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Studies on the Sulfur-containing Chelating Agents. XLII.[1] Solvent Extraction of Nickel(II) and Zinc(II) with N-(*p*-Substituted phenyl)-β-mercaptocinnamamides

Masahiko Chikuma, Akira Yokoyama, Yoriko Ueda,
and Hisashi Tanaka

Faculty of Pharmaceutical Sciences, Kyoto University[2]

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Stability constants and extraction constants of nickel(II) and zinc(II) chelates of N-(*p*-substituted phenyl)-β-mercaptocinnamamides were determined by solvent extraction method in chloroform system. Stability constants of the nickel(II) chelates were smaller than those of zinc(II) chelates. The extent of the back donation from metal to sulfur is considered to be an important factor of the order of stability in nickel(II) and zinc(II) chelates. The contribution of adduct formation of nickel(II) chelate with pyridine to synergistic effect was indicated by solvent extraction and spectrophotometric method. Hammett substituent constants of the *p*-substituted groups were found to be correlated with the stability constants, adduct formation constants, frequencies of *d—d* bands or the chemical shifts of thiol proton, in the ligands, nickel(II) chelates and their adducts.

We have extended the study on the complex formation of thio-β-diketones[3] to that on the related amides and esters in recent years. In a previous paper,[4] we reported on the difference between thio-β-diketones and the related amides that the partition coefficient of N-phenyl-β-mercaptocinnamamide between chloroform and water was smaller than that of the related thio-β-diketone, thiodibenzoylmethane, and the extraction constants of several kinds of metal ion with the former were larger than with the latter. The present paper deals with the determination of the stability constants of nickel(II) and zinc(II) chelates of N-(*p*-substituted phenyl)-β-mercaptocinnamamides shown in Chart 1, and the equilibrium constants of the adduct formation of the nickel(II) chelates with pyridine both by solvent extraction and spectrophotometric methods.

Experimental

Materials——N-(*p*-Substituted phenyl)-β-mercaptocinnamamides (I—V): The corresponding isothiuronium *p*-toluenesulfonates were hydrolyzed in 10% NaOH aqueous solution to prepare I—V. The analytical data of the obtained ligands, III and IV except for I, II, and V which were reported in our previous paper[5] are shown in Table I.

N-*p*-Tolylphenylpropiolamide (VI) and N-(*p*-Methoxyphenyl)phenylpropiolamide (VII): VI and VII were prepared by the method reported previously.[5] The analytical data are shown in Table I.

S-[1-Phenyl-2-(*p*-tolylcarbamoyl)vinyl]isothiuronium *p*-Toluenesulfonate (VIII) and S-[1-Phenyl-2-(*p*-methoxyphenylcarbamoyl)vinyl]isothiuronium *p*-Toluenesulfonate (IX): VIII and IX were prepared by the method reported previously.[5] The analytical data are shown in Table I.

N-(*p*-Substituted phenyl)-benzoylacetamides: N-(*p*-Substituted phenyl)-benzoylacetamides, which are the oxygen homologues of I—V, were prepared by the method reported by Kibler and Weissberger.[6] The

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[1] Part XLI: M. Chikuma, A. Yokoyama, and H. Tanaka, *J. Inorg. Nucl. Chem.*, 37, 199 (1975).
[2] Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto.*
[3] M. Cox and J. Darken, *Coordination Chem. Rev.*, 7, 29 (1971); S.E. Livingstone, *ibid.*, 7, 59 (1971).
[4] M. Chikuma, A. Yokoyama, and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 22, 1378 (1974).
[5] A. Yokoyama, K. Ashida, and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 12, 690 (1964).
[6] J. Kibler and A. Weissberger, "Organic Syntheses," Coll. Vol. III. ed. by E.C. Horning, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 108.

melting points of N-(*p*-substituted phenyl)-benzoylacetamides except N-*p*-ethoxyphenyl-benzoylacetamide (X) agreed with those reported in the literature.[7] The analytical data of X were shown in Table I.

Bis[N-(*p*-substituted phenyl-β-mercaptocinnamamido] nickel(II): The nickel(II) chelates (XI—XV) of I—V were prepared by the method reported previously.[8] The analytical data of XIII and XIV were shown in Table I.

