the pyrazine complex Ru(NH$_3$)$_5$(pyz) the MLCT absorption maximum was observed at 472 nm. The shift in the absorption maxima of 3320 cm^{-1} is very similar to the shift in the emission maximum of the py-containing dimer compared to that of the pyz-containing polymer.

Summary

The synthesis, structure, and spectroscopy of a new Cu(I) polymer have been reported. The luminescence observed in the polymer is compared with that of other Cu(I) complexes. The lowest excited state in the Cu(I) polymer is assigned as a Cu(I) to pyz metal-to-ligand charge transfer excited state on the basis of resonance Raman experiments, distortions determined from the resonance Raman spectra, and comparisons with similar mononuclear, dinuclear, trinuclear, and tetranuclear Cu(I) molecules.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-9509275). We thank Ian Ball and Professor Richard B. Kaner for assistance with the conductivity measurements.

Supporting Information Available: Tables of positional and thermal parameters, bond lengths and angles, and data collection and structure refinement details (6 pages). Ordering information is given on any current masthead page.

IC9610593

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