Inorganica Chimica Acta, 36 (1979) 113–120
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Complexes of 3,4-Dihydroxyphenyl Derivatives. II.* Complex Formation Processes in the Nickel(II)–L-DOPA and Zinc(II)–L-DOPA Systems

ARTHUR GERGELY, TAMÁS KISS and GYÖRGY DEÁK

Institute of Inorganic and Analytical Chemistry, Lajos Kossuth University, H-4010 Debrecen, Hungary

Received January 24, 1979

A pH-metric study (at 25 °C and 0.2 M *ionic strength) of the nickel(II)–L-3,4-dihydroxyphenylalanine (L-DOPA) and zinc(II)–L-DOPA systems was used to determine the stoichiometric compositions and stability constants of the species formed. From the results obtained for the nickel(II) and zinc(II)–alaninate–pyrocatecholate systems, and UV and visible spectral studies of the corresponding DOPA complexes, conclusions were drawn on the mode of bonding of the complexes formed. It was found that complexes containing aminoacid-like and pyrocatechol-like bonds are formed in both systems: the latter are favoured in the case of zinc(II), and the former in the case of nickel(II). This is so marked that in the nickel(II)–DOPA system the 1:2 complex containing only (O, O) bonds is not formed at all. In both systems mixed complexes containing both (N, O) and (O, O) bonds occur to appreciable extents. It was established for some species that not only a given arrangement of donor atoms belongs to a given stoichiometric composition, but complexes with different structures are in equilibrium with one another.*

Introduction

Comparatively wide-ranging studies have been made of the equilibrium processes occurring in the copper(II)–DOPA system [3–7]. It was found that aminoacid-type complexes are formed in the lower pH range, while at higher pH values the products are complexes containing pyrocatechol-type bonds and their deprotonated species. In the intermediate pH interval, cyclic and open-chain dimeric species and a complex of mixed bonding type are formed. However, our knowledge relating to the other transition metal ion–DOPA systems is deficient and in part contradictory. Gorton and Jameson [8] concluded that only aminoacid-type 1:1 and 1:2 complexes are formed in the nickel(II)–DOPA system. Clear-cut conclusions have not been drawn as regards the zinc(II)–DOPA system, but pyrocatechol-like coordination was considered to be more favoured. Equilibrium studies were carried out by Weber *et al.* [9] in a relatively narrow pH range (pH < 7.5). In both the nickel(II)–DOPA and the zinc(II)–DOPA systems, formation only of aminoacid-like complexes being observed. At the same time, in the course of their kinetic study on the formation of nickel(II)–DOPA complexes, Kustin *et al.* [10] assumed two different 1:1 species with stoichiometric compositions NiH_2A and NiHA. Nevertheless, no conclusions were made with regard to the mode of binding of the species NiHA.

The aim of the present work is to establish the stoichiometric compositions of the species formed in the nickel(II)–DOPA and zinc(II)–DOPA systems. In addition, we try to determine the donor groups taking part in the bonding, by studying the effect of complex formation on the UV band of the phenolate group of the ligand, and by a visible spectral study of the nickel(II) complexes. The possibility also arose of the formation of a complex containing both (N, O) and (O, O) bonds. As a model experiment with regard to this, a study has been also made of the nickel(II)–alaninate–pyrocatecholate, the nickel(II)–tyrosinate–dopamine, and the zinc(II)–alaninate–pyrocatecholate mixed ligand systems.

Experimental

Chemicals

The compounds used in the experiments were commercially-available products of Reanal and Fluka. The aminoacids were purified by recrystallization from a mixture of ethanol and water, and the pyrocatechol by distillation at reduced pressure. The L-3,4-dihydroxyphenylalanine (L-DOPA), a product of Fluka, was used without further purification. Stock solutions were prepared from metal chlorides of the highest analytical purity, and their concentrations were checked gravimetrically, in the form of the oxinate.

---

*Part I : ref. [3].

pH-metric Measurements

The stability constants of the nickel(II) and zinc(II) parent and mixed ligand complexes were determined by pH-metric titrations. The ionic strength was adjusted to 0.2 *M* with KCl. The titrations were carried out at eight metal ion–ligand ratios in the cases of the nickel(II)–DOPA and zinc(II)–DOPA systems, and at three different ratios in the other cases. The ligand concentration was 4×10^{-3}, 6×10^{-3} or 8×10^{-3} *M*, and the metal ion concentration was varied in the range 2×10^{-3}–8×10^{-3} *M*. In the case of the mixed ligand systems the metal ion–ligand A–ligand B ratio was 1:1:1, 1:2:1, 1:1:2 or 1:2:2.

