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Photoluminescence of Tetrameric Copper(I) Iodide Complexes in Solution

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Abstract: The colorless complexes $[Cu(py)I]_4$ and $[Cu(mor)I]_4$ (py = pyridine; mor = morpholine) were shown to be photoluminescent in noncoordinating solvents such as benzene, CH_2Cl_2, or acetone at room temperature. The red emission (λ_{max} = 698 nm) of the pyridine complex in benzene is quite intense (Φ = 0.04) and decays with a lifetime of $\tau = 0.9 \times 10^{-6}$ s. The red photoluminescence (λ_{max} = 654 nm) of the morpholine complex is much weaker (Φ = 0.004) and decays with $\tau = 0.3 \times 10^{-6}$ s. It is suggested that the emitting state of both complexes is a metal-centered $3d^94s^1$ excited state of Cu(I), but this state is strongly modified by copper–copper interaction in the tetramer which consists of a $[CuI]_4$ cubane core.

During recent years a few Cu(I)–phosphine complexes were shown to be weakly luminescent in solution at room temperature.[1,2] The emitting states were assigned to metal-to-ligand charge-transfer (CT) or perturbed intraligand (IL) excited states.[1-5] In addition, a large number of other Cu(I) complexes of the general composition Cu(L)X (L = nitrogen base and X = halogen) were observed to be intensely luminescent at ambient temperatures, but only in the solid state.[6-9] The emission behavior of these solid compounds is rather complicated, and its origin does not seem to be very clear. Some of the solid complexes show very large red shifts of the emission when it is compared with the absorption. A typical example is the complex [Cu(py)I], which emits a dual luminescence dependent on its solid-state structure.[10] As the tetramer $[Cu(py)I]_4$, the colorless compound undergoes a strong yellow emission at room temperature.[7-10]

We report here the observation of the luminescence of $[Cu(L)I]_4$ with L = pyridine (py) and morpholine (mor) in solution at room temperature. Emission quantum yields and lifetimes were determined. The emission which is quite intense in the case of the pyridine complex is attributed to a copper-centered $3d^94s^1$ excited state which is strongly modified by metal–metal interaction in the tetramers which consist of a $[CuI]_4$ cubane core.

Experimental Section

Materials. The complexes $[Cu(py)I]_4$[7,11] and $[Cu(mor)I]_4$[12] were prepared as colorless crystals by the method of Hardt et al. The crystalline materials dissolve rather slowly in weakly coordinating solvents. When precipitated from benzene solution by addition of hexane the complexes are obtained as powders which dissolve more readily. It was suggested that $[Cu(py)I]_4$ decomposes in benzene, yielding CuI.[7] According to our observations, dilute solutions of $[Cu(py)I]_4$ and $[Cu(mor)I]_4$ in benzene are stable at room temperature for several hours. Upon standing longer and at higher temperatures the solutions become cloudy due to the precipitation of CuI. Molecular weights of $[Cu(py)I]_4$ and $[Cu(mor)I]_4$ were determined by osmometry in solutions of benzene at 37 °C. At this temperature the complexes decomposed slowly. By extrapolation the following molecular weights were obtained: $[Cu(py)I]_4$ calcd 1078, found 1100; $[Cu(mor)I]_4$ calcd 1110, found 1102.

All solvents for spectroscopic measurements were spectrograde. Methyl methacrylate resin was commercial Paraloid B 72 (Roth, West Germany).

Instrumentation. Absorption spectra were measured on a Uvikon 810 absorption spectrometer. Emission spectra were obtained on a Hitachi 850 spectrofluorimeter which was equipped with a Hamamatsu 928 photomultiplier. All emission spectra were corrected for monochromator and photomultiplier efficiency. Luminescence quantum yields were determined by comparing the integrated emission intensity of the dissolved copper complexes with that of europium thenoyltrifluoroacetonate in acetone (λ_{max} = 612 nm, Φ = 0.56).[13] At the exciting wavelength λ = 313 nm the optical density of all solutions was adjusted to E = 0.69. Emission lifetimes were measured on an apparatus equipped with a nitrogen laser (λ_{exc} = 337 nm) and a gated vidicon (B and M Spectronic). This instrument will be described elsewhere.[14]

