Spectrophotometric Studies of the Metallic Chelates of 2-Picolylamine. I. The Electronic Absorption Spectra of Some Nickel, Copper(II) and Cobalt(III) Chelates

By Shunji UTSUNO and Kôzô SONE

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2-Picolylamine (2-aminomethylpyridine; abbreviation: "pic") is a chelating agent which is structurally intermediate between ethylenediamine ("en") and 2,2′-bipyridine ("bip"). Recently Sutton[1] found that 2-picolylamine forms a large number of chelates with various metals, and that their properties in many respects resemble those of ethylene diamine chelates.[2] His data on the absorption spectra of these chelates were of special interest to us, since they reflect a number of important features of their electronic structures; this interest inspired us to carry out a series of more detailed spectrophotometric studies of these and related chelates, the first results of which shall be reported in this paper.

Experimental

Reagents.—The 2-picolylamine used in this work was the product of the Aldrich Chemical Co. (Milwaukee, Wisc., U. S. A.). In the preparation of the chelates, it was used without further purification; in the spectral study of the systems contain-

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[1] G. J. Sutton, *Australian J. Chem.*, **13**, 74, 222, 473 (1960); **14**, 37, 545, 550 (1961); **15**, 232, 563 (1962).

[2] The stabilities of some of these chelates were studied also by D. E. Goldberg and W. C. Fernelius (*J. Phys. Chem.*, **63**, 1246 (1959)) and T. J. Lane, C. S. C. and J. W. Thompson (*J. Am. Chem. Soc.*, **82**, 4179 (1960)).

ing the free ligand, it was purified by vacuum distillation (b. p. 89°C/15 mmHg). All the other reagents used were "Extra Pure" chemicals, most of which were the products of the Wako Pure Chemicals Co. (Osaka, Japan).

Apparatus. — The visible, ultraviolet and near infrared spectra of the aqueous solutions of the chelates were measured with a Shimadzu QR-50 quartz spectrophotometer, using silica cells of 10 mm. and 1 mm. light paths.

The Preparation of the Chelates.—These chelates —[Co pic$_3$](ClO$_4$)$_3$, [Co pic$_2$(NO$_2$)$_2$]NO$_3$·1/2H$_2$O, Ni·pic$_2$Cl$_2$, [Ni pic$_3$]Cl$_2$·2H$_2$O and Cu pic$_2$Cl$_2$– were prepared according to the methods of Sutton.[1] When all these chelates were analyzed with respect to their metals, satisfactory agreement between experimental and theoretical values was obtained in every case. In addition, the following chelates (a)—(d) were prepared for the present study:

(a) Ni pic Cl$_2$·H$_2$O. — NiCl$_2$·6H$_2$O (2.4 g.; 10^{-2} mol.) was dissolved in 3 ml. of water by heating, and 2-picolylamine (1.1 g.; 10^{-2} mol.) was added. When the blue mixture was concentrated by heating, green crystals were formed; after cooling, they were washed with 95% ethanol and then with absolute ethanol and ether. (Yield, 2.12 g.; 83%) (Found: Ni, 22.68; C, 28.33; H, 4.04; N, 11.21. Calcd. for $C_6H_{10}N_2Cl_2ONi$: Ni, 22.95; C, 28.17; H, 3.94; N, 10.95%).

(b) Ni pic SO$_4$·2H$_2$O.—NiSO$_4$·6H$_2$O (2.6 g.; 10^{-2} mol.) was dissolved in 5 ml. of water by heating, and 2-picolylamine (1.1 g.; 10^{-2} mol.) was added. The mixture was left standing for a week or more in a dessicator or in the open air, and the greenish blue crystals which formed were filtered, washed repeatedly with ethanol and then with ether, and dried at room temperature in the open air. The obtained crystals contained about 3 molec. of water of crystallization; when they were heated at 150°C for several hours, a part of the water was lost, leaving the pale blue dihydrate. (Yield, 2.58 g.; 86%). (Found: Ni, 19.28; C, 22.84; H, 4.12; N, 9.42. Calcd. for $C_6H_{12}N_2SO_6Ni$: Ni, 19.64; C, 23.10; H, 4.04; N, 9.37%).