The pH-metric measurements were made in the manner described earlier [3], with a Radiometer pHM 64 instrument, a G 202 B glass electrode and a K 101 calomel electrode. The temperature of the measurements was 25 ± 0.1 °C.

Spectral Studies

Near infrared and visible spectrophotometric measurements were used to study the spectra of the parent complexes NiA_2 and the mixed ligand complexes NiAB of alanine and tiron (disodium pyrocatechol-3,5-disulphonate). In addition, the spectrum of the nickel(II)–DOPA system was also recorded at various pH values at a metal ion–ligand ratio of 1:2.

In the UV spectral examinations in the cases of the nickel(II)–DOPA and zinc(II)–DOPA systems, the absorbances were measured in the pH range 5.5–11.8, at a metal ion–ligand ratio of 1:2, in the range of absorption of the deprotonated phenolic hydroxy group (250–330 nm). These absorbance values were corrected by the spectral data of the free ligand. The spectral data thus obtained, therefore, are characteristic of the ligand bound to the metal ion.

The examinations were performed on a Beckman ACTA MIV double-beam recording spectrophotometer.

Calculations

The complexes formed in the systems under study can be characterized by the following general equilibrium process:

$$qM + pH + nA + rB \rightleftharpoons M_qH_pA_nB_r \qquad (1)$$

where A and B mean the fully deprotonated form of the ligands.

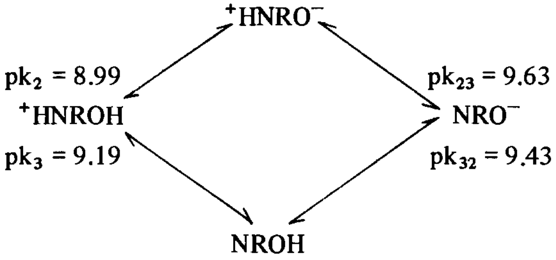
The stability constants of the species are given by:

$$\beta_{qpnr} = \frac{[M_qH_pA_nBr]}{[M]^q[H]^p[A]^n[B]^r} \qquad (2)$$

The appropriate stability constants defined by eqn. (2) were calculated from the pH-metric titration data as described earlier [11, 12].

Results and Discussion

Earlier investigations have dealt in detail with the protonation processes of L-3,4-dihydroxyphenylalanine (L-DOPA) [1–4]. In addition to the macroconstants, Martin [4] used spectrophotometry to determine the microconstants characteristic of the deprotonation of the amino group and the first phenolic hydroxy group. These measurements were repeated in this work at 0.2 *M* (KCl) and very good agreement was obtained with his results. The macro- and microconstants calculated from the pH-metric and spectrophotometric experimental data are as follows:



$$H_4A \xrightleftharpoons{pK_1 = 2.22} H_3A \xrightleftharpoons{pK_2 = 8.80} H_2A \xrightleftharpoons{pK_3 = 9.83}$$

$$HA \xrightleftharpoons{pK_4 = 13.4} A$$

To clarify whether formation of a complex containing both (N,O) and (O,O) bonds is favoured in the nickel(II)–DOPA and zinc(II)–DOPA systems too, similar model experiments were performed as in the case of copper(II)–DOPA [3]. We investigated the nickel(II)–alaninate–pyrocatecholate and zinc(II)–alaninate–pyrocatecholate mixed ligand systems, in which the potential donor groups of DOPA belong to two different ligands.

The stability constants of the parent complexes of the ligands with nickel(II) and zinc(II) ions are listed in Table I, and those of the mixed ligand complexes in Table II.

The concentration distributions of the complexes formed at a metal ion–ligand A–ligand B ratio of 1:2:2 in the mixed ligand systems are plotted as functions of the pH in Figs. 1 and 2.

The data of Table I show that at higher pH values it was also necessary to reckon with the formation of hydroxo complexes. This took place to a considerable extent particularly in the zinc(II)–alaninate and nikel(II)–pyrocatecholate systems. The stability constants obtained here for the parent complexes of type MA_n are in good agreement with the earlier results of Sigel *et al.* [13] for pyrocatechol complexes, and of Childs and Perrin [14] for alanine complexes. It may be stated from the data of Table II that formation of the mixed ligand complex of

TABLE I. Stability Constants of Nickel(II) and Zinc(II) Complexes of Alaninate and Pyrocatecholate, t = 25 °C, I = 0.2 *M* KCl.

