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⑥ Room-Temperature Fluorescence of Substituted Copper(I) Benzenethiolates

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ROOM-TEMPERATURE FLUORESCENCE OF SUBSTITUTED COPPER(I) BENZENETHIOLATES

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ABSTRACT

The room-temperature fluorescence of copper(I) complexes of substituted benzenethiols is discussed. The fluorescence can be excited over a wide range of excitation wavelengths with no change in the position of the emission band which occurs at 590 ± 5 nm. The maximum emission is observed at an excitation wavelength of 470 nm which corresponds to the maximum in the excitation spectrum. The observed transition is assigned as the π^*-d type which is inverse of the lowest energy charge-transfer transition where the Cu(I) ion d-electron is excited to a π^* orbital of the ligand. The complexes interact with pyridine to form loosely bound adducts which exhibit yellow to green fluorescence.

pi*

pi*-d

INTRODUCTION:

In the course of our studies on the electrical properties of transition metal mercaptides of 1,4-dimercaptobenzene[1], we found a weak pink-red fluorescence emission in copper(I) benzenethiolate, C_6H_5SCu, under uv illumination at room temperature. This fluorescence depends strongly on the nature of substitution on the phenyl ring. Subsequently, we prepared and examined the fluorescence characteristics of a number of copper(I) complexes of substituted benzenethiols. Of the various substituents investigated, the 4-bromo, 4-chloro and 2,5-dichloro substituents enhanced the fluorescence emission of the parent copper(I) benzenethiolate. In this communication, the absorption, emission, and the excitation spectra of the copper(I) complexes of 4-bromobenzenethiol, 4-chlorobenzenethiol, 2,5-dichlorobenzenethiol, and benzenethiol are reported. The objectives of the study were to assign the observed fluorescence transition and to gain an understanding into the mechanism of energy transfer in these complexes.

EXPERIMENTAL:

Preparation of complexes. The complexes were prepared by slowly adding an ethanolic solution of cupric chloride to boiling solution of the corresponding benzenethiol in ethanol, using a 100% excess of the thiol. The reaction mixture was refluxed for four hours under nitrogen. The bright yellow insoluble complex in each case was filtered, washed with boiling ethanol and benzene, and dried *in vacuo* at 150°C. Analysis found: C, 41.62; H, 2.92; S, 18.85; Cu, 36.88. Analysis calcd. for C_6H_5SCu: C, 41.73; H, 2.89; S, 18.56; Cu, 36.80. Analysis found: C, 29.79; H, 1.28; S, 13.42; Cu, 26.58; Cl(by difference), 28.93. Analysis calcd. for $C_6H_3(Cl_2)SCu$: C, 29.83; H, 1.24; S, 13.27; Cu, 26.30; Cl, 29.35. Analysis found: C, 28.34; H, 1.40; S, 12.70; Cu, 25.52; Br(by difference), 32.04. Analysis calcd. for $C_6H_4(Br)SCu$: C, 28.64; H, 1.59; S, 12.74; Cu, 25.53; Br, 31.76. Analysis found: C, 34.64; H, 1.91; S, 15.46; Cu, 30.58; Cl(by difference), 17.36. Analysis calcd. for $C_6H_4(Cl)SCu$: C, 34.79; H, 1.93; S, 15.48; Cu, 30.67; Cl, 17.11.

Absorption spectra. Solid state absorption spectra of the complexes were recorded using a Beckman Model DK-2 spectrophotometer. The complexes were examined as slurries in glycerol smeared on Whatman chromatographic paper.

Fluorescence spectra. The emission and the excitation spectra were recorded on a Farrand spectrofluorometer equipped with emission and excitation grating monochromators of Czerny-Turner type. A high pressure xenon lamp, operated at 150 watts, was used as a source to excite the fluorescence emission. The detector system was a IP28 RCA photomultiplier tube operated at 900 volts. The readout system was a Keithley 414S picoammeter equipped with a zero suppression control. The output from the amplifier was recorded on a Sargent Model SRG-GC strip chart recorder. All spectra were measured at room temperature and are uncorrected for the instrument response. The samples were examined as slurries applied to Whatman chromatographic paper of dimensions suitable for positioning diagonally in the sample compartment.

