



Synthesis and Structural Studies of some complexes of Ni(II) and Co(III) with Hexamethylenedibiguanide

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Abstract: Complexes of Ni(II) and Co(III) with Hexamethylenedibiguanide $[\text{Hm}(\text{BigH}^+)_2]$ of the molecular composition $\text{Ni}[\text{Hm}(\text{BigH}^+)_2](\text{OH})_2 \cdot \text{H}_2\text{O}$, $\text{Ni}[\text{Hm}(\text{BigH}^+)_2]\text{SO}_4 \cdot 4\text{H}_2\text{O}$, $\text{Ni}[\text{Hm}(\text{BigH}^+)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}_2[\text{Hm}(\text{BigH}^+)_2]_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ and $\text{Co}_2[\text{Hm}(\text{BigH}^+)_2]_3(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ have been prepared and characterized by the studies of IR, UV, electrical conductance and magnetic susceptibility measurements. The complexes of both the Ni(II) and Co(III) are found to be diamagnetic which indicates the low spin square planar structure of Ni(II) complexes and Octahedral geometry of Co(III) complexes.

Keywords: Cobalt, Complexes, Hexamethylenedibiguanide, Nickel

I. Introduction

Hexamethylenedibiguanide sulfate $[\text{Hm}(\text{BigH}_2^+)_2]\text{SO}_4 \cdot \text{H}_2\text{O}$ (Fig. 1) is a quadridentate chelating ligand and its complexes are known with only some metals. Its donor behavior has not been studied extensively.

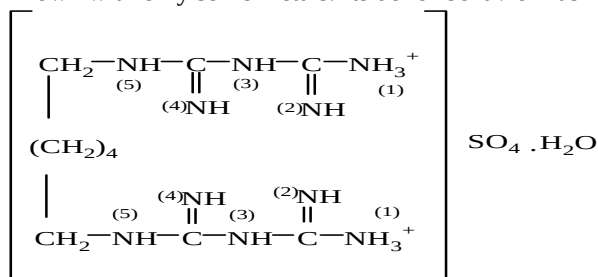


Fig. 1

This ligand coordinates with the N(2) and N(4) of both the biguanide substituent groups to form a six membered chelate ring with the metal ion.

To determine the chelating behavior of hexamethylenedibiguanide ligand, we have prepared and characterized the complexes of Ni(II) and Co(II) with this ligand.

II. Materials and Methods

The ligand Hexamethylene dibiguanide was prepared by the reported method.

Preparation of the complexes:

A. Nickel hexamethylenedibiguanidium hydroxide monohydrate, $\text{Ni}[\text{Hm}(\text{BigH}^+)_2](\text{OH})_2 \cdot \text{H}_2\text{O}$:

It was obtained by mixing the strong alkaline solution of hexamethylenedibiguanide sulphate (2.8 g) with a solution of nickel sulfate (1.2 g) and digesting it in a water bath for 3-4 hours. A yellow colored precipitate was obtained, it was filtered, washed with water, then with alcohol and was finally dried over KOH. This substance liberated ammonia from ammonium salts.

Analysis: Found (Calculated.) Ni, 14.90%(14.94); N, 35.22%(35.44); C, 30.05%(35.44),
H, 07.10%(07.09); H_2O , 04.80%(04.55)

B. Nickel hexamethylenedibiguanidium sulfate tetrahydrate, $\text{Ni}[\text{Hm}(\text{BigH}^+)_2]\text{SO}_4 \cdot 4\text{H}_2\text{O}$:

The complex Sulphate was obtained by digesting the complex Nickel hexamethylenedibiguanidium hydroxide monohydrate, with ammonium sulfate.

Analysis: Found (Calculated.) Ni, 11.30%(11.54); SO₄, 18.32%(18.78); N, 27.12%(27.39); C, 23.20%(23.48); H, 06.30%(06.26); H₂O, 14.20%(14.09).

C. Nickel hexamethylenedibiguanidium sulfate tetrahydrate, $\text{Ni}[\text{Hm}(\text{BigH}^+)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$:

The complex chloride was obtained by the action of ammonium chloride on the complex Nickel hexamethylenedibiguanidium hydroxide monohydrate.

Analysis: Found (Calculated.) Ni, 12.09%(12.14); Cl, 14.58%(14.61); C, 24.65%(24.69); H, 06.60%(06.58); H₂O, 14.65%(14.81).

