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Kinetic and Equilibrium Studies of Complex Formation of Nickel(II) with Carboxylate Ligands at High Pressure. III. Nickel(II) Malonate and Nickel(II) Tartronate

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Kinetic and equilibrium measurements were carried out for the complexation reaction of nickel(II) malonate and nickel(II) tartronate in an aqueous solution at 20 °C and at pressures up to 100 MPa. The reaction volume, ΔV^0, and the activation volume, ΔV_f^*, for the complex formation were estimated from the pressure dependence of the stability constant and the rate constant. The results are as follows: $\Delta V^0=13.5\pm1.0\,\text{cm}^3\,\text{mol}^{-1}$ and $\Delta V_f^*=14.7\pm0.5\,\text{cm}^3\,\text{mol}^{-1}$ for nickel(II) malonate, and $\Delta V^0=13.3\pm0.7\,\text{cm}^3\,\text{mol}^{-1}$ and $\Delta V_f^*=15.2\pm0.5\,\text{cm}^3\,\text{mol}^{-1}$ for nickel(II) tartronate. The larger ΔV^0 value compared with those obtained for dicarboxylate ligands which form a monodentate complex coincides with that malonate and tartronate form a chelate complex with nickel(II) in an aqueous solution. By appropriately estimating the volume changes associated with the outer-sphere complex formation and first-bond formation, the overall volume profile for the complexation reaction was obtained. A Similar feature regarding the volume profile for the complexation of nickel(II) malonate and nickel(II) tartronate suggests that tartronate forms a bidentate chelate complex by two carboxyl groups rather than by carboxyl and hydroxyl groups.

The usefulness of the activation volume as a criterion for a mechanistic study has been progressively demonstrated since a high-pressure technique was combined with rapid-reaction techniques. Recently, many kinetic investigations have been reported for metal complexation reactions in solutions under high pressure in order to understand reaction mechanisms based on the activation volume.[1–3] Previously, we studied the complex formation reactions of nickel(II) with some carboxylate ligands in aqueous solutions under high pressure using a high-pressure pressure-jump technique.[4,5] In this present paper, we report the results obtained with nickel(II) malonate and nickel(II) tartronate systems.

In a preliminary communication,[6] we presented the kinetics of a nickel(II) malonate complexation reaction under high pressure, where only the pressure-jump relaxation data were available and the overall volume profile for the reaction could not be obtained because of the poor accuracy of the kinetically determined stability constants. Hence, in the present work, the stability constants at high pressure were determined independently.

A malonate ion has two carboxylato groups which can coordinate to a nickel(II) ion to form a six-membered chelate complex in an aqueous solution, while a tartronate ion has an additional hydroxyl group on α-carbon (see Scheme 1). Considering the molecular structure of a tartronate ion, there may be possible structures of the complex with nickel(II); six-membered chelate coordinated by two carboxyl oxygens, five-membered chelate coordinated by one carboxyl oxygen and one hydroxyl oxygen, and also tridentated chelate coordinated by two carboxyl oxygens and one hydroxyl oxygen. It will be shown below that the volume profile obtained in this study can serve to elucidate not only the rate-determining step of the reaction but also the structure of the complex.

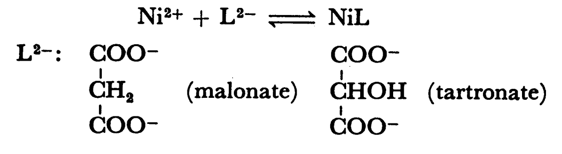
Experimental

Reagents. Stock solutions of nickel(II) malonate and nickel(II) tartronate were prepared from nickel sulfate and respective acids according to a procedure described previously.[4] The concentration of the solution was determined by titrating with an EDTA solution standardized by a standard solution of zinc nitrate. Nickel sulfate (Wako Pure Chemicals, guaranteed grade), malonic acid (Wako Pure Chemicals, >98%), and tartronic acid (Aldrich Chemical Co., 98%) were used without further purification. Each sample solution was prepared by diluting the stock solution to the desired concentration. The pH's of the sample solutions were 6.9±0.1 for nickel(II) malonate and 6.0±0.1 for nickel(II) tartronate. In these pH ranges, most of the ligands were in a fully dissociated form, considering the p*K*a values of the acids; $\text{p}K\text{a}_1=2.85$ and $\text{p}K\text{a}_2=5.67$ for malonic acid,[7] and $\text{p}K\text{a}_1=2.02$ and $\text{p}K\text{a}_2=4.24$ for tartronic acid.[8]

