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Vibronic Structure in the Emission Spectrum of the Tetranuclear Copper Cluster [$Cu_4I_4(dmpp)_4$]

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Introduction

The luminescence of tetrameric d^{10} Cu(I) cluster compounds continues to attract attention[1-10] because of its unusual and interesting properties such as luminescence thermochromism in Cu_4X_4(pyridine)$_4$ (where X is a halide)[1-5] and the uncoupled nature of the lowest electronic state from other nearby states.[8,9] The lowest energy transition in copper clusters was orginally suggested to be a cluster-centered d^{10}–d^9s^1 transition.[6] More recent work suggests that in $Cu_4I_4L_4$ (where L is pyridine or substituted pyridines) the lowest energy transition involves significant iodide to pyridine charge-transfer character.[8] In all of the emission spectra reported to date, the lowest energy emission band is broad and unstructured. The presence and characterization of structure would allow the normal modes that are changed in the excited electronic state to be identified and would assist in the assignment of the transition.

In this note we report the discovery of vibronic structure on the lowest energy emission band of Cu_4I_4(dmpp)$_4$ (where dmpp is 1-phenyl-3,4-dimethylphosphole).[11] Raman spectra are taken to obtain more information about the vibrational properties of the molecule. Time-resolved emission spectra and emission lifetimes are measured. The vibronic structure is fit and the excited-state distortions are determined by using the time-dependent theory of electronic spectroscopy. The use of these results to assign the lowest energy excited electronic state is discussed.

Experimental Section

Emission Spectroscopy. The steady-state emission spectrum was taken with an Ar ion laser excitation source. A solid sample of [Cu_4I_4(dmpp)$_4$] was mounted in a Displex closed-cycle refrigerator equipped with a thermocouple. The digital signal passed through a Spex 1702 0.75-m single monochromator. A Hamamatsu R316-02 photomultiplier tube was used to detect the signal, which was then fed into a Stanford Research System SR-400 two channel gated photon counter. The data were stored in an Apple II computer and later were transferred to a VAX 780 computer for analysis. The emission spectrum was corrected for instrumental response using a standard tungsten lamp which has an equivalent black body temperature of 2859 K. The theoretical spectrum for a black body at 2859 K is calculated by using Planck's formula.

The time-resolved visible emission spectra were taken at 20 K with the samples mounted in a Displex closed-cycle helium refrigerator. The spectra were obtained by using 406.0-nm pulsed excitation from a XeCl Excimer pumped dye laser. A Model 1211 EG&G high-voltage pulser was used to gate an optical multiplier analyzer (OMA). The digital signal was detected and recorded with a 0.3-m single-scanning monochromator and with the OMA.

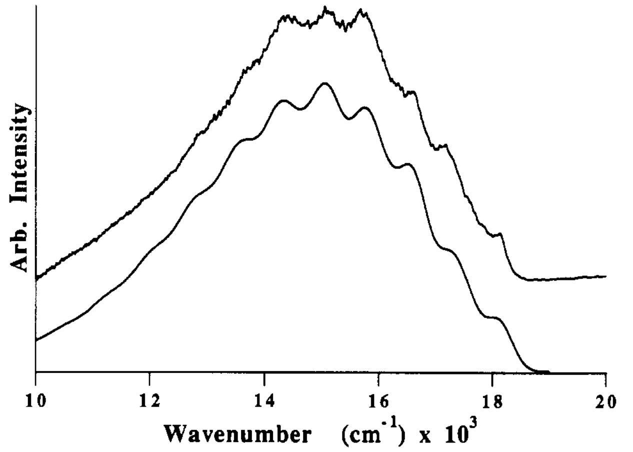

Figure 1. Top: Emission spectrum of [Cu_4I_4(dmpp)$_4$] at 15 K. Bottom: Calculated emission spectrum. The values of ω and Δ used in the calculation are given in the text.

The emission lifetime measurements were made by using 406.0-nm pulsed excitation from a XeCl Excimer pumped dye laser. The solid samples were mounted in a Displex closed cycle refrigerator. The signal was passed through a monochromator to a RCA C31034 photomultiplier and digitally stored in a Tektronix RTD 710 storage oscilloscope. The data were transferred to an IBM XT and were plotted in ln(intensity) verses time scales. Finally, the lifetime results were transferred to a VAX 780 computer for further analysis.