RESULTS:

Each complex shows a moderately strong absorption in the visible which intensifies near ultraviolet region, with an unmistakable shoulder in the 400-415 nm range which blends into much stronger bands in the ultraviolet. The absorption spectrum of copper(I) 4-bromobenzenethiolate, $C_6H_4(Br)SCu$, is shown in Fig. 1. The absorption band in the visible, which is responsible for the yellow colors of these complexes, can be readily assigned to a d-π^* charge-transfer transition arising from the excitation of a Cu(I) d-electron to a π^* orbital of the ligand. Although no well-defined maxima is readily obvious from the absorption spectrum of any of these complexes, the excitation spectrum shows a clear maximum at 470 nm. The observed emission and the excitation spectra of all complexes were similar in shape and position of the bands. Therefore, only the spectra of the copper(I) 4-bromobenzenethiolate are reproduced in Fig. 2. Also shown in Fig. 3 are the emission spectra of this complex obtained at excitation wavelengths in the range 320-470 nm. The main features of the fluorescence spectra of these complexes are noted below.

1. Each complex has a single emission band with onset located at 500 nm and maximum at 590 ± 5 nm. The excitation spectra are quite broad with a maximum at 470 nm and onset at 530 nm.
2. The emission band is located at a longer wavelength just outside the excitation band and tails into the excitation band near 510 nm. It should be a fluorescence band corresponding to the 0-0 transition.
3. The wavelength of maximum fluorescence remains constant through the 320-470 nm excitation range. The maximum emission occurs at an excitation wavelength of 470 nm. The intensity of emission decreases as the excitation is carried out below or above 470 nm.
4. The intensity of emission increases in the order: $C_6H_4(Br)SCu \approx C_6H_4(Cl)SCu > C_6H_3(Cl)_2SCu > C_6H_5SCu$.
5. Benzenethiols having substituents such as fluoro, alkyl, alkoxy, and nitro attached to the benzene ring form only weakly fluorescing complexes with copper(I). The fluorescence is visually observed in the red region of the visible spectrum but could not be detected with the instrument available to us.

DISCUSSION:

The absorption, emission and the excitation spectra of the copper(I) complexes reported herein are similar in shape and position of the bands. Each complex is characterized by having an absorption in the visible which appears to peak near 400 nm and extends into much stronger bands in the ultraviolet. Since copper(I), a closed-shell diamagnetic ion, has no empty d orbitals, the assignment of the low energy absorption band as the charge-transfer $d-\pi^*$ transition involving excitation of copper(I) d-electron to the ligand π^* orbitals is reasonable. We observed that light of wavelength shorter than 300 nm , the long wavelength edge below which transitions characteristic of the ligands occur, failed to excite any fluorescence in these complexes. Thus, energy transfer involving pure ligand electronic states is ruled out. The location of the emission band just to the long-wavelength side of the longest wavelength charge-transfer absorption band and the fact that the maximum emission occurred when the complexes are excited in the charge-transfer band, i.e., at 470 nm, would indicate energy transfer involving a π^*-d type transition which is inverse of the lowest energy charge-transfer absorption by the complexes. It is not surprising that the wavelength of maximum fluorescence of these complexes is insensitive to changes of the ligand. Although the available evidence is conflicting, it has been concluded from the ultraviolet spectra of the substituted benzenethiols that the 3d-orbitals of sulfur do not significantly mix with the π^* orbitals of the aromatic ring.[2,3] Therefore, the ligand π^* orbitals involved in the transition are probably sulfur 3d orbitals. A similar orange fluorescence reported by Anglin, et al.,[4] for the copper(I) complexes of cysteine and glutathione ligands, which lack aromatic character, further indicates that the excited charge-transfer state is formed from the transfer of charge from copper(I) d orbitals to the sulfur 3d orbitals. Because of the insolubility of the copper(I) benzenethiolates, they are only shown to fluoresce in the solid state. It is therefore possible that the fluorescence emission of these systems could arise from the crystal energy levels. A knowledge of the crystal structure and impurity levels of the above systems would be required to elucidate the mechanism of the photon emission.