Measurements. The stability constants of the complexes were determined from conductivity measurements according to the Fuoss-Kraus method.[9] The conductivity under high pressure was measured using a conductivity cell made by modifying an injector, which was immersed in a conventional high-pressure vessel. The concentration range of nickel(II) species employed for the conductivity measurements was 1×10^{-4}—$1\times10^{-3}\,\text{mol dm}^{-3}$. Kinetic measurements were made using a high-pressure pressure-jump apparatus.[6] The concentration range of nickel(II) species for kinetic measurements was 5×10^{-4}—$1\times10^{-2}\,\text{mol dm}^{-3}$ for nickel(II) malonate and 5×10^{-4}—$5\times10^{-3}\,\text{mol dm}^{-3}$ for nickel(II) tartronate. The temperature was kept at 20.0±0.1 °C throughout the measurements and the pressure was maintained within ±0.5 MPa. As the concentration of the sample solution is expressed in molarity, in the case of measurements under pressure, corrections for the molar concentration due to compression were made using the density data of water.[10]

Results

The complex formation reaction under consideration is represented in Scheme 1. Stability constants



$$Ni^{2+} + L^{2-} \rightleftharpoons NiL$$

L^{2-}: $COO^- - CH_2 - COO^-$ (malonate) $COO^- - CHOH - COO^-$ (tartronate)

Scheme 1.

of the complexes, *K*, were determined from the conductivity data according to Eq. 1 using a computer iteration technique (detail of the procedure was described previously[4]).

$$\frac{F}{\Lambda} = \frac{1}{\Lambda^0} + \left(\frac{K}{(\Lambda^0)^2}\right)\left(\frac{\Lambda c \gamma_\pm^2}{F}\right), \tag{1}$$

where *F* is the conductivity coefficient (related to the degree of dissociation of the complex, α, by $\alpha = \Lambda/\Lambda^0 F$), and other symbols have their usual meanings. Figures 1a and 1b show the plot of Eq. 1 for nickel(II) malonate and nickel(II) tartronate, respectively, at various pressures. Good linearity was observed for the whole pressure range. From the slope and intercept of these plots, the values of *K* were determined and are summarized in Table 1.

The present value of *K* for nickel(II) malonate at 0.1 MPa is in good agreement with a value found in the literature[11] ($K = 1.26 \times 10^4$ mol^{-1} dm^3 at 25 °C and $I \to 0$). For nickel(II) tartronate, the available literature value[8] is $K = 2.82 \times 10^3$ mol^{-1} dm^3 at 20 °C and $I = 0.1$. From this value, the stability constant at zero ionic strength is estimated to be 18.5×10^3 mol^{-1} dm^3 by using activity coefficient calculated from the Davies equation[12] ($\gamma_\pm \simeq 0.39$ for a divalent electrolyte at $I = 0.1$). Considerable disagreement is seen between this value and the present result at 0.1 MPa, the origin of which is not known.

