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Synthesis of Chelating Agents. X. Chelating Behavior of 1,2-Diamines with Specific Configurations: *cis*- and Diequatorial *trans*-Diamino-*trans*-decalins, *cis*- and *trans*-Diaminotetralins and 3,3-Dimethyl-1,2-diaminobutane*

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Stability constants were determined at 25 °C for the metal chelates of racemic *cis*- and diequatorial *trans*-2,3-diamino-*trans*-decalins, *cis*- and *trans*-2,3-diaminotetralins and 3,3-dimethyl-1,2-diaminobutane (BEDA), where Cu(II), Ni(II) and Zn(II) are metal ions. Alicyclic *trans*-diamines afforded 1 : 1 complexes more stable than those with *cis*-isomers, regardless of the metal ions. Stability of the metal chelates with BEDA is comparable to that of the *trans*-diamines. The difference in stability of the *trans*- and *cis*-diamine complexes increased in the order Cu-, Zn- and Ni ions. Upon formation of 1 : 2 complexes, it became greater with Ni ion, but practically no difference was observed with the others. An explanation was given on the basis of stereochemistry of the diamines and coordination structures of the divalent metal ions.

Chelating behavior with transition metal ions has been extensively studied for various aliphatic 1,2-diamines capable of internal rotation around the axis of 1,2-carbon atoms, such as ethylenediamine and 2,3-diaminobutane.1)

In order to elucidate stereochemical effects of the chelating agents on their metal complex formation, we have studied the synthesis of complexanes with certain conformations. This paper deals with the chelating behavior of some precursory 1,2-diamines such as 2(*ax*), 3(*eq*)-dimaino-*trans*-decalin [D(A,E)], 2(*eq*), 3(*eq*)-diamino-*trans*-decalin [D(E,E)], *cis*-2,3-diaminotetralin [T(A,E)], *trans*-2,3-diaminotetralin [T(E,E)] and 3,3-dimethyl-1,2-diaminobutane [BEDA].2,3) In these diamines, the stereochemical relationship between the two amino groups is considered to be restricted to a certain extent by their less flexible carbon framework or the steric hindrance of bulky substituents.4)

Experimental

Potentiometric measurements were carried out in a jacketed 100 ml titration vessel, maintained at 25.0±0.1 °C by circulation of thermostated water through the outer jacket. Ionic strength of a solution was adjusted to 0.10 by addition of potassium nitrate for the diaminodecalins D(E,E) and D(A, E) and *cis*-diaminotetralin T(A,E). Potassium chloride was used for *trans*-diaminotetralin T(E,E), since potassium nitrate caused precipitation during the course of titration, particularly for copper(II) ion even in a lower pH region.

A Hitachi-Horiba model P pH-meter fitted with glass(1026)- and calomel(2010) electrodes was calibrated by titration of an acetic acid solution with a 0.1 M potassium hydroxide free from carbonate ion, to give $-\log[\mathrm{H}^+]$. After each measurement the acetic acid solution was again titrated in order to reconfirm the variation in pH-meter reading to be within 0.02.

Titration curves for a metal ion were obtained on two solutions (1 : 1 and 1 : 2 metal to ligand ratios). The total concentration of each ligand was kept constant at 1.0×10^{-3} M, while that of a metal ion was varied correspondingly 1.0×10^{-3}—5.0×10^{-4} M. Computations were carried out by use of a FACOM 230-60 of the Computer Center in Kyushu University. Preparation of the ligand materials was described previously.2,3)

Results and Discussion

Dissociation Constants. The dissociation constants of the conjugate acids of T(E,E) and T(A,E) were calculated as dibasic acids according to Schwarzenbach.5) The results are summarized in Table 2 along with those of some related diamines.

The $\mathrm{p}K_{a2}$ values of diaminotetralins are approximately 1 unit lower than those of the other alicyclic diamines. A similar comparison for aminocyclohexane and 2-aminotetralin, with $\mathrm{p}K_a$ values 10.646) and 9.80,7) respectively, showed that the base strengths of tetralin derivatives are much weaker than those expected from Taft's polar effect of a phenethyl group,8,9) indicating the existence of a direct field effect.

