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Synthesis and Thermochromic Properties of New Five-coordinate Copper Chelates

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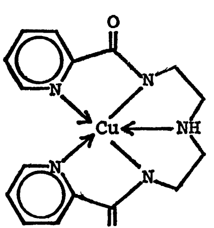
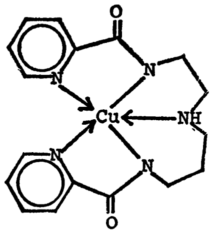
Two new five-coordinate copper(II) chelates [Cu(PCdien)] and [Cu(PCenpn)] were prepared, and the thermochromism of the former in methanolic solution was studied. When this violet-blue solution (ν_{max}: 16500 cm^{-1}) was heated nearly to the boiling point of methanol, the color of the solution became gradually yellowish (ν_{max}: 21000 cm^{-1}). The absorption spectra of these cold and hot solutions were compared with those of similar four-coordinate Cu(II) complexes in various solvents, and the yellow color was ascribed to a tetracoordinated species of [Cu(PCdien)], which is formed by the partial rupture of the pentacoordinated structure caused by the intramolecular steric strains. No thermochromic property of the PCenpn chelate was observed.

Recently we prepared two new five-coodinate copper(II) chelates shown below, and found that one of them shows a peculiar thermochromism in its methanolic solution. The results of these studies will be described in this paper.



[Cu(PCdien)] = *N*-(picolinoyl)-*N'*-(picolinoylaminoethyl)-ethylenediaminato copper(II)



[Cu(PCenpn)] = *N*-(picolinoyl)-*N'*-(picolinoylaminoethyl)-propanediaminato copper(II)

Experimental

Synthesis of the Chelates. [Cu(PCdien)] can be prepared from diethylenetriamine and methyl picolinate; 13.7 g (0.1 mol) of the latter is added dropwise into 5.2 g (0.05 mol) of the former, and the mixture is heated at 140 °C for 1 hr and then at 160 °C for 2 hr. A concentrated aqueous solution containing 12.5 g (0.05 mol) of $CuSO_4 \cdot 5H_2O$ is added to it, and then one containing 4 g (0.1 mol) of NaOH. The deep green, tarry precipitate which separates out is washed with cold methanol, and the dark blue crude crystals which remain are recrystallized from hot methanol. The product obtained is the monohydrate of [Cu(PCdien)] (Found: Cu, 16.23; N, 17.59; H_2O, 4.20%. Calcd for $C_{16}H_{17}N_5O_2Cu \cdot H_2O$: Cu, 16.17; N, 17.82; H_2O, 4.58%.); the anhydrous chelate can be obtained by its dehydration in vacuum at 90 °C, (Found: Cu, 17.00%. Calcd for $C_{16}H_{17}N_5O_2$ Cu: Cu, 16.95%).

[Cu(PCenpn)] can be obtained in a similar way from 3-(aminoethylamino)-propanediamine and methyl picolinate. After heating the ligand mixture and mixing it with solutions of $CuSO_4 \cdot 5H_2O$ and NaOH, the mixture is evaporated under reduced pressure almost to dryness, and extracted with methanol. The extract is then evaporated to dryness again, and the residue is recrystallized from water (pH 9). The product has the composition of [Cu(PCenpn)]$\cdot 1.5H_2O$ (Found: Cu, 15.27; N, 16.93; H_2O, 6.70%. Calcd for $C_{17}H_{19}N_5O_2Cu \cdot 1.5H_2O$: Cu, 15.28; N, 16.84; H_2O, 6.50%.) and can be made anhydrous as in the case of [Cu(PCdien)] (Found: Cu, 16.53%. Calcd for $C_{17}H_{19}N_5O_2Cu$: Cu, 16.34%.).

Physical Measurements. The visible absorption spectra of the solutions were measured with a Shimadzu Multiconvertible Spectrophotometer Double-40, using 5 mm and 10 mm cells. Measurements with hot and cold solutions were carried out as promptly as possible after their preparation, without use of thermospacers; this is because the thermochromic changes are quite slow and no serious error was expected to result. All other measurements were carried out with conventional techniques.

Results and Discussion

Both of the chelates are violet-blue crystals, and dissolve in methanol forming violet-blue solutions with ν_{max} and ε_{max} values shown in Table 1. When these solutions are heated almost to boiling, the color of the solution of [Cu(PCenpn)] remains nearly unchanged, but that of [Cu(PCdien)] becomes gradually green, and then remarkably yellowish. This color change is fairly slow, and the solution must be refluxed

Table 1. Characteristic data on [Cu(PCdien)] and [Cu(PCenpn)]

	[Cu(PCdien)]	[Cu(PCenpn)]
$\nu_{max}(\varepsilon_{max})^{a)}$	16500 cm^{-1}(140)	15400 cm^{-1}(250)
Molar conductivity$^{b)}$ (mho cm^2 mol^{-1})	11.55	3.18
μ_{eff} (286 K) BM	1.79$^{c)}$; 1.81$^{d)}$	1.81$^{c)}$; 1.88$^{d)}$
IR spectra ν_{N-H}	3440 cm^{-1}	3320 cm^{-1}
amide I	1637	1620
	1620	
py	1598	1598
	1581	1580
	1560	1557

a) Methanolic solutions. b) 10^{-3} M solutions in methanol: these data show that both of the chelates are only partially ionized in solution. c) Anhydrous chelate. d) Hydrated chelate.

