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Mixed Metal complexes of Copper(II), Nickel(II) and Zinc (II) Involving Dopa and Dopamine

S. Sheik Mansoor*

***Department of Chemistry , C.Abdul Hakeem College,**

Melvisharam – 632 509, India

E-mail: smansoors2000@yahoo.co.in

ABSTRACT: The stability constants of mixed metal complexes in aqueous solutions for the ligand L-dopa (3,4-dihydroxy phenylalanine) and dopamine 2-(3,4-dihydroxy phenyl) ethylamine with Cu(II)-Ni(II), Cu(II)-Zn(II), and Ni(II)-Zn have been determined by computer based analysis of the *p*H titration data. The mixed metal species of the type MAM' have been detected with dopa and dopm. A qualitative attempt has been made on the comparison of the log β values, to study the Irving-Williams order of stabilities.
Keywords: Mixed metal complexes, Dopa. Dopamine, Ligand, Stability constant.

1. INTRODUCTION

Considerable attention has been paid in recent years to the investigation of the properties of L-dopa and dopamine, because of their biological significance (1). The ligands L-dopa and dopamine are well known for their use in neurotransmission process (2) and in the treatment of Parkinson's disease (3,4). A prominent feature of Parkinson's disease is the loss of dopamine in the striatum and many therapeutic investigations for the disease are aimed at restoring dopamine signaling (5). The neurotransmitters dopamine and L-dopa mediate the generation and growth of Gold nano particles (Au-NPs). The plasmon absorption of the Au-NPs allow the quantitative colorimetric detection of the neurotransmitters (6). Dopamine has pharmacologically appropriate effects in the management of low cardiac output associated with compromised renal function, such as severe congestive heat failure (7). The biological importance of dopa and dopm prompted us to study the complex forming tendency of the ligands. This present paper deals with the mixed meal complex formation of dopa and dopamine with Cu(II)-Ni(II), Cu(II)-Zn(II), and Ni(II)-Zn in aqueous solution.

2. EXPERIMENTAL

2.1 Materials and reagents

The ligands L-Dopa and Dopamine used were of Fluka products of puriss quality. The Cu(II), Ni(II) and Zn(II) perchlorate stock solutions were prepared and estimated as reported earlier (8-10).

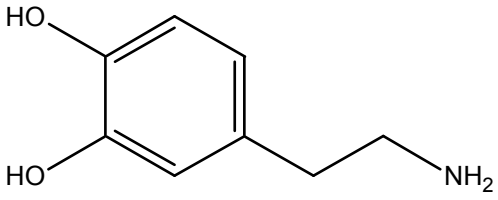
2.2 Potentiometric titrations

All the *p*H measurements were carried out with a digital *p*H meter with glass and calomel electrode with an accuracy of 0.01 *p*H unit. A double walled titration cell with inlet and outlet provisions for water circulations was used to carryout the *p*H titrations. The volumes were made up to 50 mL with deionised water prior to the titration being performed. The titration cell was maintained at 37 ± 0.1°C by circulating water using a thermostat and they were stirred magnetically under a continuous flow of nitrogen. The ionic strength was adjusted to 0.15 mol dm^{-3} with $NaClO_4$. Other details on the potentiometric *p*H titrations and data analysis and calculations have been earlier reported (11). All the calculations have been done with the aid of MINIQUAD-75 computer program (18). The auxiliary binary stability constant data under the present experimental conditions (Table 1) required for the computation of the mixed metal stability have been taken from the reported work (12).

3. RESULTS AND DISCUSSION

3.1 Binary complexes of Ni(II) and Zn(II) with Dopm

In dopamine ligand there are three coordinating groups *viz*., two hydroxyl and one amino groups. The ligand dopm possesses three protonation constants. The ligand dopm is a decarboxylted derivative of dopa.



Dopamine

In Ni(II)-dopm binary system, the binary species of the type NiAH, NiA and NiA_2H in addition to HA, H_2A and H_3A have been detected. The stability constant data reported are presented in Table 1. In Zn(II)-dopm binary system, the binary species of the type ZnAH and NiA in addition to HA, H_2A and H_3A have been detected.