The pressure dependence of the stability constant provides for an evaluation of the reaction volume for the complex formation according to the relation[13]

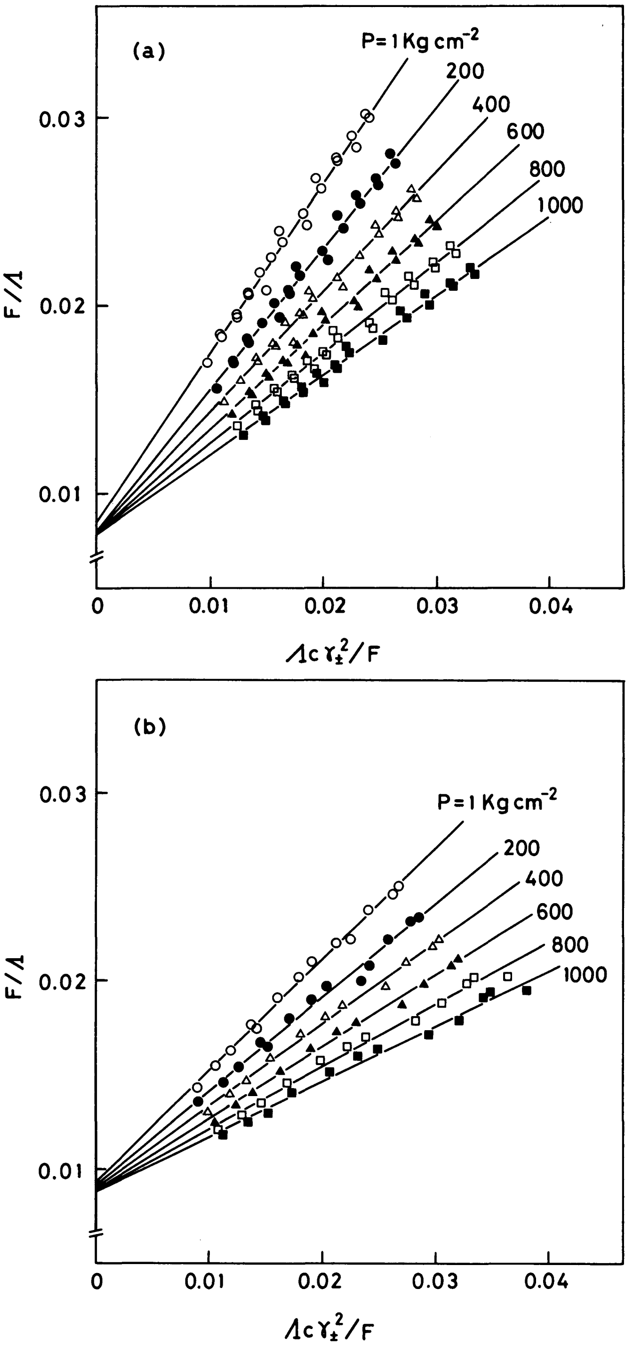


Fig. 1. Plot of conductivity data according to Eq. 1 for (a) nickel (II) malonate and (b) nickel (II) tartronate at 20 °C. Pressures are indicated in the figure.

Table 1. Stability Constants, *K*,[a] as a Function of Pressure at 20 °C and $I \to 0$

	P/MPa					
	0.1	20	40	60	80	100
Nickel(II) malonate	12.3 (1.3)	11.2 (1.2)	10.4 (1.1)	9.21 (0.87)	7.90 (0.67)	6.84 (0.54)
Nickel(II) tartronate	6.77 (0.42)	5.93 (0.46)	5.37 (0.32)	4.94 (0.31)	4.12 (0.32)	3.80 (0.31)

a) In 10^3 mol^{-1} dm^3. Standard deviations estimated from the least-squares analysis are given in parentheses.

$$RT\left(\frac{\partial \ln K}{\partial P}\right)_T = -\Delta V^0 - RT\kappa_0, \qquad (2)$$

where ΔV^0 is the reaction volume, i.e., the change in the partial molar volume at infinite dilution accompanied by the complex formation from a nickel(II) ion and ligand, κ_0 represents the solution compressibility, and other symbols have their usual meanings. In Eq. 2, $-RT\kappa_0$ is the correction term for the compression required when the concentration is expressed in terms of molarity and has a value of $1.1\ \mathrm{cm^3\ mol^{-1}}$[13a] for the present case. A plot of log K against pressure is shown in Fig. 2a, and log K shows a linear pressure dependence over the studied pressure range. From the slope of a straight line fitted using a least-squares method, the reaction volumes for nickel(II) malonate and nickel(II) tartronate were estimated according to Eq. 2. They are listed in Table 4 together with those obtained for other dicarboxylate ligands.

