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183. **Hisashi Tanaka and Akira Yokoyama**: Studies on the Sulfur-containing Chelating Agents. XI.[*1] Relationship between Chelating Ability and Chemical Structure of Ligand. (1).

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In the previous papers,1) syntheses and chelating abilities of various types of ligands, involving mercapto and carbonyl groups as shown in Chart 1, have been reported. They were found to have chelating abilities with many kinds of metals.

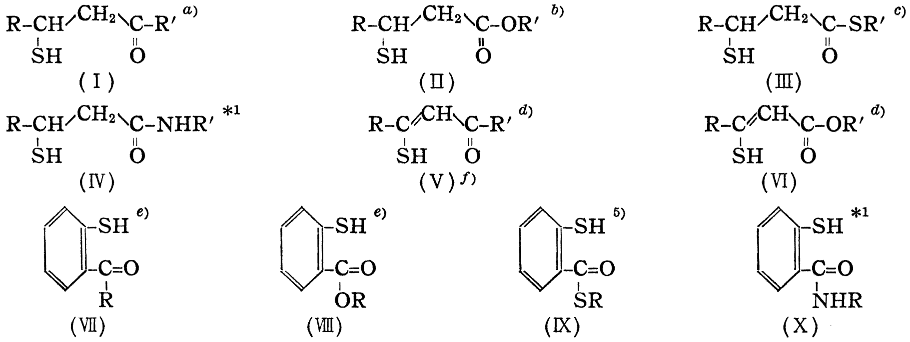
f) (V) is present thioxoform and does not have chelating ability.

Chart 1. Ligands

This paper deals with the results of the investigation on the chelating abilities of these ligands, considering a selectivity with metal ions, absorption spectra of chelates and a comparison of stabilities of the chelates produced from these ligands.

The metals which react with any of these ligands (I~X) are summarized in Table I.

Table I. Metals which reacted with Ligands (I)~(X).
Periodic Table

(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
							Fe^{2+} Co Ni
Cu^{2+}	Zn						
							Pd
Ag	Cd						
							Pt
Au	Hg	Tl	Pb	Bi			

[*1] Part X: This Bulletin, **10**, 556 (1962).

[*2] Yoshida, Sakyo-ku, Kyoto (田中 久, 横山 陽).

1) *a*) Part I: This Bulletin, 8, 275 (1960). *b*) Part V: *Ibid.*, **9**, 66 (1961). *c*) Part VII: *Ibid.*, **10**, 13 (1962). *d*) Part VIII: *Ibid.*, **10**, 19 (1962). *e*) Part IX: *Ibid.*, **10**, 25 (1962).

Since only a few S-O-chelating agents have been known, general selectivity to the metals is quite unknown. In general, sulfur as a ligand atom has a different tendency in the selectivity from that of oxygen.[2] According to Schwarzenbach,[3] the ligands in which sulfur reacts as ligand atom are rather highly selective and called "selective complexing agents." On the contrary, O-O- and N-O-chelating ligands are called "general complexing agents" which react with many kinds of metals. As to the selectivities of the ligands (I∼X), it was found that these ligands react with the metals which were precipitated readily by hydrogen sulfide, despite of the fact that these ligands involve sulfur and oxygen with different tendency in selectivity as a ligand atom.

Notwithstanding that all of the ligands (I∼X) have mercapto and carbonyl groups at the position to six membered chelate ring, considerable differences in the selectivity were observed. These differences were considered to be due to those of chelating ability of their chemical structures. As to palladium, copper, nickel, cobalt, and iron, which formed stable chelate with some of these ligands, their selectivities were compared and summarized in Table II. Palladium and copper reacted with all of these ligands, while nickel, cobalt, and iron reacted selectively. With regard to the tendency of forming coordinating bond with bivalent metals, "Irving, Williams's stability series," namely palladium>copper>nickel>cobalt>iron, is well known and this order has been confirmed with many kinds of chelates. In order to investigate whether this order could be also applicable to the ligands (I∼X), following experiments were carried out.

