BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1100—1104 (1972)

Thermochromisms of Some β-Diketone Chelate Copmlexes of Copper(II) in Pure Pyridine[1]

Hiroshi YOKOI, Mitsuru SAI, and Taro ISOBE
Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai

(Received December 3, 1971)

Two types of thermochromisms have been found for several β-diketone chelate complexes of copper(II) in pure pyridine or γ-picoline. One is observed for such complexes as bis(acetylacetonato)copper(II). In this case, the visible absorption spectra at various temperatures have well-defined isosbestic points; there are two different complex species, L and H, at equilibrium in the solvent, where L and H represent the low-temperature and high-temperature species respectively; they are different in the interaction between the complex and pyridine or γ-picoline molecules. The other is observed for such complexes as bis(salicylaldehydato)copper(II), where the spectral intensity increases remarkably with a rise in the temperature. The equilibrium for bis(acetylacetonato)copper(II) was studied over the temperature range of 0—60°C, and the results were used to derive the approximate thermodynamic parameters, $\Delta H = 4.0 \pm 1.0$ kcal/mol and $\Delta S = 13 \pm 4$ e.u., for the L→H change. The most probable structures for L and H were suggested from a spectrophotometrical point of view.

The thermochromism exhibited by many metal complexes in solution is associated with an equilibrium between the different configurations which the complexes can adopt in the solution at various temperatures.[2–6] It is interesting to us that some kinds of metal complexes change their structural configurations easily according to environmental conditions. Some of the configurations may be chemically labile. Investigations of the thermochromism are, therefore, important in understanding chemical reactions.

The purpose of this paper is to report the new experimental finding that the β-diketone chelate complexes of copper(II) in pure pyridine or γ-picoline exhibit two different types of thermochromisms and

---

[1] Preliminary report: H. Yokoi, M. Sai, and T. Isobe, *Chem. Lett.*, **1972**, 25.

[2] D. E. Scaife and K. P. Wood, *Inorg. Chem.*, **6**, 358 (1967); K. Mizutani and K. Sone, *Z. Anorg. Allg. Chem.*, **350**, 216 (1967); R. K. Scarrow and T. R. Griffiths, *Chem. Commun.*, **1967**, 425.

[3] K. Sone and M. Kato, *Z. Anorg. Allg. Chem.*, **301**, 277 (1959); C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 399, 919 (1957); F. Basolo, Y. T. Chen, and R. K. Murmann, *J. Amer. Chem. Soc.*, **76**, 956 (1954).

[4] F. A. Cotton and J. P. Fackler, Jr., *ibid.*, **83**, 2820, 3775 (1961).

[5] D. M. L. Goodgame and M. A. Hitchiman, *Inorg. Chem.*, **5**, 1303 (1966).

[6] M. Nicolini, C. Pecile, and A. Turco, *Coodin. Chem. Rev.*, **1**, 133 (1966); T. Boschi, M. Nicolini, and T. Turco, *ibid.*, **1**, 269 (1966).

to estimate the possible mechanisms for these thermochromisms. This experimental finding indicates that there are different interactions between the complex and pyridine or γ-picoline molecules.

Experimental

Materials. The β-diketone chelate complexes of copper(II) employed here are $Cu(acac)_2$, $Cu(dpm)_2$, $Cu(bzac)_2$, $Cu(sal)_2$, and $Cu(etacest)_2$, where acac, dpm, bzac, sal, and etacest are the anions of acetylacetone, dipivaloylmethane, benzoylacetone, salicylaldehyde, and ethyl acetoacetate respectively. They were prepared and purified by the same general method.[7] All the ligand agents were obtained commercially. G.R.-grade pyridine and γ-picoline were dried over potassium hydroxide and were fractionally distilled.

Spectroscopy. The visible absorption spectra for the complexes in pyridine and γ-picoline were measured over the temperature range of 0—60°C with a Cary model 14 spectrophotometer, using 1-cm quartz cells. Color changes occured reversibly with a change in the temperature for all the sample solutions.