(c) Cu pic Cl$_2$.—CuCl$_2$·2H$_2$O (1.7 g.; 10^{-2} mol.) and 2-picolylamine (1.1 g.; 10^{-2} mol.) were dissolved separately in 90% ethanol (10 ml. each). When the two solutions were mixed, a green precipitate was formed at once; this became blue when the mixture was heated for some time. After the completion of this color change, the precipitate was filtered and washed with ethanol and ether. The pale blue crystalline powder which was obtained was recrystallized by dissolving it in 10 ml. of water by heating and then adding the same volume of ethanol. (Yield, 2.16 g.; 90%). (Found: Cu, 25.92; C, 29.32; H, 3.23; N, 11.72. Calcd. for $C_6H_8N_2Cl_2Cu$: Cu, 26.19; C, 29.71; H, 3.32; N, 11.55%).

(d) Cu pic SO$_4$·2H$_2$O.—CuSO$_4$·5H$_2$O (2.5 g.; 10^{-2} mol.) was dissolved in 5 ml. of water, and 2-picolylamine (1.1 g.; 10^{-2} mol.) was added. The mixture was left standing overnight in a refrigerator, and the blue crystals which separated out were washed with ethanol and ether, dried at room temperature in the open air, and recrystallized from water. (Yield, 2.37 g.; 79%). (Found: Cu, 21.13; C, 26.71; H, 3.14; N, 10.44. Calcd.:[3] Cu, 20.91; C, 26.92; H, 3.01; N, 10.46%).

Results and Discussion

The Formation of Some Nickel and Copper Chelates. — Sutton[1] prepared a number of nickel chelates of 2-picolylamine with metal: ligand ratios of 1:2 and 1:3, and copper chelates with the ratio of 1:2. On the other hand, it is well known that both ethylenediamine and 2, 2′-bipyridine can form 1:1, 1:2 and 1:3 chelates with these metals, either in an aqueous solution or in the state of crystalline complexes; therefore, it is to be expected that 2-picolylamine can also form 1:1 chelate with nickel and copper, and a 1:3 chelate with copper, at least in aqueous solutions, and probably in the state of crystalline complexes, too. In fact, Fernelius et al.[2] found that such 1:1 complexes of considerable stability are formed in solution, and now we have found the crystals of the Ni pic Cl$_2$·H$_2$O, Ni pic SO$_4$·2H$_2$O, Cu pic Cl$_2$ and Cu pic SO$_4$·2H$_2$O chelates can be easily obtained from the solutions of their components. The nickel chelates are greenish blue (sulfate) or green (chloride), and they give blue solutions in water, while the copper chelates are blue, both in the solid state and in aqueous solutions.

The common coordination numbers of Ni^{2+} and Cu^{2+} are 6 and 4 respectively, and the tendencies of organic amines, water, Cl^- and SO_4^{2-} to form coordinate bonds with these ions generally decrease in the order: amines $>$H$_2$O$>$ anions. Therefore, the most probable coordination formulas of the copper chelates are [Cu pic Cl$_2$] and [Cu pic (OH$_2$)$_2$] SO$_4$ respectively, while the coordination of both water and anions must be assumed to explain the compositions of the nickel chelates. In aqueous solutions, however, the coordinated anions seem to be displaced by water, forming the chelate ions [Cu pic (OH$_2$)$_2$]$^{2+}$ and [Ni pic(OH$_2$)$_4$]$^{2+}$; this is proved by the fact that the solutions of all these chelates show the immediate reactions of their anions, by the fact that the absorption spectra of these solutions are practically independent of their anions (i. e., the curves of Ni pic Cl$_2$·H$_2$O and Cu pic Cl$_2$ are nearly identical with those of Ni pic SO$_4$·2H$_2$O and Cu pic SO$_4$·2H$_2$O respectively), and, further, by the fact that these spectra are quite insensitive to the addition of their anions in a considerable excess.

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[3] While the value for Cu refers to the dihydrate ($C_6H_{12}N_2SO_6Cu$), those for C, H and N refer to the anhydrous state, since this chelate loses all of its water in the course of vacuum dessication prior to the organic analysis (5 mmHg, 80°C, 2 hr.).