Reagents——Pyridine and $CHCl_3$ were distilled over NaOH and Linde 4A molecular sieves before use, respectively. All other chemicals were of analytical grade. The radioisotopes, ^{63}Ni and ^{65}Zn were obtained from the Radiochemical Center, Amersham, England as $NiCl_2$ and New England Nuclear Corp., U. S. A. as $ZnCl_2$, respectively. The buffer solution of 0.01 M acetic acid —0.01 M sodium acetate was used to adjust the pH of the aqueous phase to a desired value. Sodium perchlorate recrystallized from water added to adjust the ionic strength.

Apparatus——The β-radioactivity of ^{63}Ni was measured with a Beckman liquid scintillation system LS-233 after the treatment described previously.[4] The radioactivity of ^{65}Zn was measured with a Fujitsu well-type scintillation counter Model ATS-121 (NaI). The pH value of equilibrated aqueous phase was measured by a Hitachi-Horiba Model F-5 type pH meter. Electronic and nuclear magnetic resonance (NMR) spectra were measured with a Hitachi spectrophotometer Model EPS-2 by the use of 1 cm cells and a Varian A-60 NMR spectrometer, respectively.

Procedure——Six milliliters of aqueous solution containing nickel(II) or zinc(II) ions (1×10^{-7} M), sodium perchlorate (0.1 M) and acetic acid (0.01 M) were adjusted to a desired value of pH, and shaken with 6 ml of chloroform solution containing various amount of ligand and pyridine at $22\pm1°$ until the extraction equilibrium was reached. The distribution ratio (D) of nickel(II) and zinc(II) between $CHCl_3$ and water was measured as previously reported.[4] The distribution ratio of metal was defined as follows.

$$D=\frac{\text{total radioactivity of metal in organic phase}}{\text{total radioactivity of metal in aqueous phase}}$$

The values of P/K_a (P: the partition coefficient of ligand, K_a: the acid dissociation constant of ligand), were obtained by the extraction-spectrophotometric method reported previously.[9]

The equilibrium constants of the adduct formation of the nickel(II) chelates with pyridine or *o*-phenanthroline at 20° in $CHCl_3$ were determined by the method reported previously.[8]

NMR spectra were measured in hexadeuteroacetone by the use of trimethyl silane (TMS) as an internal standard at $25\pm1°$.

Calculations

The extraction constants (K_{ex}) and the stability constants (β_2) of the metal chelates can be calculated by the following equations.[4]

$$K_{ex}=\frac{[MR_2]_0[H]^2}{[M][HR]_0{}^n} \tag{1}$$

$$\log K_{ex}=\log D-2\log[HR]_0-2pH \tag{2}$$

$$\log\beta_2=\log K_{ex}-\log P_c+2\log(P/K_a) \tag{3}$$

where, M, H, HR, R, P_c and the subscript "o" denote a metal ion with the charge 2+, a hydrogen ion, a neutral ligand, an anion of the ligand, a partition coefficient of a metal chelate and the organic phase, respectively and the aqueous phase is represented without any subscript and the charges on the ion are omitted for simplicity.

The extraction constants ($K_{ex\ 2,n}$) of nickel(II) in the presence of pyridine and the equilibrium constants ($\beta_{2,n}$) of adduct formation in the organic phase can be calculated by the following equations.[1]

$$K_{ex\ 2,n}=\frac{[MR_2B_n]_0[H]^2}{[M][HR]_0{}^2[B]_0{}^n} \tag{4}$$

$$\begin{aligned}\log K_{ex\ 2,n}=&\log D-2\log[HR]_0-2\,pH-n\log[B]_0\\&+\log(1+\sum_{j=1}\beta'_j[B]^j)\end{aligned} \tag{5}$$

$$\log\beta_{2,n}=\log K_{ex\ 2,n}-\log K_{ex} \tag{6}$$

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7) P. van Brandt, E. De Hoffmann, and A. Bruylants, *Bull. Soc. Chim. Belges*, **73**, 782 (1964).

8) M. Chikuma, A. Yokoyama, and H. Tanaka, *J. Inorg. Nucl. Chem.*, **36**, 1243 (1974).

9) A. Yokoyama, N. Nakanishi, and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **20**, 1856 (1972).

where B, β'_j and n denote pyridine, the formation constant of nickel(II)-pyridine complex in the aqueous phase and the ratio of the base to the mother nickel(II) chelate in the adduct complex, respectively.