Results and Discussion

The visible absorption spectra at various temperatures for $Cu(acac)_2$ and $Cu(bzac)_2$ in pyridine are shown in Figs. 1 and 2 respectively. The same temperature dependences of the spectra were also observed for $Cu(dpm)_2$ in pyridine and for $Cu(acac)_2$ in γ-picoline. It is characteristic of these three complexes in pyridine and γ-picoline that the visible absorption spectra at various temperatures have well-defined isosbestic points. On the other hand, the spectra of $Cu(sal)_2$ in pyridine at various temperatures are shown in Fig. 3; almost the same temperature dependences of the spectra were observed for $Cu(etacest)_2$ in pyridine and $Cu(sal)_2$ in γ-picoline. It is characteristic of the latter two complexes in pyridine and γ-picoline that the spectral lines observed at various temperatures do not intersect with one another and that only the spectral intensities increase remarkably with a rise in the temperature. The five complexes employed here, accordingly, group themselves in two classes, the former three complexes (Class A) and the latter two complexes (Class B), according to these temperature dependences of the visible absorption. This classification is also consistent with the one based upon the stability of the complexes,[8,9] the composition of the adducts of the complexes with pyridine,[10] and the solvent effect of the positions of the absorption maximum, as are listed in Table 1.

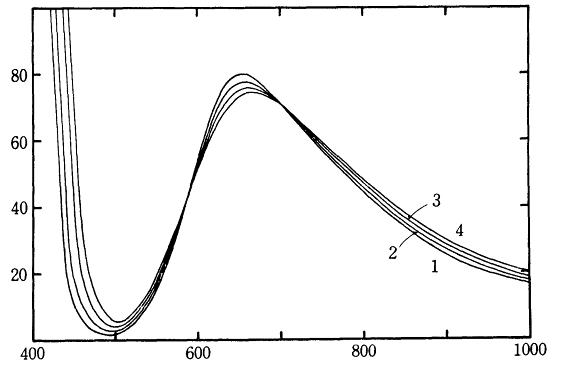

Fig. 1. Visible absorption spectra of $Cu(acac)_2$ in pyridine. (1): 0°C, (2): 20°C, (3): 40°C, (4): 60°C.

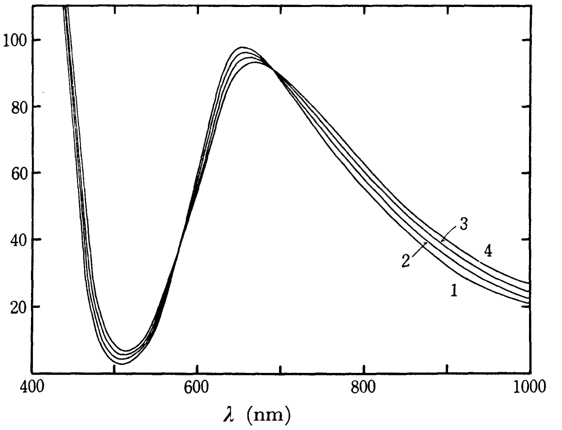

Fig. 2. Visible absorption spectra of $Cu(bzac)_2$ in pyridine. (1): 0°C, (2): 20°C, (3): 40°C, (4): 60°C.

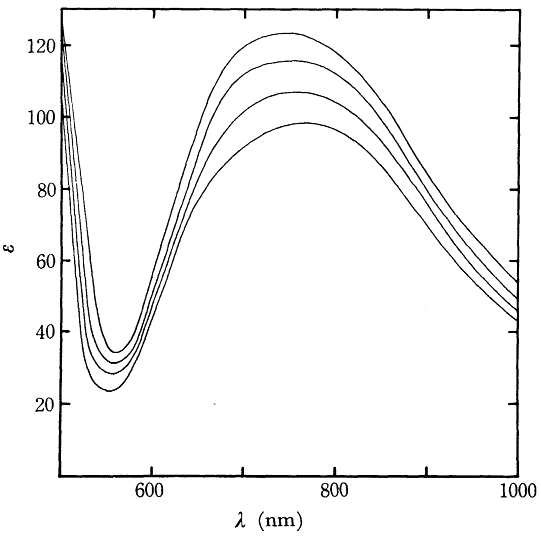

Fig. 3. Visible absorption spectra of $Cu(sal)_2$ in pyridine. (1): 0°C (the lowest line), (2): 20°C, (3): 40°C, (4): 60°C.

