BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 105—109 (1967)

Spectrophotometric Studies of the Metal Chelates of 2-Aminomethylpyridine and Its Derivatives. II. The Preparation and Electronic Absorption Spectra of Some Nickel and Copper(II) Chelates of 6-Methyl-2-aminomethylpyridine and *N*-Methyl-2-aminomethylpyridine

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(Received May 30, 1966)

Fifteen chelates of nickel and copper(II), among which twelve are new, of 6-methyl-2-aminomethylpyridine (6-methyl-2-picolylamine="mepic") and *N*-methyl-2-aminomethylpyridine (picolylmethylamine="pma") were prepared, and the electronic absorption spectra of their aqueous solutions were measured. The spectra observed were practically those of the chelate ions $[Cu\,L]^{2+}$, $[Cu\,L_2]^{2+}$, $[Ni\,L]^{2+}$, $[Ni\,L_2]^{2+}$ (L=mepic or pma) and $[Ni\,(pma)_3]^{2+}$; $[Ni(mepic)_3]^{2+}$ was found to be unstable in solution, and to dissociate into $[Ni(mepic)_2]^{2+}$ and a ligand molecule. With the exception of $[Cu(pma)]^{2+}$, the wave numbers of the absorption maxima (ν_{max}) of these chelates were all smaller than those of the corresponding 2-aminomethylpyridine (2-picolylamine ="pic") chelates as a result of the steric hindrance caused by methyl substitution in the ligands. The nature and degree of this steric hindrance in each chelate, and the probable structure of some of these chelates, can be studied by a comparison of the obtained spectra with one another and by the use of scale models of these chelates.

In a previous communication,[1] we have reported about the electronic absorption spectra of the metal chelates of 2-picolylamine (abbreviation: "pic"). We shall report here the results for the chelates of two methyl derivatives of 2-picolylamine, *i. e.*, 6-methyl-2-picolylamine ("mepic") and picolylmethylamine ("pma"). In general, it is expected that the methyl group in these ligand molecules will enhance the basicity of their nitrogen atoms and increase the ligand field strength, but they will also exert certain amounts of steric hindrance to coordination. Since the results of the stability measurements performed by Fernelius, Lane, *et al.*[2] indicated that the metal chelates of mepic and pma were less stable than the corresponding pic chelates, it seems that the influence of steric hindrance is stronger than that of the increased basicity. With this in mind, we prepared a number of nickel and copper(II) chelates of mepic and pma, and measured their electronic absorption spectra, in order to obtain some information about the influence of these methyl groups on the spectra of the chelates.

Experimental

Reagents. The ligands, 6-methyl-2-picolylamine and picolylmethylamine, used in this work were the products of the Aldlich Chemical Co. (Milwaukee, Wisc., U. S. A.) and were used without further purification. All the other reagents used were "Extra Pure" Chemicals, most of which were the products of the Hayashi Pure Chemical Co. (Osaka, Japan).

Apparatus. The visible, ultraviolet, and nearinfrared spectra of the aqueous solutions of the chelates were measured with a Shimadzu QR-50 quartz spectrophotometer, using silica cells with 10 mm and 100 mm light paths.

The Preparation of the Chelates. (a) $Cu(mepic)_2Cl_2\cdot 3H_2O$, $Cu(mepic)_2(ClO_4)_2$ and $Ni(mepic)_3(ClO_4)_2$. These were prepared according to the method of Sutton.[3]

(b) $Ni(mepic)Cl_2\cdot 3H_2O$. Nickel chloride hexahydrate (2.37 g; 10 mmol) was dissolved in 3 *ml* of water, and then mepic (1.22 g; 10 mmol) was added. The solution was evaporated on a steam bath until the crystals began to separate out on the surface of the solution. A small amount of ethanol was added, the separated crystals were dissolved by heating, and then the solution was kept in a refrigerator. The green crystals which separated were washed with ethanol and ether and dried in open air (yield, 1.92 g; 63%). (Found: Ni, 19.24; N, 9.48%. Calcd. for $C_7H_{16}N_2O_3Cl_2Ni$: Ni, 19.20; N, 9.16%).

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[1] S. Utsuno and K. Sone, This Bulletin, **37**, 1028 (1964).

