

Synthesis, Characterization and Structural Studies on the Fe(III) and Co(III) Complexes of Butyl Biguanide

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Complexes of Fe(III) and Co(III) with butyl biguanide (buformin) have been prepared and characterized using elemental analysis, magnetic moment measurements, molar conductance measurements and infrared and electronic spectroscopic techniques. The magnetic moment values are indicative of a high spin octahedral complex for Fe(III) and a diamagnetic octahedral complex for Co(III). The electronic and IR spectrum of Fe(III) and Co(III) complexes are in conformity with the octahedral structure.

Key Words: Buformin, Deprotonation, Octahedral.

INTRODUCTION

Biguanides and their derivatives are very important compounds. They have a wide range of chemotherapeutic applications and are found to be versatile ligands¹. Many biguanides and substituted biguanides are used as antimalarial, antimicrobial, antifungal and ovicidal agents². Metal complexes of biguanides with unusual oxidation states of the metals have been reported³. A comprehensive study of biguanide and substituted biguanide complexes of 3d transition metals have been made by Ray and coworkers⁴. A novel pharmaceutical formulation containing a biguanide and an angiotensin antagonist has also been reported⁵. The present work involves the synthesis of the ligand butyl biguanide commonly known as buformin and its complexes with Fe(III) and Co(III). The structure of the complexes are established with the help of elemental analysis, magnetic moment measurements, electrical conductivity and electronic and IR spectroscopic studies.

EXPERIMENTAL

Preparation of butyl biguanide (Buformin): N-Butyl amine was intimately mixed with equimolar amount of conc. HCl and cooled well. Butyl amine hydrochloride is formed. The substituted biguanide was prepared from the interaction of butyl amine hydrochloride and dicyandiamide^{6,7}.

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In a model experiment, equimolar quantities of dicyandiamide (16.8 g, 0.2 mol) and butylamine hydrochloride (0.2 mol) in 100 mL water were taken. It was refluxed in a water bath for about 2-3 h and allowed to cool. The precipitated butyl biguanide hydrochloride was collected, washed with water, then ether and dried. Buformin hydrochloride was formed as needle shaped crystals. This was dissolved in the minimum quantity of water and treated with an equimolar quantity of NaOH. The free biguanide separated was filtered and washed with water and dried.

General method for the preparation of the buformin complexes:

The complexes were prepared by refluxing an aqueous solution of the ligand and an aqueous solution of corresponding metal salt with constant stirring. The precipitated complex was filtered, washed and dried. Cobalt salt gave deep purple coloured and iron salt brownish yellow coloured complexes.

The IR spectrum was recorded on a Nicolet 5700 FT-IR spectrophotometer using KBr disc procedure in the range 4000-400 cm^{-1} . Electronic spectrum was recorded on a Perkin Elmer Lambda 25 double beam spectrophotometer. The magnetic moments were determined using the Gouy method.

RESULTS AND DISCUSSION

The metal percentage was determined by ignition method and also by gravimetric procedure⁸. The experimental percentage for Fe(III) complex is 10.54 and for Co(III) complex the value is 11.21. The analytical details are given in Table-1. Analytical data shows the metal ligand ratio to be 1:3 in both the cases. The complexes are insoluble in most organic solvents and hence conductance measurement could not be made. Using gravimetric procedure counter anions were checked and found to be absent.

TABLE-1
ANALYTICAL DATA AND COLOUR OF Co(III) AND
Fe(III) COMPLEXES OF BUFORMIN

Complex	Colour	Metal (%)	
		Theoretical	Experimental
Co(III)	Deep purple	11.3	11.21
Fe(III)	Brownish yellow	10.6	10.54

Magnetic moments were determined using the Gouy method and is given in Table-2. The magnetic moment of the iron complex is 5.8 BM which is very close to spin only value of 5.92 BM expected for Fe(III) system with five unpaired electrons⁹. This is indicative of a high spin octahedral complex. Co(III) complex is found to be diamagnetic. The ground state for a high spin octahedral complex of Co(III) is ${}^1A_{1g}$. Hence the magnetic moment data is suggestive of an octahedral structure.