The rate constants for the complex formation reaction were determined from the pressure-jump relaxation data. The observed relaxation process was characterized by a single relaxation time in the measured concentration range. A reciprocal relaxation time for the reaction of Scheme 1 is given by Eq. 3.[14]

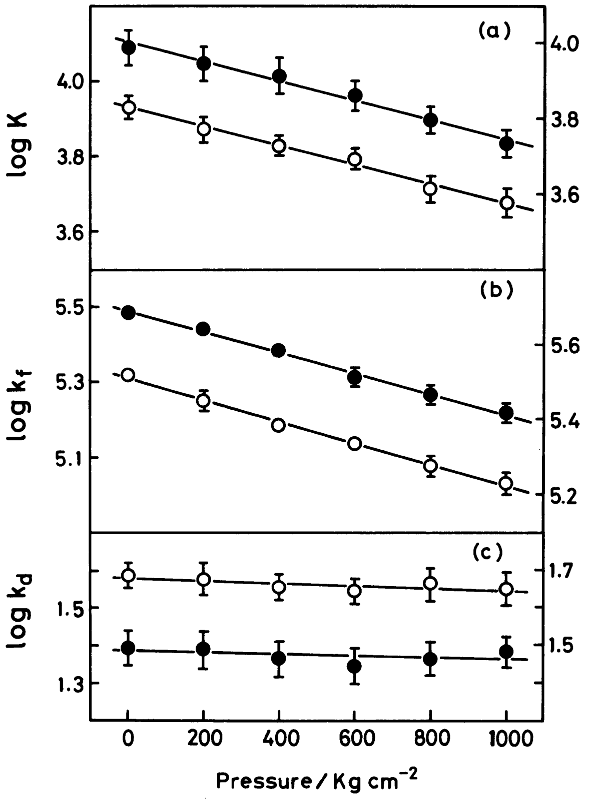


Fig. 2. Pressure dependence of (a) log K, (b) log k_f, and (c) log k_d at 20 °C: ●, nickel(II) malonate (left scale); ○, nickel(II) tartronate (right scale). Solid lines show the linear least-squares fits to the data points.

$$1/\tau = k_f[\gamma_\pm^2(c_{Ni}+c_L) + 1/K], \qquad (3)$$

where k_f is the rate constant of the complex formation at zero ionic strength, c_{Ni} and c_L are the equilibrium concentration of nickel(II) and ligand ions, and $\gamma_\pm$ is the mean activity coefficient of the free ions at a given ionic strength.

The values of k_f were determined from the relaxation time using Eq. 3, where c_{Ni}, c_L, and $\gamma_\pm$ were calculated from the stability constant by a previously described procedure.[4] Some examples of the obtained results are shown in Table 2. The dissociation rate constants of the complex, k_d, were determined from the relation

$$k_d = k_f/K \qquad (4)$$

The values of the rate constants, thus obtained, at various pressures are summarized in Table 3.

The activation volume of the reaction was estimated from the pressure dependence of the rate constant based on a relation analogous to Eq. 2.[13] Figures 2b and 2c show plots of log k_f and log k_d against pressure. In the studied pressure range, a linear relationship was obtained between the logarithm of the rate constant and the pressure. From the slope of the straight line (fitted by a least-squares method), the values of the activation volume for the complex formation, ΔV_f^*, and dissociation, ΔV_d^*, were estimated, and are listed in Table 4.

Discussion

It is considered that malonate ions form six-membered chelate complexes with nickel(II) ions in an aqueous solution, while succinate ions form monodentate complexes with nickel(II) ions rather than seven-membered chelate complexes. This may be justified from a comparison of the stability constant; the stability constant of nickel(II) succinate is much smaller than that of nickel(II) malonate. The glutarate ion and the adipate ion, which have longer methylene chains between two carboxyl groups, might also form a monodentate complexes. The difference in the structure of the complexes is reflected in the reaction volume. As can be seen in Table 4, succinate, glutarate, and adipate have similar values of ΔV^0 and are smaller than that for malonate.