To determine the equilibrium constants (K) of the adducts in dry chloroform, the equation (7)[10] was used in pyridine adduct and the equation (8) in o-phenanthroline adduct.

$$\frac{a}{A-A_0}=\frac{1}{K(\varepsilon_{\mathrm{adduct}}-\varepsilon_{\mathrm{chelate}})b^n}+\frac{1}{\varepsilon_{\mathrm{adduct}}-\varepsilon_{\mathrm{chelate}}} \tag{7}$$

$$K=\frac{(A-A_0)(\varepsilon_{\mathrm{adduct}}-\varepsilon_{\mathrm{chelate}})}{\{a(\varepsilon_{\mathrm{adduct}}-\varepsilon_{\mathrm{chelate}})-(A-A_0)\}\{b(\varepsilon_{\mathrm{adduct}}-\varepsilon_{\mathrm{chelate}})-(A-A_0)\}} \tag{8}$$

where a is the initial nickel(II) chelate concentration, b is the initial base concentration, A_0 is the absorbance of a solution of the chelate of concentration a, A is the absorbance of a solution of the chelate and the base of concentrations a and b, $\varepsilon_{\mathrm{adduct}}$ is molar absorptivity of the adduct complex, and $\varepsilon_{\mathrm{chelate}}$ is molar absorptivity of the mother chelate. The value of $\varepsilon_{\mathrm{adduct}}$ is found, by trial and error treatment, to give the most reproducible value of the formation constant, K.

Results and Discussion

Extraction of Nickel(II) and Zinc(II)

The overall stability constants were obtained by the use of the values of P/K_a, which can be determined from the relation between the distribution ratio (D_r) of the ligand and [H] in the pH region of $K_a \gg [H]$ by the extraction-spectrophotometric method. As shown in Fig. 1, the plots of log D_r *v.s.* pH gave a straight line with the slope -1. The values of P/K_a obtained are shown in Table II.

The distribution curves of nickel(II) and zinc(II) are shown in Fig. 2 and 3. The values of the extraction constants (K_{ex}), the partition coefficients (P_c) and the stability constants (β_2) of nickel(II) and zinc(II) chelates obtained are shown in Table II. The stability constants of nickel(II) and zinc(II) chelates of these ligands increase in the order I<II<III<IV<V.

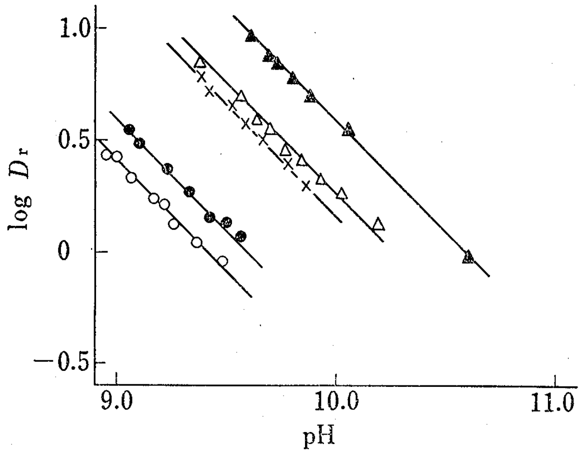

Fig. 1. Effect of pH on Distribution Ratio of Ligand

ionic strength: 0.1 ($NaClO_4$)
initial concentration of ligand: 5×10^{-5}M
○: I, ●: II, ×: III, △: IV, ▲: V

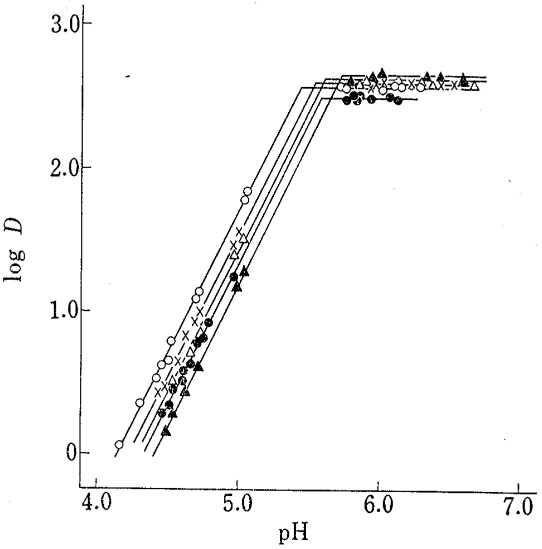

Fig. 2. Effect of pH on Distribution Ratio of Nickel (II)

initial concentration of ligand: 1×10^{-2}M
Symbols are explained in Fig. 1.