[2] a) D. E. Goldberg and W. C. Fernelius, *J. Phys. Chem.*, **63**, 1246 (1959); b) H. R. Weimer and W. C. Fernelius, *ibid.*, **64**, 1951 (1960); c) T. J. Lane and J. W. Thompson, *J. Am. Chem. Soc.*, **82**, 4179 (1960).

[3] G. J. Sutton, *Australian J. Chem.*, **16**, 371 (1963).

(3) $Ni(mepic)SO_4\cdot 3H_2O$. Nickel sulfate hexahydrate (2.59 g; 10 mmol) was dissolved in 10 m*l* of water, and then mepic (2.22 g; 10 mmol) was added. Greenish-blue crystals immediately began to separate out. After they had stood overnight in a refrigerator, they were filtered, washed with cold water, and dried over sulfuric acid (yield, 2.36 g; 71%). Since this chelate hydrolyzed in hot water and nickel hydroxide was precipitated, the yield after recrystallization was very low (yield, 0.62 g; 19%). (Found: Ni, 17.74; N, 8.49; C, 25.62; H, 4.95%. Calcd for $C_7H_{16}N_2\cdot O_7SNi$; Ni, 17.74; N, 8.46; C, 25.35; H, 4.87%).

(d) $Ni(mepic)_2Cl_2\cdot 2H_2O$. Into a solution of nickel chloride hexahydrate (1.19 g; 5 mmol) in 10 m*l* of ethanol, the amine (1.22 g; 10 mmol) was added. The blue granules which gradually separated out of the solution were filtered and washed with ethanol and ether (yield, 1.82 g; 89%). For further purification, the product was recrystallized from hot water (*ca.* 5 m*l*). (Found: Ni, 14.32; N, 13.22%. Calcd for $C_{14}H_{24}N_4O_2Cl_2Ni$: Ni, 14.29; N, 13.69%).

(e) $Ni(mepic)_2(ClO_4)_2\cdot 2H_2O$. An aqueous solution of nickel perchlorate (2.15 M, 2 m*l*; 4.3 mmol) was added to the amine (1 g; 8.2 mmol). After it had been kept in a refrigerator overnight, light blue crystals separated out. They were washed with water containing 20% ethanol and dried in open air (yield, 2.03 g; 92%). This chelate is readily soluble in methanol, ethanol and hot water, but it is only slightly soluble in cold water. Recrystallization was performed with hot water containing a small amount of nickel perchlorate. (Found: Ni, 10.86; N, 10.41; C, 31.53; H, 4.76%. Calcd for $C_{14}H_{24}N_4O_{10}Cl_2Ni$: Ni, 10.91, N, 10.41; C, 31.24; H, 4.49%).

(f) $Cu(mepic)Cl_2$ Copper chloride dihydrate (1.70 g; 10 mmol) was dissolved in 10 m*l* of ethanol, and the amine (1.22 g; 10 mmol) dissolved in 5 m*l* of ethanol, was added. The green crystals which immediately formed were filtered and washed with ethanol and ether (yield, 2.20 g; 85%). Recrystallization from hot methanol resulted in green needles. Dissolution in hot water produced a blue precipitate, which seemed to be copper(II) hydroxide. (Found: Cu, 24.32; N, 10.85%. Calcd for $C_7H_{10}N_2Cl_2Cu$: Cu, 24.76; N, 10.92%).

(g) $Cu(mepic)SO_4\cdot 2H_2O$. The amine (1.22 g; 10 mmol) was added to an aqueous solution of copper sulfate pentahydrate (2.54 g; 10 mmol) in 10 m*l* of water. From the resultant deep blue solution, blue crystals were separated out. They were filtered through a glass filter, washed with water, and dried in open air (yield, 2.83 g; 90%). They were recrystallized by adding ethanol to the aqueous solution of the crude product. (Found: Cu, 19.88; N, 8.57%. Calcd for $C_7H_{14}N_2O_6SCu$: Cu, 19.99; N, 8.82%).

(h) $Ni(pma)Cl_2$. To a solution of nickel chloride hexahydrate (1.19 g; 5 mmol) in 2 m*l* of water, the amine (0.61 g; 5 mmol) in 5 m*l* of ethanol was added. The mixture was evaporated to dryness on a steam bath. The resulting green powder was repeatedly washed with hot ethanol and was recrystallized from a water-ethanol mixture (yield, 0.97 g; 77%). (Found: Ni, 23.51; N, 11.35; C, 34.02; H, 4.12%. Calcd for $C_7H_{10}N_2Cl_2Ni$: Ni, 23.32; N, 11.13; C, 33.39; H, 4.00%).