The resultant volume change associated with the complex formation between metal ions and charged ligands may be divided into several contributions; i) the release of electrostriction due to the charge

Table 2. Relaxation Times and Rate Constants of Complex Formation for Nickel(II) Malonate and Nickel(II) Tartronate at 20 °C and $I \to 0$

$P=0.1$ MPa			$P=100$ MPa		
$c^{a)}$ / 10^{-3} mol dm^{-3}	$1/\tau$ / s^{-1}	k_f / 10^5 mol^{-1} dm^3 s^{-1}	$c^{a)}$ / 10^{-3} mol dm^{-3}	$1/\tau$ / s^{-1}	k_f / 10^5 mol^{-1} dm^3 s^{-1}
(a) Nickel(II) Malonate					
0.474	110	3.09	0.404	82.7	1.80
0.671	125	3.01	0.606	96.9	1.78
0.758	135	3.08	0.808	99.1	1.61
0.948	154	3.18	1.01	111	1.64
1.85	207	3.19	1.52	135	1.67
2.37	223	3.08	3.03	172	1.59
2.84	245	3.13	5.05	203	1.51
4.63	284	2.94	8.08	268	1.65
6.02	321	2.97	10.1	289	1.62
9.48	384	2.93			av. 1.65
		av. 3.06			
(b) Nickel(II) Tartronate					
0.578	172	3.27	0.578	135	1.85
0.771	202	3.41	0.771	150	1.84
0.962	215	3.30	1.16	151	1.57
1.16	231	3.28	1.35	186	1.82
1.35	244	3.25	1.54	187	1.74
1.54	248	3.12	1.93	200	1.69
1.93	317	3.63	2.31	222	1.75
2.31	312	3.31	2.89	238	1.71
2.89	327	3.16	3.28	227	1.55
3.28	365	3.34	3.86	249	1.59
3.86	398	3.40	4.43	265	1.61
4.43	382	3.09			av. 1.70
		av. 3.30			

a) Analytical concentration under atmospheric pressure.

Table 3. Rate Constants for the Complex Formation Reaction of Nickel(II) Malonate and Nickel(II) Tartronate as a Function of Pressure at 20 °C and $I \to 0^{a)}$

	Nickel(II) malonate		Nickel(II) tartronate	
P/MPa	$k_f/10^5$ / mol^{-1} dm^3 s^{-1}	k_d / 10 s^{-1}	$k_f/10^5$ / mol^{-1} dm^3 s^{-1}	k_d / 10 s^{-1}
0.1	3.06(0.09)	2.49(0.27)	3.30(0.15)	4.87(0.37)
20	2.76(0.14)	2.46(0.29)	2.82(0.17)	4.76(0.47)
40	2.42(0.10)	2.32(0.26)	2.43(0.12)	4.53(0.36)
60	2.05(0.12)	2.23(0.25)	2.18(0.10)	4.42(0.35)
80	1.84(0.10)	2.33(0.24)	1.90(0.12)	4.61(0.47)
100	1.65(0.09)	2.42(0.23)	1.70(0.11)	4.48(0.47)

a) Standard deviations estimated from the values at 9—13 different concentrations are shown in parentheses.

Table 4. Reaction Volumes, ΔV^0, and Activation Volumes, ΔV^*, for the Complex Formation of Nickel(II) with Carboxylate Ligands$^{a)}$