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[10] H.A. Benesi and J.H. Hildebrand, *J. Amer. Chem. Soc.*, 71, 2703 (1949).

This order suggests that the stability constants of these chelates are greatly affected by the *p*-substituted group. The values of the stability constants of zinc(II) chelates were found to be larger than those of the corresponding nickel(II) chelates. This order, which does not

Table I. Analytical Data

Compound	Formula	mp (or decomp.) (°C)	Recryst. solvent	Analysis (%) Calcd. (Found) C	H	N	S	Ni
III	$C_{16}H_{15}ONS$	105—106	abs. EtOH	71.38	5.58		11.90	—
				(71.67)	(5.61)		(11.48)	—
IV	$C_{16}H_{15}O_2NS$	139—140	abs. EtOH	67.37	5.26		11.23	—
				(67.31)	(5.41)		(11.38)	—
VI	$C_{16}H_{13}ON$	135—137	EtOH	81.70	5.53	5.96	—	—
				(81.57)	(5.79)	(5.83)	—	—
VII	$C_{16}H_{13}O_2N$	122—124	EtOH	76.49	5.18	5.58	—	—
				(76.49)	(5.25)	(5.63)	—	—
VIII	$C_{24}H_{25}O_4N_3S_2$	209—211	EtOH	59.63	5.18		13.25	—
				(59.37)	(5.35)		(13.45)	—
IX	$C_{24}H_{25}O_5N_3S_2$	203—205	EtOH	57.72	5.01		12.83	—
				(57.48)	(5.27)		(12.90)	—
X	$C_{17}H_{17}O_3N$	238—239	EtOH	72.08	6.01	4.95	—	—
				(72.12)	(6.20)	(4.99)	—	—
XIII	$C_{32}H_{28}O_2N_2S_2Ni\cdot\frac{1}{2}CHCl_3$[a]	147—149	$CHCl_3$	59.58	4.35			8.97
				(59.40)	(4.39)			(8.85)
XIV	$C_{32}H_{28}O_4N_2S_2Ni$	224—225	$CHCl_3$	61.27	4.47			9.37
				(61.45)	(4.68)			(9.10)