TABLE I. LIGAND FIELD BANDS OF ETHYLENEDIAMINE, 2-PICOLYLAMINE AND 2,2′-BIPYRIDINE CHELATES

Chelate	λ_{max} (log ε_{max})			Literature
$[\mathrm{Ni\ en\ (OH_2)_4}]^{2+}$	973 (0.68)	618 (0.54)	370 (0.76)	6a
$[\mathrm{Ni\ pic\ (OH_2)_4}]^{2+}$	960 (0.62)	610 (0.50)	367 (0.81)	*
$[\mathrm{Ni\ bip\ (OH_2)_4}]^{2+}$	942 (0.62)	595 (0.42)	(( ))	6a
$[\mathrm{Ni\ en_2\ (OH_2)_2}]^{2+}$	940 (0.81)	571 (0.71)	357 (0.87)	6a
$[\mathrm{Ni\ pic_2\ (OH_2)_2}]^{2+}$	910 (0.91)	556 (0.73)	(( ))	*
$[\mathrm{Ni\ bip_2\ (OH_2)_2}]^{2+}$	929 (0.97)	560 (0.87)	(( ))	6a
$[\mathrm{Ni\ en_3}]^{2+}$	898 (0.85)	547 (0.81)	345 (0.90)	6a, 6c
$[\mathrm{Ni\ pic_3}]^{2+}$	860 (0.96)	536 (1.03)	(( ))	*
$[\mathrm{Ni\ bip_3}]^{2+}$	789 (0.84)	519 (1.08)	(( ))	6a, 6b
$[\mathrm{Cu\ en\ (OH_2)_2}]^{2+}$		662 (1.51)		6a
$[\mathrm{Cu\ pic\ (OH_2)_2}]^{2+}$		685 (1.51)		*
$[\mathrm{Cu\ bip\ (OH_2)_2}]^{2+}$ a)		699 (1.48)		6a
$[\mathrm{Cu\ en_2}]^{2+}$		556 (1.85)		6a
$[\mathrm{Cu\ pic_2}]^{2+}$		580 (1.82)		*
$[\mathrm{Cu\ bip_2}]^{2+}$		750 (1.99)		6a
$[\mathrm{Co\ en_3}]^{3+}$		467 (1.93)	338 (1.90)	6c
$[\mathrm{Co\ pic_3}]^{3+}$		464 (2.11)	~335 (~2.2, sh.)	*
$[\mathrm{Co\ bip_3}]^{3+}$ a)		448 (1.83)	(( ))	6d
cis-$[\mathrm{Co\ en_2\ (NO_2)_2}]^{+}$		435 (2.10)	(( ))	12
trans-$[\mathrm{Co\ en_2\ (NO_2)_2}]^{+}$		429 (2.20)	(( ))	12
$[\mathrm{Co\ pic_2\ (NO_2)_2}]^{+}$		440 (2.46)	(( ))	*

(( )): The band hidden by the strong ultraviolet absorption of the ligand.
sh: Shoulder.
*: Data of the present study.
a) According to Ito (Ref. 6a), these chelates should be formulated as $[\mathrm{Cu\ bip\ (OH_2)_4}]^{2+}$ and $[\mathrm{Cu\ bip_2\ (OH_2)_2}]^{2+}$, respectively.

TABLE II. STRONG ULTRAVIOLET BANDS OF 2-PICOLYLAMINE CHELATES

Chelate	λ_{max} (log ε_{max})	Chelate	λ_{max} (log ε_{max})	
(2-Picolylamine)	260 (3.48)	$[\mathrm{Co\ pic_3}]^{3+}$	~260 (3.95, sh.)	
$[\mathrm{Ni\ pic\ (OH_2)_4}]^{2+}$	260 (3.46)	$[\mathrm{Co\ pic_2\ (NO_2)_2}]^{+}$	338 (3.70)	252 (4.34)
$[\mathrm{Ni\ pic_2\ (OH_2)_2}]^{2+}$	260 (3.74)	*cis*-$[\mathrm{Co\ en_2\ (NO_2)_2}]^{+}$	323 (3.68)a)	
$[\mathrm{Ni\ pic_3}]^{2+}$	260 (3.98)	*trans*-$[\mathrm{Co\ en_2\ (NO_2)_2}]^{+}$	339 (3.44)a)	249 (4.37)a)
$[\mathrm{Cu\ pic\ (OH_2)_2}]^{2+}$	247 (3.59)			
$[\mathrm{Cu\ pic_2}]^{2+}$	247 (3.92)			

a) Data of Kuroya and Tsuchida (Ref. 12a.). Later data of Basolo (Ref. 12b) in $\mathrm{MeOH-H_2O}$ agree reasonably well with these authors', but add one more band at 240 mμ (log ε_{max} 4.22) for *cis*-$[\mathrm{Co\ en_2\ (NO_2)_2}]^{+}$.