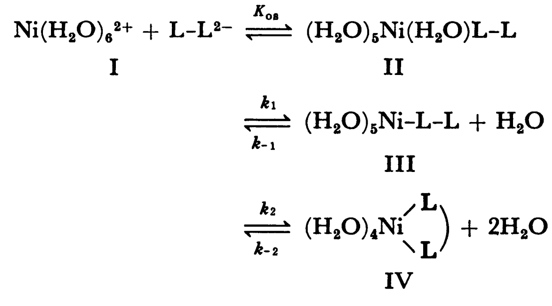
Ligands	ΔV^0	ΔV_f^*	ΔV_d^*
Succinate$^{b)}$	11.1 ± 0.9	14.1 ± 0.8	3.0 ± 0.9
Glutarate	$10.4 \pm 0.8^{c)}$		
Adipate	$11.2 \pm 0.7^{c)}$		
Malonate	13.5 ± 1.0	14.7 ± 0.5	1.2 ± 1.2
Tartronate	13.3 ± 0.7	15.2 ± 0.5	1.9 ± 0.8

a) In cm^3 mol^{-1}; Errors are standard deviations estimated from the least-squares analysis. b) Ref. 4. c) Reaction volumes determined in our laboratory by the same method.

neutralization, ii) the elimination of solvated water around the coordinating group accompanied by the coordination bond formation to produce free water, iii) the difference in coordination bond length between a metal-water bond and a metal-ligand bond, and iv) for a chelating ligand, the increase of free volume, which is too small to be occupied by the solvent molecule, resulting from the formation of ring structure. The contributions from i), ii), and iv) are positive for volume increase in the system, while the sign of the contribution from iii) may depend on the nature of metal-ligand bond. Since all ligands listed in Table 4 have the same electrical charge (−2), it can be regarded that contribution i) is the same for all ligands. The smaller values of ΔV^0 for a monodentate complex than for a chelate complex may be reasonable considering contributions ii) and iv).

The value of ΔV^0 for nickel(II) tartronate is essentially the same as that for nickel(II) malonate (Table 4). Malonate ions form six-membered chelate complexes coordinated by two carboxyl oxygens. For a chelate complex formed from a tartronate ion, three different structures may be expected; a six-membered chelate coordinated by two carboxyl oxygens, a five-membered chelate coordinated by one carboxyl oxygen and one hydroxyl oxygen, or a tridentate chelate coordinated by two carboxyl oxygens and one hydroxyl oxygen. That the ΔV^0 value of nickel(II) tartronate is comparable to that of nickel(II) malonate suggests that tartronate forms a six-membered chelate complex using two carboxyl oxygens. If tartronate forms a chelate using one carboxyl and one hydroxyl group or a tridentate chelate using two carboxyl and one hydroxyl groups, then a different ΔV^0 value from malonate should be expected from the contributions ii)—iv) described above; in fact, the reaction volume of 17.8 cm^3 mol^{-1} was obtained for nickel(II) malate which forms a chelate complex coordinated by one carboxyl and one hydroxyl groups.[15)]

The metal complexation reaction has been generally interpreted in terms of a stepwise mechanism which was postulated by Eigen and discussed further by Wilkins.[16)] For the bidentate chelate complex (as in the present case), this mechanism is represented by Scheme 2. In this scheme, I is a free ion, II is an outer-sphere complex, III is a monodentate complex with one end of the ligand left free, IV is a bidentate chelate complex, K_{os} is outer-sphere complex formation constant, and k's are the rate constants of the respective steps. Under the assumptions that I ⇄ II is very rapid compared with other steps and that III is in a steady state, the overall rate constants are related to the rate constants of each step in Scheme 2 by the equations



Scheme 2.

$$k_f = K_{os}k_1\left(\frac{k_2}{k_2+k_{-1}}\right) \tag{5}$$

$$k_d = k_{-1}\left(\frac{k_{-2}}{k_2+k_{-1}}\right) \tag{6}$$

For the complex formation of nickel(II) malonate, the rate-determining step was assigned to the first-bond formation step (i.e., the formation of III) based on an analysis of the complexation rate constant.[17,18)] This assignment is further supported from the present result that the activation volume ΔV_f^* for nickel(II) malonate is essentially the same as that for nickel(II) succinate for which the chelation process is lacking. This may also be the case for the complexation of nickel(II) tartronate, since ΔV_f^* is comparable to the other two ligands listed in Table 4. For a case in which the rate-determining step is the first-bond formation (i.e., $k_2 \gg k_{-1}$), Eqs. 5 and 6 are reduced to

