The Preparation, Infrared Spectra, and Thermal Stability in the Solid State of Nickel(II) Complexes with edda-type Polyamino Carboxylic Acids

Ichiro HIRAKO, Tasuku MURAKAMI, and Masahiro HATANO

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, 2-1-1 Katahira, Sendai 980

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Some nickel(II) complexes with optically active ethylenediamine-*N,N'*-diacetic acid(edda)-type polyamino carboxylic acids were prepared. Their electronic and infrared spectra and thermogravimetric curves were measured in the solid state. The stretching frequencies of the coordinated carboxylate group and the thermal stability of these complexes in the solid state were quite different from those of bis(amino acidato) complexes.

On the structures and thermal stabilities in the solid state of diaquabis(amino acidato)nickel(II) complexes, extensive works have been reported. The crystal structure of diaquabis(glycinato)nickel(II) is a slightly distorted octahedral, with two glycinate anions of a *trans(N,N)*-configuration in a plane, and with two water molecules occupying its apical positions.[1,2] The diaquabis(amino acidato) complexes are easily dehydrated on heating to form their anhydrous complexes, which are polymeric with bridging through the non-donating oxygen atom in the carboxylate group.[3,4]

On the other hand, not so much has been reported concerning the nickel(II) complexes with edda-type polyamino carboxylic acids, which are expected to form complexes with a *cis(N,N)*-configuration in a plane. In order to obtain information on the differences in structures and thermal stabilities between the edda-type complexes and the bis(amino acidato) complexes, we have now prepared new edda-type complexes and measured their electronic and infrared(IR) spectra and thermogravimetric(TG) curves.

Experimental

Preparation of Ligands. Ethylenediamine-*N,N'*-di-L-α-propionic acid (abbreviated to H_2eddp), ethylenediamine-*N,N'*-di-L-α-isovaleric acid (H_2eddv), ethylenediamine-*N,N'*-di-L-α-hydrocinnamic acid (H_2eddc), ethylenediamine-*N,N'*-di-L-α-(β-hydroxy)propionic acid (H_2eddh), and (*S,S*)-1,1'-ethylenedipyrrolidine-2,2'-dicarboxylic acid (H_2epro) were prepared from L-alanine (L-alaH), L-valine (L-valH), L-phenylalanine (L-phalaH), L-serine (L-serH), and L-proline (L-proH) respectively by a method similar to that described in the literature.[5] These acids were identified by their elementary analyses. The ethylenediamine-*N,N'*-diacetic acid (H_2edda) was obtained commercially. The structural formulas of these polyamino carboxylic acids are shown in Fig. 1.

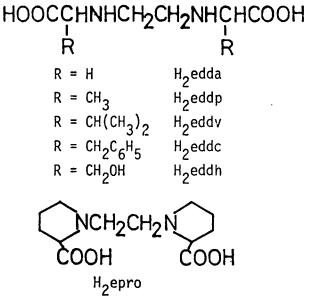

Fig. 1. edda-Type polyamino carboxylic acids. Except for H_2edda these acids are optically active.

Preparation of Nickel(II) Complexes. Hydrated Complexes: The hydrated nickel(II) complexes of these edda-type polyamino carboxylic acids were prepared by the following procedures. Basic nickel(II) carbonate was mixed with an equimolar amount of each polyamino carboxylic acid in an aqueous solution. The solution was concentrated at 70—80 °C on a water bath, and then allowed to stand. Within a few days, blue crystals separated out; they were recrystallized from water. The analytical data of these complexes are summarized in Table 1.

TABLE 1. ANALYTICAL DATA

Complex	C% Obsd (Calcd)	H% Obsd (Calcd)	N% Obsd (Calcd)
$[Ni(edda)(H_2O)_2]\cdot H_2O$	25.26 (25.06)	5.59 (5.57)	9.86 (9.76)
$[Ni(eddp)(H_2O)_2]$	32.41 (32.21)	6.61 (6.06)	9.41 (9.40)
[Ni(eddp)]	36.58 (36.52)	5.59 (5.33)	10.66 (10.63)
$[Ni(eddv)(H_2O)_2]$	42.19 (40.80)	7.55 (7.43)	7.87 (7.94)
[Ni(eddv)]	45.17 (45.40)	6.95 (6.64)	8.61 (8.84)
$[Ni(eddc)(H_2O)_2]\cdot H_2O$	50.80 (51.20)	5.69 (5.55)	6.08 (6.10)
[Ni(eddc)]	56.95 (57.82)	5.66 (5.35)	6.68 (6.67)
$[Ni(eddh)(H_2O)_2]$	29.14 (29.21)	5.47 (5.48)	9.01 (8.54)
$[Ni(epro)(H_2O)_2]$	41.00 (41.30)	5.92 (6.35)	8.10 (8.03)