a) clathrate

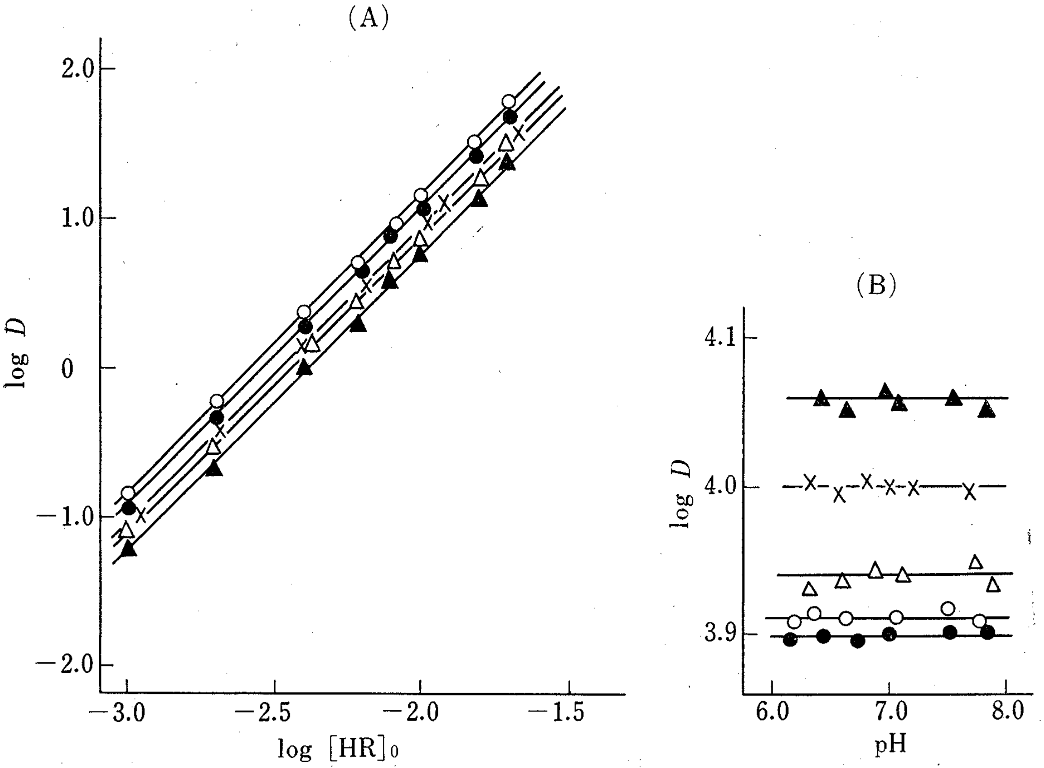

Fig. 3. Effect of Ligand Concentration and pH on Distribution Ratio of Zinc(II)

(A) ○: pH 4.00, ●: pH 4.00 ×: pH 3.98, △: pH 4.03 ▲: pH 4.01
(B) initial concentration of ligand: 2×10^{-2}M
Symbols are explained in Fig. 1.

agree with Irving-Williams' orders,[11] has been found generally in the chelates of sulfur-oxygen coordinating ligands such as thiodibenzoylmethane.[4] The extent of the back donation from the metal to sulfur which has vacant *d* orbitals probably controls the order of the stability of nickel(II) and zinc(II) chelates, as proposed in various types of sulfur-coordinating complexes.[12]

TABLE II. Extraction Constants and Stability Constants

Ligand	log (P/K_a)	Nickel(II)			Zinc(II)		
		log K_{ex}	log P_c	log β_2	log K_{ex}	log P_c	log β_2
I	9.41	−4.28	2.57	11.97	−2.84	3.91	12.07
II	9.59[a]	−4.62	2.49	12.07	−2.90	3.90	12.38
III	10.16	−4.43	2.60	13.29	−3.02	4.00	13.30
IV	10.27	−4.54	2.61	13.39	−3.16	3.94	13.44
V	10.59	−4.78	2.65	13.75	−3.24	4.06	13.88

a) 9.48 in ref.[4]

Adduct Formation of Nickel(II) Chelates with Pyridine Base

The distribution curves of nickel(II) in the presence of pyridine obtained in this study are shown in Fig. 4 and 5. The values of log β'_j, the partition coefficient in chloroform system and the pK_a of pyridine which were reported as 1.78 for $j=1$,[13] 2.83 for $j=2$,[13] $10^{1.2}$[14] and 5.18[15] respectively were used for the calculation of the concentrations of nikel(II)-pyridine complexes in the aqueous phase and free base in the organic phase.

The predominant species in the organic phase is suggested to be Ni(II)R_2B_2 from the slope shown in Fig. 4 and 5. The extraction constants ($K_{ex\,2,n}$) and the equilibrium constants ($\beta_{2,n}$) obtained are shown in Table III.

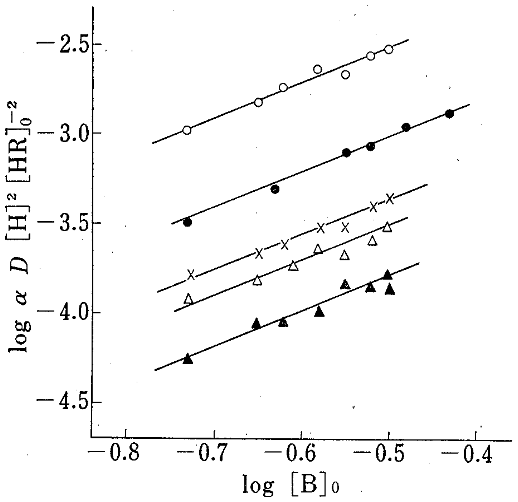

Fig. 4. Effect of Pyridine Concentration on Distribution Ratio of Nickel (II)

Symbols are explained in Fig. 1.

