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THERMOCHROMISMS OF SOME β-DIKETONE CHELATE COMPLEXES OF COPPER(II) IN PURE PYRIDINE

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Two types of thermochromisms have been found for several β-diketone chelate complexes of copper(II) in pure pyridine. One is observed for such complexes as bis(acetylacetonato)copper(II), where the visible absorption spectra at various temperatures have well-defined isosbestic points. The other is observed for such complexes as bis(salicylaldehydato)copper(II), where only the spectral intensity increases unusually with a rise in temperature.

We report here the new experimental fact that two interesting types of thermochromisms are observed for some β-diketone chelate complexes of copper(II) in pure pyridine. The complexes employed in this study are bis(acetylacetonato)copper(II), bis(benzoylacetato)copper(II), bis(dipivaloylmethanato)copper(II), bis(salicylaldehydato)copper(II), and bis(ethyl acetoacetato)copper(II), which are abbreviated as Cu(acac)$_2$, Cu(bzac)$_2$, Cu(dpm)$_2$, Cu(sal)$_2$, and Cu(Etacest)$_2$ respectively. They can group themselves in the two classes, the former three complexes and the latter two, according to the stability$^{1)}$ and to whether they form the 1:1 or 1:2 adducts with pyridine.$^{2)}$ The visible absorption spectra of Cu(acac)$_2$, Cu(bzac)$_2$, and Cu(sal)$_2$ in pyridine at various temperatures are shown in Figs. 1 – 3 respectively. The above-mentioned classification is also consistent with the one based upon the temperature dependences of the visible absorption examined in this work; the complexes of the two classes show quite different types of the temperature dependences, as is seen in Figs. 1 – 3. Some results of the visible absorption spectra are listed in Table 1.

Any of the complexes of the first class have well-defined isosbestic points in their visible absorption spectra at various temperatures, as are shown in Figs. 1 and 2. This experimental fact clearly indicates that there are two complex species, the low-temperature and high-temperature species, at equilibrium in each of the pyridine solutions, namely, that there are two different interactions of pyridine with the complexes of this class even in pure pyridine. It has been reported that the copper atom is penta-coordinated to the four oxygen atoms in the β-diketone and to the nitrogen atom of the pyridine molecule for Cu(acac)$_2$ in pyridine.$^{3)}$ The visible absorptions of these complexes in pyridine shift to somewhat longer wavelengths and their peak heights slightly decrease with a rise in temperature, but

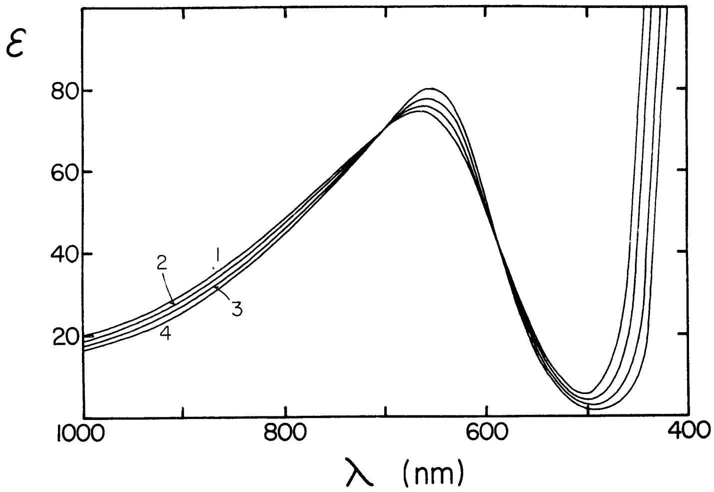

Fig. 1. Visible absorption spectra for $Cu(acac)_2$ in pyridine.
(1): 60°C, (2): 40°C,
(3): 20°C, (4): 0°C.