Raman Spectroscopy. Raman spectra of a solid sample of [Cu_4I_4(dmpp)$_4$] were taken with 457.9-, 488.0-, and 514.5-nm excitation wavelengths at room temperature. The signal was collected by using a Spex 1401 0.85-m double monochromator and an RCA C31034 photomultiplier tube. It was then fed into the Stanford Research System SR 400 gated photon counter. The data was finally stored in an Apple II computer.

[Cu_4I_4(dmpp)$_4$], [Cu_4Cl_4(dmpp)$_4$], and [Cu_4Br_4(dmpp)$_4$] were generous gifts from Professor John Nelson at the University of Nevada—Reno.[11]

Results

1. Luminescence of [Cu_4I_4(dmpp)$_4$]. The emission spectrum of [Cu_4I_4(dmpp)$_4$] in the powder form at 15 K excited at 351.0 nm is shown in Figure 1. The red luminescence has its band maximum at 15 070 cm^{-1} with a width at half-height of 4245 cm^{-1}. The wavenumber of the highest energy vibronic peak is 18 141 cm^{-1}. A striking feature of the spectrum is the vibronic structure. The most obvious features are the resolved peaks that are separated by $\sim 10^3$ cm^{-1} near the maximum of the spectrum. A small number of shoulders and resolved peaks are observed near the origin at 17 943, 17 889, 17 621, 17 301, 17 138, and 16 618 cm^{-1}. The separation of these peaks from the 18 141-cm^{-1} origin are 198, 252, 520, 840, 1003, and 1523 cm^{-1}.

The emission lifetime of a powdered sample of [Cu_4I_4(dmpp)$_4$] was measured at 17 K. Plots of the log of the intensity versus time are nonlinear. The plot can be fit with two exponentials corresponding to lifetimes of 15 and 58 μs.

Time-resolved emission spectra of solid [Cu_4I_4(dmpp)$_4$] at 20 K were taken in order to determine if multiple excited states are contributing to the emission spectrum. Spectra were taken with gate widths of 9.5 and 3 μs and with delays ranging from 1.1 to 101 μs. The energy, bandwidth, and vibronic structure were unchanged.

2. Luminescence of Comparison Compounds. The emission spectrum of the pure phosphole ligand was taken to determine if a ligand-centered transition was responsible for the observed luminescence. A blue luminescence is observed when the ligand at 20 K is excited at 351 nm. The emission spectrum contains

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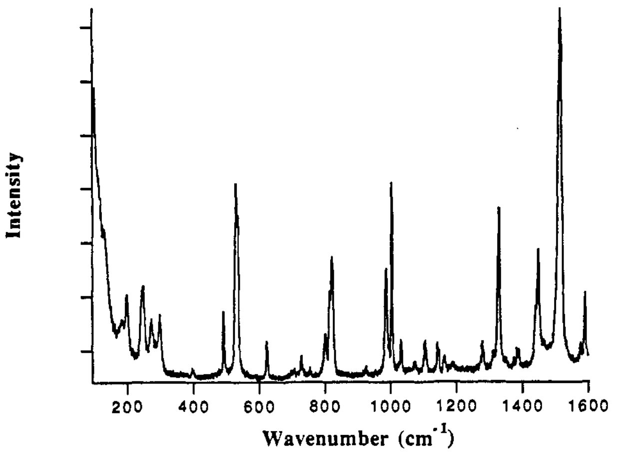

Figure 2. Raman spectrum of $[Cu_4I_4(dmpp)_4]$ excited at 457.9 nm.

a broad band with a maximum at 21 000 cm^{-1}, its full-width at half-height of 5150 cm^{-1} and its origin at about 26 450 cm^{-1}.