D. Dicobaltic (III) tris-hexamethylenedibiguanidium hydroxide monohydrate,

$\text{Co}_2[\text{Hm}(\text{BigH}^+)_2]_3(\text{OH})_6 \cdot \text{H}_2\text{O}$

A solution of hexamethylenedibiguanide sulfate (0.5 g) in water (200 ml) was made strongly alkaline with NaOH solution (20ml, 4N NaOH) and treated with 1.6 g cobalt sulfate solution (30 ml). The mixture was heated on the water bath. As ammonia was given off, the complex base separated as a soft mass. This was cooled and filtered after 1.5 hours. The product was washed as usual and dried over KOH. It forms dark red crystals, insoluble in water and alcohol.

Analysis: (Calculated.) Co, 10.80%(10.82); N, 38.48%(38.53); C, 32.80%(33.03); H, 07.36%(07.34); H₂O, 01.68%(01.65).

E. Dicobaltic (III) tris-hexamethylenedibiguanidium sulphate hexahydrate,

$\text{Co}_2[\text{Hm}(\text{BigH}^+)_2]_3(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$

The sulphate was obtained by digesting the Dicobaltic(III) tris-hexamethylenedibiguanidium hydroxide monohydrate with ammonium sulphate.

Analysis: (Calculated.) Co, 08.38%(08.64); N, 30.50%(30.74); SO₄, 20.89%(21.08); C, 26.32%(26.35); H, 06.18%(06.15); H₂O, 07.99%(08.10).

III. Result and discussion

It has been found that hexamethylenebiguanide, $\text{Hm}(\text{BigH})_2, (\text{C}_{10}\text{H}_{24}\text{N}_{10})$ forms complexes with the first row transition metal ions in alkaline medium. The ease with which parent biguanide, $\text{BigH}, (\text{C}_2\text{H}_7\text{N}_5)$ forms complexes with general transition metal ions is not retained in case of hexamethylenedibiguanide, $\text{Hm}(\text{BigH})_2$

with cobalt (II) and nickel (II). $\text{Hm}(\text{BigH})_2$ forms complexes slowly in ammoniacal medium on gentle refluxation. The cobalt (II) complex could not be isolated as it gets oxidized to cobalt (III) and sparingly soluble

product of the composition $\text{Co}_2[\text{Hm}(\text{BigH}^+)_2]_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ is formed. In case of simple biguanide, phenylbiguanide and alkylbiguanide, both cobalt(II) and cobalt (III) complexes have been isolated. The cobalt (II) complexes of parent biguanide are susceptible to aerial oxidation and cobalt (III) complexes are formed

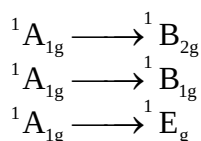
immediately. The complex base of composition $\text{Co}_2[\text{Hm}(\text{BigH}^+)_2]_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ was formed by this ligand in sodium hydroxide solution. The complex base after refluxing with appropriate ammonium salt gave complex chloride and sulphate. These complex salts have low solubility in cold water but get dissolved appreciably on heating. The aqueous solution of complex salts are conducting, indicating their ionic character ($\Lambda_a > 400 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$). The complex salts are diamagnetic indicating their low spin octahedral geometry in oxidation state +1. The electronic absorption spectrum of complex chloride in aqueous

solution displays one broad band at 490 cm^{-1} and a shoulder near 360 cm^{-1} . The electronic absorption bands are attributed to $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ transitions in octahedral field.

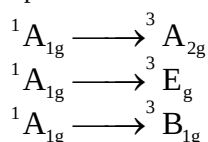
Nickel (II) has been found to form a cream yellow complex $\text{Ni}[\text{Hm}(\text{BigH}^+)_2]_3(\text{OH})_2 \cdot \text{H}_2\text{O}$ in strongly alkaline solution of hexamethylenedibiguanide sulphate in NaOH and nickel (II) sulphate solution in water at reflux temperature. The complex sulphate and chloride of composition $\text{Ni}[\text{Hm}(\text{BigH}^+)_2]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}[\text{Hm}(\text{BigH}^+)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ respectively were obtained by refluxing complex base with excess of ammonium sulphate/chloride in aqueous suspension. These complex salts of nickel (II) are quite stable and retain water molecules at room temperature but gradually lose water molecule on heating. At 110°C - 120°C the complex base as well as other salts completely eliminate all water molecules and become anhydrous. The complex base becomes an anhydro base such as $[\text{Ni Hm}(\text{BigH}^+)_2]$. The complex base is sparingly soluble in water whereas the complex chloride and complex sulphate are slightly soluble in hot water. The aqueous solutions of complex salts are conducting ($\Lambda_\alpha \approx 180\text{-}190\text{ ohm}^{-1}\text{ mol}^{-1}\text{ cm}^2$) indicating their ionic character. At room temperature the complexes are diamagnetic supporting their square planar structure with dsp^2 covalent hybrid bonding.

