



Synthesis, Resolution and Characterization of 2(2- Pyridyl) - Benzimidazolebisbiguanidiniumcobalt(III) Complexes

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Abstract: When diamminebisbiguanidiniumcobalt (III) complex salts are treated with 2(2-pyridyl) – benzimidazole solution in suitable acid and heated on steam bath for some time, the complex salts of the corresponding acids are obtained. Other derivatives have been prepared from the complex chloride. The conductivity measurements have indicated the tri positive charge on the complex ion. The electronic absorption spectrum shows the octahedral configuration of cobalt (III). The complex has been resolved by the formation of diastereoisomers with d-camphorsulphonic acid. It shows “asymmetric transformation of second order”. Several salts, viz., sulphate, chloride etc. have been prepared.

Keywords: Resolution, Diastereoisomers, Antipod, Benzimidazole, Imidazole, 2(2-bipyridyl), d-camphorsulphonic acid.

I. Introduction

2(2-Pyridyl)-benzimidazole is an interesting ligand containing $\text{—H} = \text{C}^* \sim \text{C} = \text{N}^{\sim}$ grouping *

It was found that several metals formed stable and charged complexes with the reagent much in the same manner as 2(2-bipyridyl) and o-phenanthroline. The preparation, analytical aspects and infrared spectra of the metal chelates of imidazole derivatives, such as 2(2-pyridyl)-benzimidazole and 2(2-pyridyl)-imidazole, have been reported.¹

The diamminebisbiguanidiniumcobalt (III) complex² salt when treated with 2(2-pyridyl) – benzimidazole in suitable acid medium and heated on steam bath, gave the corresponding complex salt on cooling. The complex salts were found to be very stable as they were formed in strong acid medium. The oxalato oxalate and μ -thiosulphatotetrakisbiguanidedithiosulphatodicobalt could not be isolated from the complex by the usual method. The conductivity measurement also indicated that the complex was very stable in aqueous solution, there being very little hydrolysis. The equivalent conductivity at 1024 dilution at 29° was found to be of the

same order as that of $[\text{Co}(\text{BigH})_2(\text{en})]\text{Cl}_3^+$. The values are 133.9 and 139.3 $\text{ohm}^{-1} \text{cm}^2$ respectively. From conductivity data the valency of the cation has been found to be 3.

The electronic absorption spectrum revealed only one peak around 480 m μ . There was too much absorption below 360 m μ probably due to charge transfer effect. It could be resolvable into its optical isomers through diastereoisomeric salt formation with d- camphorsulphonic acid. The complex sulphate was treated with calculated amount of barium d- camphorsulphonate solutions. After filtering off the precipitated barium sulphate, the filtrate was left in air for fractional crystallisation. Several crops were collected and analysed. All fractions showed a constant dextro rotation. Only the last two fractions (very small in amount) showed the laevo rotation. Here the dextro form is less soluble than the laevo form. The filtrate, after removing the dextro antipode, quickly changed into the dextro form, as in case of the di(methylamine)bisbiguanidiniumcobalt(III) chloro d-tartrate³. Here also the laevo $\rightarrow$ dextro conversion is found to be rapid.

The optically active simple complex salts, however, could not be obtained by decomposition of the complex d- camphorsulphonate either with potassium iodide or with ammonium sulphate. The resolution showed “asymmetric transformation of second order” almost similar to that found in case of trisbiguanidiniumcobalt(III) chloride, though a very small amount of laevo could be obtained in the last two fractions.³

The structure of the complex may be represented by an octahedral structure.

II. Experimental

2(2-Pyridyl)-benzimidazolebisbiguanidiniumcobalt(III) sulphate:

The complex salt has been prepared by adding a solution of 2(2-pyridyl)-benzimidazole in dilute sulphuric acid to that of a solution of diammine bisbiguanidiniumcobalt(III) sulphate in water. The diammine heterochelate was prepared by the method of Ray and Ghosh.³ The mixed solution was heated on steam bath for some time.

On cooling, deep red crystals separated out. The crystals were filtered, washed with water and alcohol and dried in air. The air dried sample on analysis was found to contain:

$[\text{Co}(\text{Big H})_2(\text{PBMZ})]_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$: where " Big H^+ " stands for one molecule of biguanide²⁺ and "PBMZ" for one molecule of 2(2-pyridyl)-benzimidazole:

Analysis: Found (Calcd.) Co, 9.17% (9.26%), N, 27.92% (2.61%), SO_4 , 22.40% (22.64%), H_2O , 5.51% (by loss at 110°C) (5.66%).