Emission spectra of the chloride and bromide derivatives of the copper phosphole cluster were taken in order to assist in assigning the electronic transition (vide infra). The emission spectrum of $[Cu_4Cl_4(dmpp)_4]$ at 10 K was obtained by using 472.7-nm excitation. The spectrum has its origin at about 18 200 cm^{-1} and peaks at about 14 900 cm^{-1}. Poorly resolved vibronic structure was observed. The separations between the features and the origin are 200, 950, 1590, 2250, and 3600 cm^{-1}. The emission spectrum of $[Cu_4Br_4(dmpp)_4]$ at 15 K was taken with 472.7-nm excitation. The spectrum has its origin at 18 250 cm^{-1} and its band maximum at 15 100 cm^{-1} with a width of 2600 cm^{-1}. The separations between the poorly resolved vibronic features and the origin are 250, 900, 2505, and 3250 cm^{-1}.

3. Raman Spectrum of $[Cu_4I_4(dmpp)_4]$. The vibrational frequencies of solid $[Cu_4I_4(dmpp)_4]$ were obtained from the room-temperature Raman spectrum. Figure 2 shows a spectrum obtained by using 457.9-nm excitation. The most intense peaks (those having intensities greater than 0.1 of that of the most intense peak in the spectrum at 1517 cm^{-1}) are at 198, 246, 270, 298, 492, 529, 819, 986, 1004, 1329, 1448, 1517, and 1591 cm^{-1}. Using the peak at 2930 cm^{-1} assigned to the C–H stretch as an "internal standard", the intensities of the peaks at 529, 819, 1329, 1448, and 1517 cm^{-1} do not change as the laser excitation frequencies vary from 457.9 to 514.5 nm. The intensity of the peak at 1004 cm^{-1}, however, increases at 514.5-nm excitation.

Discussion

1. Assignment of Vibronic Peaks. Ligand-centered normal vibrational modes are prominent in the vibronic structure in the emission spectrum. The presence of these modes is indicative of significant structural changes in the ligand upon excitation of the complex. The modes observed in the emission spectrum are the most intense (or among the most intense) bands observed in the Raman spectrum. Two of the vibronic features can be readily assigned. First, a prominent band at 1003 cm^{-1} from E_0 in the emission spectrum corresponds to the second most intense peak (1004 cm^{-1}) in the Raman spectrum. Peaks at 1004 cm^{-1} are also found in the Raman spectra of $[Cu_4Br_4(PPh_3)_4]$ and $[Ag_4I_4(PPh_3)_4]$. This normal mode is assigned to the p-ring vibration of the phenyl group of the ligand.[12] Second, the prominent peak in the emission spectrum at about 1523 cm^{-1} corresponds to the most intense peak in the Raman spectrum at 1517 cm^{-1}. It is assigned to a ligand-centered mode because its frequency is too high to be a metal–ligand or cluster mode.[13,14] It cannot be assigned to a ligand phenyl group mode because it is not found in the Raman (or emission) spectra of the comparison compounds $[Cu_4Br_4(PPh_3)_4]$ or $[Ag_4I_4(PPh_3)_4]$ and because there is no corresponding peak in the Whiffen analysis of phenyl modes.[12] It is assigned to a C=C stretch in the phosphole ring portion of the ligand.

The remaining prominent bands at 252, 520, and 840 cm^{-1} in the emission spectrum and their corresponding bands at 246, 529, and 819 cm^{-1} in the Raman spectrum cannot be definitely assigned. The 252-cm^{-1} mode may be a μ X-sens phenyl vibration;[12] this assignment was made for a 256-cm^{-1} mode in $[Rh_2(O_2CCH_3)_4(PPh_3)_2]$.[15] Alternatively it may be a Cu–P stretch. This assignment was made for a 262-cm^{-1} mode in the PEt_3 complex.[13] A corresponding band is found in the Raman spectra of $[Cu_4Br_4(PPh_3)]_4$ and $[Ag_4I_4(PPh_3)]_4$. The modes at 529 and 109 cm^{-1} were not found in the spectra of either $[Cu_4Br_4(PPh_3)_4]$ or $[Ag_4I_4(PPh_3)_4]$. Hence, these modes are probably not phenyl ring modes. They may be a phosphole ligand-centered torsional mode and a C–C stretching mode, respectively. Vibrational modes of the cubane core occur at less than 200 cm^{-1}.