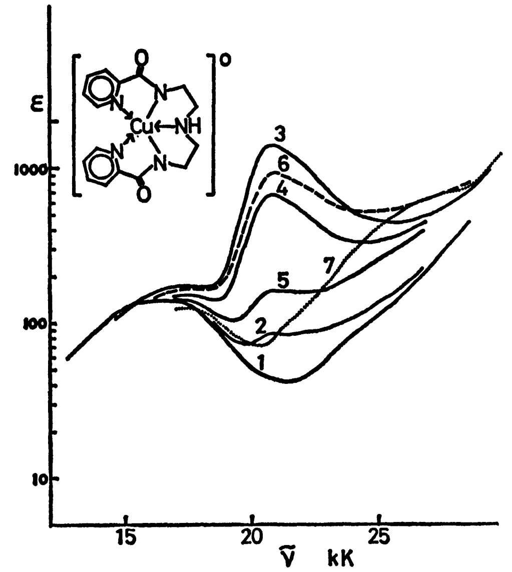


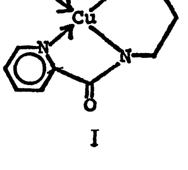
Fig. 1. Absorption spectra of [Cu(PCdien)] in methanol.

for some minutes for its full development. The reverse change from yellow to violet-blue occurs on cooling, but this change is much slower, and the solution reverts to its original violet-blue state only after standing for several days in a freezer (*ca.* −15 °C).

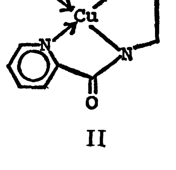
The general outlook of the spectral changes observed in the course of this process is shown in Fig. 1. Curve 1 shows the spectrum of a fresh, cold solution (2.0×10^{-3} M) prepared by keeping the weighed sample together with methanol in a freezer overnight. When this solution is left standing at room temperature (26 °C) for some time (*ca.* 1/2 hr), a weak band at *ca.* 21000 cm^{-1} is observed (Curve 2).[1] This band becomes very much stronger by heating; Curve 3 is the spectrum of the same solution after refluxing at *ca.* 68 °C for 10 min, when the apparent color change appears to be nearly complete. Curve 4 is observed when the refluxed solution is cooled and kept in a freezer for a day; Curve 5, after four more days, and Curve 6 when the solution is then refluxed again.

The spectral changes can thus be repeated; however, as can be seen from these Curves, the amount of the observed spectral change tends to decrease in the course of repetition. This seems to be due to an irreversible decomposition of the chelate, which, also slowly, takes place in solution; in fact, when we let the solution stand for a long time (5 days) at room temperature, the solution becomes remarkably greenish and only poorly thermochromic. Curve 7 shows the absorption curve of such an "aged" solution.

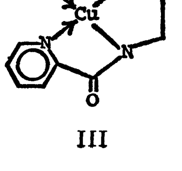
Although the exact mechanism of this thermochromism is still unknown, a clue for its understanding can be found in the earlier work of Ojima.[2] Figure 2 shows his data on the absorption curves of the chelate I in various solvents.



I



II



III

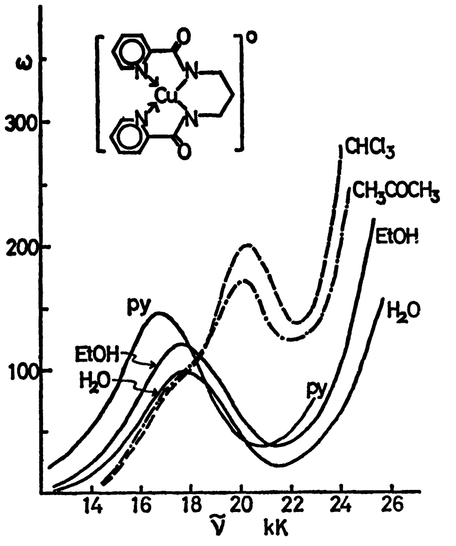


Fig. 2. Absorption spectra of I in various solvents.