TABLE II. Selectivities of Ligands

Ligands		Metals reacted				
Aromatic thiols	Aliphatic thiols					
	Ketone (I)	Pd	Cu^{2+}			
Ketone (VII)	Acid ester (II) Acid amide (IV)	Pd	Cu^{2+}	Ni		
Acid ester (VIII) Acid amide (X)	Thiolic acid ester (III)	Pd	Cu^{2+}	Ni	Co	
Thiolic acid ester (IX)	α,β-Unsat. acid ester (VI)	Pd	Cu^{2+}	Ni	Co	Fe^{2+}

The apparent stability constants of the chelates were measured by Ishidate and Yamane's method.[4] From the results of these experiments, the chelating abilities of those ligands were compared with each other.

Methods and Results

1) Investigations on the "Irving, Williams's stability series": (similar experiments were carried out with all of the ligands, but as an example, an experiment on the ligand (III) is described.) ethanol solution of the ligand (III) ($10^{-2}M$) and $10^{-2}M$ aqueous solution of Pd^{2+}, Cu^{2+}, Ni^{2+}, and Co^{2+} were prepared from $PdCl_2 \cdot 2H_2O$, $(AcO)_2Cu \cdot 2H_2O$, $NiSO_4 \cdot 7H_2O$ and $(AcO)_2Co \cdot 4H_2O$ respectively and these solutions were mixed in a manner as shown in foot note of Figs. 1 and 2. After shaken for 5 hours, chelate was extracted with 10 cc. of chloroform, and whose absorption spectrum in chloroform was measured. The spectra of the extracts from the solutions (1), (2), (3), and (4) containing only one kind of metal ion, were compared with those of the solutions (5), (6), (7), and (8) in which are contained two or more kinds of metal ions. As observed in Figs. 1 and 2, in the case of the solutions (5) and (6), the absorption spectra coincided with that of palladium

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2) N.V. Sidgwick: J. Chem. Soc., **1941**, 441.
3) G. Schwarzenbach: Anal. Chem., **32**, 6 (1960).
4) M. Ishidate, Y. Yamane: Yakugaku Zasshi, **77**, 386 (1957).

chelate. This showed the formation of only palladium chelate. In the case of the solution (8), the absorption spectrum coincided with that of copper chelate. Therefore the formation of only copper chelate was observed. From these facts, it is under stood that palladium and copper chelates were far more stable than nickel and cobalt chelates. However, in the case of the solution (7), the absorption spectrum did coincide neither with that of nickel chelate nor cobalt chelate. This fact suggested that the stabilities of nickel and cobalt chelates are not greatly different from each other.

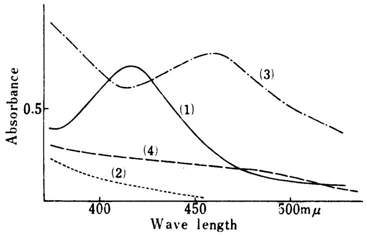

Fig. 1. Absorption Spectra obtained from Solutions (1), (2), (3) and (4)

Composition of Solutions for Measurement of Absorption Spectra

(1) Ligand (1 cc.) + Pd^{2+} (1 cc.) + H_2O (2 cc.)
(2) Ligand (1 cc.) + Cu^{2+} (1 cc.) + H_2O (2 cc.)
(3) Ligand (1 cc.) + Ni^{2+} (1 cc.) + H_2O (2 cc.)
(4) Ligand (1 cc.) + Co^{2+} (1 cc.) + H_2O (2 cc.)

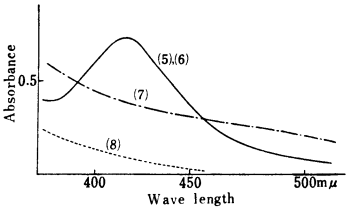

Fig. 2. Absorption Spectra obtained from Solutions (5), (6), (7), and (8)

Composition of Solutions for Measurement of Absorption Spectra

(5) Ligand (1 cc.)+Pd^{2+}(1 cc.)+Ni^{2+}(1 cc.)+Co^{2+}(1 cc.)
(6) Ligand (1 cc.)+Pd^{2+}(1 cc.)+Cu^{2+}(1 cc.) +H_2O (1 cc.)
(7) Ligand (1 cc.)+Ni^{2+}(1 cc.)+Co^{2+}(1 cc.) +H_2O(1 cc.)
(8) Ligand (1 cc.)+Cu^{2+}(1 cc.)+Ni^{2+}(1 cc.)+Co^{2+}(1 cc.)

