



Preparation, Spectral Studies and Resolution of Bisbiguanidiniumdinitrocobalt (III) Complexes

R.K. Prasad¹, Bina Rani², M.K. Singh¹, Abhay Kumar¹, D.K. Verma¹, Prahlad Kumar¹,
Sanjay Kumar³, Randhir Kumar³ & Renu Kumari Sinha⁴

¹P.G. Dept. of Chemistry, Patna University, Patna-800 005, Bihar, INDIA.

²Dept. of Chemistry, M.M. College, (P.U.) Patna-800 001, Bihar, INDIA.

³Dept. of Chemistry, Patna Science College, Patna University, Patna-800 005, Bihar, INDIA.

⁴St. Joseph's Convent, Bankipore, Patna-800 004, Bihar, INDIA.

Abstract: The *Cis-bisbiguanidiniumdinitrocobalt(III) complex chloride* has been prepared by substitution of two pyridine molecules from *bisbiguanidiniumdipyridinecobalt (III) chloride* by sodium nitrite. The several salts of the complex, viz, sulphate, nitrate, chloride, bromide, and iodide have been prepared and characterized. From chemical reactions electronic absorption and i.r. spectral bands the *cis- octahedral* configuration has been suggested for the complex. The conductivity measurement reveals and univalency of the complex ion. The electronic absorption spectrum of complex salts show the two usual *d-d*-transition around 335m μ and 465m μ . Like *cis- bisethylenediaminedinitrocobalt(III)* salts, the attempt to resolve the *bisbiguanidiniumdipyridinecobalt (III) camphor - d-sulphonate* into pure optical active *d-l* antipodes were unsuccessful, due to the second order asymmetric transformation of the isomers.

Keywords: Resolution, *d*-Camphorsulphonate, Asymmetric transformation, molar rotation, Octahedral,

I. INTRODUCTION

Nitrite ion is known to coordinate metal ion in four different ways¹⁻⁶. As a monodentate ligand it may coordinate through the nitrogen atom forming the well-known nitro complexes and through the oxygen atom forming the less common nitrito complexes. It may also function as a bridging ligand forming bond through the nitrogen as well as with oxygen between two metal atoms⁷. It may also function as a bidentate chelating group⁸. Since the nitro groups lie toward the stronger end of the spectrochemical series as compared with the nitrito groups, nitro complexes are more common. They form usually strong σ bonds with low spin d^6 systems. Werner studied the isomerism in yellow xantho $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{++}$ complex and the brick red "iso xantho" $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{++}$.

The cobaltdinitrotetrammine (III) complexes have been known in both the trans and cis forms⁹. The bisethylenediaminedinitrocobaltdinitro(III) nitrite has also been obtained in both the trans and cis forms. The trans form has been prepared by air oxidation of mixture of cobalt(II) nitrate, and ethylenediamine and sodium nitrite in neutral solution. The cis form was prepared by the action of ethylenediamine on sodium ehexanitrocobaltat (III). Recently it has been prepared from trans cobaltdichlorobisethylenediamine(III) chloride by Harbulak and Albinak¹⁰.

Celap, Radanovic and Janjic¹¹ have studied the bisglycinatodinitrocobaltate (III) and have determined the configuration by resolving the complex by preparing the diastereoisomers of (+) cinchonine bisglycinatodinitrocobaltate(III).

Boucher and Bailar Jr.¹² have studied the preparation and properties of sodium bisacetylacetonatodinitrocobaltate(III) and some complexes of the type amminebisacetylacetonatodinitrocobaltate(III).

Rosenhein and Gorfunkel¹³ prepared bisacetylacetonatodinitrocobaltate(III) by the action of acetylacetone on sodium cobaltinitrite. Both cis and trans forms of the complex have been identified by infra red spectroscopy¹⁴. Here we report the preparation and characterization of cis bisbiguanidiniumdinitrocobalt (III) salts.

II. RESULTS DISCUSSION

We have found that usual method of oxidizing the bisbiguanidiniumcobalt (II) hydroxide in presence of NaNO_2 , to isolate bisbiguanidiniumdinitrocobalt(III) failed to produce the desired complex. However the cis

isomer can be prepared by substitution of the pyridine groups from cis bisbiguanidiniumdipyridinecobalt (III) chloride in aqueous medium by adding sodium nitrite. The evolution of pyridine from depyridone complex started immediately which was accelerated by warming over the steam bath, with the separation of an orange crystalline substance. From this several complex salts, viz., sulphate, chloride, bromide, iodide nitrate and d-camphorsulphonate have been prepared. Attempts to prepare the trans- bisbiguanidiniumdinitrocobalt (III) complex by the action of biguanide sulphate on sodium hexanitrocobaltate (III) also failed and no pure product could be isolated through this reaction.

The I.r. spectrum of $[\text{Co}(\text{Big H})_2(\text{NO}_2)_2]\text{Cl}$ was recorded to find out the nature of coordination of the NO_2 groups. It has been found¹⁵ that ν_{as} and ν_{s} stretches of NO_2 groups in complexes are shifted due to coordination of NO_2 . In nitro complexes ν_{as} and ν_{s} are reported to be shifted to higher frequency while in nitrito complex ν_{as} is increased but ν_{s} is shifted to lower vibrations¹⁶. It has been shown by Gatehouse¹⁶ that in case of cis-configuration ν_{as} band splits into two bands and an additional absorption is observed at 1335-1355 cm^{-1} . Table (I) below shows the frequencies (cm^{-1}) of the above complex and reported cis $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{Cl}$.