Ligand		$\log\beta$				
		MA	MA_2	MA_3	MAH_{-1}	MA_2H_{-1}
Alaninate	Ni(II)	5.32	9.74	12.80	–	−1.79
	Zn(II)	4.56	8.51	–	−3.6	−0.15
Pyrocatecholate	Ni(II)	8.72	14.67	–	−1.8	–
	Zn(II)	9.72	17.75	–	–	6.53

TABLE II. Stability Constants of Mixed Ligand Complexes of Alaninate (A) and Pyrocatecholate (B), t = 25 °C, I = 0.2 *M* KCl.

Ligand		$\log\beta_{MAB}$	$\Delta\log\beta_{MAB}^{a}$	$\log\beta_{MABH_{-1}}$	$\log\beta_{MA_2B}$
Alaninate–Pyrocatecholate	Ni(II)	13.03	0.53	2.61	16.5
	Zn(II)	13.92	0.49	2.75	–

[a] $\Delta\log\beta_{MAB} = \log\beta_{MAB}^{exp} - 1/2(\log\beta_{MA_2} + \log\beta_{MB_2} + \log 4)$.

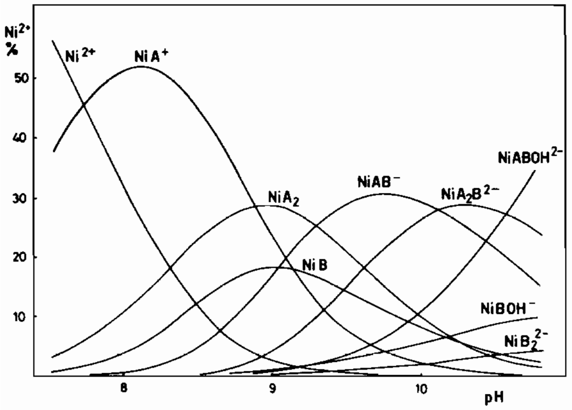


Fig. 1. pH-dependence of the concentration distribution of the complexes formed in the nickel(II)–alaninate (A), –pyrocatecholate (B) system at a metal ion–ligand–ligand ratio of 1:2:2.

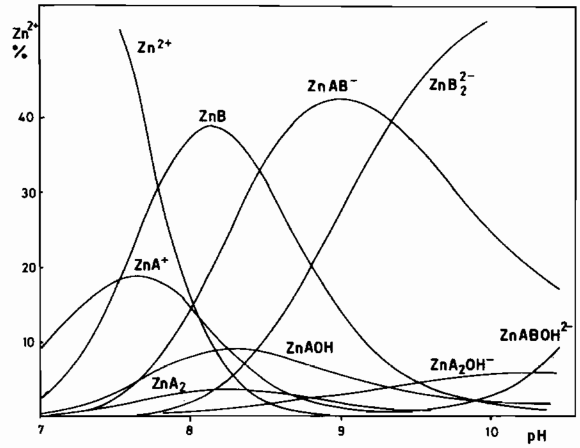


Fig. 2. pH-dependence of the concentration distribution of the complexes formed in the zinc(II)–alaninate (A), –pyrocatecholate (B) system at a metal ion–ligand–ligand ratio of 1:2:2.

composition MAB is favoured for both metal ions ($\Delta\log\beta_{MAB} \sim 0.5$). This is well illustrated by the concentration distribution curves in Figs. 1 and 2 as well. In the nickel(II)–alaninate–pyrocatecholate system, the complex NiA_2B is also formed in appreciable concentration, but not the species $NiAB_2$ containing one alaninate and two pyrocatecholates. This may be explained in that formation of the pyrocatecholate parent complex NiB_2 itself is sterically hindered, as reflected by the log K_1/K_2 value of 2.77. Similarly as for the parent complexes, in the systems containing the B ligand it is also necessary to reckon with the formation of hydroxo complexes. On the basis of the data obtained for the mixed ligand complexes, therefore, it may be assumed that complexes of similar mixed bonding type may be formed in the nickel(II)–DOPA and the zinc(II)–DOPA systems too. Further, because of the existence of the complex NiA_2B, the presence of the species with a composition of 1:3 cannot be excluded in the nickel(II)–DOPA system.