2) Reaction of palladium ion with nickel chelate : An upper metal ion in the "Irving, Williams's stability series" reacted with a chelate of the lower metal. As an example, the reaction of palladium ion and nickel chelate is described. Aqueous solution of palladium ion($10^{-2}M$) and $10^{-2}M$ chloroform solution of nickel chelate were mixed and shaken for 5 hours. An absorption spectrum in chloroform was measured and was found to be coincident with that of palladium chelate. The results of experiments 1) and 2) are summarized in Table III.

TABLE III. Result from Experiments 1) and 2)

Pd^{2+} + Ni-chelate $\longrightarrow$ Pd-chelate + Ni^{2+}
Pd^{2+} + Ni^{2+} + Ligand $\longrightarrow$ Pd-chelate
Cu^{2+} + Ni^{2+} + Co^{2+} Ligand $\longrightarrow$ Cu-chelate
Ni-chelate + Co^{2+} $\rightleftharpoons$ Co-chelate + Ni^{2+}
Ni^{2+} + Co^{2+} + Ligand $\longrightarrow$ Ni-chelate + Co-chelate

TABLE IV. Degree of Dissociation (α) and Apparent Stability Constant, log K

Ligand	log K, (α)		
	Ni-chelate	Co-chelate	Fe-chelate
(II)	10.95 (0.13)	—	—
(III)	11.18 (0.085)	12.12 (0.65)	—
(IV)	9.37 (0.31)	—	—
(VI)	12.65 (0.028)	15.43 (0.10)	12.38 (0.50)
(VII)	11.18 (0.085)	—	—
(VIII)	11.51 (0.066)	12.69 (0.43)	—
(IX)	12.05 (0.044)	13.23 (0.33)	—
(X)	11.00 (0.097)	11.53 (0.71)	—

Chelate : $5\times10^{-5}M$, Ligand : $1\times10^{-3}M$, pH : 5.8.
Pd- and Cu-chelate do not dissociate.
Ligands ; (I) R, R'=C_6H_5, (II) R=C_6H_5, R'=C_2H_5, (III) R=C_6H_5, R'=C_2H_5,
(IV) R, R'=C_6H_5, (VI) R=C_6H_5, R'=C_2H_5, (VII) R=C_6H_5,
(VII) R=C_2H_5, (IX) R=C_2H_5, (X) R=C_6H_5

3) Measurement of apparent stability constant: The apparent stability constants of the chelates were measured in EtOH-$CHCl_3$-H_2O (5:4:1) by Ishidate and Yamane's method.[4] (As these chelates are insoluble in water, measurement was only possible in such a solvent mixture). Measurements were carried out using absorption curves of each chelate reported in the previous papers.[*1,1] Degree of dissociation (α) and stability constant (K) were calculated from the equation,[4] and listed in Table IV.

Discussion

From the results of the experiments 1), 2), and 3), it was found that "Irving, Williams's stability series" is applicable to the case of the ligands (I~X). However, as seen in Fig. 2 and Table III, the order of nickel and cobalt was not distinct. The stabilities of nickel and cobalt chelates will be reported in the following paper in detail.

When the chelating abilities of the ligands (I~X) were compared, judging from the applicability of "Irving, Williams's stability series," it is presumed that the ligand which reacts even with lower metal in this series, has stronger chelating ability. Namely, as seen in Table II, the ligands (VI) and (IX) which react with iron has the strongest chelating ability. As to the chelating ability of the aromatic and aliphatic mercapto compounds, the former has stronger chelating ability if the type of carbonyl group is same.

From the result of experiment 3), as seen in Table IV, stability constants of the chelates of (VI) and (IX) are high and the constants decrease in order of (VIII), (VII), (III), (X), (II), and (IV). These results also support the presumptions mentioned above, although they were obtained in the solvent in which the proportion of water is small.