(i) $Ni(pma)_2Cl_2$. Nickel chloride hexahydrate (1.19 g; 5 mmol) was dehydrated with 5 m*l* of 2, 2-dimethoxypropane. After the mixture had stood for an hour at room temperature, *n*-butanol was added and the solution was heated on a steam bath for about 30 min, in order to drive off the acetone, the methanol, and the excess of the dehydrating reagent. The solution was then poured into a beaker containing the amine (1.22 g; 10 mmol). A light blue powder was immediately separated out. It was filtered and washed with ethanol and ether (yield, 1.72 g; 92%). (Found: Ni, 15.70; N, 14.89; C, 44.86; H, 5.38%. Calcd for $C_{14}H_{20}N_4Cl_2Ni$: Ni, 15.70; N, 14.98; C. 44.97; H, 5.39%).

(j) $Ni(pma)_3(ClO_4)_2$. Nickel perchlorate hexahydrate (1.22 g; 3.33 mmol) was dehydrated with 3 m*l* (10% in excess) of 2, 2′-dimethoxypropane. The dehydration is endothermic, and after the resulting cold solution had warmed up to room temperature, it was diluted with 30 m*l* of methanol and heated until 20 m*l* of the solvents were distilled out. Then the amine (1.32 g; 11 mmol) was added, and the resulting red solution was filtered. The filtrate was heated gently and evaporated to dryness. To the red gum obtained, an additional amount of methanol was added; evaporation was repeated until purplish-pink crystals finally separated out. They were washed with cold methanol until the washings were pink, and then dried in open air (yield, 1.46 g; 70%). They were recrystallized from warm water containing 30% methanol. The synthesis of this chelate using water, ethanol, or *n*-butanol as a solvent was unsuccessful because the red gum precipitated was difficult to crystallize in these solvents. (Found: Ni, 9.32; N, 13.49; C, 40.07; H, 4.76%. Calcd for $C_{21}H_{30}N_6O_8Cl_2Ni$: Ni, 9.41; N, 13.47; C, 40.41; H, 4.85%).

(k) $Cu(pma)Cl_2$. The e) procedure was applied using pma instead of mepic. Blue needles. (Found: Cu, 24.74; N, 10.82; C, 32.77; H, 4.06%. Calcd for $C_7H_{10}N_2Cl_2Cu$: Cu, 24.76; N, 10.91; C, 32.76; H, 3.93%).

(l) $Cu(pma)SO_4\cdot 4H_2O$. Picolylmethylamine (0.5 g; 4.2 mmol) was added to an aqueous solution of copper sulfate pentahydrate (1.5 g; 4.2 mmol in 5 m*l* of water). The resulting solution was kept over sulfuric acid. The blue crystals which separated out were filtered through a glass filter and washed with 50% ethanol. They were dissolved in hot water (3 m*l*) and then ethanol was added to the solution. After they had stood overnight in a refrigerator, the separated blue crystals were filtered, washed with 50% ethanol, and dried in open air (yield, 1.1 g; 74%). (Found: Cu, 18.52; N, 7.81; C, 23.66; H, 4.51%. Calcd for $C_7H_{18}N_2O_8SCu$: Cu, 17.96; N, 7.91; C, 23.76; H, 5.13%).

(m) $Cu(pma)_2ClO_4)_2$. An aqueous solution of copper perchlorate (1.35 g; 5 mmol in 10 m*l* of water) was mixed with the amine (1.22 g; 10 mmol). The separated violet crystals were filtered, washed with cold water, and dried in open air (yield, 2.20 g; 89%). They were recrystallized from hot water. (Found: Cu, 12.50; N, 11.25; C, 33.27; H, 4.13%. Calcd for $C_{14}H_{20}N_4O_8Cl_2Cu$: Cu, 12.54; N, 11.06; C, 33.18; H, 3.98%).