2. Calculated Emission Spectrum. The emission spectrum of $[Cu_4I_4(dmpp)_4]$ shows evidence for distortions along seven normal coordinates and thus requires that a seven-dimensional potential surface be used in the calculation. The spectrum is calculated by using the time-dependent theory of electronic spectroscopy.[16] Because details of both the method and its applications to the spectra of molecules distorted along many normal modes in excited electronic states have been presented and reviewed previously,[17-20] only the relevant equations required for the spectrum of $[Cu_4I_4(dmpp)_4]_4$ are presented here.

The emission intensity $I(\omega)$ at frequency ω is given by

$$I(\omega) = C\omega^3 \int_{-\infty}^{\infty} e^{i\omega t} \langle \phi | \phi(t) \rangle \, dt \qquad (1)$$

where C is a constant. The time-dependent overlap is given by

$$\langle \phi | \phi(t) \rangle =$$

$$\exp\left\{ \sum_k \left[-\frac{\Delta_k{}^2}{2}(1 - \exp(-i\omega_k t)) - \frac{i\omega_k t}{2} \right] - iE_0 t - \Gamma^2 t^2 \right\} \qquad (2)$$

where ω_k is the vibration frequency, Δ_k is the displacement of the kth normal mode, E_0 is the electronic origin, and Γ is a phenomenological damping factor.

The experimental emission spectrum is fit by using modes observed in the experimental spectrum and frequencies of these modes that are accurately obtained from the Raman spectrum. The best-fit spectrum is compared to the experimental spectrum in Figure 1. In the calculation, an E_0 of 18 150 cm^{-1} (found from the experimental emission spectrum) and a damping factor of $\Gamma = 160$ is used. The values of the displacements Δ and the frequencies for the seven modes are respectively 0.5, 198 cm^{-1}; 0.5, 246 cm^{-1}; 1.4, 529 cm^{-1}; 1.76, 819 cm^{-1}; 0.57, 986 cm^{-1}; 0.75, 1004 cm^{-1}; and 1.85, 1517 cm^{-1}.

The values of Δ determined from the best fit provide quantitative information about the bond length and bond angle changes in the excited electronic state. Conversion of the units to Å and degress requires a normal coordinate analysis. However, a rough approximation for interpretative purposes can be made if it is

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crudely assumed, for example, that the mass involved in the C═C stretching mode of the phosphole is the reduced mass of the C═C unit and that $\Delta = (1/\sqrt{2})(\delta(C_1{=}C_1) + \delta(C_2{=}C_2))$. With these assumptions, the change δ in an individual C═C bond length in the excitated state is 0.06 Å.[21] This ligand-centered distortion, the largest in the molecule, is of reasonable magnitude given the approximate nature of the conversion to the individual bond-length change.

3. Assignment of Emission Band. The emission spectrum is assigned to a one-electron transition terminating on the phosphole ligand on the basis of the vibronic structure observed in the spectrum and the calculated distortions. The transition could either be a copper metal to dmpp ligand charge transfer (MCLT) or an iodide ligand-to-ligand phosphate charge transfer (LLCT). The LLCT assignment can be ruled out because there is no significant shift in the energies of the emission bands of $[Cu_4Cl_4(dmpp)_4]$, $[Cu_4Br_4(dmpp)_4]$, and $[Cu_4I_4(dmpp)_4]$ when the halide is changed from chloride to bromide to iodide. The transition is spin-forbidden on the basis of the measured microsecond lifetime. Because of the significant distortions in the phosphole ligand determined from the intensities of the vibronic structure in the emission band, the similarities of the emission energies when the halide ligand is changed, and the microsecond lifetime, the emitting state of $[Cu_4I_4(dmpp)_4]$ is assigned to a spin-forbidden metal-to-ligand charge transfer.

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(21) The formula to convert the dimensionless displacement Δ into Å is

$$\delta = \sqrt{\frac{6.023 - 10^{23}}{m} - \frac{\hbar}{2\pi c\omega}} - 10^{8} - \Delta$$

where m is the mass involved in the vibration in the units of gram atomic weight (e.g. mass of C = 12 g), ω is the wavenumber of the vibrational mode in cm^{-1}, $\hbar = h/2\pi$, where h is Planck's constant in g $\mathrm{cm}^2\,\mathrm{s}^{-1}$, c is the speed of light in cm s^{-1}, δ is the displacement in Å, and Δ is the dimensionless displacement.