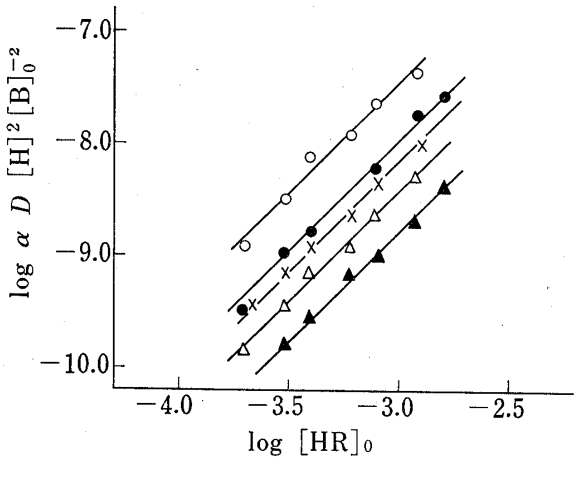

Fig. 5. Effect of Ligand Concentration on Distribution Ratio of Nickel (II) in the Presence of Pyridine

initial pyridine concentration: 2×10^{-1}—4×10^{-1}M
pH 5.84—6.33
Symbols are explained in Fig. 1.

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11) H. Irving and R.J.P. Williams, *J. Chem. Soc.*, **1953**, 3192.
12) S.E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965).
13) J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).
14) Fa-chun Chou and H. Freiser, *Anal. Chem.*, **40**, 34 (1968).
15) L.G. Sillén and A.E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

The values of $\beta_{2,n}$ decrease in the order XI>XII>XIII>XIV>XV. This order is reverse to that of the stability of the mother nickel(II) chelates as generally expected. The relationship between log β_2 for nickel(II) chelate and log $\beta_{2,n}$ is linear as shown in Fig. 6.

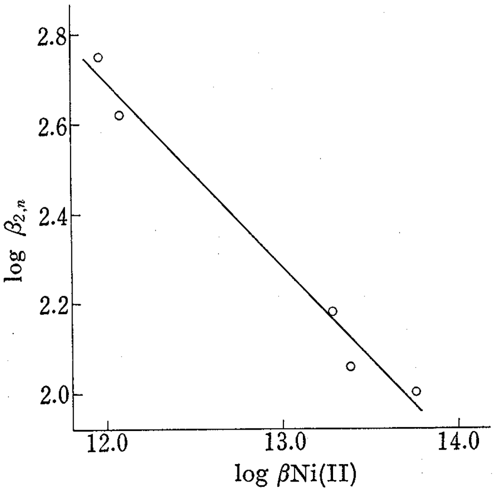

Fig. 6. Relationship between the Stability Constants of Nickel (II) Chelates and the Equilibrium Constants of Their Pyridine Adducts Determined by Extraction Method

TABLE III. Extraction Constants of Nickel(II) Chelates in the Presence of Pyridine and Equilibrium Constants of Adduct Formation

Ligand	log $K_{ex,2,2}$	log $\beta_{2,2}$
I	−1.53	2.75
II[a]	−2.00	2.62
III	−2.25	2.18
IV	−2.48	2.06
V	−2.78	2.00

a) ref.[1]

The equilibrium constants (K) of the adduct formation with pyridine in dry chloroform are shown in Table IV. It is found that two molecules of pyridine and one molecule of *o*-phenanthroline coordinate respectively to the central nickel(II) atom of the chelate. Much higher values were obtained as the equilibrium constants for the adduct formation by the solvent extraction method, namely in wet chloroform than in dry chloroform by the spectrophotometric method. Similar difference between the values obtained in wet and dry solvents was reported in zinc(II)-thenoyltrifluoroacetone and tri-*n*-octylphosphine oxide-carbon tetrachloride systems.[16] It is presumed that the difference in the equilibrium constants obtained by these method may be essentially attributed to the presence or the absence of the water molecules.[16] The linear relationship between the equilibrium constants in wet and dry chloroform suggests the contribution of the adduct formation with pyridine to the synergistic effect. This suggestion was supported by the features in the electronic spectra of the extracts described later.

d-d Bands of the Nickel(II) Chelates and Their Adducts

The spectral data of the nickel(II) chelates in chloroform pyridine and chloroform containing excess *o*-phenanthroline are shown in Table V. In the electronic spectra of these five nickel(II) chelates, absorption bands with low intensity ($\varepsilon<130$), which may be provisionally assigned as the *d-d* transition band,[17] in the region 650 to 670 nm are always observed, and the color of these chelates is reddish brown. This spectral feature indicates that the structures of these nickel(II) chelates are similar to that of XII, which is verified to have square-planar structure of S-O type coordination and *cis*-configuration by X-ray crystallographic analysis[18] and the measurement of the magnetic susceptibility.[8]

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[16] W.R. Walker and N.C. Li, *J. Inorg. Nucl. Chem.*, **27**, 411 (1965).