Results and Discussion

Some Properties of the Chelates. As has been described in the Experimental section, we succeeded in isolating a number of 1 : 1 and 1 : 2 chelates of nickel and copper(II), and 1 : 3 chelates of nickel, using either 6-methyl-2-picolylamine or picolylmethylamine. Among these, the 1 : 1 nickel chelate of the later ligand was very difficult to prepare. When nickel sulfate was used as the starting material, green crystals were obtained from an aqueous solution containing the ligand in the molar ratio of Ni : pma = 1 : 1 after it had stood over sulfuric acid or after had been added ethanol; these crystals did not contain the amine, however, and were proved to be nickel sulfate. Even when an excess of the ligand was used, only nickel sulfate precipitated from the solution. The nitrate of the 1 : 1 chelate could not be crystallized either. Only when nickel chloride was used as the starting material was a water-soluble crystalline chelate obtained.

The preparation of 1 : 2 and 1 : 3 chelates from nickel perchlorate and 6-methyl-2-picolylamine or picolylmethylamine was also very difficult, although a crystalline solid could be obtained by appropriate methods (see "Experimental section"). Although these chelates were scarcely soluble in water, it was very difficult to obtain them in crystalline forms. Therefore, attempts to prepare them in an aqueous solution were unsuccessful, and only resinous substances were separated out from the solutions. In the preparation of $Ni(mepic)_2(ClO_4)_2 \cdot 2H_2O$, it was found that, when a stoichiometric amount of nickel perchlorate was used, a blue gum was obtained which solidified in a refrigerator. However, a pure crystalline product could be obtained when a slight excess of nickel ions was present.

The 1 : 3 nickel chelate of 6-methyl-2-picolylamine seems to be unstable in an aqueous solution, and it seems to dissociate strongly in the following way:[4]

$$[Ni(mepic)_3]^{2+} \rightarrow [Ni(mepic)_2]^{2+} + \text{mepic} \quad (1)$$

This can be seen from the fact that the absorption spectrum of an aqueous solution of $Ni(mepic)_3(ClO_4)_2$ was nearly identical with that of $Ni(mepic)_2(ClO_4)_2$ or $Ni(mepic)_2Cl_2 \cdot 3H_2O$. This may be the reason why only blue crystals of $Ni(mepic)_2 Cl_2 \cdot 3H_2O$ can be isolated from an aqueous solution containing nickel chloride and the amine in the ratio of 1 : 3.

The Electronic Absorption Spectra of the Chelates. The visible, near-ultraviolet and near-infrared absorption spectra of aqueous solutions of all the chelates prepared were measured. Representative curves are shown in Figs. 1, 2 and 3. In every case, Beer's law holds fairly well throughout the concentration range studied, 3×10^{-3}—3×10^{-4} M for copper chelates and 4×10^{-2}—4×10^{-3} M for nickel chelates. Anions had practically no effect on the spectrum. In other words, each spectrum seems to be practically characteristic of the chelate cation $[Ni\ L_n]^{+2}$ or $[Cu\ L_n]^{+2}$ (L = mepic or pma, n = 1—3) contained in

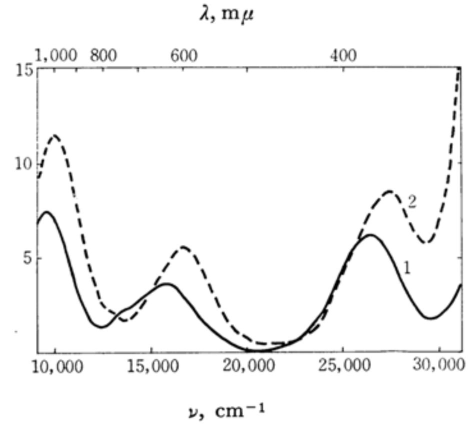

Fig. 1. Absorption curves of 1, $[Ni(mepic)]^{2+}$; 2, $[Ni(mepic)_2]^{2+}$.

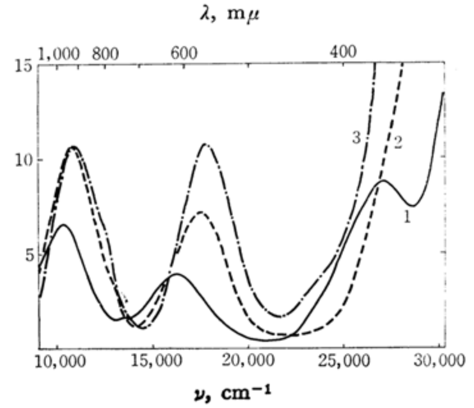

Fig. 2. Absorption curves of 1, $[Ni(pma)]^{2+}$; 2, $[Ni(pma)_2]^{2+}$; 3, $[Ni(pma)_3]^{2+}$.