The log β_{NiA} value of 9.66 obtained in the Ni(II)-dopm system under present experimental conditions is comparable to the value of 8.72 (at temp = 25°C and I = 0.2M KCl) for the Ni(II)-pyrocatechol system (13). This demonstrates the pyrocatechol mode of binding of dopm in its NiA species with the non-involvement of the terminal amino group in binding. The log β_{ZnA} value of 11.43 obtained in this system compares favorably with the log β_{ZnA} value for Zn(II)-pyrocatecholate system (13). This indicates that dopm binds the metal in a pyrocatechol manner with its amino group in the deprotonated form.

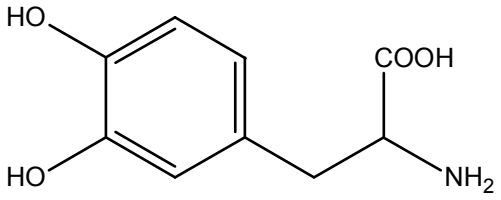
In the NiAH and ZnAH species, the proton can be attached with the terminal amino group and the protonated ligand binds the metal in a pyrocatechol like manner. In the NiA(AH) species in the Ni(II)-dopm system, both the ligands bind the metal in a pyrocatechol manner and the extra protons resides with the terminal amino group of any one of the ligand.

Table 1 : Proton ligand stability constants and stability constants of Cu(II), Zn(II) and Ni(II) complexes with dopm. (I = 0.15 mol dm^{-3} ($NaClO_4$) ; temp. = 37°C)

Parameters	Metal ions		
	Cu(II) (12)	**Ni(II)**	**Zn(II)**
log β_{HA}	11.48(5)	-	-
log β_{H2A}	21.61(3)	-	-
log β_{H3A}	30.34(4)	-	-
log β_{MAH}	22.07(6)	18.12(2)	18.89(6)
log β_{MA}	15.44(5)	9.66(12)	11.43(11)
log β_{MA2H}	-	26.07(44)	-
log β_{MA2}	23.25(26)	-	-
log K^{MA}_{MA2}	7.81	-	-
log K^{MAH}_{MA2H}	-	7.95	-
log P	11.94	7.99	8.76
pk^{H}_{MAH}	6.63	8.46	7.46

3.2 Binary complexes of Ni(II) and Zn(II) with Dopa

In the dopa ligand, there are four coordinating groups *viz.,* two hydroxyl, one amino and one carboxylate groups. The ligand dopa possesses four protonation constants. Two of these will be phenolate protons. The first proton to coordinate (a phenolate proton) has a very high affinity for the A^{3-} ion. Hence it can only be removed in solutions of very high *p*H. The second and third pk_a values correspond to the dissociation of phenolato oxygen and the amine nitrogen hydrogen atoms. The fourth proton to coordinate is the carboxyl proton. Since dopa has four potential coordination sites, different types of metal complexes can be envisaged. At low *p*H values amino acid side-chain (N,O) bonding is expected and at high *p*H values ortho phenolic hydroxyl groups (O,O) bonding can be expected.



Dopa

In the Ni(II)-dopa system, the binary species of the type NiH_2, NiA, NiA_2H_4 and NiA_2H_3 in addition to HA, H_2A,H_3A and H_4A have been detected. In Zn(II)-dopa system, the binary species $ZnAH_2$ and ZnA in addition to HA, H_2A,H_3A and H_4A have been detected. The stability constant data reported are given in Table 2.

In NiA dopa species has been found to be favored at higher *p*H ranges. This suggests that Ni(II) in NiA species binds the ligand through the phenolic hydroxyl groups. This become more evident if it is noted that the log β_{NiA} value of 10.84 obtained in the Ni(II)-dopa system is comparable to that value of 9.66 obtained in the Ni(II)-dopm system (Table 1), where the ligand binds the metal in a pyrocatechol manner. In the case of $NiAH_2$ dopa, the complex formation was found to be more favored at lower *p*H. This demonstrates that the ligand binds the metal in a glycine-like mode with its phenolate oxygens protonated.

The formation of ZnA complex has been detected at higher *p*H as in the case of NiA dopa species and it may be concluded that in the ZnA dopa species also the ligand binds the metal *via* the pyrocatechol (O,O) mode. The log β_{ZnA} value of 12.37 obtained for the Zn(II)-dopa system is comparable to that value of 11.43 obtained in the Zn(II)-dopm system (Table 1), where the dopm ligand binds the metal through the pyrocatechol (O,O) mode.