[17] *a*) H.B. Gray and C.J. Ballhausen, *J. Amer. Chem. Soc.*, **85**, 260 (1963); *b*) C.K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962); *c*) A. Ouchi, M. Hyodo, and Y. Takahashi, *Bull. Chem. Soc. Japan*, **40**, 2819 (1967).

[18] M. Shiro, private communication.

Table IV. Equilibrium Constants for Adduct Formation of Nickel (II) Chelates with Pyridine and *o*-Phenanthroline at 20° in Chloroform[a]

Ni(II) chelate		Pyridine	*o*-Phenanthroline
XI[b]	log *K*	0.54	5.15
		(380)	(366)
	$\varepsilon_{\text{adduct}}$	23000	26000
XII[b]	log *K*	0.34	5.12
		(374)	(364)
	$\varepsilon_{\text{adduct}}$	22200	23800
XIII[c]	log *K*	0.21	4.63
		(375)	(365)
	$\varepsilon_{\text{adduct}}$	23300	24200
XIV[c]	log *K*	0.06	4.54
		(370)	(364)
	$\varepsilon_{\text{adduct}}$	26200	26500
XV[b]	log *K*	−0.05	5.03
		(364)	(364)
	$\varepsilon_{\text{adduct}}$	27100	27100

a) Analytical wavelengths (λ_{max}: nm) are designated in parentheses.
b) ref.[8]
c) This work.

On the other hand, in pyridine or in chloroform containing excess *o*-phenanthroline, the absorption spectra indicate the octahedral configuration of these complexes but the splitting of $^3T_{2g}\leftarrow{}^3A_{2g}$ transition suggests that a nickel(II) ion is situated in a distorded octahedral field.[19] Two added pyridine molecules or one *o*-phenanthroline molecule occupy two unsaturated coordination positions of central nickel(II) atom to form the six-coordinated complex. Further, similar absorption maxima in the near infrared region are observed in the extracts of all nickel(II)-pyridine-chloroform extraction systems. These facts indicate that the predominant species in the organic phase of the extraction system containing pyridine are six-coordinated complexes and the strongly coordinated pyridine molecules may form axial bonds with central nickel(II) atom.

Table V. *d-d* Bands of Nickel (II) Chelates in Chloroform, Pyridine and Chloroform Containing Excess *o*-Phenanthroline[a]

Ni(II) chelate	$CHCl_3$	Pyridine[b]		$CHCl_3$ containing *o*-Phenanthroline[b]		
XI	670(95)[c]	880sh(19)	1010(37)	840sh(18)	895[c]	(20)
XII	660(87)[c]	885sh(14)	1020(25)	840sh(31)	900[c]	(34)
XIII	655(92)	890sh(19)	1025(29)	840sh(24)	905	(28)
XIV	650(130)	890sh(22)	1030(36)	845sh(27)	910	(29)
XV	650(100)[c]	890sh(20)	1040(30)	847sh(29)	915[c]	(31)

a) Extinction coefficients are designated in parentheses.
sh: shoulder
b) The absorption spectrum shows a discernible shoulder at shorter wavelength side of the main absorption band. These two bands are suggested to be based on the splitting of $^3T_{2g}\leftarrow{}^3A_{2g}$ transition.
c) ref.[8]

The relationship between the stability constant and the frequencies of the *d-d* bands in these nickel(II) chelates or those of the pyridine adducts is shown in Fig. 7. This relationship is expected from the correlation between the stability of mother chelates and that of their adducts as shown in Fig. 6.

Jørgensen[17b] described a spectrochemical series in some low spin square planar nickel(II) chelates, namely, diethyl dithiophosphate(dtp), ethyl xanthate (exan), and N,N-dimethyldithiocarbamate (dtc). In the nickel(II) chelates, presented in this paper (XI—XV), and

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19) B.N. Figgis, "Introduction to Ligand Fields," (translated by S. Yamada) Nankodo, Tokyo, 1969.

