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Nickel(II) Complexes of Ethylenediaminemonoacetic Acid (EDMA). The Preparation and Thermal Decomposition of Nickel(II)-EDMA Complexes

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The following nickel(II) complexes containing ethylenediaminemonoacetate anion(s) (edma) were newly prepared from an aqueous solution containing nickel(II) ion and edma: $[Ni(edma)(H_2O)_3]X$ (X=Cl and Br), $[Ni(edma)I]_4$, and $[Ni(edma)_2]\cdot 2H_2O$. By the thermal decomposition of $[Ni(edma)(H_2O)_3]X$, $[Ni(edma)X]_4$-type complexes (X=Cl and Br) were also prepared. By absorbing three molecules of water in an atmosphere, two new, mixed complexes containing a halogen anion and water molecule(s), $[Ni(edma)Cl(H_2O)_2]\cdot H_2O$ and $[Ni(edma)Br(H_2O)]_2\cdot 4H_2O$ (dimer), were prepared from $[Ni(edma)X]_4$. By the measurements of the absorption spectra, the magnetic moments, and the dehydrations, their structures were all assigned to octahedral. The $[Ni(edma)X]_4$ complexes (X=Cl, Br and I) were presumed to have the tetramer structure, where four halogen anions are triply bridged to the nickel(II) ion. The difference between the $[Ni(edma)(H_2O)_3]X$, $[Ni(edma)Cl(H_2O)_2]\cdot H_2O$, and $[Ni(edma)Br(H_2O)]_2\cdot 4H_2O$ complexes were clearly observed on the basis of their derivatographic behavior. The mechanisms of the dehydrations were also discussed.

In the previous paper, the stability constants of nickel(II)-EDMA complexes with 1-to-1 and 1-to-2 compositions were reported.[1] From the spectrophotometric evidence, it was concluded that the formation of a mixed complex containing chloride ions could be ruled out in an aqueous solution. This conclusion is reasonable because it is known that the formation constant of a nickel(II)-hexaquo complex with chloride ions is very small.[2] However, it can not always be said that the information obtained by the solution equilibrium study safely holds for solid-state chemistry. Therefore, in order to obtain much information concerning the complex formation reaction, it would be necessary to prepare the complexes and characterize them.

In these circumstances, in order to obtain information on mixed nickel(II)-EDMA complexes containing halogen anions and in order to compare the properties in the solution state and those in the solid state, the preparation and thermal decomposition of nickel(II)-EDMA complexes were examined.

Experimental

Preparation of the Complexes. *1) Ethylenediaminemonoacetatotriaquonickel(II) Chloride,* [Ni(edma)-

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[1] M. Kodama, Y. Fujii and T. Ueda, This Bulletin, **43**, 2085 (1970).

[2] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964), p. 282.

(H$_2$O)$_3$]Cl (I). To an aqueous solution containing 2.4 g (0.01 mol) of nickel(II) chloride hexahydrate, 2.5 g (0.012 mol) of ethylenediaminemonoacetic acid dihydrochloride monohydrate (EDMA·2HCl·H$_2$O)[3] were added, and the solution was warmed at 70—80°C. After adjusting the solution's pH to 6—7 by adding sodium bicarbonate, the resulting solution was concentrated to about 15 m*l*. Three or four volumes of alcohol were then added to the solution, and the resulting solution was cooled to 0°C for a day. Light blue crystals were separated out. They were recrystallized from water-alcohol. Yield, about 2.0 g (75%). Found: C, 18.81; H, 5.93; N, 10.97; H$_2$O, 20.6%. Calcd for $C_4H_{15}NiN_2O_5Cl$: C, 18.55; H, 5.62; N, 10.67; H$_2$O, 20.37%.

2) Tetramer of Ethylenediaminemonoacetatochloronickel(II), [Ni(edma)Cl]$_4$ (II). The complex I was heated at about 180°C for half an hour. A light green powder was thus obtained. This complex was cooled and preserved in a desiccator with silica gel. Found: C, 22.41; H, 4.26; N, 12.58%. Calcd for $C_4H_9NiN_2O_2Cl$: C, 22.11; H, 4.18; N, 12.89%.

3) Ethylenediaminemonoacetatochlorodiaquonickel(II) Monohydrate, [Ni(edma)Cl(H$_2$O)$_2$]·H$_2$O (III). The complex II was allowed to stand in an atmosphere for two or three days at room temperature. The color thus changed gradually from light green to light blue. Found: C, 18.40; H, 5.92; N, 10.44; H$_2$O, 20.2%. Calcd for $C_4H_{13}NiN_2O_4Cl\cdot H_2O$: C, 18.55; H, 5.62; N, 10.67; H$_2$O, 20.37%.