Stability Constants. Titration curves of the diaminodecalins are shown in Figs. 1 and 2. Similar curves were obtained for the diaminotetralins and BEDA.

The equilibria on the chelate formation might be represented as follows.

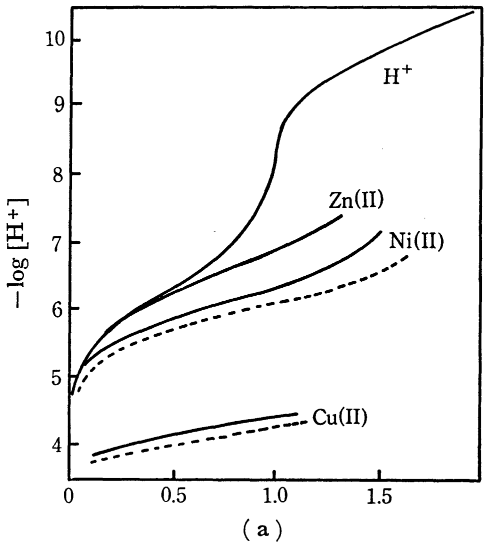

Fig. 1. Potentiometric titration curves of D(A, E) in the presence of various cations, —— 1 : 2 solution, and ---- 1 : 1 solution.

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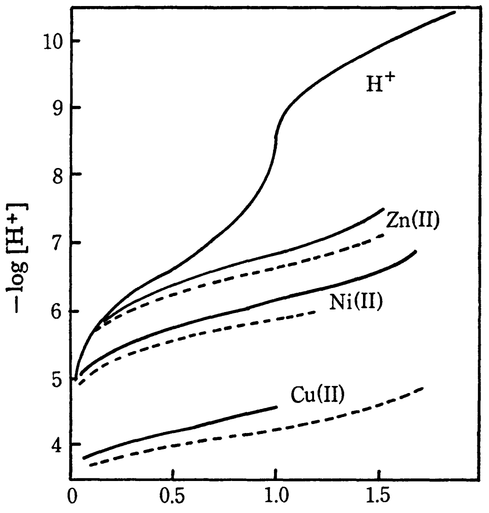
TABLE 1. ELEMENTAL ANALYSES OF PRECIPITATES RESULTING FROM TITRATION OF 1 : 2 SOLUTIONS

Compound	Molecular formula	Elemental analysis C% Found	C% Calcd	H% Found	H% Calcd	N% Found	N% Calcd
$CuT(E,E)_2(NO_3)_2$	$C_{20}H_{28}N_6O_6Cu$	46.69	46.89	5.53	5.51	16.48	16.42
$CuT(E,E)_2(NO_3)_2$[a]	$C_{20}H_{28}N_6O_6Cu$	46.89	46.89	5.47	5.51	16.29	16.42
$NiT(E,E)_2Cl_2(H_2O)_2$[a]	$C_{20}H_{32}N_4O_2Cl_2Ni$	48.86	49.00	6.54	6.53	11.24	11.44
$ZnT(E,E)_2(NO_3)_2$	$C_{20}H_{28}N_6O_6Zn$	46.54	46.73	5.86	5.49	15.94	16.36
$ZnT(E,E)Cl_2$[a]	$C_{10}H_{14}N_2Cl_2Zn$	40.36	40.21	4.77	4.69	9.40	9.38
$CuT(A,E)_2(NO_3)_2$	$C_{20}H_{28}N_6O_6Cu$	46.80	46.89	5.51	5.51	16.43	16.42
$CuD(E,E)_2(NO_3)_2$	$C_{20}H_{40}N_6O_6Cu$	45.28	45.85	7.64	7.64	16.14	16.05
$NiD(E,E)_2(NO_3)_2$	$C_{20}H_{40}N_6O_6Ni$	46.32	46.27	7.64	7.71	16.13	16.19
$CuD(A,E)_2(NO_3)_2$	$C_{20}H_{40}N_6O_6Cu$	45.21	45.85	7.53	7.64	15.81	16.05
$CuD(A,E)_2(NO_3)_2$[a]	$C_{20}H_{40}N_6O_6Cu$	45.56	45.85	7.60	7.64	15.87	16.05
$NiD(A,E)_2(NO_3)_2$	$C_{20}H_{40}N_6O_6Ni$	46.04	46.27	7.60	7.71	16.01	16.19

a) resulting from a 1 : 1 solution.