We also tried to prove our second expectation, i. e., the formation of the chelate ion. $[\mathrm{Cu\ pic_3}]^{2+}$, and we found rather convincing evidence for its existence in solution. Figure 1 shows three representative curve taken from our data on the absoprtion spectra of aqueous solutions containing $[\mathrm{Cu\ pic_2}]^{2+}$ and free 2-picolylamine; it can be seen that, with the increase in free ligand concentration, the absorption band of $[\mathrm{Cu\ pic_2}]^{2+}$ at 580 mμ is gradually intensified and shifted toward a longer wavelength, until, in a 8.46 M solution of 2-picolylamine (the highest concentration tried), the λ_{max} and ε_{max} values become 612 mμ and 109 respectively. A comparison of these data with the spectra of the $[\mathrm{Cu\ en_2}]^{2+}$-ethylenediamine system studied by Bjerrum and Nielsen[4] reveals the general resemblance of these two systems, and an approximate analysis of the data by their method indicates that the chelate ions $[\mathrm{Cu\ pic_3}]^{2+}$ are progressively formed in these solutions. The third stability constant (k_3) of this chelate was estimated to be 2~3, which is somewhat larger than the k_3 value (~0.1) of $[\mathrm{Cu\ en}]^{2+}$ reported by Bjerrum and Nielsen, but much

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[4] J. Bjerrum and E. J. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948).

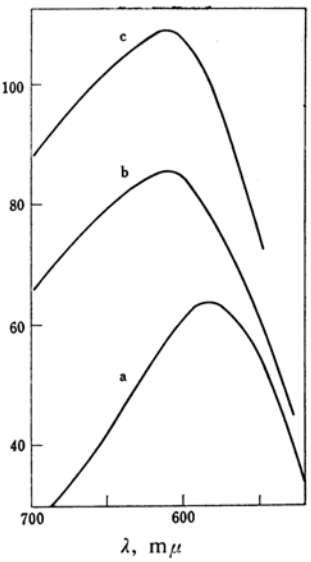

Fig. 1. The effect of excess 2-picolylamine on the spectrum of [Cu pic_2]$^{2+}$.

a: [Cu pic_2]$^{2+}$ (6.82×10^{-3} M)
b: [Cu pic_2]$^{2+}$ (5.09×10^{-3} M) + 2-picolylamine (7.901×10^{-1} M) + HNO_3 (6.87×10^{-2} M)
c: [Cu pic_2]$^{2+}$ (5.09×10^{-3} M) + 2-picolylamine (8.465 M). Temp.: 25°C
μ: 1 M KNO_3; cell thickness: 10 mm.

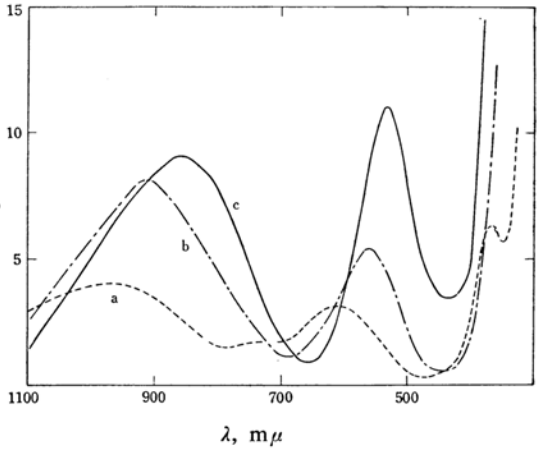

Fig. 2. Absorption spectra of nickel chelates.
a: [Ni pic$(OH_2)_4$]$^{2+}$
b: [Ni $pic_2(OH_2)_2$]$^{2+}$
c: [Ni pic_3]$^{2+}$
Concn.: $10^{-1}\sim5\times10^{-2}$ M; temp: 13°C; cell thickness: 10 mm.