It can be seen that the ν_{max} and ε_{max} values are largest in $CHCl_3$ (20200 cm^{-1} and 200, respectively), and the ν_{max} decreases in the order of $CHCl_3 \rightarrow CH_3COCH_3 \rightarrow H_2O \rightarrow$ EtOH→py, while the ε_{max} seems to pass through a minimum and then increases again. Table 2 summarizes these data, and similar data observed with the chelates II and III.[3]

In $CHCl_3$, which is a poorly coordinating solvent, we can expect the chelate I to assume a four-coodinate structure. This structure will be approximately planar, but the formation of a perfectly planar structure will be hindered by the strains in the chelate rings and by the repulsion between the hydrogen atoms on the pyridine rings. Going to a more strongly coordinating solvent, however, the chelate will become gradually tetragonal, and when the solvent becomes very basic (*e.g.* pyridine), the chelate may become eventually pentacoordinated. The spectral changes in Fig. 2 and Table 2 can probably be taken as the reflection of these structral changes.[4]

We now see that the absorption curves of [Cu(PCdien)] in cold and hot methanol are, respectively, very similar to those of I in pyridine and chloroform. Model studies show that the pentacoordinated structure of [Cu(PCdien)] is, although sterically possible (trigonal bipyramid seems to be more favorable than square pyramid), quite highly strained; therefore, though the chelate may retain its pentacoordinated structure in a very cold solution, a rupture of the chelate ring (probably at the Cu←NH bond) will take place on heating, leading to a tetracoordinated structure. The spectral analogy mentioned above can thus be understood, at least in a qualitative way. The tetracoordinated structure is, however, again expected from model studies to be considerably strained; indeed, the very high ε_{max} value of the high-temperature species observed in Fig. 1 (apparent value: 1400 at 20800 cm^{-1}) may be related to this high strain and poor

TABLE 2. ν_{max} AND ε_{max} VALUES OF THE CHELATES I—III IN VARIOUS SOLVENTS

Chelate	ν_{max} ($10^3\,cm^{-1}$: ε_{max} in parentheses)				
	$CHCl_3$	CH_3COCH_3	H_2O	EtOH	py
I	20.2(198)	20.0(171)	17.7(97)	17.3(117)	16.3(145)
II	20.4(397)	—	18.5(225)	18.5(252)	17.4(252)
III	17.1(216)	—	18.7(212)	18.3(228)	17.5(256)

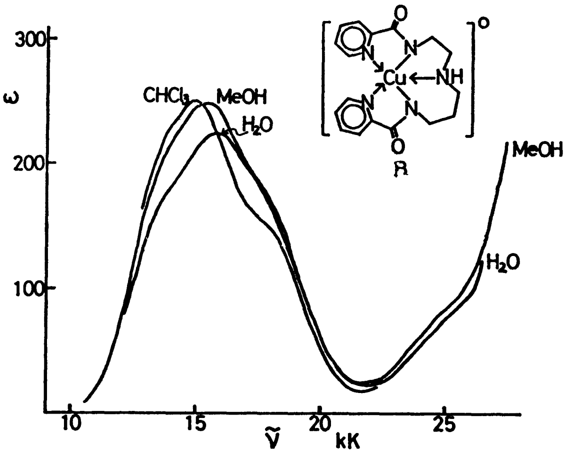


Fig. 3. Absorption spectra of [Cu(PCenpn)] in various solvents.

symmetry of the chelate. Moreover, the change between these two structures will need a large amount of conformational change, so that it (and the reverse reaction, too) will need a large activation energy, and a part of the chelate may be lost in the course of these changes by some kind of decomposition.

It is also of interest to note that the chelate [Cu(PCenpn)], which is not thermochromic in methanol (and H_2O and $CHCl_3$, in which it is also soluble), shows absorption curves which are all very similar (Fig. 3), and characteristic of the CuN_5-type pentacoordinated chelates already studied by Ojima and Nonoyama.[5] The slight structural change from [Cu(PCdien)] to [Cu(PCenpn)], *i.e.* the introduction of one 6-ring instead of a 5-ring, seems to greatly lessen the intramolecular strain, and avoid the rupture of the chelate ring upon heating.

Our thanks are due to Miss Junko Ida for her help in the experiments.

References

1) When the solution is kept longer at room temperature, however, this band does not gain in intensity so much, and the solution begins gradually to "age", *i.e.*, to show a curve similar to Curve 7 and to become poorly thermochromic.

2) H. Ojima, *Nippon Kagaku Zasshi*, **88**, 333 (1967).

3) A serious exception among these data is that of the chelate III in $CHCl_3$; here ν_{max} and ε_{max} are much lower than expected from other data. This, however, may be due to the effect of intermolecular association leading to an apparently higher coordimation number of copper(II), which will be favored in such a poorly coordinating solvent.

4) It may be pointed out that the spectral change from H_2O or EtOH to py resembles, to some extent, the change observed when $[Cu(NH_3)_4(OH_2)_2]^{2+}$ is transformed in aqueous solution into $[Cu(NH_3)_5(OH_2)]^{2+}$, which probably holds its water only very weakly; *cf.*, *e.g.*, B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).

5) H. Ojima and K. Nonoyama, *Z. Anorg. Allg. Chem.* **401**, 207 (1973).