4) Ethylenediaminemonoacetatotriaquonickel(II) Bromide, [Ni(edma)(H$_2$O)$_3$]Br (IV). To an aqueous solution of the complex I (7 g, 0.0264 mol), an aqueous solution of silver nitrate (5.1 g, 0.03 mol) was added. The silver chloride which resulted was filtered off, and then potassium bromide (9.4 g, 0.07 mol) was added to the filtrate. The precipitate of silver bromide was filtered off, and the resulting solution was concentrated to about 15 m*l*. Three or four volumes of alcohol were added to the solution, which was then cooled to 0°C for a day. After filtering off the potassium bromide thus precipitated, the filtrate was concentrated to a volume of about 25 m*l*. When it was cooled to 0°C, light blue crystals were separated out. They were recrystallized from water-alcohol. Yield, about 5 g (61%). Found: C, 15.75; H, 4.78; N, 9.27; H$_2$O, 17.7%. Calcd for $C_4H_{15}NiN_2O_5Br$: C, 15.51; H, 4.89; N, 9.04; H$_2$O, 17.45%.

5) Tetramer of Ethylenediaminemonoacetatobromonickel(II), [Ni(edma)Br]$_4$ (V). This compound was prepared from the complex IV by the same way as was employed for the complex II. Found: C, 18.58; H, 3.77; N, 10.49%. Calcd for $C_4H_9NiN_2O_2Br$: C, 18.35; H, 3.47; N, 10.70%.

6) Bis(ethylenediaminemonoacetato)diaquo-μ-dibromodinickel(II) Tetrahydrate, [Ni(edma)Br(H$_2$O)]$_2$·4H$_2$O (VI). This compound was prepared from the complex V in the same manner as has been described for the complex III. Found: C, 15.92; H, 4.44; N, 9.45; H$_2$O, 17.1%. Calcd for $C_4H_{11}NiN_2O_3Br\cdot 2H_2O$: C, 15.51; H, 4.89; N, 9.04; H$_2$O, 17.45%.

7) Tetramer of Ethylenediaminemonoacetatoiodonickel(II), [Ni(edma)I]$_4$ (VII). An aqueous solution of the complex I (7 g, 0.0264 mol) was treated with a silver nitrate solution. After filtering off the silver chloride thus precipitated, potassium iodide was added to the filtrate. The resulting solution was treated in the same manner as in the case of the complex IV. When the alcoholic solution was then concentrated to about 30 m*l* and allowed to stand for a day, light green crystals were separated out. They were washed with 50% alcohol. Yield, about 2 g (24%). Found: C, 15.76; H, 2.92; N, 9.47%. Calcd for $C_4H_9NiN_2O_2I$: C, 15.56; H, 2.94; N, 9.08%.

8) Bis(ethylenediaminemonoacetato)nickel(II) Dihydrate, [Ni(edma)$_2$]·2H$_2$O (VIII). To an aqueous solution of nickel(II) chloride hexahydrate (2.4 g, 0.01 mol), 8.4 g (0.08 mol) of ethylenediaminemonoacetic acid dihydrochloride monohydrate were added. The solution was warmed to about 80°C, and the solution's pH was adjusted to 10—11 by adding a 6 N sodium hydroxide solution. The resulting solution was concentrated to about 10 m*l*. The sodium chloride thus precipitated was filtered off. About 60—70 m*l* of alcohol were added to the filtrate, and the resulting solution was allowed to stand in a refrigerator for 2—3 weeks. Blue crystals could thus be separated out. They were washed with 80% alcohol. Yield, about 1.0 g (34%). Found: C, 29.39; H, 6.91; N, 16.94%. Calcd for $C_8H_{18}NiN_4O_4\cdot 2H_2O$: C, 29.20; H, 6.75; N, 17.03%.

Measurements. The visible and far-infrared absorption spectra of aqueous solutions were recorded on a Hitachi EPS-3 pen-recording spectrophotometer. The reflection spectra were measured with a Hitachi Perkin-Elmer 139 spectrophotometer with a standard Hitachi reflection attachment. The infrared absorption spectra were taken on Nujol mulls between sodium chloride or on potassium bromide disks using a Hitachi EPI-S2 spectrometer. The TGA, DTA, and DTG curves were automatic-photographically recorded with a single sample by means of a Metrimpex Derivatograph, type-OD-102. The magnetic susceptibility was determined with a Gouy balance at room temperature. The elemental analyses were performed by the conventional combustion method, using a Yanagimoto C.H.N. Corder, MT-1.