Anhydrous Complexes: The anhydrous complexes of eddc and eddv were separated out from concentrated hot (70—80 °C) aqueous solutions. The anhydrous eddp complex was obtained on heating its hydrate *in vacuo* at 250 °C. See Table 1 for the results of analyses.

Bis(amino acidato) Complexes: Some bis(L-amino acidato)-nickel(II) complexes were prepared from basic nickel(II) carbonate and L-amino acids according to the method in the literature.[6] These bis(amino acidato) complexes were identified by means of their elementary analyses.

Measurements. The electronic and IR spectra were recorded with Hitachi EPS-3T and EPI-S_2 or EPI-G_2 spectrophotometers respectively, using KBr pellets. The TG curves were obtained with a Perkin-Elmer TGS-1 thermobalance at a heating rate of 8 °C/min in a nitrogen stream. All of the samples used for the TG measurements were ground

and sieved to obtain finely powdered fractions below 100 mesh.

Results and Discussion

The electronic spectra in the solid state of the hydrated nickel(II) complexes of edda, eddp, and eddc exhibited three absorption peaks, at about 10200, 13300 and 16200 cm^{-1}, which are characteristic of the octahedrally coordinated nickel(II) ion. Their anhydrous complexes also showed similar spectra, the peaks of which shifted to slightly lower wave numbers. This spectral profile of the edda-type complexes is identical with that of bis(amino acidato) nickel(II) complexes, suggesting that the anhydrous edda-type complexes are also polymeric, with bridging through the carboxylate groups, like the anhydrous bis(amino acidato) complexes.[4]

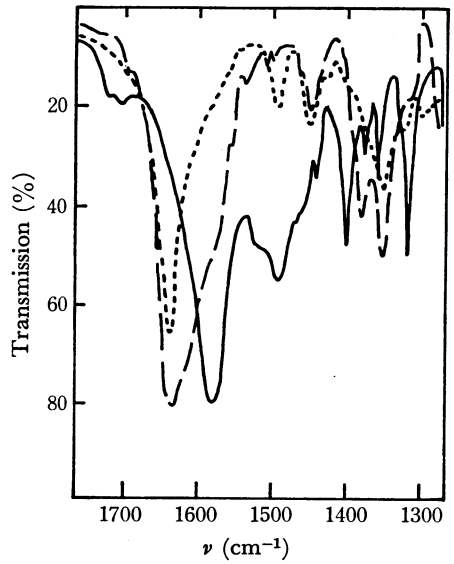

Fig. 2. IR spectra (1700—1300 cm^{-1}) of [Ni(eddp)-$(H_2O)_2$] (—), [Ni(eddp)](---), and [Ni(eddc)] (···).

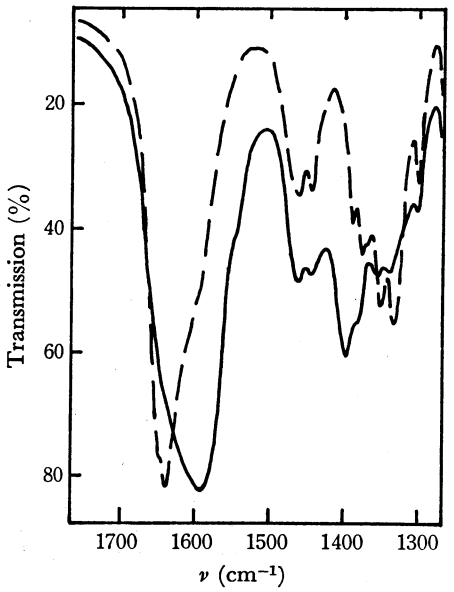

Fig. 3. IR spectra (1700—1300 cm^{-1}) of [Ni(eddv)-$(H_2O)_2$] (—) and [Ni(eddv)] (---).

