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Study of some mixed-ligand ternary complexes of Ni (II) ion with drug dapsone as primary ligand and different amino acids as secondary ligand

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ABSTRACT

Mixed -ligand ternary complexes of Ni (II) ion with drug dapsone and different amino acids are synthesized and characterized. In this process drug dapsone is used as primary ligand and different amino acids such as prolein, glycine, alanine, histidin, arginine, threonine, valein, methionine, tryptophan and lysine are used as secondary ligand. The prepared ternary complexes were characterized by elemental analysis, UV-Visible and IR spectral analysis as well as magnetic measurements. The general formula [Ni(dap)L]. xH_2O were found for the ternary complexes, where L is amino acid and x is the number of coordinated water molecules. From the analytical and spectral data, the stoichiometry has been found to be 1:1:1 for the complexes.

Keywords: Dapsone, Spectral analysis, Mixed-ligand complexes, Magnetic measurements.

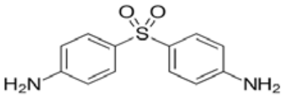
INTRODUCTION

Mixed ligand complex formation is widely in systems where metal ion and two or more ligands are present [1]. They also play an important role in catalytic centre of mtalloenzymes and metal activated enzymes. Thus, investigation and the interaction between various transition metals and amino acids and their ternary complexes can be used as metalloenzyme models [2].

Amino acids with one or more than one coordination site along with different functional group has a significant role in complexes of drugs play an important role in numerous chemical and biological systems [3]. The role of transition metal ions and their complexes are involved in metabolism, transportation and catalytic procceses in systems [4]. Nickel catalyse reactions proceed through cycles involving the nickel in various oxidation states. The catalytic applications of nickel complexes have been explained extensively [5-12].

The main attempt of this work is to know the proper mechanism of action of drugs and lower side effects [13]. The complexes of drugs has higher efficacy than potent drug [14]. Dapsone is antileprotic drug [15-16], nearly water insoluble and very weakly basic drug. It is used in the treatment of dermatitis herpetiformis, rheumatic and connective tissue disorders [17].

The literature survey shows that there is very limited work of ternary complexes of transition metals like Ni (II) ion with drug and different amino acids have reported. Hence the present paper deals with the systematic study of Ni (II) complexes with drug dapsone as primary ligand and different amino acids as secondary ligand.



Structure of dapson

MATERIALS AND METHODS

During the study all chemicals were used A.R. grade.0.025 molar aqueous solution of drug and different amino acids was added with freshly prepared nickel hydroxide precipitate. The mixture was heated on water bath for two hours. After that filter the hot solutions and evaporate on water bath. Blue coloured complexes are obtained. These complexes were separated and crystallized by distilled water. The crystals were dried in vaccum at 600C.

RESULTS AND DISCUSSIONS

Elemental analysis

The elemental analysis data along with some physical properties of the synthesized ternary complexes are given in table 1. The prepared ternary complexes are water soluble. From the elemental data the tentative molar ratio of the ternary complexes via Metal:L_1:L_2 comes out to be 1:1:1, where L_1=drug as primary ligand and L_2=amino acids as secondary ligand respectively.

Table 1: Elemental data of synthesized ternary complexes.