Such isosbestic points as are shown in Figs. 1 and 2 indicate that the complexes of Class A are present as two different complex species at equilibrium, even in a pure solvent of pyridine or γ-picoline. The two complex species will hereafter be called the low-temperature species, L, and the high-temperature species,

---

[7] P. Pfeiffer, E. Breith, E. Lubbe, and T. Tsumaki, *Ann.*, **503**, 84 (1933); A. E. Finn, G. G. Hampson, and L. E. Sutton, *J. Chem. Soc.*, **1938**, 1254.

[8] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-ion Complexes," (Special Publication No. 7), The Chemical Society, Burlington, London (1964).

[9] M. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, **67**, 2003 (1945).

[10] D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961); Y. Muto, This Bulletin, **31**, 56 (1958); H. Yokoi, M. Sai, and T. Isobe, *ibid.*, **43**, 1078 (1970).

TABLE 1. VARIOUS PROPERTIES OF THE β-DIKETONE CHELATE COMPLEXES OF COPPER(II)

Class	Copper(II) complex	Stability[a]	Adduct with pyridine[c]	Visible absorption spectra: Absorption maximum (at 20°C) Solvent: C-E[d] λ(nm); ε	Pyridine λ(nm); ε	Temperature dependence in pyridine solution λ(nm); ε
A	Cu(acac)$_2$	17.4	[Cu(acac)$_2$·Py]	654; 44	655; 77	two isosbestic points 585; 38 700; 71
	Cu(dpm)$_2$	ca. 19[b]		658; 44[e]	645; 98	576; 32 686; 83
	Cu(bzac)$_2$	18.0	[Cu(bzac)$_2$·Py]	654; 53	660; 96	562; 33 726; 77
B	Cu(sal)$_2$	13.0	[Cu(sal)$_2$·Py$_2$]	660; 59	760; 108	Changes in intensity without crossings of spectral lines
	Cu(etacest)$_2$	14.2	[Cu(etacest)$_2$·Py$_2$]	650; 40	710; 72	

a) Ref. 9. b) an approximately estimated value. c) Ref. 10, Py represents a pyridine molecule. d) an equivolume mixture of chloroform and ethanol. e) A shoulder was observed at about 530 nm.

H.

$$\mathrm{L} \rightleftharpoons \mathrm{H} \tag{1}$$

The equilibrium constant, K, for this equilibrium may be obtained from the following equation:

$$K = \frac{[\mathrm{H}]}{[\mathrm{L}]} = \frac{x}{c^0 - x} = \frac{D - D_\mathrm{L}}{D_\mathrm{H} - D} \tag{2}$$

where c^0 represents an initially-given concentration, where D is the measured optical density at any suitable wavelength, and where D_L and D_H are the optical densities at the same wavelength which would be found for the pure L and H species respectively at the concentration of c^0. Unfortunately, neither D_L nor D_H could be determined directly here, but an attempt has been made to estimate them for Cu(acac)$_2$, using the following method.

The measured spectra in the neighborhood of the two isosbestic points are shown in Fig. 4, where the bold line represents the peak position for the measured spectra and the one estimated by extrapolation for the spectra at temperatures besides 0—60°C. Accordingly, if we properly estimate the two temperatures at which the L and H species are present in solution in their pure forms, the spectral peak positions at the temperatures will be determined by the bold line. Since the spectral lines of D_L and D_H pass through the two isosbestic points and the peak positions estimated for them, we can draw smooth curves like the measured spectral lines through the three points; the curves are regarded as assumed spectral lines of D_L and D_H and are shown by dotted lines in Fig. 4. The equilibrium constant at any temperature can then be determined at any suitable wavelength within the range of 585—700 nm by using Eq. (2). The results are listed in Table 2. It is expected, from a consideration of the absorption-line shapes, that the true temperatures at which the L and H species are present in solution in their pure forms do no deviate extremely from the assumed ones listed in Table 2. Although the values of ΔH and and ΔS for the equilibrium were finally determined to be 4.0±1 kcal/mol and 13±4 e.u. respectively, such large errors were introduced for extra safety because of some uncertainty in the values of D_L and D_H.