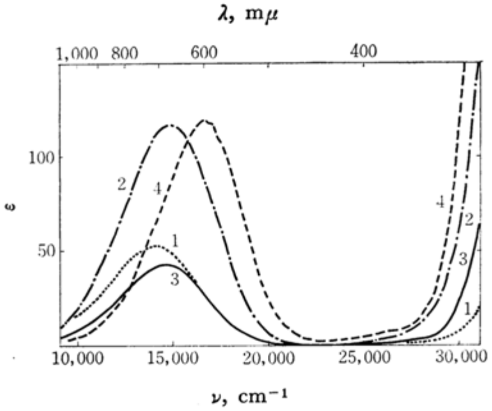

Fig. 3. Absorption curves of 1, $[Cu(mepic)]^{2+}$; 2, $[Cu(mepic)_2]^{2+}$; 3, $[Cu(pma)]^{2+}$; 4, $[Cu(pma)_2]^{2+}$.

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[4] In these and following formulae of chelate ions, the coordinated water molecules are not shown for the sake of simplicity.

TABLE 1. LIGAND FIELD BANDS OF 6-METHYL-2-AMINOMETHYLPYRIDINE, *N*-METHYL-2-AMINOMETHYLPYRIDINE AND 2-AMINOMETHYLPYRIDINE CHELATES

Chelate ion	ν_{max}, cm^{-1} (log ε_{max})			$\Delta\nu_{max}$, cm^{-1} a)	
	mepic	pma	pic	mepic	pma
$[\text{Ni L}]^{2+}$	9600 (0.87)	10400 (0.82)	10400 (0.62)	800	0
	15700 (0.55)	16300 (0.60)	16400 (0.50)	700	100
	26400 (0.78)	27100 (0.95)	27200 (0.81)	800	100
$[\text{Ni L}_2]^{2+}$	10000 (1.06)	10800 (1.03)	11000 (0.91)	1000	200
	16700 (0.75)	17600 (0.86)	18000 (0.73)	1300	400
	27200 (0.92)	b	b	—	—
$[\text{Ni L}_3]^{2+}$	—	10900 (1.03)	11600 (0.96)	—	700
	—	17900 (1.03)	18700 (1.03)	—	800
	—	b	b	—	—
$[\text{Cu L}]^{2+}$	14100 (1.72)	14700 (1.64)	14600 (1.51)	500	−100
$[\text{Cu L}_2]^{2+}$	14800 (2.07)	16700 (2.08)	17200 (1.82)	2400	500

a) $\Delta\nu_{max}$ means $\nu_L - \nu_{pic}$, where ν_L and ν_{pic} are the ν_{max} of $[\text{M L}_n]^{2+}$ and $[\text{M(pic)}_n]^{2+}$, and L is mepic or pma.

b) The band hidden by the strong ultraviolet absorption of the ligand.

the respective chelate, with the exception of $\text{Ni(mepic)}_3(\text{ClO}_4)_2$ mentioned above. The wave numbers of the absorption maxima, ν_{max}, taken from these curves are summarized in Table 1, together with the data for the corresponding 2-picolylamine chelates.

Judging from these ν_{max} values and from their intensities, it is obvious that all these absorption bands are due to the splitting of 3d orbitals of nickel or copper ions. In the case of nickel chelates, where two or three bands were observed for each chelate, the general outlook of the spectra indicates that they are all of the high-spin, six-coordinated type, and that the band with the lowest ν_{max} should correspond to the $^3A_{2g}\rightarrow{}^3T_{2g}$ transition, the next higher one, to $^3A_{2g}\rightarrow{}^3T_{1g}$ (F), and the highest, to $^3A_{2g}\rightarrow{}^3T_{1g}$(P).5)

From the data in Table 1, it can be seen that the ν_{max} values of the chelates of 6-methyl-2-picolylamine and picolylmethylamine are, in general, somewhat lower than those of the corresponding 2-picolylamine chelates. The decreases in ν_{max} (*i. e.*, the weakening of the ligand field) are small in pma chelates, and in the case of $[\text{CuL}]^{2+}$, the ν_{max} for pma is even slightly higher than that for pic; the decreases in mepic chelates are, however, much larger, showing a remarkable weakening of the ligand field.