S.NO.	**Name of complexes**	**Molecular formula**	**Molecular weight**	**% analysis**					
				%C	**%H**	**%N**	**%O**	**%S**	**%M**
1.	$[Ni(dap)(pro)].5H_2O$	$C_{17}H_{21}N_3O_4S.5H_2O$	520.69	39.17% (38.05)	5.95% (5.22)	8.06% (7.90)	29.38% (29.35)	6.14% (6.00)	11.27% (11.10)
2.	$[Ni(dap)(gly)].6H_2O$	$C_{14}H_{17}N_3O_4S.6H_2O$	489.69	34.30% (33.01)	5.92% (5.87)	8.57% (8.00)	32.67% (32.01)	6.53% (6.14)	11.98% (10.87)
3	$[Ni(dap)(ala)].3H_2O$	$C_{15}H_{19}N_3O_4S.3H_2O$	449.69	40.02% (39.56)	5.55% (5.34)	9.33% (9.25)	24.90% (23.98)	7.11% (7.68)	13.00% (12.97)
4.	$[Ni(dap)(hist)].7H_2O$	$C_{18}H_{21}N_5O_4S.7H_2O$	587.69	36.75% (36.45)	5.95% (5.84)	11.91% (10.67)	29.94% (29.87)	5.44% (5.41)	9.98% (9.12)
5.	$[Ni(dap)(arg)].8H_2O$	$C_{18}H_{26}N_6O_4S.8H_2O$	624.69	34.57% (33.58)	6.72% (6.66)	13.44% (12.85)	30.73% (29.56)	5.12% (5.00)	9.39% (8.66)
6.	$[Ni(dap)(threo)].4H_2O$	$C_{16}H_{21}N_3O_5S.4H_2O$	497.69	38.57% (38.22)	5.82% (5.78)	8.43% (8.41)	28.93% (26.87)	6.42% (6.52)	11.79% (11.02)
7.	$[Ni(dap)(val)].6H_2O$	$C_{17}H_{23}N_3O_4S.6H_2O$	531.69	38.36% (37.26)	6.58% (6.45)	7.80% (7.60)	30.09% (29.65)	6.01% (5.78)	11.03% (10.12)
8.	$[Ni(dap)(meth)].5H_2O$	$C_{17}H_{23}N_3O_4S_2.5H_2O$	545.69	37.38% (36.58)	6.02% (6.00)	7.69% (7.65)	26.38% (25.64)	5.86% (5.48)	10.57% (9.98)
9.	$[Ni(dap)(tryp)].3H_2O$	$C_{23}H_{24}N_4O_4S.3H_2O$	564.69	48.87% (47.59)	5.31% (5.34)	19.83% (18.64)	9.91% (8.69)	5.66% (5.62)	10.39% (9.36)
10.	$[Ni(dap)(lys)].4H_2O$	$C_{18}H_{26}N_4O_4S.4H_2O$	524.69	41.16% (40.62)	6.48% (6.32)	10.67% (10.35)	24.39% (23.87)	6.09% (6.00)	11.18% (11.00)

UV-Visible Spectral analysis

The UV-Visible spectral details of the prepared ternary complexes are given in table 2. All ternary complexes show two absorption peaks in the uv-visible region, one strong peak at the range 320-385 nm and the other peak at 620-640 nm. The first band assigned to ligand to metal charge transfer while the second band can be ascribed to an intraligand transition of the amino acid moieties. These bands were assigned to $^3A_{2g}$-$^3T_{1g}$(F) and $^3A_{2g}$-$^3T_{1g}$(P) transitions respectively, which correspond to an octahedral structure for Ni^{2+} complexes [18].

Table 2: UV-Visible data of the synthesized ternary complexes.

S.N.	**Name of complexes**	λ_{max}	**Absorbance** (cm^{-1})	**Wave no.**	**Energy**	**Frequency (Hz)**	ε_{max}
1.	$[Ni(dap)(pro)].5H_2O$	640,320	0.154	15625.00	1.9373	468	15.40
2.	$[Ni(dap)(gly)].6H_2O$	620,320	0.168	16129.03	1.9997	483	16.80
3.	$[Ni(dap)(ala)].3H_2O$	615,325	0.624	16260.16	2.0160	487	62.40
4.	$[Ni(dap)(hist)].7H_2O$	641,320	0.239	15586.03	1.9342	467	23.90
5.	$[Ni(dap)(arg)].8H_2O$	616,325	0.114	16233.77	2.0127	486	11.40
6.	$[Ni(dap)(threo)].4H_2O$	598,300	0.007	16722.41	2.0733	501	0.70
7.	$[Ni(dap)(val)].6H_2O$	635,350	2.844	15748.03	1.9525	472	248.40
8.	$[Ni(dap)(meth)].5H_2O$	640,385	0.154	15625.00	1.9373	468	15.40
9.	$[Ni(dap)(tryp)].3H_2O$	628,320	0.114	15923.57	1.9743	477	2.40
10.	$[Ni(dap)(lys)].4H_2O$	620,325	0.168	16129.03	1.9997	483	16.80

IR Spectral studies

The careful inspection of the FTIR spectra free ligands and its ternary complexes is based on some references [19-21]. Table 3 shows the measured IR band positions of the ternary chelatesin order to facilitate the assigned of these bands in the free ligands and their metal chelates.