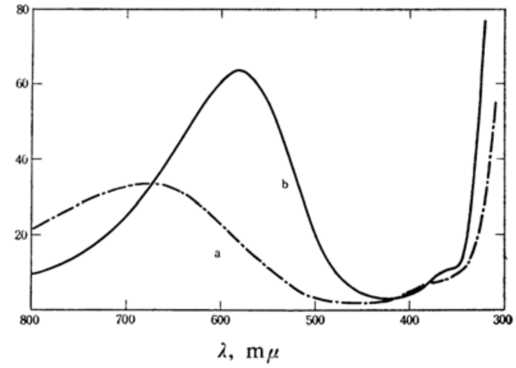

Fig. 3. Absorption spectra of copper chelates.
a: [Cu pic$(OH_2)_2$]$^{2+}$　b: [Cu pic_2]$^{2+}$
Concn.: $10^{-2}\sim7\times10^{-3}$ M; temp.: 18°C; cell thickness: 10 mm.

smaller than the value of [Cu bip_3]$^{2+}$ (~2000) reported by Irving and Mellor.⁵⁾ This fact, and the fact that the λ_{max} and ε_{max} values of [Cu pic_3] given above are quite near to the values of [Cu en_3]$^{2+}$ reported by Bjerrum and Nielsen, are new examples of the close resemblance between 2-picolylamine and ethylenediamine chelates, a resemblance which has already been pointed out by Sutton¹⁾ and which will be discussed further in the next section.

The Electronic Absorption Spectra of the Chelates.—The visible, ultraviolet and near infrared spectra of the chelates prepared are summarized in Figs. 2—4 and in Tables I and II. Table I shows the λ_{max} and $\log\varepsilon_{max}$ values of the relatively weak absorption bands appearing between 350 and 1000 mμ, bands which are undoubtedly due to the ligand-field splittings of the metal 3d orbitals; this table also presents the data of the corresponding ethylenediamine and 2, 2′-bipyridine chelates taken from the literature.⁶⁾ The results already mentioned in the preceding section, and the remark of Sutton¹⁾ that Ni pic_2 Cl_2 and Cu pic_2 Cl_2 are converted into [Ni pic_2 $(OH_2)_2$]$^{2+}$ and [Cu pic_2]$^{2+}$ in their aqueous solutions, were taken into account in the preparation of this table.

It can be seen from this table and from the corresponding curves in Figs. 2—4 that, in general, the spectrum of a 2-picolylamine chelate is intermediate between those of the ethylenediamine and 2, 2′-bipyridine chelates of the corresponding structure. This is what one can expect from the structure of 2-picolylamine; however, it can be seen further that, in most cases, the spectral similarity to the ethylenediamine chelates is more apparent than that to the 2, 2′-bipyridine chelates. This fact is in conformity with the remark of Sutton mentioned above; two groups of chelates can be distinguished in this respect: (i) those in which the λ_{max} values decrease in the order: ethylenediamine $\gtrsim$ 2-picolylamine > 2, 2′-bipyridine and (ii) those in which they increase in

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5) H. Irving and D. H. Mellor, *J. Chem. Soc.*, **1962**, 5222.

6) a) H. Ito, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1383 (1956); b) K. Sone and M. Kato, *Naturwiss.*, **45**, 10 (1958); c) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1497 (1954); d) B. Martin and G. M. Waind, *J. Chem. Soc.*, **1958**, 4284.

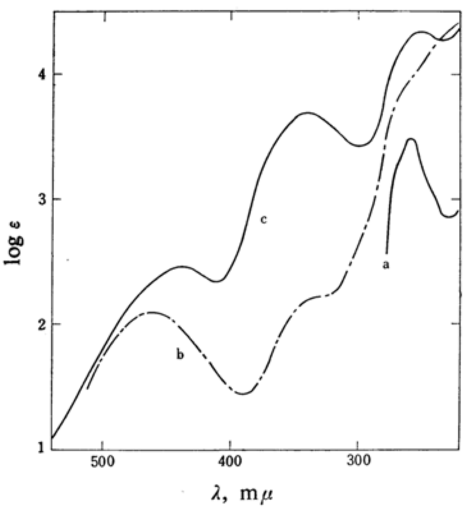

Fig. 4. Absorption spectra of cobalt chelates.

a: 2-picolylamine
b: [Co pic_3]$^{3+}$
c: [Co $pic_2(NO_2)_2$]$^{+}$
Concn.: $2\times10^{-3}\sim10^{-4}$ M; temp.: 18~24°C; cell thickness: 10 mm. and 1 mm.

the order: ethylenediamine $\lesssim$2-picolylamine$<$ 2, 2′-bipyridine.