The 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.[11,12] The oscillator strength at t°C will hereafter be expressed as f_t. Assuming that $\nu_n = 150$—$300\ \mathrm{cm}^{-1}$, we can calculate the (f_{60}/f_0) ratio to be 1.15—1.19 according to the coth rule mentioned above for the copper(II) complexes in pure forms. The spectral data of the β-diketone chelate complexes of copper(II) in pyridine and γ-picoline are listed in Table 3.

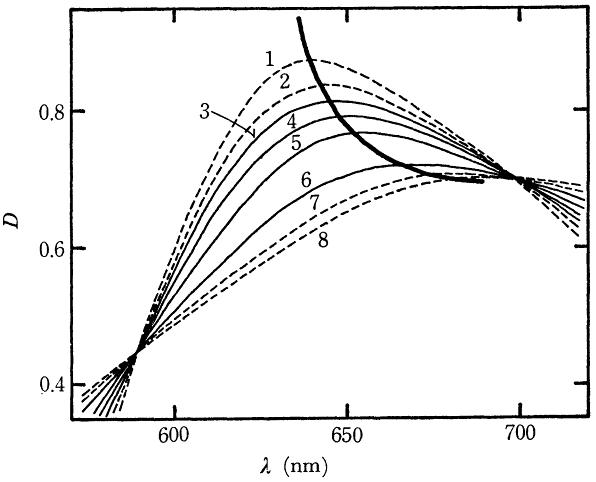

Fig. 4. The measured and estimated spectra in the neighborhood of isosbestic points for Cu(acac)$_2$ in pyridine (——: the measured spectra, ----: the estimated spectra, the bold line shows the spectral peak position).
(1): −60°C, (2): −40°C, (3): 0°C, (4): 20°C, (5): 40°C, (6): 60°C, (7): 110°C, (8): 130°C.

---

[11] A. D. Liehr and C. J. Ballhausen, *Phys. Rev.*, **106**, 1161 (1957); J. H. Van Vleck, *J. Phys. Chem.*, **41**, 67 (1937); R. S. Mulliken and C. A. Rieke, *Repts. Progr. Phys.*, **8**, 231 (1941).

[12] J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, **37**, 1569 (1962).

TABLE 2. THE EQUILIBRIUM AND THERMODYNAMIC CONSTANTS OF $L \rightleftharpoons H$ FOR $Cu(acac)_2$ IN PYRIDINE

Assumed temperature[a] (°C)		K				ΔH (kcal/mol)	ΔS (e.u.)
L	H	0°C	20°C	40°C	60°C		
−40	110	0.71	1.11	2.12	3.12	4.7	16
−60	130	0.98	1.40	2.43	3.33	3.9	12
−60	110	1.05	1.53	2.77	4.00	4.3	13
−40	130	0.66	1.02	1.85	2.63	4.4	13
						av.[b] 4.0±1.0	13±4

a) The assumed temperature at which L or H is present in solution in a pure form.
b) Such large errors were adopted for extra safety.

TABLE 3. SPECTRAL DATA OF THE β-DIKETONE CHELATE COMPLEXES OF COPPER(II) IN PYRIDINE AND γ-PICOLINE

Copper(II) complex	Solvent[a]	Absorption maximum		Oscillator strength, f[b]		f_{60}/f_0[d]
		0°C λ(nm); ε	60°C λ(nm); ε	0°C ($\times 10^3$)	60°C ($\times 10^3$)	
$Cu(acac)_2$	Py	652; 80	667; 75	1.76	1.95	1.10
	γ-Pic	660; 88	675; 81	1.97	2.07	1.05
$Cu(dpm)_2$	Py	660; 98	670; 94	2.20	2.33	1.05
$Cu(bzac)_2$	Py	645; 114	652; 94	2.25	2.44	1.08
$Cu(sal)_2$	Py	*ca.* 750; 98[c]	*ca.* 750; 123[c]	2.72	3.68	1.35
	γ-Pic	*ca.* 740; 107[c]	*ca.* 730; 129[c]	3.01	3.84	1.27
$Cu(etacest)_2$	Py	730; 67	730; 77	1.63	1.99	1.22

a) Py: pyridine, γ-Pic: γ-picoline. b) Corrected values at 20°C (the observed f value at t°C was multiplied by the ratio of the density of pyridine at 20°C to the density of pyridine at t°C). c) These systems exhibited broad absorption peaks. d) f_t represents the oscillator strength at t°C.

