



Spectral and Magnetic Aspects of some mixed ligand complexes of Co (III) ion with Acetylacetone and Biguanide

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Abstract: Complexes of Co(III) with biguanide and acetylacetone having molecular composition $[\text{Co}(\text{BigH}^+)_2(\text{acac})]X_n \cdot n\text{H}_2\text{O}$ have been prepared and characterized with the help of IR, UV and magnetic studies. The complexes of Co(III) were found to be diamagnetic. The results of spectral analysis and magnetic studies suggest an octahedral structure for the mixed ligand complexes of Co (III).

Keywords: Cobalt, mixed ligands, diamagnetic, IR, UV

I. Introduction

Complexes of biguanide and substituted biguanides with different metal ions are known from a long time¹⁻³ due to their strong coordination power and medical significance as a diabetic drug. Biguanide metal complexes are also known for their antimicrobial activities¹². Biguanide is bidentate ligand and it coordinates to the central metal here Co (III) through its imino and amino N-atoms. Acetyl acetone is also a bidentate ligand and it forms coordinate bond with the metal ion through the donor O-atoms in its enol-form.

Here, to study the chelating behavior, we have prepared and characterized the mixed ligand complexes of Co (III) with biguanide and acetyl acetone.

II. Materials and Methods

Materials: Dicyandiamide, Aluminium chloride, acetyl acetone, copper sulphate and all other chemicals required were available commercially and used as such.

Physical Measurements: The results of C, H, S and N were obtained from Central Drug Research Institute, Lucknow. The anions and metal ions were estimated by standard methods⁴⁻⁷. Magnetic properties were measured as reported earlier¹.

The result of U-V spectra was recorded on Carry 5000 UV-VIS-NIR spectrophotometer at SAIF STIC and the IR spectra were recorded on Perkin Elmer at Central Drug Research Institute, Lucknow. And the magnetic measurements (VSM) were done from CIF, IIT Guwahati.

The ligands and the complexes were prepared by the reported method³.

Synthesis of Ligand

Biguanide sulphate⁸ (m.p. 231–232°C) $\text{C}_2\text{H}_7\text{N}_5 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$

Biguanide sulphate was prepared according to the method described by Smolka and Friedrich with slight modification which resulted in a better yield. In this method, a mixture of ammonium chloride (NH_4Cl) and dicyandiamide, $\text{C}_2\text{H}_4\text{N}_4$ [dried at 100°C] in 2:1 proportion was mixed thoroughly in mortar and pestle and the mixture so obtained was then transferred to a dry pyrex beaker and heated over asbestos board by means of a Bunsen burner. During this process, the mixture was constantly stirred with the help of a glass rod and the temperature was raised gradually to 155°C. At this temperature, the mixture changed to a thick liquid and was maintained at this temperature $[155 \pm 2]^\circ\text{C}$ for ten minutes. The molten mass was then poured into a large volume of water and then treated with a solution of Cuprammonium sulphate, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$. As a result, rose-red coloured precipitate of copper biguanide sulphate was obtained at once. This was filtered in a Buchner funnel and was washed thoroughly with cold water. The precipitate should be kept over the Buchner funnel till water gets drained. The moist copper biguanide sulphate was then decomposed with cold solution of about 10% sulphuric acid. A blue solution was obtained which on keeping in cold $[12^\circ\text{C}]$ deposited large crystals of biguanide sulphate.

The yield was found to be best when a mixture of 8 gm of dicyandiamide with 16 gm of ammonium chloride was fused.

Found: C = 10.11%; N = 29.90%

$C_2H_7N_5 \cdot H_2SO_4 \cdot H_2O$ requires:

C = 10.21%; N = 29.78%

Preparation of Complexes

(a) Acetylacetonatobisbiguanidinium cobalt (III) hydroxide: The Bisbiguanidinium cobalt (III) hydroxide was prepared by adding with stirring calculated amount of biguanide sulphate, dissolved in slight excess of sodium hydroxide to a solution of cobalt sulphate. The yellow silky precipitate obtained was filtered quickly to avoid oxidation, on a Buchner funnel and was washed with ice cold water. This was then transferred to an aeration flask in which a suspension was made with a little water. Diamminebisbiguanidinium cobalt (III) hydroxide was prepared by passing a brisk current of air through a mixture of bisbiguanidinium cobalt (III) hydroxide and liquor ammonia for several hours, fresh ammonia being added from time to time the silky yellow bisbiguanidinium cobalt (III) hydroxide gradually dissolved to a red solution. The solution containing diamminebisbiguanidinium cobalt (III) hydroxide was filtered. The filtrate on acidification gave the diamminebisbiguanidinium cobalt (III) salt. Acetylacetonatobisbiguanidinium cobalt (III) hydroxide was prepared by heating a solution of diamminebisbiguanidinium cobalt (III) hydroxide, as prepared above, with acetyl acetone on steam bath. Acetyl acetone was added in small portions from time to time to compensate the loss by evaporation. When no further ammonia evolved, the solution on cooling deposited light red crystals in small amounts. The crystals were filtered, washed with water and alcohol. The compound was dried in a CO_2 free atmosphere. It was slightly soluble in water and aqueous solution is alkaline to litmus. On heating it decomposed to cobalt oxide with the evolution of acetyl acetone and ammonia. On analysis it was found to contain:

Co = 12.64%, N = 30.31%

Required for $[Co(BigH^+)_2(acac)](OH)_2 \cdot 4H_2O$ where “ $BigH^+$ ” stands for one molecule of biguanide and ‘acac’ for one molecule of acetyl acetone:

Co = 12.63%, N = 30.04%

(b) Acetylacetonatobisbiguanidinium cobalt (III) sulphate: The complex was prepared by heating a solution of diamminebisbiguanidinium cobalt (III) sulphate with acetyl acetone on a steam bath till the evolution of ammonia ceased. On cooling the solution, dark red crystals separated. The crystals were filtered, washed with water and alcohol and then dried in air. The complex is soluble in water. The air-dried sample on analysis was found to contain:

Co = 12.23%, N = 29.25%, SO_4 = 20.18%, H_2O = 3.82% (by loss at $110^\circ C$)

Required for $[Co(BigH^+)_2(acac)]SO_4 \cdot H_2O$:

Co = 12.43%, N = 29.54%, SO_4 = 20.24%, H_2O = 3.79%

(c) Acetylacetonatobisbiguanidinium cobalt (III) chloride: It was prepared by heating a solution of diamminebisbiguanidinium cobalt (III) chloride with acetylacetone on steam bath. The solution was concentrated to a small volume which on cooling deposited some orange crystals of trisbiguanidinium cobalt (III) chloride. These were filtered off. The filtrate on further cooling deposited dark violet red crystals. The crystals were filtered, washed with a small quantity of ice cold water and with alcohol. The air dried sample on analysis was found to contain:

Co = 13.26%, N = 31.41%, Cl = 15.64%, H_2O = 3.97% (by loss at $110^\circ C$)

Required for $[Co(BigH^+)_2(acac)]Cl_2 \cdot H_2O$:

Co = 13.12%, N = 31.19%, SO_4 = 15.79%, H_2O = 4.01%

(d) Acetylacetonatobisbiguanidinium cobalt (III) nitrate: Diamminebisbiguanidinium cobalt (III) hydroxide prepared as described above was neutralized with dilute nitric acid in cold. The solution on cooling deposited red crystals of diamminebisbiguanidinium cobalt (III) nitrate. This was then heated on steam bath with acetylacetone. The colour of the solution changed to dark red. On cooling, red needle shaped crystals separated. The crystals were filtered, washed with water and alcohol. The air dried substance on analysis was found to contain:

Co = 11.84%, N = 33.35%, NO_3 = 24.96%, H_2O = 3.52% (by loss at $105^\circ C$)

Required for $\left[\text{Co}(\text{BigH}^+)_2(\text{acac})\right](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$

Co = 11.73%, N = 33.47%, $\text{NO}_3 = 24.68\%$, $\text{H}_2\text{O} = 3.58\%$

(e) Acetylacetonatobisbiguanidinium cobalt (III) oxalate: It was prepared by adding a solution of sodium oxalate to a solution of the complex chloride. The first crop of orange crystals was filtered out. The filtrate on cooling gave fine reddish violet crystals of the complex oxalate. The crystals were filtered, washed with water and alcohol and dried in air. The air dried compound on analysis was found to contain:

Co = 11.15%, N = 26.66%, $\text{C}_2\text{O}_4 = 16.72\%$

Required for $\left[\text{Co}(\text{BigH}^+)_2(\text{acac})\right]\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$

Co = 11.33%, N = 26.92%, $\text{C}_2\text{O}_4 = 16.91\%$

When a solution of the complex oxalate was heated with an excess of oxalic acid on the steam bath dark violet crystals of oxalatooxalate were obtained, which on analysis was found to contain:

Co = 14.01%

Required for $\left[\text{Co}(\text{BigH}^+)_2(\text{C}_2\text{O}_4)_2\right]\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$

Co = 13.95%

III. Results and Discussions

Electronic spectra⁹

The Co (III) complexes show two bands, one at around 480 – 490 nm is attributed to $(^1\text{A}_{1g} \longrightarrow ^1\text{T}_{1g})$ and other at around 260 – 265 nm due to $(^1\text{A}_{1g} \longrightarrow ^1\text{T}_{2g})$ and charge transfer transitions.

The diamagnetic behaviour and absorption at these bands suggests octahedral structure for the complexes of Co (III) ion with biguanide and acetyl acetone ligands.

Infra Red Spectra^{10,11}

In the free ligand ‘biguanide’ the band due to $-\text{NH}_2$ group is observed at 3389.82 cm^{-1} , N–H stretching in $-\text{NH}_3^+$ group is present at 3019.47 cm^{-1} and 2399.56 cm^{-1} .