The chelates [Ni R $(OH_2)_4$]$^{2+}$, [Ni R_3]$^{2+}$, and [Co R_3]$^{3+}$ belong to the first group. According to the concept of the spectrochemical series,7) this type of spectral change means that the strength of the effective ligand field increases in the order; ethylenediamine $\lesssim$ 2-picolylamine $<$ 2, 2′-bipyridine. In fact, this is a very conceivable order, because it is generally accepted that, in the 2, 2′-bipyridine chlates, there is a special stabilization of the resonance system of the bipyridine molecule because of the chelate formation, presumably through the formation of metal-ligand π-bonds and the introduction of some "aromaticity" into the chelate ring. On the other hand, such effects are absent in ethylenediamine chelates, and, in the case of 2-picolylamine chelates, it is apparent that they are, at most, much smaller than in 2, 2′-bipyridine chelates, since there is only one pyridine ring and no conjugation between the ring and the $-CH_2NH_2$ chain in their ligand. Therefore, we can expect that the most effective binding of the metal ions, or, in other words, the operation of the strongest ligand field, is realized in 2, 2′-bipyridine chelates, and that the corresponding effects decrease in ethylenediamine and 2-picolylamine chelates in just the observed order.

[Cu R_2]$^{2+}$ and [Cu R $(OH_2)_2$]$^{2+}$ belong to the second group. Here the chief factor governing the spectra seems to be a different one, i. e., the steric effect. It has formerly been pointed out by Ito8) that the spectro-chemical series in its simple form is not obeyed by many of the copper(II) complexes; according to him, their λ_{max} values are strongly influenced by their actual coordination number. A similar opinion was expressed by Jørgensen, who further argued that it is possible to study the shape of a copper(II) complex from the magnitude of the σ_{Cu}/σ_{Ni} ratio for it, i. e., the ratio between the wave number of its absorption band and that of the first band of the corresponding nickel complex. According to him, the complex is highly tetragonal if this ratio is 1.6~1.8, and if it is smaller than this, the tetragonality is accordingly lower; for example, [Cu en_2]$^{2+}$ (the 1.73 ratio) belongs to the former group, while [Cu bip_2]$^{2+}$ (the 1.1 ratio) belongs to the latter, most probably because of the steric repulsion caused by the 6, 6′-H atoms of bipyridine molecules, a repulsion which deforms the chelate strongly from the planar structure favored by copper(II).5)

Now the λ_{max} value of [Cu pic_2]$^{2+}$ is much closer to that of [Cu en_2]$^{2+}$ than to that of [Cu bip_2]$^{2+}$, and the value of σ_{Cu}/σ_{Ni} is 1.56. These data indicate that this chelate is nearly tetragonal in shape, and that the repulsion between the ligands is quite small. This indication is again a very reasonable one, since it can be expected that this chelate exists chiefly in the trans-planar form in solution, and the model of this form is practically free from the repulsion of this kind.

In the chelates [Cu R $(OH_2)_2$]$^{2+}$, the steric repulsion of this kind should be completely absent. The differences among the λ_{max} values of the three chelates of ethylenediamine, 2-picolylamine and 2, 2′-bipyridine are, accordingly, quite small, but they are still in the same order as those of [Cu R_2]$^{2+}$. This may be due to the existence of some kind of steric effect even in this case, although we cannot be very certain about its nature.9,10)

In the chelates, [Ni R_2 $(OH_2)_2$]$^{2+}$ the spectral order is rather irregular (ethylenediamine$>$

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7) Cf. C. K. Jørgensen, "Absorption Spectra and Chemical Binding in Complexes," Pergamon Press, London (1962), Chapter 7.

8) H. Ito, Ref. 6a.