We observed that fine crystals of copper(I) benzenethiolate, C_6H_5SCu, grown from pyridine-benzenethiol solution fluoresced yellow to green under uv illumination at room temperature. These crystals contained variable amounts of pyridine. The orange fluorescence was restored when pyridine was removed either by vacuum-drying or washing with methanol. A possible explanation for the yellow to green emission in these crystals would be a transfer of charge from the Cu-S bond to the π^* orbitals of pyridine and emission of energy via the reverse transition. The transfer of charge to pyridine as a result of solvation of the Cu-S bond, however, occurs at the expense of sulfur. As a result, the orange emission characteristic of the Cu-S bond disappears upon complexation with pyridine but reappears when pyridine is removed. These observations lend further support that the fluorescence emission of the copper(I) benzenethiolates originates from the π^*-d type charge-transfer transition in which a copper(I) d electron is excited to sulfur 3d-orbitals of the ligands. The previously studied yellow to green fluorescence in the 1 to 1 complexes of cuprous halides with pyridine arising from π^*-d type transition is in accord with these results.[5]

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LEGENDS:

Figure 1: Absorption spectrum of copper(I) 4-bromobenzenethiolate, $C_6H_4(Br)SCu$.

Figure 2: Fluorescence spectrum of copper(I) 4-bromobenzenethiolate, $C_6H_4(Br)SCu$.
(a) Excitation spectrum.

(b) Emission spectrum at 365 nm excitation wavelengths.

Figure 3: Emission spectrum of copper(I) 4-bromobenzenethiolate, $C_6H_4(Br)SCu$, at excitation wavelengths indicated.

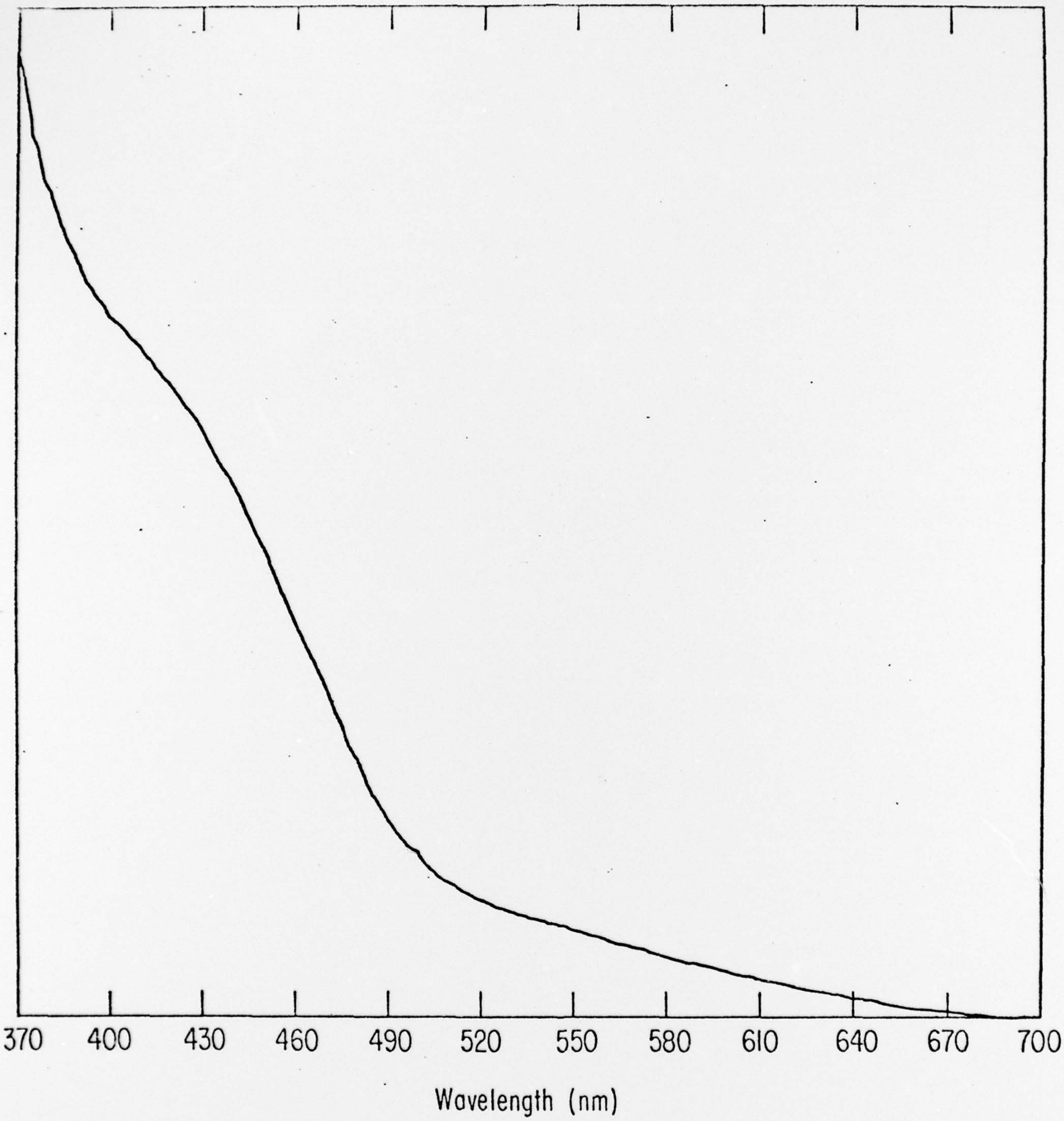

FIG. 1. Absorption spectrum of copper(I) 4-bromobenzenethiolate, $C_6H_4(Br)SCu$.