Table I

Complexes	In Potassium bromide disc		
	ν_{as}	ν_{s}	δ
cis $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{Cl}$	1422 s	1344 s 1312 s	837
cis $[\text{Co}(\text{Big H})_2(\text{NO}_2)_2]\text{Cl}$	1385 s	1340 s 1315 ms (cis)	830

For this it can be suggested that $[\text{Co}(\text{Big H})_2(\text{NO}_2)_2]\text{Cl}$ is a nitro groups bonded in complex at cis position.

The electronic absorption spectrum of the complex has been recorded and the two usual peaks around 335 $\text{m}\mu$ and 465 $\text{m}\mu$ have been obtained corresponding to the octahedral configuration of the cobalt (III) complex. The shifts were observed towards violet side.¹⁷⁻²⁰

The equivalent conductivity of an aqueous M/1000 solution of the complex nitrite was measured at 30°C and was found to be 114.06 $\text{ohm}^{-1} \text{cm}^2$, corresponding to the 1 : 1 ion, i.e., the complex dissociated into two ions.

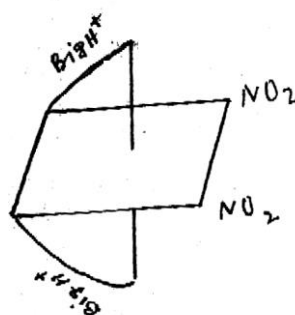
Attempts to resolve the complex into optically active antipodes were rather unsuccessful. Though the d-camphor sulphonate of the complex was isolated in different fractions and analysed. The optical rotation noted leavo, was very small with all the fractions. But the rotation is so small that it is rather qualitative, though definitely a phenomenon of "asymmetric transformation of second order" was established.

The low values of the specific and molar rotation. $[d]_{\text{D}} = -37.5^\circ$ and $[M]_{\text{D}} = -219.2^\circ$ respectively are comparable to the corresponding low values of the dinitro bisethylenediamine-cobalt(III) d-camphorsulphonate, prepared and resolved by Werner¹⁷ in which case the values are:

$$[d]_{\text{D}} = -16^\circ$$

$$[M]_{\text{D}} = -80.2^\circ$$

Still higher value in case of the (–) bisbiguanidiniumdinitro-cobalt (III) d-camphorsulphonate is due to the fact that though like ethylenediamine, biguanide molecule is symmetrical, it is asymmetrically coordinated, thus rendering the whole complex more asymmetric.



III. Experimental

Bisbiguanidiniumdinitrocobalt(III) nitrite :

A freshly prepared solution of cis-bisbiguanidiniumdipyridinecobalt(III) chloride was treated with slight excess of sodium nitrite with constant stirring. The resulting solution was warmed at 60-70°C when smell of pyridine came out and slowly orange red crystals were deposited. The whole content was cooled overnight and deposited red crystals were filtered. The crystals were washed with cold water and alcohol and then dried in air. The air dried substance on analysis was found to contain :

Co – 14.83%

N – 45.96%

Required for $[\text{Co}(\text{Big H})_2(\text{NO}_2)_2]\text{NO}_2$:

Co – 14.77%

N – 45.60%

The molar conductance of an aqueous M/1000 solution of the complex nitrite at 30°C was measured and was found to be $114.06 \text{ ohm}^{-1} \text{ cm}^2$, corresponding to 1 : 1 ions.

The electronic absorption spectrum of the complex nitrite in M/2000 solution in water has been recorded. There was too much absorption in u.v. regions. The two peaks were obtained around 335 mμ and 465 mμ.

Bisbiguanidiniumdinitrocobalt (III) sulphate and other salts

The complex salts were prepared by methathesis of the complex nitrite and appropriate potassium salts. When a solution of potassium sulphate was added to the solution of the Bisbiguanidiniumdinitrocobalt(III) nitrite warmed for one hour at 60-70°C and left overnight in cold, orange red crystals separated out. These were filtered, washed with water and alcohol. The products were dried over CaCl_2 . The complex salts

$[\text{Co}(\text{Big H})_2(\text{NO}_2)_2]\text{X}$ ($\text{X} = \frac{1}{2} \text{SO}_4^{2-}$, Cl, Br, I, NO_3 or d-camphor sulphonate).

The analytical results of complex salts correspond to expected elemental analyses of suggested formula.

(-) Bisbiguanidiniumdinitrocobalt(III) d-camphorsulphonate :

The compound was prepared by the action of calculated amount of the barium d-camphorsulphonate on the dinitro-bis-biguanidiniumcobalt(III)sulphate. The precipitated barium Sulphate was filtered off. The filtrate was then evaporated in air for fractional crystallization. The different crops obtained were isolated and analysed M/100. Solution of different fraction were prepared and their optical rotation measured. It was found that all fractions are laevo rotatory. This different crops collected were again dissolved in water and fractionated again. It gave the same rotation. The air dried substance was found to contain :

Co – 10.12%

N – 28.80%

Required for $[\text{Co}(\text{Big H})_2(\text{NO}_2)_2]\text{CS}$; where 'CS' stands for one d-camphorsulphonate ion.

Co – 10.09%

N – 28.76%

For a 0.04% solution of the complex d-camphorsulphonate in water, at 31°C in a four decimeter polarimeter tube, the optical rotation was :

$$[d]_D = -0.06^\circ$$

$$[d]_D^{31} = -37.5^\circ$$

$$[M]_D = -219.2^\circ$$

This proved the cis configuration of the complex but both d and l forms could not be separated due to second order asymmetric transformation¹⁰.

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