Results and Discussion

IR Spectra. The infrared absorption spectra were measured in order to confirm whether or not the carboxylate group was coordinated to the nickel(II) ion. All the spectra of the complexes showed the νCOO-Ni band in the range from 1585 to 1660 cm^{-1} (Table 1). Therefore, it is clear

Table 1. Infrared absorption spectra (in cm^{-1}) and mangetic moments

Complex	νCOO-Ni asym. str.	νN-H def.	μ (B.M.)
I	1645	1575	3.26
II		1585 (overlapped)	3.26
III	1650	1570	3.27
IV	1645	1570	3.08
V		1585 (overlapped)	3.15
VI		1585 (overlapped)	3.06
VII		1605 (overlapped)	3.10
VIII	1660	1575	3.06

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[3] Y. Fujii, E. Kyuno and R. Tsuchiya, This Bulletin, **43**, 786 (1970).

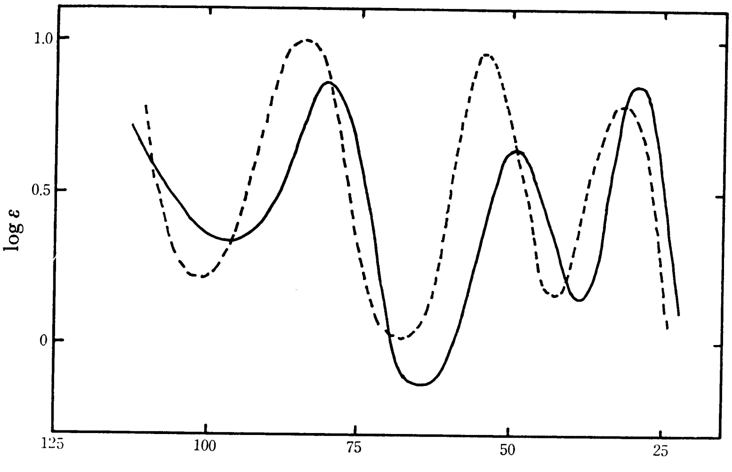

Fig. 1. Absorption spectra: complexes I and IV (——), VIII (----).

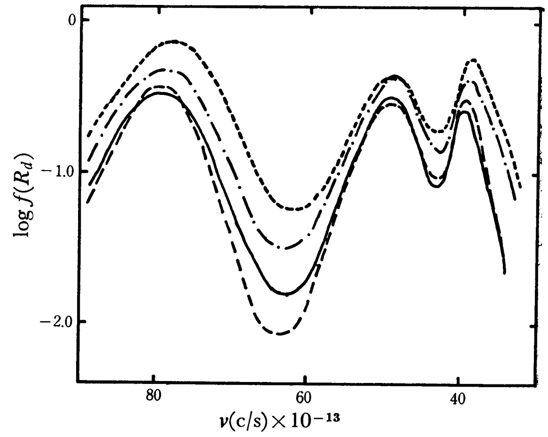

Fig. 2. Absorption spectra by the diffuse-reflectance method: I (——), III (—·——·—), IV (— — —), VI (----).

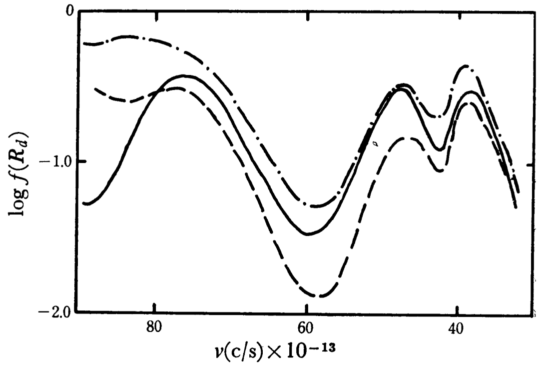

Fig. 3. Absorption spectra by the diffuse-reflectance method: II (——), V (—·——·—), VII (———).

that the carboxylate group is coordinated to the nickel(II) ion.[4] In the cases of the complexes II, V, VI, and VII, the νCOO–Ni band is shifted to lower energy sites than those of the other complexes. This fact may indicate that the COO–Ni bonds of the complexes II, V, VI, and VII are slightly weakened as compared with those of the other complexes because of the distortion of their structures. On the other hand, the complexes I, III, IV, and VIII, in which they take the monomer structure, showed the νCOO–Ni band at higher energy sites than those of the complexes II, V, VI, and VII. Therefore, though it is difficult to distinguish the difference in the structure between the complexes III and VI on the basis of their absorption spectra (shown in the next paragraph), it can be suggested from their clearly different νCOO–Ni bands that the complex VI has a different structure than the complex III.