Results

The complexes $[Cu(py)I]_4$ and $[Cu(mor)I]_4$ are soluble in a variety of solvents such as benzene, CH_2Cl_2, acetone, acetonitrile, and pyridine. A determination of the molecular weight in benzene confirmed the tetrameric composition. However, in coordinating solvents such as pyridine the tetrameric structure is apparently broken off. It was shown previously that $[Cu(py)I]_4$ converts to monomeric $[Cu(py)_3I]$.[7]

The absorption spectra of $[Cu(py)I]_4$ and $[Cu(mor)I]_4$ (Figure 1) in benzene and other solvents are rather featureless and characterized by an increase of the extinction extending from about 400 nm to shorter wavelength. The solvent cutoff below 300 nm prevents measurements at shorter wavelength.

Upon excitation of $[Cu(py)I]_4$ at λ = 366 nm, a quite intense red luminescence appeared at λ_{max} = 698 nm (Figure 1). The quantum yield of emission is $\Phi = 0.04 \pm 0.01$ and only slightly quenched in the presence of air ($\Phi = 0.03 \pm 0.01$). The emission decayed with a lifetime of $\tau = 0.9 \times 10^{-6}$ s. In other noncoordinating or weakly coordinating solvents such as CH_2Cl_2 or acetone, the red emission appeared too but was distinctly weaker than that observed in benzene. In pyridine or acetonitrile the emission was completely absent. The luminescence is apparently restricted to the tetrameric structure. The monomeric complex $[Cu(py)_3I]$ which is formed in pyridine solution is known to be not luminescent at room temperature even in the solid state.[7] For an evaluation of the influence of solvent viscosity on the emission wavelength the complex $[Cu(py)I]_4$ was incorporated into a matrix of methyl methacrylate resin. The complex and the resin were dissolved in toluene. Upon evaporation of the solvent at room temperature the resin formed a film on a glass disk. The emission of $[Cu(py)I]_4$ in this matrix appeared at λ_{max} = 610 nm.

The emission behavior of $[Cu(mor)I]_4$ is quite analogous to that of $[Cu(py)I]_4$. In benzene solution $[Cu(mor)I]_4$ shows the red luminescence at λ_{max} = 654 nm (Figure 1). However, the quantum yield ($\Phi = 0.004 \pm 0.002$) was much lower than that of the

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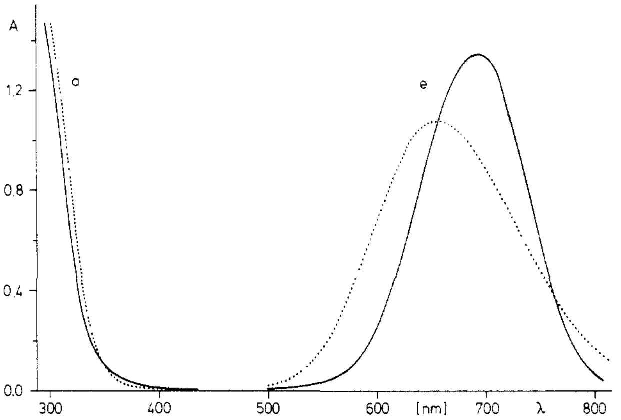

Figure 1. Electronic absorption (a) and emission (e) spectra of $[Cu(py)I]_4$ (—) and $[Cu(mor)I]_4$ (···) in benzene at 298 K. Absorption: 0.82 × 10^{-3} M $[Cu(py)I]_4$ and 0.45 × 10^{-3} M $[Cu(mor)I]_4$ concentration, 1-cm cell. Emission: $\lambda_{exc} = 313$ nm, intensity in arbitrary units.

corresponding pyridine complex. The emission decayed with a lifetime of $\tau = 0.3 \times 10^{-6}$ s.