Table 2: Proton ligand stability constants and stability constants of Cu(II), Zn(II) and Ni(II) complexes with dopa. (I = 0.15 mol dm^{-3}($NaClO_4$) ; temp. = 37°C)

Parameters	Metal ions		
	Cu(II) (12)	**Ni(II)**	**Zn(II)**
log β_{HA}	11.45(5)	-	-
log β_{H2A}	21.10(4)	-	-
log β_{H3A}	29.73(4)	-	-
log β_{H4A}	32.38(8)	-	-
log β_{MAH2}	29.20(5)	25.93(9)	26.07(7)
log β_{MAH}	23.92(8)	-	-
log β_{MA}	18.08(7)	10.84(6)	12.37(7)
log β_{MA2H4}	-	51.16(11)	-
log β_{MA2H3}	-	43.36(23)	-
log P	14.27	-	-
pk^{H}_{MAH}	5.84	-	-

The $NiAH_2$ and $ZnAH_2$ species has been found to be formed at low *p*H values and amino-acid type binding is expected with phenolate oxygens protonated. The $M(AH_2)_2$ type of species containing amino acid type bonds is formed only with Ni(II) and not with Zn(II). This is in agreement with the observation of Gorton *et al* (14) that Ni(II) ion has greater tendency than Zn(II) ion to form bonds with ligands containing (N,O) donor atoms. The NiA_2H_3 species formed by the stepwise deprotonation of the NiA_2H_4 species via some structural rearrangement, containing mixed mode of bonding involving both (N,O) and (O,O) bonds.

3.3 Mixed metal complex equilibria involving Dopa

From the studies of a number of binary species in the metal dopa systems, different type of mixed metal species are expected and a number of computer models have been included during computation and the final results showed the presence of MAM' mixed metal species in good concentration. The stability constant values for the mixed metal complex species are reported in Table 3.

Cu(II)-dopa-Zn(II) mixed metal system

In the dopa ligand there are two possibilities for the binding of dopa in the Cu(II)-dopa-Zn(II) system. The first possibility is Cu(II) binds the ligand in a pyrocatechol manner and Zn(II) binds the ligand in a glycine-like manner. The other possibility is Cu(II) binds the ligand in a glycine-like manner and Zn(II) binds the ligand in a pyrocatechol manner. Considering the fact that CuA dopa species is more stable compared to ZnA dopa species, it is favorable to choose the first possibility. If one assumes the first possibility, the approximate log β value for the formation of CuAZn mixed metal species should be the sum of log β value of 15.44 obtained in the Cu(II)-dopa binary system (Table 2), where the ligand binds the metal in a pyrocatechol manner and the log β value of 5.03 for ZnA species in the Zn(II)-glycine binary system (15), which comes to be 20.47 log units. This value compares favorable with the experimentally found log β value of 21.45 for the CuAZn dopa species. So the structure proposed for CuAZn in the title system appears to be reasonable.

Cu(II)-dopa-Ni(II) mixed metal system

Similar to Cu(II)-dopa-Zn(II) mixed metal system, the approximate log β value for the formation of CuANi mixed metal species should be the sum of log β value of 15.44 (Cu(II)-dopa) and 5.86 (Ni(II)-glycine), which comes to be 21.30 log units. This value compares favorably with the experimentally found log β value of 20.86.

Ni(II)-dopa-Zn(II) mixed metal system

The approximate log β value for the formation of NiAZn mixed metal species should be the sum of log β_{NiA} value of 10.84 obtained in the Ni(II)-dopa (Table 2) binary system and the log β value of 5.03 for ZnA species in Zn(II)-glycine binary system which comes to be 15.87 log units. This values compares favourably with log β_{NiAZn} value of 15.50 obtained in the NiAZn dopa system. Hence, the structure proposed for NiAZn in the title system appears to be reasonable.

Table 3 Values of log β for mixed metal complexes

(I = 0.15 mol dm^{-3} ($NaClO_4$) ; temp. = 37°C)

Equilibrium	log β
$Cu^{2+} + dopa^{3-} + Zn^{2+} \rightleftharpoons [Cu(dopa)Zn]^{+}$	21.45(9)
$Cu^{2+} + dopa^{3-} + Ni^{2+} \rightleftharpoons [Cu(dopa)Ni]^{+}$	20.88(9)
$Ni^{2+} + dopa^{3-} + Zn^{2+} \rightleftharpoons [Ni(dopa)Zn]^{+}$	15.50(9)
$Cu^{2+} + dopm^{2-} + Zn^{2+} \rightleftharpoons [Cu(dopm)Zn]^{2+}$	19.87(10)
$Cu^{2+} + dopm^{2-} + Ni^{2+} \rightleftharpoons [Cu(dopm)Ni]^{2+}$	18.92(10)
$Ni^{2+} + dopm^{2-} + Zn^{2+} \rightleftharpoons [Ni(dopm)Zn]^{2+}$	14.52(9)

3.4 Mixed metal complex equilibria involving dopm

Similar to dopa containing mixed metal systems, dopm also forms only one type of mixed metal species MAM'.