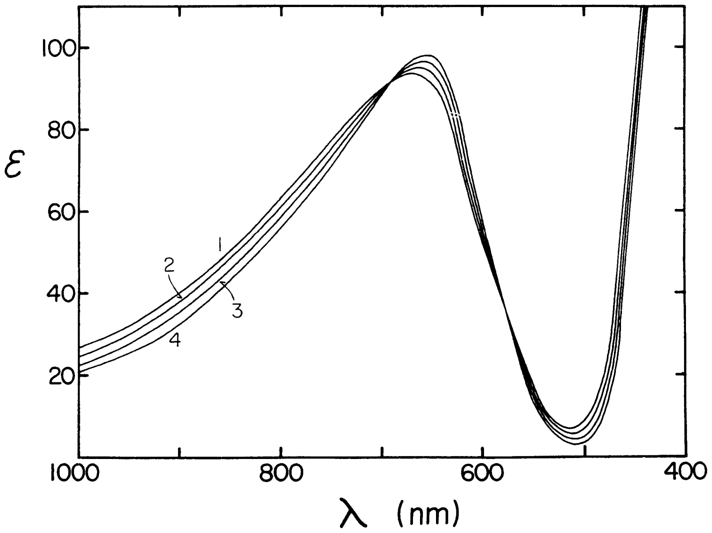

Fig. 2. Visible absorption spectra for $Cu(bzac)_2$ in pyridine.
(1): 60°C, (2): 40°C,
(3): 20°C, (4): 0°C.

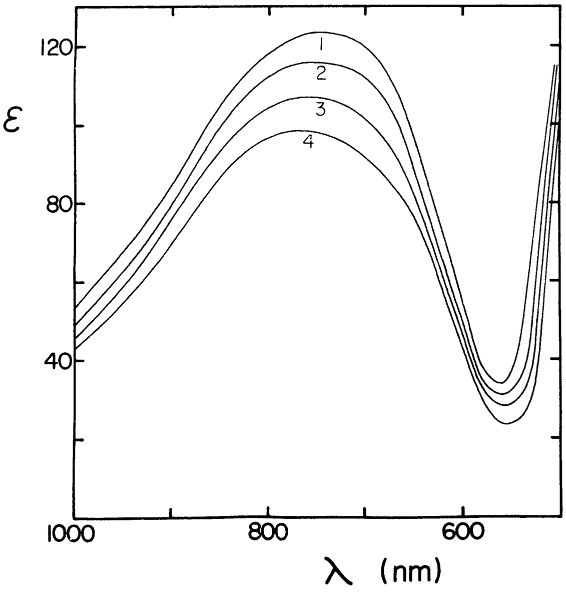

Fig. 3. Visible absorption spectra for $Cu(sal)_2$ in pyridine.
(1): 60°C, (2): 40°C,
(3): 20°C, (4): 0°C.

TABLE 1. VISIBLE ABSORPTION SPECTRA IN PYRIDINE

Copper(II) complex	Isosbestic point		Absorption peak				Oscillator strength	
			0°C		60°C		0°C	60°C
	λ (nm)	ε	λ (nm)	ε	λ (nm)	ε	($\times 10^3$)	($\times 10^3$)
$Cu(acac)_2$	585 700	38 71	652	80	667	75	1.76	1.95
$Cu(bzac)_2$	576 686	32 83	660	98	670	94	2.20	2.33
$Cu(dpm)_2$	562 726	33 77	645	114	652	94	2.25	2.44
$Cu(sal)_2$			ca. 750	98	ca. 750	123	2.72	3.68
$Cu(Etacest)_2$			730	67	730	77	1.63	1.99

it is reasonably considered that the oscillator strengths of the visible absorptions listed in Table 1 hardly vary with temperature, when such a substantial temperature dependence of spectral intensity as described below is taken into consideration. This result of the oscillator strengths indicates that there is almost no difference in the symmetry of the copper ion environment between the low-temperature and high-temperature species,4) and, furthermore, the experimental fact that the visible absorptions of the high-temperature species appear at somewhat longer wavelengths than those of the low-temperature species suggests that the in-plane coordination bonding becomes weaker and the axial one, stronger in the high-temperature species than in the low-temperature one.5) It seems, therefore, probable that the copper atom lies in the plane of the four oxygen atoms in the low-temperature species but is displaced to a slight extent from the plane in the direction of the nitrogen atom of the coordinated pyridine molecule in the high-temperature species, as has been often observed in many crystals of the metal complexes.6)

On the other hand, the visible absorption spectra of $Cu(sal)_2$ and $Cu(Etacest)_2$, the complexes of the second class, remarkably increase their intensities with a rise in temperature, as is shown in Fig. 3. The thermochromism of $Cu(acac)_2$ in some solvents is thought to be the same type.6) Temperature affects the intensity of an electronic transition induced by a vibrational mode n according to $\coth(h\nu_n/2kT)$, in the simplest theory,8) and it was found that the increases in the oscillator strength with a rise in temperature for these complexes in pyridine exceed the expectations based upon the coth rule. It seems, therefore, probable that the changes in structure accompanying a change in spectral intensity take place continuously according to temperature for the complexes of the second class in pyridine.

All the above-described facts indicate that the metal complexes essentially have the property of changing their structures flexibly under appropriate conditions, and some of those structures may be considered as the ones of reaction intermediates.

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