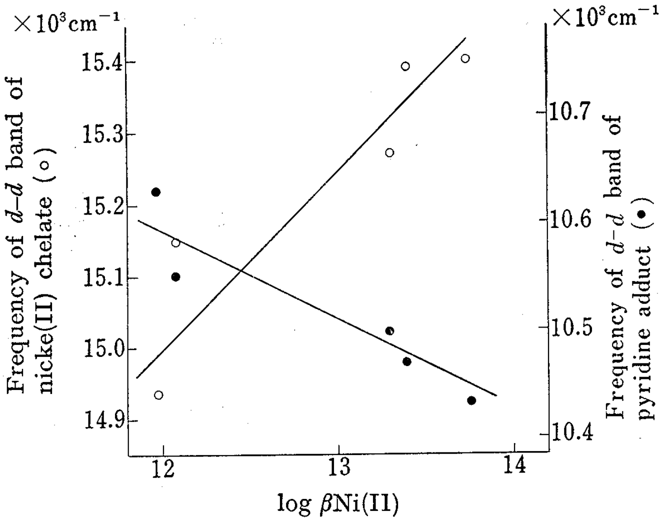

Fig. 7. Relationships between the Stability Constants of Nickel (II) Chelates and the Frequencies of *d-d* Bands of the Nickel (II) Chelates or Their Pyridine Adducts

The mean value of the frequencies of splitting bands shown in Table V, which is only approximate to the energy of $^3T_{2g} \leftarrow {}^3A_{2g}$ transition but is of the correct order of magnitude, is used in this figure, because the true frequency value corresponding to $^3T_{2g} \leftarrow {}^3A_{2g}$ cannot be estimated without some assumptions.

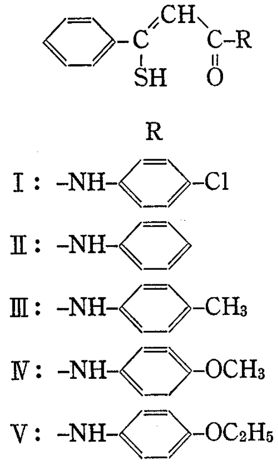

Chart 1

the related nickel(II) chelates reported previously,[8] the ligands may be placed in the following spectrochemical series: dtp,<R=OEt, R=SEt,<I,<II,<III,<IV,<V,<R=Ph,<exan,< dtc (R. in Chart 1).

NMR Spectra of Ligands

The results of the NMR measurements of I—V and their oxygen homologues, benzoylacetanilides in hexadeuteroacetone are shown in Table VI. It is easy to distinguish the signal of enol proton from that of secondary amide proton in benzoylacetanilides because the signal of the former was found in lower field. In these ligands, linear relationship is found between Hammett substituent constants[20] and the chemical shifts of the enol and secondary amide protons, or the pK_a values[7] included in Table VI.

The chemical shifts of thiol protons of I—V may be assigned on the basis of the fact that the signal of thiol protons are more sharp than those of secondary amide protons which

TABLE VI. PMR Data in Acetone-d_6[a]

	N-Phenyl-β-mercaptocinnamamides (ppm)		Benzoylacetanilides[b] (ppm)			Hammett's substitution constants[d]
	SH	-CONH-	OH	-CONH-	pK_a[c]	
I	9.35	9.60	16.08	9.58	8.80	0.227
II	9.65	9.50	16.22	9.47	8.96	0
III	9.80	9.38	16.23	9.35	9.14	−0.170
IV	9.88	9.30	16.32	9.33	9.18	−0.25
V	9.92	9.30	16.28	9.32	—	−0.268

a) conc. 0.2M at 25°
b) Homologous compounds according to N-phenyl-β-mercaptocinnamamides (I—V).
c) ref.[7]
d) ref.[20]

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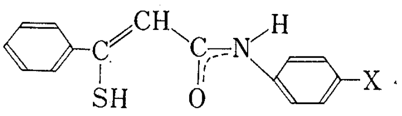
20) H.H. Jaffe, *Chem. Rev.* (London), 53, 191 (1953).

are generally broadened due to the quadrupolar relaxation effects of nitrogen atoms, although their signals are observed closely each other. A linear correlation between the chemical shifts of the thiol protons and Hammett substituent constants is found in N-phenyl-β-mercaptocinnamamides. Further, the stability constants of the nickel(II) chelates, the equilibrium constants of their adduct formation, the frequencies of *d-d* bands of the chelates and their adducts and Hammett substituent constants are found to be correlated one another. These facts suggest that the effect of *p*-substituent groups of anilide may be transmitted on to the thiol group through amide and vinyl linkages.

In addition, the mesomeric effect due to a long conjugated system shown in the following formula (**1**) on the basis of double bond character of C-N linkage may facilitate the transmission of the electronic effect of the *p*-substituted group.



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