TABLE-2
MAGNETIC MOMENT OF THE Fe(III) AND
Co(III) COMPLEXES OF BUFORMIN

Complex	Magnetic moment	
	Theoretical	Experimental
Fe(BG) ₃	5.92 BM	5.8 BM
Co(BG) ₃	Diamagnetic	Diamagnetic

In octahedral Fe(III) complexes, the ground state is ${}^6A_{1g}$ derived from 6S ground term for free ion. For the high spin complexes of Fe(III) having sextet ground state all the $d-d$ transitions are forbidden and therefore it is difficult to have a spectrum structure correlation¹⁰. The electronic spectrum of the Fe(III) complex has a weak absorption around 490 nm. This can be due to the spin forbidden transitions, ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$. This observation is in conformity with an octahedral structure. Two $d-d$ transitions can be expected for Co(III) in an octahedral ligand field¹¹. They are, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$. These transitions generally occur in the region 500 to 475 nm and the other around 360 nm. This complex gives an absorption at 485 nm. However the one around 360 nm could not be located. From this observation it can be concluded that Co(III) complex of buformin also has an octahedral geometry.

The IR spectral bands of buformin and their complexes along with the tentative assignments are provided in Table-3. The ligands and the complexes show strong bands in the region 3332-3209 cm^{-1} . This can be assigned to the symmetric and asymmetric stretching vibrations of the NH and NH_2 groups^{12,13}. Medium bands in the region 2973-2447 cm^{-1} can be attributed to the C-H vibrations of the butyl group. Strong absorption bands seen around 1660 cm^{-1} both in the ligand and its metal complexes can be assigned to the stretching vibrations of the C=N group^{12,14}. These bands however suffer red shift in the complex probably due to the involvement of the nitrogen of the C=N group for coordination. $\nu(\text{M-N})$ vibration is also seen at 420 cm^{-1} in the cobalt complex and at 425 cm^{-1} in the iron complex¹⁵.

Coordination number and geometry: The metal ligand ratio for the complexes as per analytical data is 1:3. Molar conductance data in conjunction with analytical data show that the complexes are non electrolytes. Magnetic moment data and electronic spectra are suggestive of an octahedral structure. It can be inferred that the three ligands get attached to the metal in the anionic form. This is highly probable, because computational studies have shown that, biguanides in the anionic form are more stable and that the H lost is from the nitrogen coming in between the carbon atoms¹. Based on these observations, the structure of these complexes can be represented as given in the Fig. 1.

TABLE-3
 INFRARED SPECTRAL BANDS (cm^{-1}) OF THE BIGUANIDE AND ITS
 COMPLEXES OF Fe(III) AND Co(III)

Assignment	Buformin	Co(BG) ₃	Fe(BG) ₃
$\nu(\text{N-H})$	3332	3300	3320
$\nu(\text{N-H})$	3305	3280	3280
$\nu(\text{N-H})$	3209	3200	3212
$\nu(\text{C-H})$ butyl group	2973	2970	2970
$\nu(\text{C-H})$ butyl group	2933	2935	2930
$\nu(\text{C-H})$ butyl group	2885	2884	2886
$\nu(\text{C-H})$ butyl group	2860	2850	2845
$\nu(\text{C-H})$ butyl group	2730	2730	2730
$\nu(\text{C-H})$ butyl group	2447	2447	2445
$\nu(\text{C=N})$	1660	1640	1636
$\delta(\text{N-C-N})$	1640	1630	1632
$\delta(\text{N-C-N})$	1597	1580	1577
$\nu(\text{N-H})$	1571	1568	1566
$\delta(\text{N-H})$	1534	1520	1520
$\delta(\text{C-H})$ butyl group	1471	1470	1463
$\delta(\text{C-H})$ butyl group	1450	1445	1440
$\delta(\text{C-H})$ butyl group	1402	1400	1393
$\delta(\text{N-H})$	1372	1350	1348
$\delta(\text{N-H})$	1356		
BG group	1310	1300	1310
$\nu(\text{C-N})$	1197	1180	1190
$\nu(\text{C-N})$	1158	1150	1146
$\nu(\text{M-N})$	—	420	425

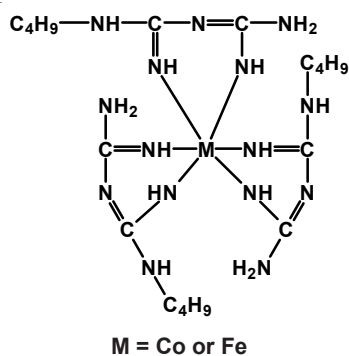


Fig. 1.

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