Because of the earlier inconsistent data, by analysis of the complex formation curves we attempted to establish whether the equilibria in the nickel(II)–DOPA and zinc(II)–DOPA systems can be described by the formation of complexes containing bonds only of aminoacid type or only of pyrocatechol type. The formation curves calculated on this assumption for various metal ion–ligand ratios did not coincide from pH 7.5 for the nickel(II)–DOPA system, and in the entire pH range for the zinc(II)–DOPA system. This also indicates that the existence of species of other bonding types must also be reckoned with in these systems.

On the basis of the results obtained for the model systems and from analysis of the formation curves, we attempted to evaluate the titration data by the assumption of various complexes containing (N,O), (O,O) and mixed bonds. With the combined treatment of the titration curves recorded at the different metal ion–ligand ratios, the best agreement between the measured and the calculated titration curves was obtained by the assumption of the species with the stoichiometric compositions shown in Table III. The average difference between the measured and calculated titration curves characteristic of the quality of the fit [11, 12] was 0.0076 cm^3 in the case of the nickel(II)–DOPA system (calculated from 137 experimental points), and 0.0066 cm^3 for the zinc(II)–DOPA system (calculated from 129 experimental points).

TABLE III. Stability Data on the Nickel(II)–DOPA and Zinc(II)–DOPA Complexes.

$$\beta_{qpn} = \frac{[M_qH_pA_n]}{[M]^q[H]^p[A]^n},\ t = 25\ °C,\ I = 0.2\ M\ \mathrm{KCl}.$$

Complex	Composition qpn	M = Ni(II)	M = Zn(II)
MH_2A	121	28.13 ± 0.02	27.00 ± 0.08
MHA	111	19.9 ± 0.10	20.23 ± 0.03
MH_4A_2	142	55.06 ± 0.02	–
MH_3A_2	132	47.19 ± 0.08	47.18 ± 0.05
MH_2A_2	122	38.19 ± 0.08	38.59 ± 0.05
MHA_2	112	28.57 ± 0.05	28.92 ± 0.05
MA_2	102	17.10 ± 0.10	18.50 ± 0.05

For the easier comparison with the stability data of other systems, the equilibrium constants relating to the successive complex formation processes were derived from these data. They are listed in Table IV.

TABLE IV. Equilibrium Constants of the Nickel(II)–DOPA and Zinc(II)–DOPA Complexes, t = 25 °C, I = 0.2 *M* KCl.

Process	log K	Metal Ion	
$M^{2+} + H_2A^- \rightleftharpoons MH_2A^+$	$\log K_1$	Ni(II)	4.90
		Zn(II)	3.77
$MH_2A^+ + H_2A^- \rightleftharpoons M(H_2A)_2$	$\log K_2$	Ni(II)	3.70
		Zn(II)	–
$M(H_2A)_2 \rightleftharpoons MH_3A_2^- + H^+$	$-\log K_2^{-1}$	Ni(II)	7.87
		Zn(II)	–
$MH_3A_2^- \rightleftharpoons MH_2A_2^{2-} + H^+$	$-\log K_2^{-2}$	Ni(II)	9.00
		Zn(II)	8.59
$MH_2A_2^{2-} \rightleftharpoons MHA_2^{3-} + H^+$	$-\log K_2^{-3}$	Ni(II)	9.62
		Zn(II)	9.67
$MHA^{3-} \rightleftharpoons MA_2^{4-} + H^+$	$-\log K_2^{-4}$	Ni(II)	11.47
		Zn(II)	10.42

The pH-dependence of the concentration distribution of the complexes formed at a metal ion–ligand ratio of 1:2 in the nickel(II)–DOPA system is shown in Fig. 3, and that in the zinc(II)–DOPA system in Fig. 4.

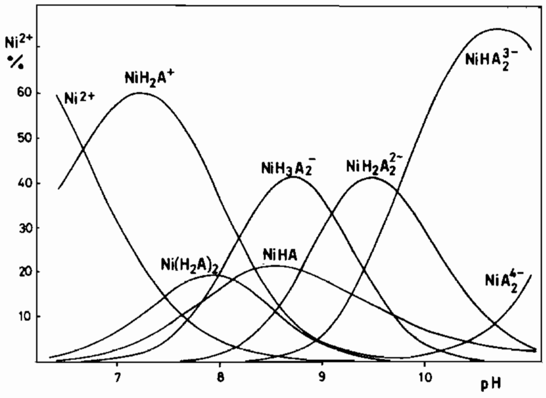


Fig. 3. pH-dependence of the concentration distribution of the complexes formed in the nickel(II)–DOPA system at a metal ion–ligand ratio of 1:2.