To conclude this presumptions, comparing the chelating ability of the ligands (I~X) qualitatively, the order would be (VI, IX)>(VIII, III, X)>(VII, IV, II)>(I).

In order to give some endorsements to the above-mentioned comparison of the stabilities, a relationship between stability and absorption spectrum of the chelate was investigated. Sekido reported on the relationship between stabilities of the chelates and visible and ultraviolet absorption spectra in metal oxinates as follows.[5] In various kinds of oxinates, absorption maxima were observed in the region of 380~400 mμ in every case. These maxima are considered to be the characteristics to the oxinates, and it was proved that the more stable the chelate, the larger the shift of the maximum to the longer wave length. As to the chelates of the ligands (I~X), absorption curves were investigated, taking nickel chelates as examples. As previouly reported,[1b~e)*1] the maximum was observed at 460 mμ in each case, as also seen in nickel dimethylglyoximate,[6] and nickel oxinate.[5] This maximum was observed always at 460 mμ regardless the type of the ligands, while another absorption maximum was observed in the region of 350~400 mμ in all cases, and the difference of the wave length of this maximum depended upon the ligands of the chelates. The wave lengths of these maxima were compared in a manner as reported by Sekido[9] with the metal oxinates. In the chelates of the aromatic mercapto compounds (VIII, IX, X) and the unsaturated mercapto compound (VI), the absorption maxima were found in the longer wave length (at 380~400 mμ), while in the chelates of aliphatic mercapto compounds (II, III, IV), they were found to be shifted to the shorter wave length (at 360~370 mμ). Therefore, the chelates of the ligands (VIII, IX, X, VI) are considered to be more stable than others. As reported before,[1d,e)*1] in the infrared spectra, shifts of the bands of

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5) E. Sekido: Nippon Kagaku Zasshi, **80**, 1011 (1959).
6) E.B. Sandell: "Colorimetric Determination of Traces of Metals" 471 (1950). Interscience Publishers. Inc., New York.

the carbonyl group were observed remarkably in the chelates of (VI), (IX), and (X) but not in the chelates of (I), (II), (III), and (IV). These observations also support the presumptions mentioned above on the chelating ability.

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Summary

Stabilities of copper, palladium, nickel, cobalt and iron chelates of various types of ligands involving mercapto and carbonyl groups was compared with each other qualitatively, and "Irving and Williams' stability series" was found to be applicable to these chelates. Apparent stability constants of these chelates were determined. From the results of these experiments, relationship between chelating abilities and chemical structures of the ligands were investigated.

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184. **Hisashi Tanaka and Akira Yokoyama** : Studies on the Sulfur-containing Chelating Agents. XII. Relationship between Chelating Ability and Chemical Structure of Ligand. (2).[*1]

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In an attempt to make clear the relationship between chelating abilities and chemical structures of S-O-chelating ligands, shown in Chart 1 of Part 1,[*1] qualitative investigations of their chelating abilities and apparent stability constants of the chelates were reported.[*1] It was found that "Irving and Williams' stability series" was almost completely applicable to the chelates of the ligands (I~X). However, the order of the stabilities of both nickel and cobalt chelates could not been clarified, due to the difference of the ratio of ligand to metal at the time of accomplishment of chelate formation. The ratio was 2:1 and 3:1 in nickel and cobalt chelates, respectively. This paper deals with further investigations on the comparison of relative stabilities of the chelates and on the relationship between the chelating abilities and the chemical structures of the ligands obtained from the experimental results. In order to ascertain the comparison of the relative stabilities of the chelates, pH values were measured at the point of 50% extraction of the chelates in chloroform and also at the point of incipient chelate formations.

Relationship between Stabilities and pH at the Time of Extraction

Stability constants of the chelate are usually determined by the titrimetric, spectrophotometric and polarographic methods. However, in the case of neutral inner complex, as it is difficult to determine stability constant by the common methods, the pH at 50% extractability or at incipient precipitation have been used for the comparison

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[*1] Part 1 : This Bulletin, **10**, 1129(1962).

[*2] Yoshida-konoe-cho, Sakyo-ku, Kyoto (田中　久, 横山　陽).