(a)

Fig. 2. Potentiometric titration curves of D(E, E) in the presence of various cations, —— 1 : 2 solution, and ---- 1 : 1 solution.

$$M + L \rightleftarrows ML \qquad K_{ML} = \frac{[ML]}{[M][L]} \tag{1}$$

$$ML + L \rightleftarrows ML_2 \qquad K_{ML_2} = \frac{[ML_2]}{[ML][L]} \tag{2}$$

$$ML(OH^-) + H^+ \rightleftarrows ML \qquad K_{MLOH} = \frac{[ML]}{[ML(OH^-)][H^+]} \tag{3}$$

$$2ML \rightleftarrows ML_2 + M \tag{4}$$

where M and L stand for a divalent metal cation and a diamine ligand, respectively. Reactions (1) and (3) should play important roles in the 1 : 1 solution, and (1) and (2) in the 1 : 2 solution. If this is the case, a set of K_{ML} and K_{MLOH} and one of K_{ML} and K_{ML_2} might be calculated from the titration data of the 1 : 1 and 1 : 2 solutions, respectively, in combination with mass- and charge balance. The stability constants of the diaminodecalins thus obtained are summarized in Table 2. Titration data from the 1 : 1 solutions of the diaminotetralins and BEDA, however, could not be analyzed by the above procedure. Precipitates of 1 : 2 composition (metal to ligand) were formed during the course of titration of the 1 : 1 solutions

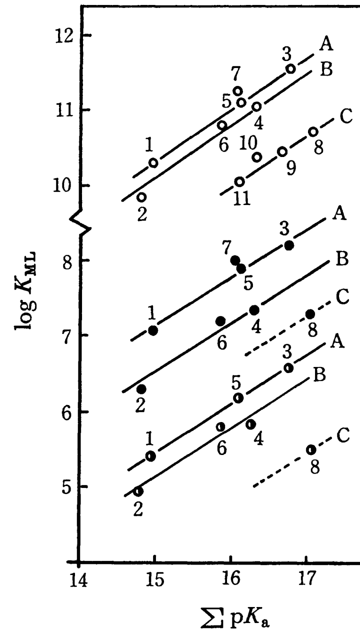


Fig. 3. Relationship of the 1 : 1 chelate stabilities against the total basicities of 1,2-diamines.

1, T(E,E); 2, T(A,E); 3, D(E,E); 4, D(A,E); 5, *t*-CYDA; 6, *c*-CYDA; 7, BEDA; 8, ethylenediamine;[a] 9, 1,2-diaminopropane;[b] 10, 1,2-diaminobutane;[b] and 11, 1,2-diamino-2-methylpropane.[b] ○, Cu chelate; ●, Ni chelate; and ◑, Zn chelate.

a) For chelate stability, T. Davis, S. S. Singer, and L. A. K. Staveley, *J. Chem. Soc.*, **1954**, 2304; measured at 25 °C under $\mu=0.1$, and for acid dissociation, H. K. Powell and N. F. Curtis, *J. Chem. Soc. B*, **1966**, 1205; measured at 25.0 °C under $\mu=0.1$ ($NaClO_4$-$Ba(ClO_4)_2$).

b) For chelate stability, H. K. Powell and N. F. Curtis, *J. Chem. Soc. A*, **1967**, 1441; measured at 25.0 °C under $\mu=0.1$ ($NaClO_4$-$Ba(ClO_4)_2$, and for acid dissociation, the same reference as cited in a).

