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NOTE

Spectrochemical, EXAFS and XANES Studies of Cu(II), Ni(II) and Co(II) Complexes of *m*-Mercaptoacetamido Phenol

V.W. BHAGWAT,* P.C. NAHAR and ASHUTOSH MISHRA†
School of Studies in Chemistry, Vikram University, Ujjain-456 010, India

Complexes of Cu(II), Ni(II) and Co(II) with *m*-mercaptoacetamido phenol (*m*-MAP) 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 group.

m-Mercaptoacetamido phenol (*m*-MAP) is a condensed product of thioglycolic acid and *m*-amino phenol. It acts as strong chelating agent because of the presence of acidic —SH group and coordinating —C=O group but surprisingly it forms chelates with sulphide forming cations. The ligand has been used as a gravimetric reagent, as a reductant, as a selective detection reagent and as a spectrophotometric reagent for quantitative estimation of trace amounts of Co(II)[1–4]. In the present communication we are reporting the electronic and infrared spectral studies, magnetic moment and EXAFS and XANES studies of Cu(II), Ni(II) and Co(II) complexes.

The ligand was synthesised by refluxing thioglycolic acid and *m*-amino phenol in 1 : 1 ratio at 120°C in CO_2 atmosphere[4]. It was washed with 10% HCl to remove unreacted amino phenol and was crystallised from 50% ethanol. The complexes were prepared by adding alcoholic solution of the ligand to the metal sulphates in 1 : 2 [MSO_4 : Ligand]. Copper complex precipitated at pH 2.0 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 copper(II) is reduced to copper(I). This was confirmed by first reducing copper(II) to copper(I) by SO_2 water. All these complexes are insoluble in almost all solvents except DMF and sodium hydroxide solution.

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. Sulphur and metal ions were estimated by usual methods. Magnetic moment measurements were carried out using Gouy balance with $Hg[Co(CNS)_4]$ as a standard. EXAFS and XANES studies were carried out by usual techniques.

The magnetic moments for Co(II) and Ni(II) complexes are of the order of

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†Department of Physics, D.A.V.V. Campus, Khandawa Road, Indore-452 001, India.

4.68 BM and 2.90 BM respectively indicating that the cmplexes are octahedral[5]. The copper complex is diamagnetic as expected. Analytical data indicate $ML_2 \cdot 2H_2O$ stoichiometry for Co(II) and Ni(II) complexes while $ML \cdot 2H_2O$ for copper complex. The presence of water molecule has been confirmed by infrared spectrum which has a peak around 860 cm^{-1} typical of coordinated water molecule[6]. The sharp band around 2530 due to —SH is missing in the complex while the peak at 1670 cm^{-1} due to —C=O is shifted slightly towards the higher side. This suggest the involvement of —SH and —C=O in bonding. Thus the *m*-MAP acts as a bidentate ligand and forms a chelate ring with water molecules occupying the axial position.

Three bands at 29410 cm^{-1}, 21280 cm^{-1} and 17860 cm^{-1} are observed for Co(II) complex and are assigned to $4A_{(2g)}{}^{F} \longleftarrow 4T_{(1g)}{}^{F}$, $4T_{(1g)}{}^{P} \longleftarrow 4T_{(1)}{}^{F}$ and $4T_{(2g)}{}^{P} \longleftarrow 4T_{(1g)}{}^{F}$ transitions. Nickel complex of *m*-MAP shows two maxima at 23260 cm^{-1} and 15630 cm^{-1} corresponding to $3T_{(1g)}{}^{P} \longleftarrow 3A_{(2g)}$ and $3T_{(1g)}{}^{F} \longleftarrow 3A_{(2g)}$. The calculated values[7] of 10 Dq, B and β are 15198 cm^{-1}, 591 cm^{-1} and 0.527 respectively for Co(II) complex and 8413 cm^{-1}, 793 cm^{-1} and 0.773 respectively for Ni(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. The shift in the principal absorption maxima is 16.67 and ΔE_k is 6.96. The average bond length is 2.43 Å. For copper complex the shift in the principal absorption maximum is 24.1 and ΔE_k is 2.57. Similar lower values of ΔE_k have been observed in case of Cu(I) thiovenol complex by Nigam and Shrivastav[8] and for CuCl and CuI by Ballal and Mande[9]. Thus the lower value of the suggests that copper is present as Cu(I) in the complex of *m*-MAP. The average bond length for Cu(I) complex is 1.95 Å.

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