2(2-Pyridyl)-benzimidazolebisbiguanidiniumcobalt(III) chloride:

This was prepared by adding a solution of 2(2-pyridyl)-benzimidazole in dilute hydrochloric acid to a solution of diaminebisbiguanidiniumcobalt(III) chloride in water and heating on steam bath for a while. On cooling, orange red crystals separated. The crystals were purified by recrystallization from water. The crystals were filtered, washed with water and alcohol and dried in air. The air dried compound was found to contain:

$[\text{Co}(\text{Big H})_2(\text{PBMZ})]\text{Cl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$:

Analysis: Found (Calcd.) Co, 9.76% (9.69%), N, 30.02% (29.95%), Cl, 17.48% (17.51%), H_2O , 7.34% (by loss at 105°C) (7.41%).

The equivalent conductivity of the complex chloride in aqueous solution was measured⁴ at different dilution at 28.5°C. The result are tabulated below:

Dilution in litres	32	64	128	256	512	1024
$\wedge_v$	101.2	105.7	113.7	119.3	128.06	133.9

The equivalent conductivity at infinite dilution was calculated from the formula $\wedge_\infty = \wedge_v (1 + n_1 n_2 0.692 v^{1/2})$ where n_1 and n_2 are the valencies of cation and anion and v is the dilution in litre. The value of $\wedge_\infty$ (mean) was found to be 137.07 $\text{ohm}^{-1} \text{cm}^2$. The valency of the cation was found to be 3.

The electronic absorption spectrum of the complex chloride has been recorded, showing one absorption band around 480 nm.

2(2-Pyridyl)-benzimidazolebisbiguanidiniumcobalt(III) iodide:

The complex was prepared by metathesis with potassium iodide. The orange red coloured precipitate obtained was filtered, washed and dried as usual. The air dried sample on analysis was found to contain:

$[\text{Co}(\text{Big H})_2(\text{PBMZ})]\text{I}_3 \cdot 2\text{H}_2\text{O}$.

Anal: Found (Calcd.) Co, 6.81% (6.75%), I, 43.42% (43.61%).

(+) 2(2-Pyridyl)-benzimidazolebisbiguanidiniumcobalt(III) d-camphorsulphonate:

The (+) complex d-camphorsulphonate was prepared by adding barium d-camphorsulphonate to the complex sulphate. Barium sulphate was precipitated gradually and was removed by filtration. The filtrate was then evaporated in air for fractional crystallization. The first four fractions were found to be dextro rotator. More than 85% of the (+) complex diastereoisomer separated in this way. The complex on analysis was found to contain:

$[\text{Co}(\text{Big H})_2(\text{PBMZ})] \cdot (\text{C.S})_3 \text{H}_2\text{O}$

Where C.S. is d-camphorsulphonate ion.

Analysis: Found (Calcd.) Co, 5.01% (5.04%), N, 15.61% (15.59%).

For a 0.1% solution of the complex in water at 29°C in a four decimeter tube, the optical rotation was:

$\alpha_D = +0.12^\circ$, $[\alpha]_D^{29} = +30^\circ$, $[M]_D = +350.5^\circ$

(-) 2(2-Pyridyl)-benzimidazolebisbiguanidiniumcobalt(III) d-camphorsulphonate:

From the mother liquor, left after removing the dextro diastereoisomer, deposited some impure crystals, which were rejected. The crystals then obtained, were found to be laevo rotator. The compound on analysis was found

to contain: $[\text{Co}(\text{Big H})_2(\text{PBMZ})] \cdot (\text{C.S})_3 \text{H}_2\text{O}$

Analysis: Found (Calcd.) Co, 5.08% (5.04%), N, 15.78% (15.59%).

For a 0.072% solution of the complex in water at 29°C, in a four decimeter tube, the rotation was:

$\alpha_D = -0.10^\circ$, $[\alpha]_D^{29} = -34.6^\circ$, $[M]_D = -404.2^\circ$

The specific and molar rotations of the complex d-camphorsulphonate were much lower in comparison with the corresponding values of the α -picolinatobisbiguanidiniumcobalt(III) d-camphorsulphonate:

Complexes	$[\alpha]_D$	$[M]_D$
$[\text{Co}(\text{BigH})_2^+(\text{PlCH})](\text{C} \cdot \text{S})_2 6\text{H}_2\text{O}$	– 250°C	– 238.5°
$[\text{Co}(\text{BigH})_2(\text{PBMZ})](\text{C} \cdot \text{S})_3 \text{H}_2\text{O}$	– 34.6°	–404.2°C

III. References

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