$$k_f \simeq K_{os}k_1 \quad \text{and} \quad k_d \simeq k_{-1}/K_2, \tag{7}$$

where $K_2 = k_2/k_{-2}$. Then, the overall activation volume can be approximately expressed by

$$\Delta V_f^* = \Delta V_{os}^0 + \Delta V_1^*, \tag{8}$$

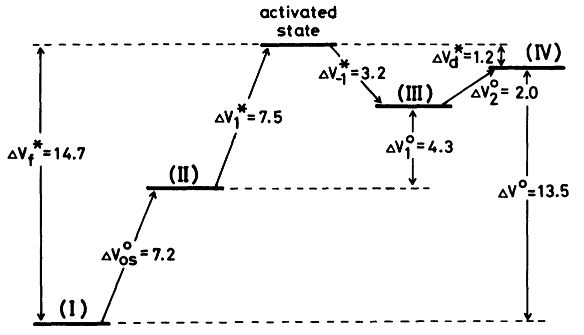
$$\Delta V_d^* = \Delta V_{-1}^* - \Delta V_2^0, \tag{9}$$

where ΔV_{os}^0 and ΔV_2^0 are the reaction volumes for the outer-sphere complex formation and the chelate formation from monodentate intermediate, and ΔV_1^* and ΔV_{-1}^* are the activation volumes for the first bond formation and breaking.

The value of ΔV_{os}^0 is estimated to be approximately 7.2 cm^3 mol^{-1} for 2-2 electrolyte at 20 °C according to Hemmes[19)] as mentioned in a previous paper.[4)] Then, the values of ΔV_1^* can be estimated from Eq. 8 as follows; $\Delta V_1^* = 7.5 \pm 0.5$ cm^3 mol^{-1} for nickel(II) malonate and 8.0 ± 0.5 cm^3 mol^{-1} for nickel(II) tartronate. These values show a close resemblance to the activation volume of the water exchange of the aquanickel(II) ion, $\Delta V_{H_2O}^* = 7.2 \pm 0.3$ cm^3 mol^{-1}, obtained from a high-pressure NMR study.[20)] This result suggests that the activated state for the first-bond formation process is the same as that for the water exchange process, where the bond between nickel(II) and leaving water molecule is loosened and somewhat lengthened.

The volume profile diagrams obtained for the complexation reaction of nickel(II) malonate and nickel(II) tartronate are shown in Fig. 3. The value of ΔV_1^0, which represents the volume difference between II and III, was estimated to be 4.3 cm^3 mol^{-1} from ΔV^0 and ΔV_{os}^0 for nickel(II) succinate.[4)] This estimation is based on the facts that ΔV_1^0 corresponds to the volume change associated with the coordina-

(a) nickel(II) malonate



(b) nickel(II) tartronate

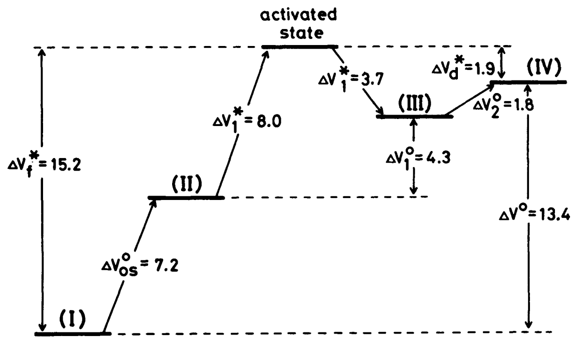


Fig. 3. Volume profile diagrams for the complex-formation reaction of nickel(II) malonate (a) and nickel(II) tartronate (b). I, II, III, and IV correspond to the species in Scheme 2. The values of volume change in cm^3 mol^{-1} are shown in the figure.

tion-bond formation by a carboxyl group after an outer-sphere complex forms, and nickel(II) succinate forms a monodentate complex coordinated by a single carboxyl group. An initial volume increase occurs due to the release of electrostriction upon forming the outer-sphere complex(II). It is followed by a volume increase due to the loosening of water-nickel(II) bonds to reach an activated state. Then, a volume decrease occurs upon going from the activated state to the monodentate complex(III) due to the completion of the coordination bond. It is again followed by a volume increase due to another coordination-bond formation to form a final chelate complex(IV). The positive ΔV_1° and ΔV_2° may be ascribed to the elimination of solvated water around the coordinating group due to the bond formation, which produces the free water and the resulting volume increase.