Figures 2 and 3 show the IR spectra of the complexes of eddp, eddv, and eddc in the region of 1300—1700 cm^{-1}. The strong band at 1590 cm^{-1} and the medium band at 1400 cm^{-1}, both of which appeared for the hydrated complex of eddp, can be assigned to the antisymmetric and symmetric stretching vibrations of the coordinated COO^- group respectively, as in the case of the bis(amino acidato) complexes.[4,6] When the hydrate was dehydrated on heating, the strong band shifted to 1640 cm^{-1}, with a shoulder at 1580 cm^{-1}. Similarly, the strong band at 1590 cm^{-1} which appeared for the hydrated complex of eddv shifted to 1640 cm^{-1} in its anhydrous complex. Further, the anhydrous eddc complex exhibited the strong band at 1640 cm^{-1}, Therefore, it can be concluded that the antisymmetric COO^- vibration appears at 1640 cm^{-1} for the anhydrous nickel(II) complexes of the edda-type polyamino carboxylic acids. Such a high frequency of the antisymmetric COO^- stretching vibration has also appeared for palladium(II) and platinum(II) complexes of amino acids.[7]

On the other hand, the medium band at 1400 cm^{-1} disappeared in the anhydrous complexes, as may be seen in the figures. Instead of this band, two medium bands appeared at 1380 and 1350 cm^{-1} for the anhydrous eddp complex. Either of these two bands can be expected to correspond to the symmetric COO^- vibration. The anhydrous eddv complexes also exhibited two bands at 1350 and 1330 cm^{-1}. For the anhydrous eddc complex, only one band appeared at 1350 cm^{-1} with a medium strength. From these findings, it seems plausible to assign the band at 1350 cm^{-1} to the symmetric COO^- stretching vibration of the anhydrous complexes.

TABLE 2. THE COO^- STRETCHING FREQUENCIES (cm^{-1})

Complex	ν_{asym}	ν_{sym}	$\Delta\nu$
$[Ni(edda)(H_2O)_2]\cdot H_2O$	1585	1393	192
[Ni(edda)]	1580	1395	185
	1640sh	1350sh	290
$[Ni(eddp)(H_2O)_2]$	1580	1400	180
[Ni(eddp)]	1640	1350	290
		(1380)	(260)
$[Ni(eddv)(H_2O)_2]$	1590	1400	190
[Ni(eddv)]	1640	1350	290
		(1330)	(310)
[Ni(eddc)]	1640	1350	290
$[Ni(eddh)(H_2O)_2]$	1600	1400	200
$[Ni(epro)(H_2O)_2]$	1595	1395	200
$[Ni(L\text{-}ser)_2(H_2O)_2]$	1600	1420	180
$[Ni(L\text{-}ser)_2]$	1580	1410	170
$[Ni(gly)_2(H_2O)_2]$[a]	1599	1410	189
$[Ni(gly)_2]$[a]	1583	1400	183

a) From Ref. 4.

Table 2 lists the symmetric (ν_{sym}) and antisymmetric (ν_{asym}) stretching frequencies of the coordinated COO^- group observed for the hydrated or anhydrous complexes of the edda-type polyamino carboxylic acids, together with those of the bis(L-serinato) and bis(glycinato) complexes. It is very interesting that the frequency separation ($\Delta\nu$) between

Table 3. Temperature range and mass loss

Complex	Dehydration		Decomposition	
	Temperature range, °C	Mass loss, % Obsd (Calcd)	Temperature range, °C	Mass loss, % Obsd (Calcd)[a]
$[Ni(edda)(H_2O)_2]\cdot H_2O$	70—140(H_2O) 140—180($2H_2O$)	16.6 (18.8)	310—460	55.6 (55.5)
$[Ni(eddp)(H_2O)_2]$	150—230	13.2 (12.2)	310—470	56.3 (62.6)
[Ni(eddv)]			310—440	77.0 (76.3)
$[Ni(eddc)(H_2O)_2]\cdot H_2O$	50—320	8.2 (11.5)	330—490	72.1 (72.7)
$[Ni(gly)_2(H_2O)_2]$	140—210	15.8 (14.8)	330—385	53.9 (54.5)
$[Ni(L\text{-}ala)_2(H_2O)_2]\cdot 2H_2O$	50—110($2H_2O$) 110—130($2H_2O$)	23.5 (23.2)	280—325	56.6 (52.5)
$[Ni(L\text{-}val)_2(H_2O)_2]$	50—150	11.7 (11.0)	275—340	70.2 (66.1)
$[Ni(L\text{-}phala)_2(H_2O)_2]$	80—140	8.4 (8.5)	280—410	71.8 (74.0)
$[Ni(L\text{-}ser)_2(H_2O)_2]$	90—180	14.1 (12.0)	230—375	57.4 (63.0)

a) For a residue of nickel oxide.