Cu(II)-dopm-Zn(II) mixed metal system

The experimental log β_{CuAZn} value obtained for the title system is 19.87. Considering the fact that CuA dopm species is more stable compared to ZnA dopm species, it is reasonable to assume that Cu(II) binds the ligand in a pyrocatechol manner. The binding of Zn(II) to the ligand may be assumed to be *via* the amino group and by bridging any one of the phenolato oxygens. The coordination of Zn(II) can occur in two ways. In the first case, Zn(II) binds between the amino group and the 3-phenolato oxygen. In the second case, Zn(II) binds the amino group and 4-phenolato oxygen. Even though chelate rings with higher sizes are considered to be sterically unfavorable, the first way of binding in the formation of eight membered chelate ring will be stable compared to the latter involving nine membered chelate ring. The pyrocatechol mode binding of Cu(II) to the ligand accounted 15.44 log units and the remaining value of 4.43 log units may be attributed to he binding of Zn(II) between the amino group and the 3-phenolato oxygen.

Cu(II)-dopm-Ni(II) mixed metal system

As in the case of Cu(II)-dopm-Zn(II) mixed metal system, in the Cu(II)-dopm-Ni(II) mixed metal system also Cu(II) binds the ligand in a pyrocatechol manner. The binding of Ni(II) takes place between the amino group and 3-phenolato oxygen. The log β value obtained for CuANi species is 18.92. The pyrocatechol binding of Cu(II) to the ligand accounted 15.44 log units and the remaining value of 3.48 log units may be attributed to the binding of Ni(II) between the amino group and the 3-phenolato oxygen

Ni(II)-dopm-Zn(II) mixed metal system

As in the case of Ni(II)-dopa-Zn(II) mixed metal system, in the Ni(II)-dopm-Zn(II) mixed metal system also Ni(II) binds the ligand in a pyrocatechol manner. The bridging of Zn(II) can occur between the amino group and 3-phenolato group of dopm ligand. The log β value obtained for the system is 14.52. The pyrocatechol binding of Ni(II) to the ligand accounted 9.66 log units and the remaining value of 4.86 log units may be attributed to the binding of Zn(II) between the amino group and the 3-phenolato oxygen.

It should be mentioned here that in all the above cases, while calculating the expected log $\beta_{MAM'}$, statistical factors resulting from the decrease in number of coordination groups in mixed metal complex species compared to those in the MA and MA' complexes have not been taken into consideration. If this factor is considered, the above calculated values would be lesser by 1 or 2 log units. Thus in all the cases, the experimentally found log $\beta_{MAM'}$ is higher than theoretically expected values indicating higher stability for the mixed metal species.

3.5 Stability comparison of mixed metal complexes of dopa and dopm ligands:

The MAM' mixed metal species in the Cu(II)-dopa-Zn(II) and Cu(II)-dopm-Zn(II) is more stable than Ni(II)-dopa-Zn(II) and Ni(II)-dopm-Zn(II) system. This is in accordance with the Irving-Williams (16) order of stabilities. However, in the Cu(II)-dopa / dopm – Zn(II) and Cu(II)-dopa / dopm – Ni(II) systems, the former systems have higher stabilities than the latter systems. This type of observations against Irving- William series may be accounted for by considering the different geometrical preference of Zn(II) and Ni(II) in their complexes. The tetrahedral arrangement of Zn(II) leads to an increase in flexibility and more favorable arrangement in the mixed metal species unlike in the Ni(II) system which prefers a square planar geometry. Similar trends have also been observed earlier (17).

In conclusion the MAM' dopa type of species detected in the present investigation, the results indicate that one of the metal ions binds the ligand in a pyrocatechol manner and the other metal binds in a glycine-like mode depending upon their stability in the parent binary systems. In MAM' dopm type of species, the results indicate that one of the metal ions binds the ligand in a pyrocatechol manner depending upon their stability and the other meal binds the ligand through the amino group and the 3-phenolato oxygen.

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