The well-defined peak at 3223 cm^{-1} in the spectrum of dapsone is assigned to the ν(N-H) vibration. The other series of weak bands at 1589 cm^{-1},1631 cm^{-1} and 1435 cm^{-1} are related to νC=O,δ (NH_2) and νC-O vibrations. The band located at 428 cm^{-1} assigned to ν(M-N), which indicate the interaction between metal ion N-atom of aromatic ring of amino acids. After complexation ν(NH_2) vibration shows positive shift from the spectrum of free amino acids.

A distinct band appearing in the 1573-1593 cm^{-1} region in the IR spectrum of various complexes is typical of the stretching of coordinated COO- group. The amino acid ligands are coordinated to the metal ion as divalent anion via oxygen atom of the carboxylate groups [22]. Further, the observed weak band at 1411-1498 cm^{-1} in the spectra is responsible for the symmetric vibration frequency of the coordinated COO- group and is further evidence for the participation of the carboxylate group in the coordination with the central metal ion.

Some important bands in the spectrum of dapsone at 1435 cm^{-1} (νC-O) and 563 cm^{-1} (πC-O) are disappear in the spectrum of some ternary complexes. This change indicates that these groups are in coordination with the central metal ion.

Table 3: IR spectral data of synthesized ternary complexes.

S. No	**Name of complexes**	**ν NH_2**	**ν C=O**	**ν C-O**	**δ C=O**	**ν MN**	**C-W**
1.	[Ni(dap)(pro)].5H_2O	3340	1593	-----	781	449	852
2.	[Ni(dap)(gly)].6H_2O	3273	1589	1411	738	412	858
3.	[Ni(dap)(ala)].3H_2O	3242	1573	1435	786	445	821
4.	[Ni(dap)(hist)].7H_2O	3308	1581	1411	713	420	817
5.	[Ni(dap)(arg)].8H_2O	3294	1585	1460	744	420	850
6.	[Ni(dap)(threo)].4H_2O	3230	1593	1419	711	435	800
7.	[Ni(dap)(val)].6H_2O	3319	1593	1496	-----	447	844
8.	[Ni(dap)(meth)].5H_2O	3379	1580	1454	794	464	868
9.	[Ni(dap)(tryp)].3H_2O	3227	1579	1425	713	468	856
10.	[Ni(dap)(lys)].4H_2O	3265	1570	1444	788	445	852

Magnetic measurement

The magnetic moment data of the ternary complexes are presented in table 4. These values are closer to those reported in some similar type of complexes [23-24]. These values are in the range 1.8-2.5 indicates that the presence of two unpaired electron in the central metal ion.

Table 4: Magnetic measurement data of ternary complexes.

S.N.	**Name of complexes**	**Mol. Wt.**	**Sus.mass**	**Suss. Mol.**	**μ_{eff}**
1.	[Ni(dap)(pro)].5H_2O	520.69	3.26	0.001697	1.9
2.	[Ni(dap)(gly)].6H_2O	489.69	3.13	0.001532	1.8
3.	[Ni(dap)(ala)].3H_2O	449.69	3.46	0.001555	1.9
4.	[Ni(dap)(hist)].7H_2O	587.69	4.31	0.002532	2.4
5.	[Ni(dap)(arg)].8H_2O	624.69	2.32	0.001449	1.8
6.	[Ni(dap)(threo)].4H_2O	497.69	3.12	0.001552	1.9
7.	[Ni(dap)(val)].6H_2O	531.69	5.29	0.002812	2.5
8.	[Ni(dap)(meth)].5H_2O	513.69	4.14	0.002126	2.2
9.	[Ni(dap)(tryp)].3H_2O	564.69	4.42	0.002495	2.4
10.	[Ni(dap)(lys)].4H_2O	524.69	3.12	0.001637	1.9

CONCLUSION

It can be concluded on the basis of the above conducted studies that drug dapsone act as a bidentate ligand and coordinates with the metal ion via oxygen atom and sulfer atoms of carboxylate and thiole groups respectively, while amino acid moieties utilize the nitrogen atom of amino group and oxygen atom of the carboxylate group for coordinate bond formation. Finally, we suggest the octahedral geometry for the synthesized metal complexes.

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