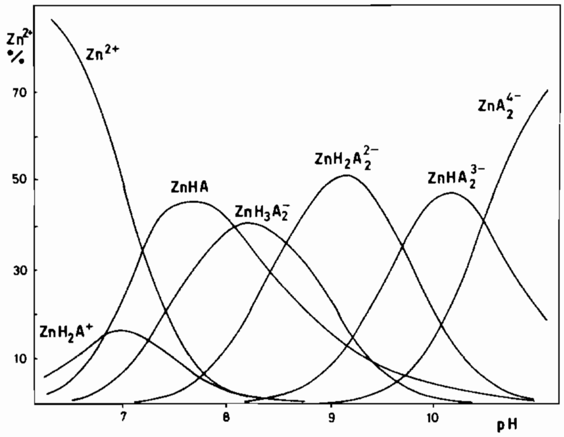


Fig. 4. pH-dependence of the concentration distribution of the complexes formed in the zinc(II)–DOPA system at a metal ion–ligand ratio of 1:2.

It is clear from the data of Table III that a stability constant for the 1:3 complex could not be obtained from the pH-metric data in the nickel(II)–DOPA system (this was also the case in the event of a considerable ligand excess). At the same time the results obtained for the model system do not exclude the existence of complexes of such type. It could be assumed, therefore, that the binding of a third ligand is sterically hindered because of the size of the DOPA molecule, and the possible intramolecular hydrogen-bonding between the donor groups of the side-chain and the coordinately non-bonded phenolic hydroxy groups. In an attempt to confirm this, we studied the nickel(II)–tyrosinate–dopamine mixed ligand system,

TABLE V. Stability Constants of Tyrosinate (A) and Dopamine (B) Parent and Mixed Ligand Complexes of Nickel(II).

$$\beta_{qpnr} = \frac{[M_qH_pA_nB_r]}{[M]^q[H]^p[A]^n[B]^r},\ t = 25\ ^\circ C, I = 0.2\ M\ KCl.$$

Complex	Composition qpnr	$\log\beta_{qpnr}$	Complex	Composition qpnr	$\log\beta_{qpnr}$
MHA	1110	15.00 ± 0.02	MHB	1101	19.37 ± 0.02
$M(HA)_2$	1220	29.39 ± 0.02	MB	1001	9.42 ± 0.05
MHA_2	1120	20.07 ± 0.02	$M(HB)_2$	1202	35.66 ± 0.02
MA_2	1020	10.15 ± 0.02	MHB_2	1102	25.61 ± 0.04
$M(HA)_3$	1330	42.29 ± 0.03	MB_2	1002	14.81 ± 0.04
MH_2A_3	1230	33.25 ± 0.03	MH_2AB	1211	33.60 ± 0.06
MHA_3	1130	22.84 ± 0.04	MHAB	1111	24.01 ± 0.06
MA_3	1030	12.78 ± 0.05	MAB	1011	13.41 ± 0.06

where the steric hindrance factors outlined above play a role, but where, in contrast with DOPA, neither ligand contains two pairs of chelate-forming donor groups. The stability constants of the parent and mixed complexes of these ligands with the nickel(II) ion are given in Table V.

The data of Table V support the assumption of the occurrence of steric hindrance: the nickel(II)–tyrosinate–dopamine system could be described by the formation merely of 1:1:1 complexes (this also refers to the case when the system with a metal ion–ligand–ligand ratio of 1:2:1 was examined, this ratio being the most suitable for the formation of MA_2B).