The N–H deformation band is observed at 929.11 cm^{-1} and the N–H out of plane vibration occurs at 769.74 cm^{-1} . The C–N stretching vibration is shown at 1069.67 cm^{-1} . A strong band at 1215.88 cm^{-1} is due to the vibration of SO_4^{2-} group.

The C = N stretching vibration in free ligand is shown at 1626.49 cm^{-1} while in complexes a higher shift in $\nu(\text{C}=\text{N})$ vibration ($1633.07\text{--}1646.60\text{ cm}^{-1}$) is observed. A higher shift in $\nu(\text{C}=\text{N})$ stretching frequency on complex formation could be attributed to the formation of a metal – nitrogen bond¹².

The metal complex shows a broad band in the range $3000\text{--}3400\text{ cm}^{-1}$ assignable to the vibrations due to $-\text{NH}$ and $-\text{OH}$ groups. In the complexes band around $1385\text{--}1403\text{ cm}^{-1}$ are due to N–C–N vibration and C = C and C = O stretching vibrations due to the acetylacetonate group. The vibration due to $-\text{CH}_3$ group is shown at $1068.45\text{--}1069.88\text{ cm}^{-1}$.

In metal complexes the intensity of metal nitrogen bond is very weak and generally observed below 500 cm^{-1} . Since the IR spectra of the complex in the region $500\text{--}400\text{ cm}^{-1}$ is not well resolved therefore, the band due to metal-ligand vibrations could not be assigned¹³.

IV. Conclusion

On the basis of stoichiometry, magnetic measurements, spectral studies (IR & electronic absorption) and physico-chemical properties octahedral structure have been proposed for these mixed ligand metal biguanide complexes.

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VI. References

- [1]. R. K. Prasad, (Mrs) Bina Rani and Dhananjai Singh, J. Indian Chem. Soc., 83, 718, (2006).
- [2]. R.K. Prasad, (Mrs) Bina Rani, Divya Singh and Dhananjai Singh, AIJRSTEM, 2, 108, (2014).
- [3]. P. Ray, Chem. Rev., 61, 313, (1961).
 - a. S. P. Ghosh, R. K. Prasad and (Mrs) Bina Rani, J. Indian Chem. Soc., 80, 912, 914 ; (2003).
 - b. S. P. Ghosh, R. K. Prasad, J. Indian Chem. Soc., 64, 765, (1987).

- c. S. P. Ghosh, H. M. Ghosh, J. Indian Chem. Soc., **33**, 899, (1956).
- d. P. Ray and N. R. Sengupta, J. Indian Chem. Soc., **36**, 201, 1959.
- e. S. P. Ghosh and A. I. P. Sinha, J. Indian Chem. Soc., **38**, 179, (1961).
- f. J. Inorg. Nucl. Chem., **41**, 330, (1964).
- g. T. R. Bera and J. Konar, J. Indian Chem. Soc., **74**, 528, (1997).
- h. S. Ghosh, C. C. Mukhopadhyay, G. S. De and A. K. Ghosh, J. Indian Chem. Soc., **75**, 219, (1998).
- i. Tannistha Roy Barman and G. N. Mukherjee, J. Chem. Sci., **118**, 411, (2006).
- j. A. Syamal, Chem. Educ. **4**, 33, 1987; **5**, 26, (1988).
- k. W. E. Swartz. Jr. and R. A. Afanzo, J. Electron, Spectrosc, Relat Phenom., **406**, 124, (1974).
- l. S. N. Nandi and D. Banerjee; Z. Anorg. Allg. Chem., **406**, 124, (1974).
- m. T. C. Creitz, R. Gsell and D. L. Wampler, J. Chem. Soc., Chem. Soc., Chem. Commun. 1371, (1969).
- n. D. Sen, J. Chem. Soc. (D), **52**, 174, (1975).
- [4]. R.K. Prasad, (Mrs.) Bina Rani and Dhananjai Singh, J. Indian Chem. Soc., **83**, 718 (2003).
- [5]. P. Ray and K. Chakravarty, J. Indian Chem. Soc., **18**, 609, (1941).
- [6]. P. Ray and N. N. Ghosh, J. Indian Chem. Soc., **15**, 350, (1938).
- [7]. A textbook of Quantitative Inorganic Analysis A.I. Vogel Longman Scientific and Technical copublished by John Wiley & Sons, (5th Edition) 1989.
- [8]. Smolka and Friedrich, Monatsh., **9**, 227 (1888).
- [9]. F. Albert Cotton, Geoffrey Wilkinson, Carlos A. Murillo, Manfred Bochmann, Advanced Inorganic Chemistry, 6th Edition.
- [10]. P. Ray and A. Choudhary, J. Indian Chem. Soc., **27**, 615, (1950).
- [11]. Infrared and Raman Spectra of Inorganic and Coordination Compound, K. Nakamoto, John Wiley, New York, 1988.
- [12]. R.K. Ray and G.B. Kauffman, Metal and Non-Metal Biguanide Complexes, 1st Edition, (2010).
- [13]. Divya Singh, Bina Rani and R.K. Prasad, AIJRSTEM, Issue 19, Vol. 1, (75-78), 2017.