Discussion

What is the nature of the emitting excited state of $[Cu(py)I]_4$ and $[Cu(mor)I]_4$? The most remarkable observation is the extremely large energy difference between absorption and emission (Figure 1). Due to the relatively long lifetime the emission is most likely associated with a spin-forbidden transition. Since the ground state is a singlet, the emitting state is probably a triplet. It may not be observed in absorption due to a very low extinction coefficient. For many first-row transition-metal complexes, spin-forbidden transitions cannot be easily detected in absorption because spin-orbit coupling ("heavy-atom effect") is rather small compared to that of second- and third-row transition metals.[15] This may explain in part the large shift from absorption to emission. A large excited-state distortion seems also to contribute to this red shift as discussed below.

Of which parentage are the orbitals involved in this emission? For Cu(I) with the filled d-shell (d^{10}), LF states do not exist. CT transitions from the ligand to the metal certainly do not occur at low energies since Cu(I) is rather reducing and not oxidizing as it would be required for low-energy CT transitions of this type. CT transition in the opposite direction from the metal to the ligand (MLCT) may be expected to appear at low energies in the case of the pyridine complex since this ligand has available empty π^* orbitals. However, the morpholine ligand as an aliphatic amine is saturated and does not provide empty low-energy orbitals. Consequently, low-energy MLCT transitions are not possible for $[Cu(mor)I]_4$. In view of the similarity of the absorption and emission spectra of the morpholine and pyridine complex it is assumed that the emitting state of both complexes is of common origin but not of the CT type.

We suggest that the emitting state is related to the metal-centered excited state $3d^94s^1$ of Cu(I).[16,17] However, only the tetrameric complexes, but not the monomer $[Cu(py)_3I]$, show the emission.[7] The tetramers consist of a $[CuI]_4$ cubane core with rather short Cu–Cu distances which are 2.69 Å for the pyridine[11] and between 2.59 and 2.71 Å for the morpholine complex.[12] It follows that the emitting $3d^94s^1$ state of Cu(I) should be strongly modified by the copper–copper interaction in the tetramer.

In the ground state of $[Cu(L)I]_4$ the metal–metal bonding is certainly rather weak.[18] The d-orbital overlap of the 4 Cu atoms should not lead to any bonding[18] when the resulting bonding (a_1 + e + t_2) and antibonding (t_1 + t_2) orbitals are completely occupied by 24 electrons of the 4 Cu(I) ions.[19] The remaining 16 electrons occupy orbitals (e + t_1 + t_2) which are essentially Cu–Cu nonbonding.[19] However, in analogy to certain binuclear Pt(II) complexes such as $[Pt_2(H_2P_2O_5)_4]^{4-}$[20-23] a configuration interaction of these MOs of d-parentage with empty orbitals generated by the overlap of 4s and 4p atomic orbitals of the Cu_4 unit yields some net bonding for the filled d-orbitals.[18] The lowest energy transition of the Cu_4 core may involve the promotion of an electron from an antibonding d-orbital to an empty s-orbital at higher energies. The excited state thus formed is expected to be strongly contracted and distorted. The contraction should take place because of an increase of Cu–Cu bonding in the excited state. Strong distortions were also observed for Fe_4S_4 clusters when the number of electrons populating metal–metal antibonding d-orbitals of the Fe_4 unit changed.[24] Taking into account these considerations, the huge long-wavelength displacement of the emission of $[Cu(py)I]_4$ seems to be caused, at least partially, by a large Stoke's shift due to a strong excited-state distortion. When compared with the yellow emission of solid $[Cu(py)I]_4$ (λ_{max} = 585 nm)[10] the red shift for the luminescence in solution can be explained by larger structural changes which can take place in solution but not in the rigid lattice of the solid. This assumption is supported by the emission of the complex incorporated in a polymer matrix. This matrix is certainly not as rigid as the solid state, but the flexibility should be restricted in comparison to the fluid solution. In agreement with this assumption the emission maximum of $[Cu(py)I]_4$ in the resin appears at λ = 610 nm.

In summary, it should be emphasized that the observation of emission of these tetrameric copper(I) complexes in solution at room temperature adds an interesting new system to the general subject of photoluminescence of coordination compounds. The complexes $[Cu(L)I]_4$ are easily synthesized starting from rather inexpensive materials. One can anticipate a variety of interesting experiments utilizing the luminescence of these compounds.

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Registry No. $[Cu(py)I]_4$, 62121-41-9; $[Cu(mor)I]_4$, 55188-35-7.

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