

NOTE

Spectrochemical, EXAFS and Studies of Co(II), Ni(II) and Cu(II) Complexes of Thioglycolanalide

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Complexes of Co(II), Ni(II) and Cu(II) with thioglycolanalide (TGA) have been synthesised. Analytical studies show a 1 : 2 (M : L) stoichiometry for Ni(II) and Co(II) complexes while for copper the stoichiometry is found to be 1 : 1 and copper is present in the complex in Cu(I) state. The electronic spectral studies suggest octahedral geometry for Co(II) and Ni(II) complexes and is supported by EXAFS and XANES. Infrared studies indicate bonding through >C=O and —SH groups.

Key Words: Spectrochemical, TGA, EXAFS, XANES, Metal complexes

Thioglycolanalide (TGA) is a condensed product of thioglycolic acid and aniline. It acts as a strong chelating agent because of the presence of acidic —SH group and coordinating >C=O group but surprisingly it forms chelates with sulphide forming cations¹. The ligand has been used as a gravimetric reagent, as a reductant, as a selective detection reagent and a spectrophotometric reagent for quantitative estimation of trace amount of Co(II) as in *m*-MAP²⁻⁵. In the present communication we are reporting the electronic and infrared spectral studies, magnetic moment and EXAFS and XANES studies of Co(II), Ni(II) and Cu(II) complexes.

The ligand was synthesised by refluxing thioglycolic acid and aniline in 1 : 1 ratio at 115°C in CO₂ atmosphere⁵. It was washed with 10% HCl to remove unreacted aniline and was crystallised by 40% ethanol. The complexes were prepared by adding alcoholic solution of the ligand to the metal sulphate in 1 : 2 [MSO₄ : ligand] ratio. Copper complex precipitated at pH 2.0–2.5 while nickel and cobalt complexes precipitated between pH 6.0–7.5. In case of copper first a black precipitate was obtained which immediately changed to yellow. This suggested that before complexation Cu(II) is reduced to Cu(I). This was confirmed by first reducing Cu(II) to Cu(I) by SO₂ water. All these complexes are insoluble in almost all solvents except DMF and sodium hydroxide solution.

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Solid state reflectance spectra of all the complexes were recorded in the region 200–900 nm with MgO as a standard. Infrared spectrum was recorded on Perkin-Elmer 210 in KBr. Elemental analysis of the complexes was done at CDRI, Lucknow. Sulfur and metal ions were estimated by usual methods. Magnetic moment measurements were carried out using Gouy balance with $\text{Hg}[\text{Co}(\text{CNS})_4]$ as a standard. EXAFS and XANES studies were carried out by usual techniques.

The magnetic moment for Ni(II) and Co(II) complex is of the order of 2.40 BM and 4.69 BM respectively indicating that the complexes are octahedral^{6,7}. The copper complex is diamagnetic as expected. Analytical data indicate $\text{ML}_2 \cdot 2\text{H}_2\text{O}$ stoichiometry for Co(II) and Ni(II) complexes, while $\text{ML} \cdot 2\text{H}_2\text{O}$ for copper complex. The sharp band around 2570 cm^{-1} due to $\nu(\text{—SH})$ is missing in the complex while the peak at 1748 cm^{-1} due to $\nu(>\text{C}=\text{O})$ is shifted slightly towards the higher side. This suggests the involvement of —SH and $>\text{C}=\text{O}$ in bonding. The presence of water molecule has been confirmed by infrared spectrum which has a peak around 850 cm^{-1} due to coordinated water molecule⁸. Thus the ligand TGA acts as a bidentate and forms a chelate ring with water molecules occupying the axial position.

Three bands at 23810 , 14710 and 13107 cm^{-1} are observed for Ni(II) complex and are assigned to $3\text{T}_{1g}^{\text{P}} \leftarrow 3\text{A}_{2g}$, $3\text{T}_{1g}^{\text{F}} \leftarrow 3\text{A}_{2g}$ and $1\text{E}_g \leftarrow 3\text{A}_{2g}$ transitions respectively. The weak band appearing around 13000 cm^{-1} can be treated as the forbidden triplet singlet transition. Co(II) complex of TGA shows two maxima at 23260 and 15630 cm^{-1} corresponding to $4\text{A}_{2g}^{\text{F}} \leftarrow 4\text{T}_{1g}^{\text{F}}$ and $4\text{T}_{1g}^{\text{P}} \leftarrow 4\text{T}_{1g}^{\text{F}}$ transitions respectively. The calculated values⁹ of 10 Dq , B and β are 8762 cm^{-1} , 748 and 0.69 respectively for Ni(II) complex and 10377 cm^{-1} , 567 and 0.506 respectively for Co(II) complex.

Non-splitting behaviour of the K-absorption edge in case of Co(II) complex suggests that the complex is not a distorted octahedral complex. A comparison of the values of chemical shifts for cobalt complex with the one reported by other workers¹⁰ reveal that the cobalt ion is present in +2 oxidation state in the complex. The shift in the principal maximum 14.29 and ΔE_{K} is 6.82 . The average bond length is 2.41 \AA . For copper complex the shift in the principal maximum 16.42 and ΔE_{K} is 0.35 . Similar lower values of ΔE_{K} have been observed in case of Cu(I) thioenol complex by Nigam and Shrivastava¹¹ and for Cu_2Cl_2 and Cu_2I_2 by Ballal and Mande¹². Thus the lower value of the shift suggests that copper is present as Cu(I) in the complex of TGA. The average bond length for Cu(I) complex is 2.13 \AA .

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