These results are in accord with the results of the stability measurements by Fernelius *et al.* and Lane *et al.* cited above;2) according to them, the chelates of mepic and pma are generally less stable than those of pic; this decrease in stability is relatively small in pma chelates, while it is much larger in mepic chelates. Thus, both these spectral data and their stability data show clearly that, in the mepic and pma chelates, the weakening of the ligand field caused by steric hindrance is stronger than the opposite effect caused by the increased basicity of nitrogen atoms, and that the steric hindrance in mepic chelates is much larger than that in pma chelates. In the case of $[\text{Cu(pma)}]^{2+}$, however, the slight increase in ν_{max} mentioned above may mean the predominance of the effect of increased basicity over that of steric hindrance.

Scale-model studies of these chelates can clarify these situations to some extent. In a 1 : 1 pma chelate, the model shows that the water molecules occupying the remaining coordination sites barely touch the chelating ligand, so that the steric hindrance is nearly absent. Accordingly, the value of $\Delta\nu_{max}$, *i. e.*, the shift of the ν_{max} value from that of the corresponding pic chelate, is quite small in $[\text{Ni(pma)}]^{2+}$, and even negative in $[\text{Cu(pma)}]^{2+}$. In the case of 1 : 1 mepic chelates, on the other hand, the model shows that a very strong repulsion between the methyl group and the nearest water molecule occurs; this leads to a remarkable weakening of the metal-nitrogen (pyridine) bond and to a large deformation of the whole chelate. Accordingly, the $\Delta\nu_{max}$ in $[\text{Cu(mepic)}]^{2+}$ and $[\text{Ni(mepic)}]^{2+}$ are quite large.

In the cases of 1 : 2 and 1 : 3 chelates, the steric repulsion between two or three chelating ligands must also be considered. The models show that this type of repulsion is larger than that between a chelating ligand and neighboring water molecules, and very much larger in mepic chelates than in pma chelates. These situations are reflected in the $\Delta\nu_{max}$ values of these chelates. First of all, they increase in the order $[\text{Cu L}]^{2+} < [\text{Cu L}_2]^{2+}$ and $[\text{Ni L}]^{2+} < [\text{Ni L}_2]^{2+} < [\text{Ni L}_3]^{2+}$. Moreover, the value for a mepic chelate $[\text{M(mepic)}_n]^{2+}$ is always much larger than that for the corresponding pma chelate $[\text{M(pma)}_n]^{2+}$, and the difference

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5) W. Manch and W. C. Fernelius, *J. Chem. Ed.*, **38**, 192 (1961).

between the $\Delta\nu_{max}$ values of $[M(mepic)_n]^{2+}$ and $[M(pma)_n]^{2+}$ increases with an increase in the n value. It is interesting that the gradual increase in steric hindrance from $[Cu\ L]^{2+}$ to $[Cu\ L_2]^{2+}$, and from $[Ni\ L]^{2+}$ to $[Ni\ L_3]^{2+}$ can also be observed in the log k_n values of Fernelius, Lane, *et al.*[2]

In the case of $[Cu(mepic)_2]^{2+}$, the $\Delta\nu_{max}$ is the largest. This is certainly due to the fact that the two mepic molecules cannot form the planar structure which is preferred by the central copper(II) ion; this breakdown of the planar structure will certainly lead to a notable weakening of the ligand field.[6] In this case, and also in the case of $[Ni(mepic)_2]^{2+}$, the expected structure is the one in which the two pyridine-N atoms are at the *trans*, and the two amino-N atoms are at the *cis* positions, while all the other conceivable structures will suffer considerable steric repulsion between the two mepic molecules. The instability of $[Ni(mepic)_3]^{2+}$ mentioned above can also be ascribed to the especially large steric hindrance among the three ligand molecules.

Another correlation between the ν_{max} values of the chelates and their structures can be obtained by comparing the values of the ratios, R, defined as:

$$R = (\nu_L - \nu_{aq.})/(\nu_{en} - \nu_{aq.}) \qquad (2)$$

where ν_L and ν_{en} are the ν_{max} values of $[M\ L_n]^{2+}$ and $[M(en)_n]^{2+}$ respectively in aqueous solutions, and $\nu_{aq.}$ is that of hydrated metal ions. In the case of nickel chelates, where two or three bands are observed on each spectra, the ν_{max} to be used in R is that for the ${}^3A_{2g}\rightarrow{}^3T_{2g}$ transition. In addition to the fact that this R is a measure of the ligand field strength of L in comparison with en and H_2O, we can get some information of the stereochemical conditions of coordinated L by comparing the R values of different chelates. For example, if the R values of $[M\ L]^{2+}$ and $[M\ L_2]^{2+}$ are nearly the same, this probably indicates that another molecule of L can be combined with $[ML]^{2+}$ without any special difficulty, just as in the formation of $[M(en)_2]^{2+}$ from $[M(en)]^{2+}$ and ethylenediamine. On the other hand, if the R for $[M\text{-}L_2]^{2+}$ is appreciably smaller than that for $[M\ L]^{2+}$, the existence of a steric hindrance in the formation of $[ML_2]^{2+}$ is indicated.

TABLE 2. R VALUES FOR 6-METHYL-2-AMINOMETHYLPYRIDINE, N-METHYL-2-AMINOMETHYLPYRIDINE, 2-AMINOMETHYLPYRIDINE AND 2, 2′-BIPYRIDINE CHELATES

Chelate ion	R			
	mepic	pma	pic	bip*
$[Ni\ L]^{2+}$	0.64	1.06	1.07	1.19
$[Ni\ L_2]^{2+}$	0.70	1.08	1.15	1.06
$[Ni\ L_3]^{2+}$	—	0.90	1.19	0.90
$[Cu\ L]^{2+}$	0.65	0.86	0.83	0.73
$[Cu\ L_2]^{2+}$	0.45	0.77	0.87	0.20

* The absorption maxima of bip chelates are taken from the data of Ito (H. Ito, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **77**, 1383 (1956)).

Table 2 shows the R values of the chelate ions studied, and also those for 2-picolylamine and 2, 2′-bipyridine (bip) chelates. We can clearly see that the values for mepic chelates are much smaller than those for pma chelates, confirming again the remarkable weakening of the ligand field in the former.

As for the stereochemical conditions in the copper chelates, a striking contrast is observed if we compare the R values of pic and bip chelates. In pic chelates, the steric hindrance accompanying the formation of $[CuL_2]^{2+}$ from $[Cu\ L]^{2+}$ and L is nearly absent ($R_{[Cu\ L]^{2+}} \lesssim R_{[Cu\ L_2]^{2+}}$), but in bip chelates it occurs very strongly ($R_{[Cu\ L]^{2+}} \gg R_{[Cu\ L_2]^{2+}}$). The values of pma and mepic chelates are between these two extremes, indicating that the steric hindrance of this type is relatively weak in pma chelates, but quite strong in mepic chelates.

As for the nickel chelates, the R values of $[Ni(pic)]^{2+}$, $[Ni(pic)_2]^{2+}$, and $[Ni(pic)_3]^{2+}$ are not very different; the small increase from $[Ni(pic)]^{2+}$ to $[Ni(pic)_3]^{2+}$ may be due to an origin which is not steric, *e. g.*, the effect of the increasing π-character of the nickel-N (pyridine) bond. In bip chelates, the R value gradually falls from $[Ni(bip)]^{2+}$ to $[Ni(bip)_3]^{2+}$, very probably due to some steric effect acting between coordinated bip molecules. The pma chelates show an intermediate trend; *i. e.*, the R increases only slightly from $[Ni(pma)]^{2+}$ to $[Ni(pma)_2]^{2+}$, and then decreases to $[Ni(pma)_3]^{2+}$, showing that some steric hindrance exists in the formation of the third (and possibly also the second) chelate.

It remains still unexplained why the R for $[Ni(mepic)]^{2+}$ is somewhat smaller than that for $[Ni(mepic)_2]^{2+}$. However, on the whole, it can be seen that these R values can furnish useful information concerning the stereochemical conditions in these chelates.

One of the authors (S. U.) wishes to express his cordial thanks to Professor Kazuo Yamasaki of Nagoya University, in whose laboratory most of the experiments were carried out during the period of 1964—1965. A part of the expenses of this work was defrayed by a grant-in-aid of the Ministry of Education.

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[6] Studies of a number of $[Cu(mepic)_2]^{2+}$-containing chelates in solid state and in non-aqueous solutions indicated the existence of five-coordinated structures (S. Utsuno and K. Sone, *J. Inorg. Nucl. Chem.*, **28**, 2647 (1966)); the existence of such a five-coordinated species in aqueous solution of such $[Cu(mepic)_2]^{2+}$, however, cannot be proved as yet with certainty.