Table 2. Acid dissociation and chelate stability constants of various diamines measured at 25.0 °C under $\mu=0.10$ with KNO_3

Cation		T(E,E)[b]	T(A,E)	D(E,E)	D(A,E)	*t*-CYDA[c]	*c*-CYDA[c]	BEDA
H^+	pK_{a1}	5.98	5.79	6.68[a]	6.36[a]	6.34	6.04	6.26[d]
	pK_{a2}	8.97	9.00	10.08	9.93	9.77	9.80	9.78
	$\sum pK_a$	14.95	14.79	16.76	16.29	16.11	15.84	16.04
Cu^{2+}	$\log K_{ML}$	10.29	9.86	11.55[e]	11.06[f]	11.09	10.82	11.26
	$\log K_{ML_2}$	8.89	8.71	10.23	10.13	9.64	9.50	9.92
	$\sum \log K$	19.18	18.57	21.78	21.19	20.73	20.37	21.18
Ni^{2+}	$\log K_{ML}$	7.09	6.31	8.22[g]	7.34	7.88	7.20	8.00
	$\log K_{ML_2}$	6.07	5.02	7.09	5.70	6.78	5.87	6.67
	$\sum \log K$	13.16	11.33	15.31	13.04	14.66	13.07	14.67
Zn^{2+}	$\log K_{ML}$	5.39	4.95	6.57	5.86	6.19	5.82	
	$\log K_{ML_2}$	4.82	4.74	5.73	5.23	5.36	5.43	
	$\sum \log K$	10.21	9.69	12.30	11.09	11.55	11.25	

a) Ref. 2, 25.0 °C, $\mu=0.10$ (KNO_3). b) 25.0 °C, $\mu=0.10$ (KCl). c) C. R. Bertsch, W. C. Fernelius, and B. P. Bloch, *J. Phys. Chem.*, **62**, 444 (1958); interporated from the data at 20.0 and 30.0 °C, and converted into $\mu=$zero by Debye-Hückel equation. d) Ref. 3, 25.0 °C, $\mu=0.10$ (KCl). e) Paired $\log K_{MLOH}=5.01$. f) Paired $\log K_{MLOH}=5.26$. g) Paired $\log K_{MLOH}=6.60$.

(Table 1). The results suggest that even in the 1 : 1 solution, the disproportionation reaction (4) takes place, to give a complex ML_2. Stability constants of of the diaminotetralins and BEDA (Table 2) are thus obtained only from the titration data of the 1 : 2 solutions, where those of BEDA complex with zinc(II) could not be obtained because of fluctuation of pH-meter readings probably due to an extremely slow reaction to attain equilibrium.

Stability of the 1 : 1 metal chelate increases in the order T(A,E), T(E,E), *c*-CYDA,** D(A,E), *t*-CYDA,** and D(E,E), in general agreement with the increase in the total basicity of the diamino group, as expressed by ($pK_{a1}+pK_{a2}$), irrespective of metal ion.

Plots of log K_{ML} against the total basicity of diamines (Fig. 3) indicate that the 1,2-diamines can be classified into three groups: the alicyclic diamines of *trans*-configuration (line A), those of *cis*-configuration (line B) and acyclic diamines capable of rotational isomerism, such as ethylenediamine and propylenediamine (line C). The data for each group fall on straight lines parallel to each other.

According to the conformation theory regarding a cyclohexane ring, it is well-known that a conformation with an *axial* bulky substituent is less stable than one with the same group in the *equatorial* position. If one refers to the conformation of the metal chelates with the ligand of a *trans*-group against those with the ligand of a *cis*-group, either one of amino group must be in the *axial* position of the ligand molecule for the latter chelate group. The coordination of aquo ion to this site might cause considerable steric hindrance. In the case of the former groups, however, both amino groups are in the *equatorial* position, so that the coordination of an aquo ion to these sites causes little steric hindrance.