In both the nickel(II)–DOPA and the zinc(II)–DOPA systems there is overlap between the processes of formation of metal complexes of aminoacid and pyrocatechol type and the processes of deprotonation of the donor groups not bound to the metal ions. Accordingly, in some cases different arrangements of the donor groups can belong to a given stoichiometric composition. UV spectral examinations were performed to elucidate the binding modes in the species formed. The formation of complexes of pyrocatechol type was followed via the change in the absorption band of the phenolate group of the ligand. The absorbance of DOPA was studied in the presence and absence of nickel(II) and zinc(II) ions, in the wavelength interval 250–330 nm and in the pH range between 6 and 12. The spectrum of the solution of the ligand was also recorded at pH ~ 15 (in 4 *M* KOH solution), for determination of the spectral characteristics of DOPA containing both phenolic hydroxy groups in deprotonated form. From studies made in the presence of the nickel(II) and zinc(II) ions at a metal ion–ligand ratio of 1:2 it could be stated that from pH ~ 11 the spectral data became constant, *i.e.* the degree of deprotonation of the phenolic hydroxy groups did not change further. The positions of the absorption maxima measured under these conditions are listed in Table VI, together with the values of the molar absorption coefficients.

TABLE VI. UV Spectral Data on the Phenolate Group of DOPA in the Presence and Absence of Metal Ions.

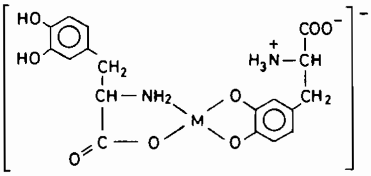
	pH	UV Spectrum [nm]	ϵ
DOPA	2.1	280	2760
DOPA	11.0	294	4350
DOPA	~15.0	309	4830
Ni(II):DOPA 1:2	11.8	303	3930
Zn(II):DOPA 1:2	11.8	301	5050

From the data in Tables IV and VI and the distribution curves in Figs. 3 and 4, and also taking into account the UV spectral examinations, the following findings may be made with regard to the complexes occurring in the nickel(II)–DOPA and the zinc(II)–DOPA systems.

(*i*) The complex MH_2A containing bonds of aminoacid type is formed in fairly significant concentration in the case of nickel(II), and in lower concentration for zinc(II); at the same time the species of composition $M(H_2A)_2$, similarly containing aminoacid-type bonds, is formed only in the nickel(II)–DOPA system. This is in agreement with the earlier observation [8] that the nickel(II) ion has a greater tendency than the zinc(II) ion to form coordinate bonds with ligands containing (N,O) donor atoms. The derived equilibrium constants given for these complexes in Table IV are only in an approximate agreement with the stability data obtained for alanine (Table I). This can be explained by the deprotonation microconstants of the ligand. If these derived constants are calculated not with the macroconstant (pK_3 = 9.83) but with the corresponding microconstant (pk_{32} = 9.43) characteristic of the protonation of the phenolate group, values of log K_1 = 5.30 and log K_2 = 4.10 are obtained for the DOPA complexes of nickel(II) and log K_1 = 4.17 for the complex of zinc(II), which are in good agreement with the stability constants of the alanine complexes of the metals.

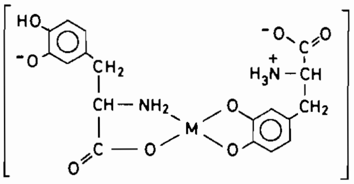
(*ii*) In the complex MHA, presumably in the case of both metal ions, there is a pyrocatechol-type bond and the amino group of the side-chain is protonated. Namely, the deprotonation constant of the complex MH_2A is 1.2 and 2.7 log unit respectively, lower than the microconstant value for dissociation of the -OH group of the ligand (pk_{32} = 9.43). Thus, such a considerable decrease of the pk value cannot be attributed to the electron withdrawing effect of the metal ion, because of its great distance from the OH group.

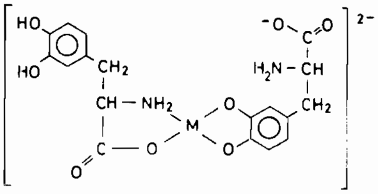
(*iii*) The mixed complex-like structure I, containing both (N,O) and (O,O) bonds, is strongly suggested for the species MH_3A_2.

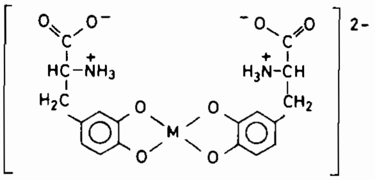

I

This is supported by the fact that formation of the mixed ligand complex is favoured for both metal ions in the model systems studied. In the case of zinc(II) the complex containing only aminoacid-type bonding can be excluded, among others for the reason that the species of composition $Zn(H_2A)_2$ is not formed either, while for the nickel(II) complex the deprotonation constant log K_2^{-1} is about one and a half orders of magnitude smaller than the microconstant pk_{32} characteristic of the deprotonation of the ligand.