Electronic Spectra. The absorption spectra in an aqueous solution and those obtained by the diffuse-reflectance method are shown in Figs. 1, 2, and 3. The numerical values are summarized in Table 2, together with those of the related compounds.

The spectra of the complexes I and IV in an aqueous solution are similar to those which are characteristic for the octahedral Ni-N_2O_4-type complexes.[5] The aqueous solutions of the complexes I and IV were adsorbed by a cation exchanger, but not by an anion exchanger. Therefore, in an aqueous solution, the complexes I and IV must be cationic and the coordination of the halogen anion to the nickel(II) ion can be ruled out. This result agrees well with the finding obtained in the previous study.[1] In the solid state, the diffuse-reflectance spectra of the complexes I and IV also show spectra similar to those in an aqueous solution, although the peak near 30×

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[4] T. Sakaguchi and K. Ueno, "Metal Chelates," Vol. II, Nankodo, Tokyo (1963), p. 43.

[5] H. Ito, *Nippon Kagaku Zasshi*, **77**, 1383 (1956).

TABLE 2. ABSORPTION SPECTRA FOR THE COMPLEXES

Complex	ν (log ε)	ν (log ε)	ν (log ε)
I	80.0 (0.86) 80.0 (−0.47)*	49.2 (0.64) 49.6 (−0.49)*	29.1 (0.85) 40.0 (−0.58)*
II	76.0 (−0.44)*	46.9 (−0.50)*	38.0 (−0.50)*
III	77.9 (−0.33)*	48.8 (−0.35)*	39.5 (−0.38)*
IV	80.0 (0.86) 80.0 (−0.45)*	49.2 (0.64) 49.6 (−0.54)*	29.1 (0.85) 40.0 (−0.51)*
V	83.3 (−1.97)*	46.9 (−0.45)*	39.2 (−0.35)*
VI	77.9 (−0.14)*	48.4 (−0.34)*	39.5 (−0.24)*
VII	76.9 (−0.50)*	46.9 (−0.80)*	39.2 (−0.58)*
VIII	84.0 (1.02)	54.1 (0.97)	30.8 (0.79)
$[Ni en(H_2O)_4]SO_4 \cdot H_2O$[5]	81.0 (0.76)	48.5 (0.54), 41.0 (0.25)	30.8 (0.68)
$[Ni(gly)_2(H_2O)_2]$[5]	80.8 (0.90)	48.8 (0.68)	29.3 (0.85)
$[Ni(en)_2(H_2O)_2](ClO_4)_2$[5]	84.0 (1.02)	54.8 (0.81)	33.4 (0.85)

The frequency is given in 10^{13} sec^{-1}.

* Data by the diffused-reflectance method, ( ) is the value of $\log f(R_d)$.

10^{13} c/s observed in an aqueous solution shifts to a shorter wavelength. Though there is a possibility that the halogen anion coordinates to the nickel(II) ion in the case of the solid state, this can be safely ruled out on the basis of the facts that the complexes in which the halogen anion is coordinated to the nickel(II) ion can be isolated by another method (the complexes III and VI) and that the behavior of the dehydration, as measured by the derivatograph, is clearly different between the complexes I, IV and III, VI. Therefore, the complexes I and IV can be concluded to have an octahedral structure, $[Ni(edma)(H_2O)_3]X$ (X= Cl and Br), where three molecules of water are all coordinated to the nickel(II) ion, in both an aqueous solution and a solid crystal.

The reflectance spectra of the complexes II, V, and VII show three peaks with nearly the same intensities in the visible and far-infrared regions. Their magnetic-moment data indicate that their structures are octahedral or tetrahedral (Table 1). If these complexes have a tetrahedral structure, only one peak would be expected in this absorption region.[6-8] The existence of three peaks with nearly identical intensities can, then, be thought to be characteristic of the octahedral nickel(II) complexes.[5] Therefore, on the basis of absorption spectra, the structures of the complexes II, V, and VII can be identified as octahedral.