Thus the vertical difference between the correlation lines of a *trans*-group and a *cis*-group could be regarded as values proportional to the stabilization free energy of the *trans*-group over the *cis*-group upon metal complex formation with respective metal ions. The difference is the highest in the nickel chelates, and ascribable to the octahedral hexacoordination structure of nickel(II) ion, which is the most bulky in comparison with tetrahedral zinc(II) and square planar copper(II). A small separation between the correlation lines of *trans*- and *cis*-diamine copper complexes might be regarded to indicate a loose aquation along the axis perpendicular to the square coordination plane of copper ion, to form a distorted octahedral structure in the 1 : 1 chelates.

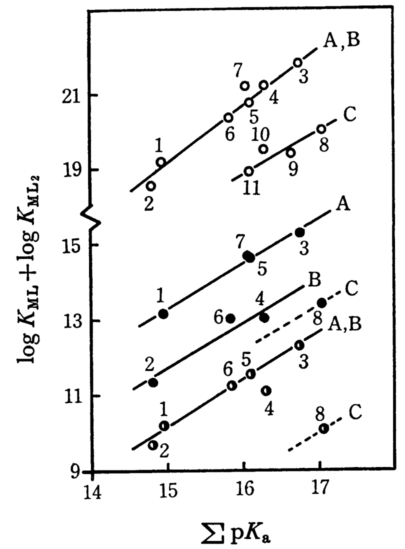


Fig. 4. Relationship of the 1 : 2 chelate stabilities against the total basicities of 1,2-diamines. Notation and references are the same as described in Fig. 3.

Diamines with free internal rotation show a relatively lower chelate stability despite their higher

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** *c*- and *t*-CYDA are abbreviations of *cis*- and *trans*-1,2-diaminocyclohexanes, respectively.

basicities. This can be explained by the loss of freedom in the internal rotation with the chelate ring formation. It should be noted that BEDA is aligned with the *trans*-diamines on a line. A bulky *t*-butyl group hinders the internal rotation in the free ligand molecule to fix the two amino groups in a *gauche* position favorable to form a chelate ring. The entropy loss upon chelation becomes to a certain extent similar to that of alicyclic *trans*-diamines of rigid structures.

Relationships between the stability of 1 : 2 metal-diamine complexes, as expressed by ($\log K_{\mathrm{ML}}+\log K_{\mathrm{ML_2}}$), and the total basicity (Fig. 4) differ somewhat from those observed (Fig. 3). The data for copper- and zinc complexes of the *trans*- and *cis*-diamines can be correlated with single lines, in contrast to nickel chelates, in which each *trans*-diamine afforded 1 : 2 complexes more stable than those of the *cis*-isomer.

The *dl-trans*- and *dl-cis*-diaminodecalins may possibly afford two and four kinds of diastereomeric 1 : 2 copper complexes, respectively, with respect to the configurations of chelate rings around the central metal atom. Molecular model study suggests that the coordinated diamines would be sterically hindered with a ligand, if present on the *z*-axis, in two of the diastereomeric complexes with the *cis*-diamines. The *dl-trans*- and *cis*-diaminocyclohexanes can also afford two diastereomeric copper complexes, and the coordinated diamines in one diastereomer with the *cis*-diamine is subject to steric hindrance with a ligand on the *z*-axis to a greater extent than in the other.

The situation in the nickel complexes would be similar to the above if the 1 : 2 chelates took configurations in which the four amino groups were arranged in a square plane.

Thus the results seem to suggest that the completion of a square ligand field with four amino-nitrogen atoms on the *x*-*y* plane in the 1 : 2 copper chelates leads to dissociation of aquo-ligands on the *z*-axis,[10] while in the nickel chelates aquo-ligands on the *z*-axis remain intact even in the 1 : 2 chelates.

The fact that the data on the 1 : 2 zinc chelates of *trans*- and *cis*-diamines fall on a single correlation line can be regarded as an evidence for a very small inter-ligand interaction in the tetrahedral coordination sphere of zinc(II) ion. If this is the case, the separation between correlation lines in the 1 : 1 zinc chelates should be ascribed to penta- or hexacoordination structures[11] of 1 : 1 diamine–zinc complexes in aqueous solutions rather than to the tetrahedral structure. The former structure would be transformed into the latter with completion of a coordination sphere by four amino groups in 1 : 2 complexes.

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