Features of the volume profiles for nickel(II) malonate and nickel(II) tartronate resemble each other. It is inferred from this result that the hydroxyl group on an α-carbon present in a tartronate ion has no significant role regarding both the mechanism of the complexation reaction and the final structure of the complex.

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References

1) E. F. Caldin, M. W. Grant, and B. B. Hasinoff, *J. Chem. Soc., Faraday Trans. 1*, **68**, 2247 (1972); M. W. Grant, ibid., **69**, 560 (1973); M. W. Grant and C. J. Wilson, ibid., **72**, 1362 (1976); B. B. Hasinoff, *Can. J. Chem.*, **52**, 910 (1974); B. B. Hasinoff, ibid., **54**, 1820 (1976); B. B. Hasinoff, ibid., **57**, 77 (1979); E. F. Caldin and R. C. Greenwood, *J. Chem. Soc. Faraday Trans. 1*, **77**, 773 (1981).

2) S. Funahashi, K. Ishihara, and M. Tanaka, *Inorg. Chem.*, **20**, 51 (1981); K. Ishihara, S. Funahashi, and M. Tanaka, ibid., **22**, 194 (1983); K. Ishihara, S. Funahashi, and M. Tanaka, ibid., **22**, 2564 (1983); S. Funahashi, Y. Yamaguchi, and M. Tanaka, ibid., **23**, 2249 (1984).

3) P. J. Nichols, Y. Ducommun, and A. E. Merbach, *Inorg. Chem.*, **22**, 3993 (1983).

4) T. Inoue, K. Kojima, and R. Shimozawa, *Inorg. Chem.*, **22**, 3972 (1983).

5) T. Inoue, K. Sugahara, K. Kojima, and R. Shimozawa, *Inorg. Chem.* **22**, 3977 (1983).

6) T. Inoue, K. Kojima, and R. Shimozawa, *Chem. Lett.*, **1981**, 259.

7) E. Gelles and G. H. Nancollas, *J. Chem. Soc.*, **1956**, 4847.

8) E. Campi, *Ann. Chim. (Rome)*, **53**, 96 (1963).

9) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 476 (1933). R. M. Fuoss, ibid., **57**, 488 (1935).

10) P. W. Bridgman, "The Physics of High Pressure," G. Bell, London (1949).

11) V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, **1961**, 4367.

12) C. W. Davies, *J. Chem. Soc.* **1938**, 2093.

13) a) K. E. Weale, "Chemical Reactions at High Pressures," E. & F. N. Spon Ltd., London (1967); b) N. S. Isaacs, "Liquid Phase High Pressure Chemistry," John Wiley & Sons, New York (1981).

14) G. H. Czerlinski, "Chemical Relaxation," Marcel Dekker Inc., New York (1966).

15) The author's unpublished data.

16) M. Eigen and R. G. Wilkins, "Mechanisms of Inorganic Reactions," Adv. Chem. Ser. No. 49, American Chemical Society, Washington, DC (1965); R. G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1974).

17) J. L. Bear and C. T. Lin, *J. Phys. Chem.*, **72**, 2026 (1968).

18) F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965); G. Calvaruso, F. P. Cavasino, and E. Di Dio, *J. Chem. Soc., Dalton Trans.* **1972**, 2632.

19) P. Hemmes, *J. Phys. Chem.*, **76**, 895 (1972).

20) Y. Ducommun, W. Earl, and A. E. Merbach, *Inorg. Chem.*, **18**, 2754 (1979); Y. Ducommun, K. E. Newman, and A. E. Merbach, ibid., **19**, 3696 (1980).