In the planar field, the d orbital of nickel (II) complexes splits into four energy level b_{1g} , b_{2g} , a_{1g} and e_g . The metal s orbital also spans a_{1g} while p orbitals span e_u and a_{1g} representation. The ligand orbitals transform as b_{1g} , a_{1g} and e_u state. Thus, in square planar field the splitting of the orbitals raises the energy of $d_{x^2-y^2}$ (b_{1g}) orbital at relatively higher energy from the other three d levels viz; $a_{1g}(d_{z^2})$, $b_{2g}(d_{xy})$ and $e_g(d_{xz}, d_{yz})$. The ground state for low spin d^8 configuration is thus, $a_{1g}^2, e_g^4, b_{1g}^4(^1A_{1g})$. The ligand field excited states are $^3A_{2g}$, $^1A_{2g}$, (b_{2g}, b_{1g}), ^3E_g , $E_g(e_g, b_{1g})$ and $^3B_{1g}(a_{1g}, b_{1g})$. Therefore, one should expect three spin allowed and three spin forbidden bond.

The spin allowed bands are:



and three spin forbidden bonds:



Due to relatively low ϵ_{max} value of spin forbidden transition the singlet triplet transitions are not observed in planar nickel (II) complexes.

The planar Ni (II) complexes can also display spin forbidden transitions of very low ϵ_{max} value in case of σ -bonding ligands. In present investigation Ni (II) complex $\text{Ni}[\text{Hm}(\text{BigH}^+)_2](\text{OH})_2 \cdot \text{H}_2\text{O}$ and $\text{Ni}[\text{Hm}(\text{BigH}^+)_2]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ display broad shoulder near 460 nm attributable to $^1A_{1g} \longrightarrow ^1B_{1g}$ transition in planar field.

Hence, the probable structure of Ni (II) complexes is square planar.

Unlike Co (II), the majority of Co (III) complexes are diamagnetic and low spin type. The term for free Co (III) ion (d^6) is ^5D . The free ion ground state energy level term ^5D splits into $^5T_{2g}$ and ^5E_g states in spin free

complex ion. Due to high cationic charge on Co^{III} (compared to Fe^{II} , d^6 system), $^1\text{A}_{1g}$ state originating from one of the high energy singlet (^1I) state of the free ion drops very rapidly and crosses the $^5\text{T}_{2g}$ state at a very low value of Δ . Thus, all Co (III) complexes known (except CoF_6^{3-}) are low spin type. The visible absorption spectra of cobalt (III) complexes display absorption from the $^1\text{A}_{1g}$ ground state to next upper energy level $^1\text{T}_{1g}$ and $^1\text{T}_{2g}$ state. In complexes of trivalent cobalt the spin forbidden transition $^1\text{A}_{1g} \longrightarrow ^5\text{E}_g$ or $^1\text{A}_{1g} \longrightarrow ^5\text{T}_{2g}$ are seldom observed. The complexes show absorption bands attributed from $^1\text{A}_{1g} \longrightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \longrightarrow ^1\text{T}_{2g}$. In D_{4h} symmetry the transition $^1\text{A}_{1g} \longrightarrow ^1\text{T}_{1g}$ splits or broadened due to splitting of $^1\text{T}_{1g}$ state. The electronic absorption spectra of complex sulphate (very qualitatively due to incomplete dissociation) displayed a broad band at 490 nm and second shoulder at 380 nm attributed from $^1\text{A}_{1g} \longrightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \longrightarrow ^1\text{T}_{2g}$ transitions respectively in octahedral field. Thus, from above experimental finding the probable structure of cobalt (III) complexes is octahedral.

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