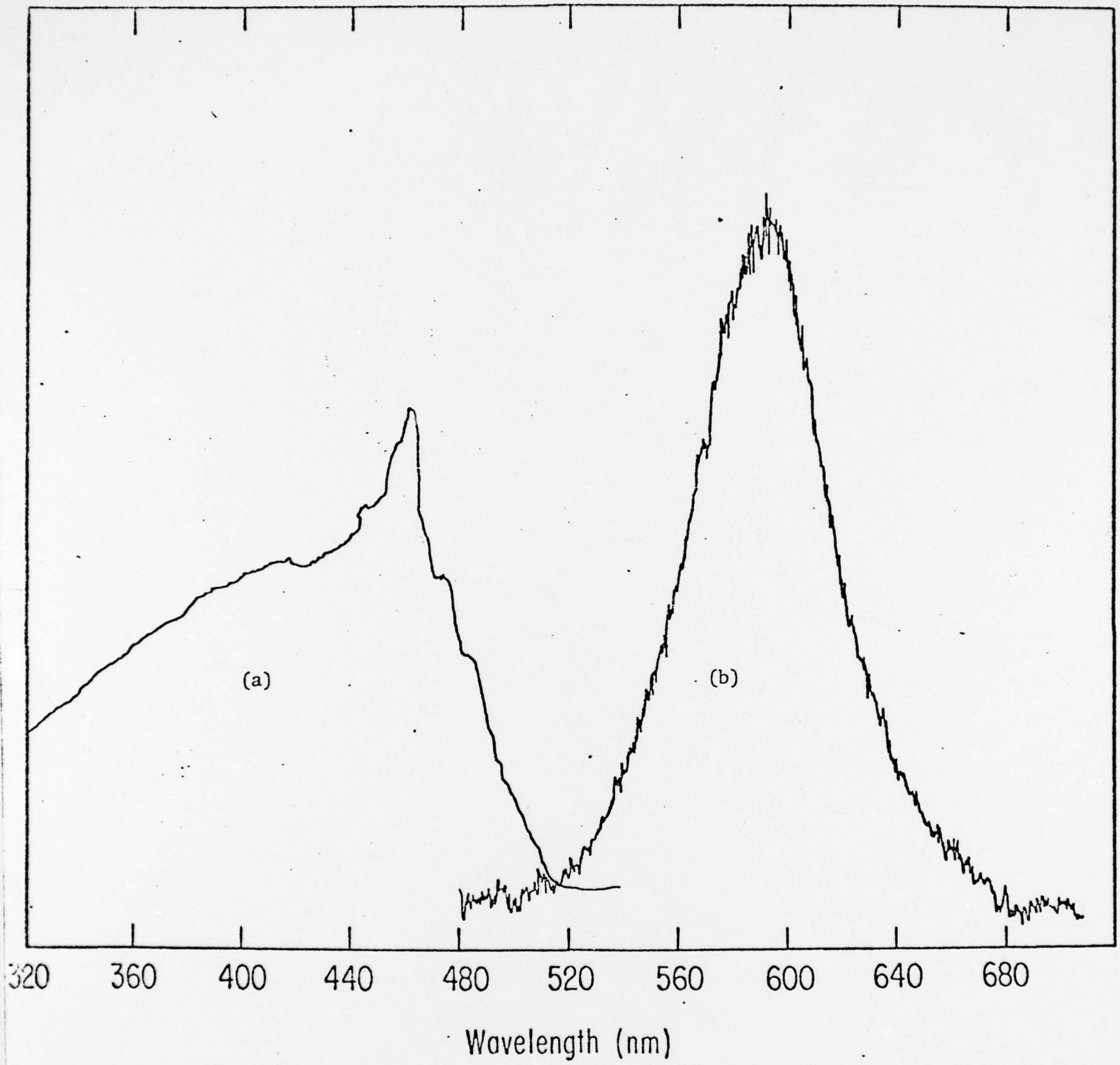

FIG. 2. Fluorescence spectrum of copper(I) 4-bromobenzenethiolate, $C_6H_4(Br)SCu$.
(a) Excitation spectrum, (b) Emission spectrum at 365 nm excitation wavelength.