(*iv*) For the species ZnH_3A_2 the dissociation constant log K_2^{-2} = 8.59. With the assumption of a mixed complex-like bonding mode, this cannot be ascribed unambiguously to dissociation either of the phenolic hydroxy or of the $-NH_3^+$ group. Consequently, it is probable that the deprotonation process is in part accompanied by a structural rearrangement and that a pyrocatechol-type complex with 1:2 composition is also formed. However, the structural rearrangement is not complete. If the complex ZnH_2A_2 were to have a structure involving merely (O,O) bonds, then from pH > 9.5 (where, as Fig. 4 shows, only this species and its deprotonated forms exist) the absorbance of the phenolate group could no longer change. In contrast with this, the UV spectral examination reveals that the absorbance still increases considerably up to pH ~ 10.2. This can be explained by the part that not only one single structure can be ascribed to the composition ZnH_2A_2; instead, the complexes with structures II and III, of mixed bonding type, and structure IV, of pyrocatechol type, are in equilibrium with one another. The mixed-bonding species may have two structures, depending on whether the phenolic hydroxy group or the chain-terminal $-NH_3^+$ is deprotonated.


II


III


IV

Since there is no significant difference between the microconstants of the -OH and $-NH_3^+$ groups (pk_{32} = 9.43; pk_{23} = 9.63), the presence of the species with structures II and III, involving the mixed bonding mode, can be assumed.

The constant log K_2^{-2} for the complex NiH_3A_2 is about half an order of magnitude smaller than the values of the above mentioned microconstants. On this basis it cannot be decided whether rearrangement to a species containing pyrocatechol-type bonds occurs in the nickel(II)–DOPA system. Evidence against the structural rearrangement is that the mixed ligand complex is the predominant species even at pH ~ 10–11 in the nickel(II)–alaninate–pyrocatecholate model system, the complex Ni(pyrocatecholate)$_2$ involving (O,O) bonding being present only in negligible concentration. In order to decide therefore, whether the further deprotonation processes of the nickel(II)–DOPA complexes are accompanied by a continuous rearrangement to structure IV or whether the complexes remain of mixed bonding type, again we carried out visible spectral examinations. Besides the parent complexes NiA_2 and mixed complexes NiAB of alanine and tiron, we additionally recorded the spectrum of the nickel(II)–DOPA

TABLE VII. Spectral Data on the Nickel(II) Complexes in Aqueous Solution.

	pH	Visible and NIR Spectrum[a] [nm]
Ni(II):alanine:OH$^-$ 1:2:2	7.5	368 ;616;1004
Ni(II):tiron:OH$^-$ 1:2:4	11.0	395 ;680;1112
Ni(II):alanine:tiron:OH$^-$ 1:1:1:3	10.5	375s;645;1064
Ni(II):DOPA:OH$^-$ 1:2:2	8.5	567s;608;1028
Ni(II):DOPA:OH$^-$ 1:2:4	9.5	660;1064
Ni(II):DOPA:OH$^-$ 1:2:6	10.5	625s;665;1060
Ni(II):DOPA:OH$^-$ 1:2:8	11.4	625s;665;1060

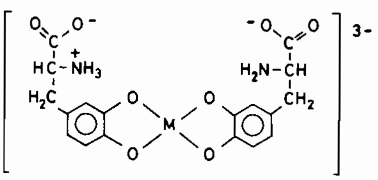
[a] s = shoulder.

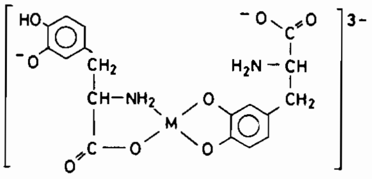
system at various pH values at a metal ion–ligand ratio of 1:2. The wavelength of the absorption maxima are given in Table VII.

The third band in the nickel(II)–DOPA system could not be measured because of the oxidation product of the ligand displaying a considerable absorbance in the wavelength range 350–400 nm. From a comparison of the data of Table VII it can be stated that from pH ~ 9.5 the spectral characteristics of the nickel(II)–DOPA complexes undergo practically no change, and agree well with the data on the nickel(II)–alaninate–tiron mixed ligand complex. On this basis it is probable that in contrast to the ZnH_2A_2 the species NiH_2A_2 remains of mixed bonding type, and thus only the equilibrium of structures II and III must be assumed in the case of this complex.