9) It is interesting to compare the spectral data in Table I with the values of the stability constants of these chelates reported by Irving and Mellor (Ref. 5) and by Goldberg and Fernelius (Ref. 2). Although the data of these two sets of authors are not strictly comparable with each other, it can be seen that there exists a certain degree of parallelism between the spectral and stability data; for example, the order of stabilities for the chelates [Ni R_3]$^{2+}$ is; ethylenediamine$<$2-picolylamine$\ll$2, 2′-bipyridine, while that for [Cu R_2]$^{2+}$ is: ethylenediamine$>$ 2-picolylamine$\gg$2, 2′-bipyridine.

10) The existence of some steric effect in [Cu bip-$(OH_2)_2$]$^{2+}$ and [Cu phen$(OH_2)_2$]$^{2+}$ was also pointed out by Irving and Mellor (Ref. 5).

2, 2′-bipyridine > 2-picolylamine). If R is a symmetrical ligand (ethylenediamine or bipyridine), this type of chelate can exist in either a cis or in a trans form; if R is unsymmetrical (2-picolylamine), two cis and two trans forms are possible. However, as in the case of the copper chelates, the formation of the trans chelate will be hindered in the case of $[\mathrm{Ni \cdot bip_2(OH_2)_2}]^{2+}$, and the cis form will be formed predominantly in solution; on the other hand, in the case of ethylenediamine and 2-picolylamine chelates, the trans forms will be more stable because of their higher symmetries, and, therefore, they will be formed predominantly in solution. This difference may be, at least in part, the reason for the irregular order observed here.[11]

Apart from the bands shown in Table I, the chelates studied also have a band or bands in the ultraviolet region which are much stronger than those in Table I (cf. Table II). 2-Picolylamine itself shows a strong band at 260 mμ while the nickel chelates also show a band at this wavelength. In the case of the copper chelates, this band is considerably broadened, and the apparent maximum is shifted to 247 mμ. $[\mathrm{Co\ pic_3}]^{3+}$ also shows a shoulder at abuot 260 mμ. $[\mathrm{Co\ pic_2(NO)_2}]^+$ shows two strong bands at 338 and 252 mμ, the latter of which is still much stronger than the band of 2-picolylamine. A comparison of the absorption curve of this chelate with those of the two isomers of $[\mathrm{Co\ en_2(NO_2)_2}]^+$ indicates that these bands are not due to the absorption of coordinated picolylamine, and that they should, rather, be ascribed to the absorption of coordinated $\mathrm{NO_2}^-$ ions, which probably occupy trans positions with regard to each other.[12] Thus, these spectral data support the original view of Sutton[1] that this chelate has the trans structure, although the corresponding cis isomer could not be obtained by him, and our several trials in this direction all ended in failure.

Summary

1) In addition to the nickel chelates (1 : 2 and 1 : 3) and copper chelates (1 : 2) already described by Sutton, it has been found that 2-picolylamine also forms 1 : 1 chelates (chlorides and sulfates) with these metals, which can be obtained in the state of crystals, and the chelate ions $[\mathrm{Cu\ pic_3}]^{2+}$ of low stability, in solution.

2) A comparison of the electronic absorption spectra of all these chelates and two cobalt(III) chelates of 2-picolylamine with those of the chelates of ethylenediamine and 2, 2′-bipyridine has indicated that, in general, the spectrum of a 2-picolylamine chelate is intermediate between the spectra of the corresponding chelates of the latter two ligands; however, the similarity to the ethylenediamine chelate is more apparent in most cases.

3) Certain structural features of the 2-picolylamine chelates have been discussed on the basis of these spectral data.

Chemical Laboratory
Aichi Gakugei University
Higashi-ku, Nagoya (S. U.)

Chemical Laboratory
Department of General Education
Nagoya University
Chikusa-ku, Nagoya (K. S.)

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[11] However, the spectrum of $[\mathrm{Ni\ bip_2(OH_2)_2}]^{2+}$ cited in Table I is that in its alcoholic solution, and, therefore, it is also possible that this irregularity is due to some effect of this solvent on the structure or electronic state of chelate. All the other data in this table refer to the spectra of aqueous solutions.

[12] a) H. Kuroya and R. Tsuchida, This Bulletin, **15**, 427 (1940); b) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).