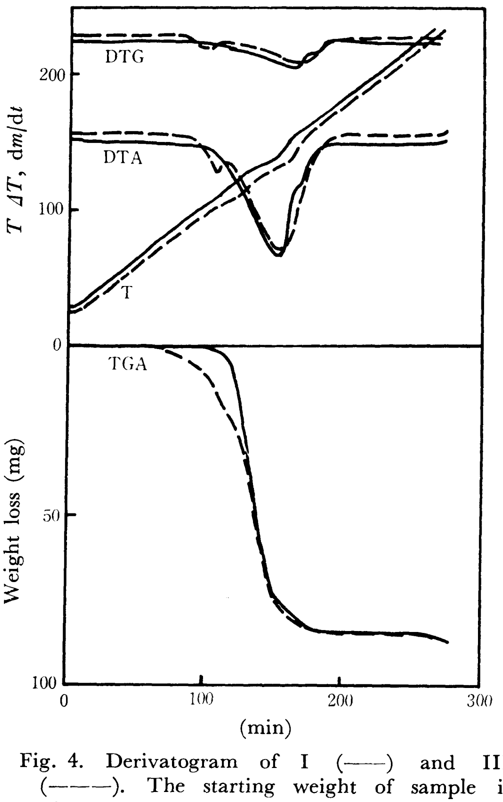

Fig. 4. Derivatogram of I (——) and III (– – –). The starting weight of sample is 400 mg.

The reflectance spectra of the complexes III and VI are nearly identical with those of the complexes I and IV, except that all the peaks of the complexes III and VI are shifted to slightly lower energy sites than the peaks of the complexes I and IV. This is thought to be due to the coordination of the halogen anion. Therefore, an octahedral structure can be assigned to them. These explanations were confirmed by the behavior of their dehydrations. The details will be discussed in the next paragraph. Here, it is enough to note that the difference in the coordination between one molecule of water and one molecule of the halogen anion (Cl^- and Br^-) do not show any considerable difference in their absorption spectra.

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6) G. P. Smith, C. H. Liu and T. R. Griffiths, *J. Amer. Chem. Soc.*, **86**, 4796 (1964).

7) H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).

8) C. R. Boston and G. P. Smith, *J. Amer. Chem. Soc.*, **85**, 1006 (1963).

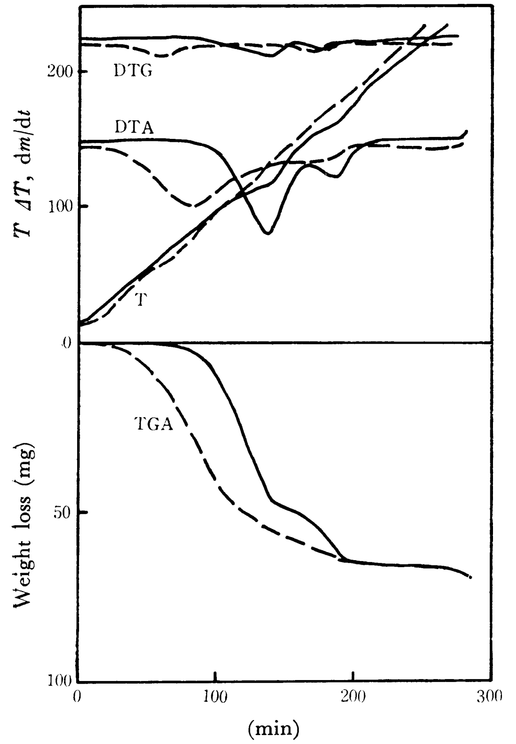

Fig. 5. Derivatogram of IV (——) and VI (– – –). The starting weight of sample is 400 mg.

The 1-to-2-ratio complex, VIII, shows a spectrum similar to those of Ni–N_4O_2-type complexes.[5] Therefore, an octahedral structure can be assigned to the complex VIII, although the configuration of the coordinated edma is not clear in detail.