There is a clear difference in the observed ratio (f_{60}/f_0) between the complexes of Class A and Class B, as may be seen in Table 3. The ratios observed for the complexes of Class B are larger than those calculated theoretically according to the coth rule; furthermore, the spectral intensities of the complexes increased remarkably without any crossings of spectral lines with a rise in the temperature, as has been mentioned above. It seems, therefore, probable that a change in structure accompanying a change in spectral intensity takes place continuously according to the temperature for the complexes of Class B in pyridine or γ-picoline.

On the other hand, the observed ratio (f_{60}/f_0) for the complexes of Class A is much smaller than for the complexes of Class B, as may be seen in Table 3. The ratio (f_H/f_L) for $Cu(acac)_2$ in pyridine at any temperature was evaluated to be about 1.1, using the following values: $K_{60°C}=3.3$, $K_{0°C}=1.2$, $f_0=1.76$, $f_{60}=1.95$, and $(f_{60,H}/f_{0,H})=(f_{60,L}/f_{0,L})=1.17$. These results indicate that the spectral intensity of L is almost equal to that of H, and that, therefore, there is almost no difference in the symmetry of the copper-ion environment between L and H.[13] The fact that, for the planar copper(II) complexes, the visible absorption bands shift to longer wavelengths as the axial coordination bondings strengthen, or as the planar coordination bondings weaken, has been confirmed both theoretically and experimentally.[14,15] This gives a basis for the interpretation of the experimental fact that the absorption maximum for H appears at a somewhat longer wavelength than that for L, as is shown in Table 3. 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 at any temperature.[16,17] Many X-ray diffraction studies have shown that, when the planar metal complexes form some penta-coordinated 1 : 1 adducts,

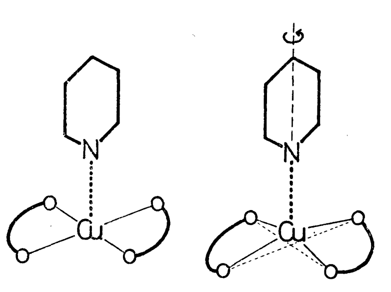

Fig. 5. The estimated structures of L and H for $Cu(acac)_2$ in pyridine.

---

[13] R. L. Belford and W. A. Yeranos, *Mol. Phys.*, **6**, 121 (1963); C. R. Hare, "Spectroscopy and Structure of Metal Chelate Compounds," ed. by K. Nakamoto and P. J. McCarthy, John Wiley & Sons, New York (1968), p. 98.

[14] R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

[15] D. P. Graddon, *J. Inorg. Nucl. Chem.*, **14**, 161 (1960); H. Yokoi, M. Sai, and T. Isobe, This Bulletin, **42**, 2232 (1969).

[16] D. P. Graddon, *Nature*, **183**, 1610 (1959); D. P. Graddon and E. C. Watton, *ibid.*, **187**, 1021 (1960).

[17] H. Yokoi, M. Sai, and T. Isobe, to be published.

the metal ion is displaced from the plane in the direction of the fifth coordinating atom.[18] On the basis of all these facts concerning the structures of Cu(acac)$_2$ in pyridine, the most probable structures of L and H were estimated to be those shown in Fig. 5, where both structures are of an approximate C_{2v} symmetry in the copper-ion environment. It may be said that the displacement of the copper atom from the plane of the four oxygen atoms is somewhat larger for H than for L. If we assume that the pyridine molecule in H rotates freely, as is shown by an arrow in Fig. 5, the entropy change can be calculated to be 14.8 e.u. Interestingly, this value is almost equal to the observed entropy change for L→H. The possibility that the pyridine molecule in H may rotate freely can be fully expected, since the difference in structure between L and H seems to be too small to give rise to such a large entropy change because of the environmental difference between them, and since it is considered, from a structural point of view, that the pyridine molecule rotates more easily in H than in L.

---

18) E. Frasson, R. Zannetti, R. Bardi, S. Bezzi, and G. Giacometti, *J. Inorg. Nucl. Chem.*, **8**, 452 (1958); P. R. H. Alderman, P. G. Owston, and J. M. Row, *J. Chem. Soc.*, **1962**, 668; S. Ooi and Q. Fernando, *Chem. Commun.*, **1967**, 532.