the antisymmetric and symmetric COO^- vibrations is much greater for the anhydrous edda-type complexes than for their hydrates, while in the bis(amino acidato) complexes the $\Delta\nu$ values of the hydrates are slightly greater than those of their anhydrous complexes.[4] It has been accepted by several authors[6,7] that, as the covalent character of the bond between the metal ion and the coordinated oxygen atom increases, the coordinated carboxylate group becomes more asymmetric, and that, as a result, the increase in the covalent character results in an increase in the frequency separation ($\Delta\nu$) between the two COO^- stretching bands. For example, large $\Delta\nu$ values(about 270 cm^{-1}) have been obtained for the bis(glycinato)palladium(II) and -platinum(II) complexes, in which the covalent character of the metal-oxygen bond is said to be very strong.[7] Therefore, the abnormal large values of $\Delta\nu$ observed for the anhydrous edda-type complexes suggest that the coordinated carboxylate group becomes more asymmetric on dehydration, in spite of the polymerization through the non-donating oxygen atom in the carboxylate group; we might conclude that the covalent character of the metal-oxygen bond in one complex molecule increases also.

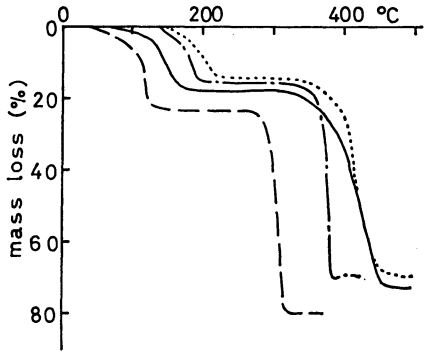

Fig. 4. TG curves of $[Ni(edda)(H_2O)_2]\cdot H_2O$ (—), $[Ni(eddp)(H_2O)_2]$ (···), $[Ni(gly)_2(H_2O)_2]$ (-·-), and $[Ni(L\text{-}ala)_2(H_2O)_2]\cdot 2H_2O$ (---).

Figure 4 shows the TG curves of the hydrated complexes of edda, eddp, glycine and L-alanine. The temperature range and the percentage of mass loss obtained from the TG curves are summarized in Table 3. As may be seen in Fig. 4, the hydrated complexes of edda and L-alanine released three or four moles of water in two steps in the temperature range from 50 to 180 °C. The step in the lower temperature range corresponds to the dehydration of lattice water(s), and the other step, to that of coordinated waters. However, the lattice water was dehydrated over a wider temperature range than the coordinated water. Though the hydrated eddc complex has three moles of water, the two steps corresponding to the dehydrations of lattice and coordinated waters were not distinguished.

The anhydrous edda-type complexes decomposed at a higher temperature than the anhydrous bis(amino acidato) complexes; further, the decomposition of the edda-type complexes was very slow, as may be seen in Fig. 4. These findings show that the edda-type anhydrous complexes are thermally more stable than the bis(amino acidato) complexes in the solid state. This high thermal stability of the edda-type complexes probably results from the increase in the covalent character in the intra-molecular metal-oxygen bond, as is to be expected from the behavior of the COO^- vibrations.

As may be seen in Table 3, bis(L-serinato)nickel(II), which has been established by X-ray analysis to have a *cis*(*N*,*N*)-configuration,[8] decomposed in a lower temperature range than did the edda-type complexes. Similarly, the bis(glycinato) complex, with a *trans*(*N*,*N*)-configuration, also decomposed in the lower temperature range. Further, the bis(L-serinato) complex shows a difference($\Delta\nu$) between the two COO^- vibrations similar to that of the bis(glycinato) complex (Table 2). These findings indicate that the *cis-trans* isomerism is not very significant for the thermal stability and the COO^- vibrations. Therefore, the high stability and the abnormal behavior in the COO^- vibrations observed for the edda-type complexes are expected to result from some structural factors, such as the tetradentate character of the ligands, other than the *cis-trans* isomerism.

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