(*v*) The constant log K_2^{-3} relating to deprotonation of the species MH_2A_2 is approximately the same for the two metal ions and corresponds to the microconstant characteristic of the dissociation of the -NH_3^+ group of the ligand. In the case of the zinc(II) complex, however, the absorbance of the phenolate group still increases significantly, and thus this process too is in part accompanied by a structural rearrangement. The pyrocatechol-type structure V can be ascribed to a large extent to the complex $ZnHA_2$. This is supported by the result obtained for the zinc(II)–alaninate–pyrocatecholate model system. From the concentration distribution curve for this system in Fig. 2 it can be seen that between pH 9 and 11 the pyrocatechol displaces the amino-acid ligand from the mixed ligand complex, and the complex Zn(pyrocatecholate)$_2$ is formed. As confirmed by the visible spectral data and by the constancy of the absorbance of the phenolate group in this range, the complex $NiHA_2$ remains of mixed bonding type and can be characterized by structure VI.

(*vi*) In agreement with the above, the deprotonation constant K_2^{-4} in the case of the zinc(II) complex can probably be ascribed to the dissociation of the -NH_3^+ group of the complex with structure V. Its value is larger than the corresponding microconstant of this group, which in all probability can be interpreted by the different charge conditions. On the basis of the spectral characteristics of the nickel(II) complex, however, it may be concluded that the ligands in the complex are invariably of mixed bonding type. At the same time the value characteristic of the dissociation of the second phenolic hydroxy group of the ligand is pK_4 = 13.4, and even on the effect of the metal ion this cannot decrease to such an extent that its deprotonation would be appreciable at pH ~ 11. When these considerations are taken into account, further proton-losing process occurring for the complex $NiHA_2$ can only be interpreted by the formation of a hydroxo complex. This is supported by the experience that a slight degree of hydroxo complex formation was observed in the nickel(II)–alaninate and the nickel(II)–alaninate–pyrocatecholate system too.


V


VI

From the considerations outlined above, it could be stated that the stability macroconstants calculated from the pH-metric titration data can be ascribed only to complexes with a given stoichiometric composition, but not with an unambiguous structure. Since the formation of complexes with pyrocatechol-type bonding can be followed separately in the UV spectrum of the ligand, similarly to the determination of the deprotonation microconstants of the ligand [4], combined evaluation of the pH and UV spectral data may in principle give a possibility for the determination of the constants of the complex formation microprocesses. For this, however, greater experimental accuracy is also necessary in the spectral examinations; in the present case this could not be achieved because of oxidation of the ligand. Accordingly, we plan to carry out studies of such a nature on simpler systems.

References

1 J. E. Gorton and R. F. Jameson, *J. Chem. Soc. A*, 2615 (1968).
2 J. E. Gorton and R. F. Jameson, *J. Chem. Soc. A*, 304 (1972).
3 A. Gergely and T. Kiss, *Inorg. Chim. Acta, 16,* 51 (1976).
4 R. B. Martin, *J. Phys. Chem., 75,* 2657 (1971).
5 J. R. Pilbrow, S. G. Carr and T. D. Smith, *J. Chem. Soc. A*, 723 (1970).
6 S. G. Carr, T. D. Smith and J. R. Pilbrow, *J. Chem. Soc. A*, 2569 (1971).
7 Whei-Lu Kwik, E. Purdy and E. I. Steifel, *J. Am. Chem. Soc., 96,* 1638 (1974).
8 J. E. Gorton and R. F. Jameson, *J. Chem. Soc. A*, 310 (1972).
9 B. Grgas-Kuznar, V. L. Simeon and O. A. Weber, *J. Inorg. Nucl. Chem., 36,* 2151 (1974).
10 M. L. Barr, K. Kustin and Sung-Tsuen Liu, *Inorg. Chem., 12,* 1486 (1973).
11 I. Nagypál, *Acta Chim. Acad. Sci. Hung., 82,* 29 (1974).
12 A. Gergely, I. Nagypál and E. Farkas, *Acta Chim. Acad. Sci. Hung., 82,* 43 (1974).
13 R. Griesser and H. Sigel, *Inorg. Chem., 10,* 2229 (1971).
14 C. W. Childs and D. D. Perrin, *J. Chem. Soc. A*, 1039 (1969).