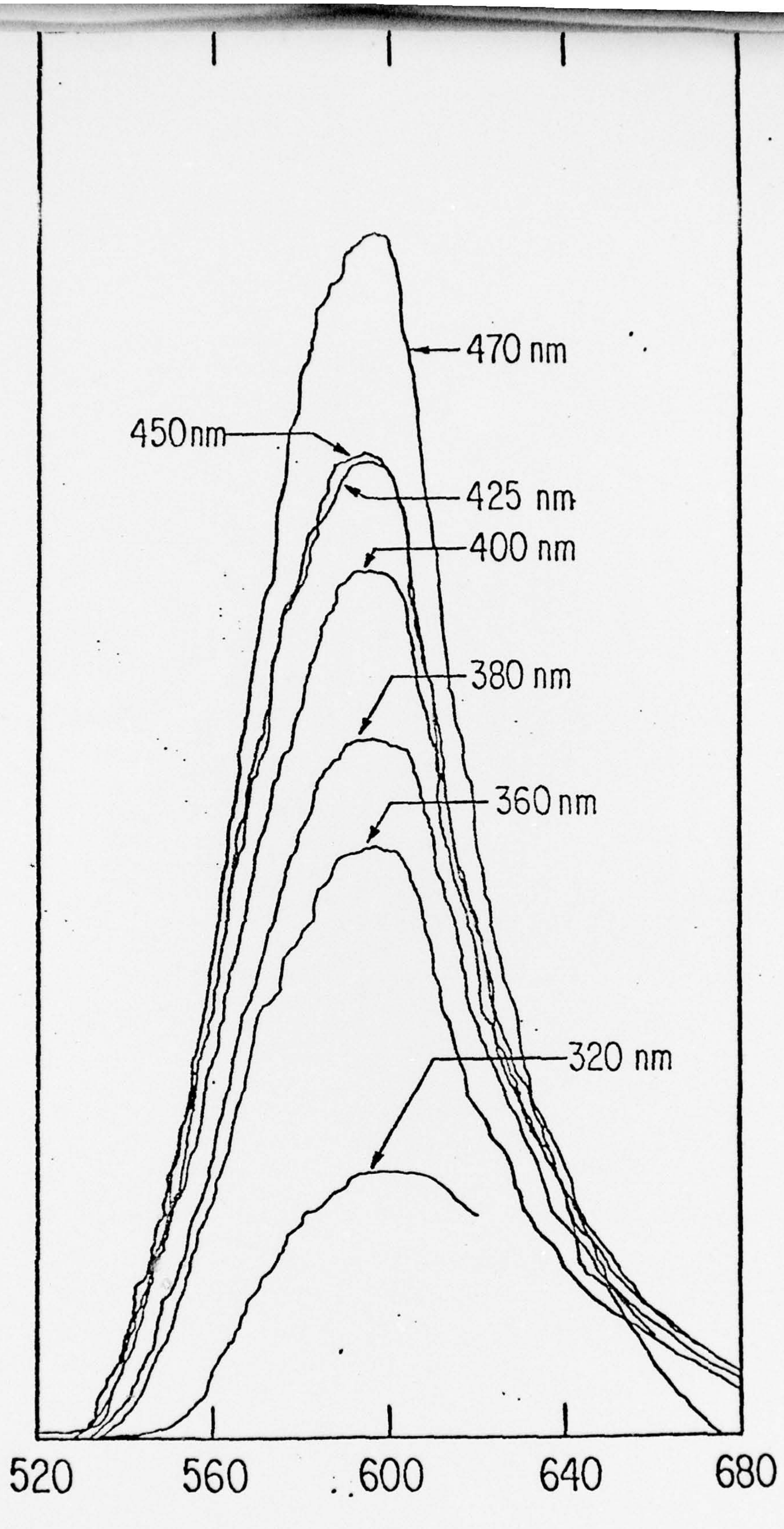

FIG. 3. Emission spectrum of copper(I) 4-bromobenzenethiolate, $C_6H_4(Br)SCu$, at excitation wavelengths indicated.