Derivatogram and Magnetic Moments. From the TGA, DTA, and DTG curves[9] (Figs. 4 and 5), it was observed that two molecules of water dehydrated from 110°C to 140°C, and another molecule of water, from 140°C to 175°C, for the complex I. On the other hand, in the case of the complex III, one molecule of water dehydrated from a very low temperature (from about 50°C to 110°C), and other two molecules of water, from 110°C to 175°C. These facts indicate that the structure of the complex I is clearly different from that of the complex III. The low temperature of the dehydration of one molecule of water for the complex III can be ascribed to the dehydration of crystalline water. Therefore, the structure of the complex III can be presumed to be $[Ni(edma)Cl(H_2O)_2]\cdot H_2O$, where the chloride ion is coordinated to the nickel(II) ion, and the structure of the complex I to $[Ni(edma)(H_2O)_3]Cl$, where the three molecules of water are all coordinated to the nickel(II) ion. The high temperature of the dehydration of one molecule of water for the complexes I and III may suggest that the dehydration proceeds through the intermediate of the dimer structure in which two molecules of the chloride ion are bridged to the nickel(II) ion as is shown in Fig. 6 (A). Further information which gives strong support to the explanation presented above was obtained by the dehydration of the complex IV. The difference in the dehydration between two molecules of water (from 80°C to 125°C) and one molecule of water (from 125°C to 175°C) is clearly distinguished in the case of the complex IV. The high temperature of the dehydration of the last molecule of water clearly indicates that the dehydrations proceed through the intermediate of the dimer structure in which two bromide ions are bridged and in which the two molecules of water are coordinated to the nickel(II) ions, as is shown in Fig. 6 (A).

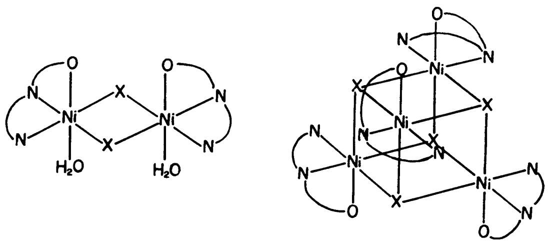

Fig. 6. The probable structure of the dimer and tetramer structures.
A: $[Ni(edma)X(H_2O)]_2$ (X=Cl and Br)
B: $[Ni(edma)X]_4$ (X=Cl, Br and I)

On the other hand, in the case of the complex VI, the dehydration of two molecules of water takes place from a very low temperature (from 35°C to about 100°C) compared with the case of the complex IV, and the last molecule of water dehydrates from about 100°C to 175°C. The low temperature of the dehydration of the two molecules of water is ascribed to two molecules of crystalline water. Therefore, the structure of the complex VI is assigned to the dimer of $[Ni(edma)Br(H_2O)]\cdot 2H_2O$, where the bromide ion is bridged. This assignment agrees well with the suggestion of the IR spectra that the complex VI may take a different structure from that of the complex III.

The values of the effective magnetic moment of the complexes are listed in Table 1. All the complexes show values near 3.10 B.M. These values suggest that all the complexes have an octahedral structure, for the nickel(II) complexes with a tetrahedral structure have been established generally to have the effective magnetic moments from 3.50 to 4.00 B.M.[10]

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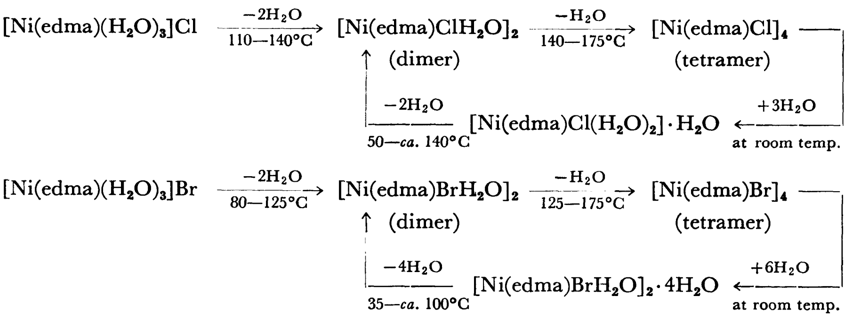
[9] R. Tsuchiya, Y. Kaji, A. Uehara and E. Kyuno, This Bulletin, **42**, 1881, 1886 (1969).

[10] D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Amer. Chem. Soc.*, **83**, 4161 (1961).



Scheme 1. The mechanism of dehydrations.

On the basis of these results and discussions, as the structure of the complexes II, V, and VII, tetramer in which the four halogen anions are triply bridged to the four nickel(II) ions may be considered reasonable (Fig. 6 (B)). Here, it is established that two nitrogen atoms and one oxygen atom of edma coordinate to the nickel(II) ion, making a facial form.

As the mechanism of the dehydration process, the above scheme can be proposed (Scheme 1).

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