

Spectral, magnetic and thermal studies of transition metal complexes of δ (3-carboxy, 4-hydroxy benzoyl) pentanoic acid

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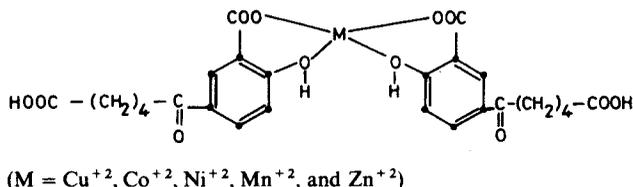
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Abstract. Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) form 1:2 complexes while Fe(III) forms 1:3 complex with δ (3-carboxy, 4-hydroxy benzoyl) pentanoic acid. Their structures have been proposed on the basis of analytical, spectral, thermal and magnetic measurements. The infrared spectra provide an evidence for the replacement of the aromatic carboxylic group hydrogen but not the phenolic group hydrogen.

Keywords. δ (3-carboxy, 4-hydroxy benzoyl) pentanoic acid; salicylic acid; transition metal complexes

1. Introduction

In recent years metal carboxylates have attracted considerable attention in chemistry because of their importance in industry and their interesting structure (Bassi *et al* 1980). Inoue *et al* (1964) reported magnetic moment of Cu(II) salicylate. Koppikar and Soundararajan (1976) studied diiodosalicylates of rare earths. A large number of derivatives of salicylic acid with metal halides have been reported (Goyal and Khosla 1980). However no study of transition metal complexes of δ (3-carboxy, 4-hydroxy benzoyl) pentanoic acid has been reported so far. Hence this study.



2. Experimental

2.1 Preparation of pentanoic acid

Polyphosphoric acid (50 g) was added to a mixture of salicylic acid (0.05 mol, 6.9 g) and adipic acid (0.075 mol, 10.95 g). After mixing, the reaction mixture was heated at 110°C for 4 hr. The solid obtained was added to the ice-cold water, filtered and washed with hot water. It was purified by dissolving in 10% alkali solution and precipitated as a brownish green coloured compound with ice cold 10% HCl. It is soluble in alcohol with a melting point of 150°C.

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2.2 Preparation of complexes

The complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Fe(III) were prepared by mixing the solution of metal chloride in water and solution of $\delta(\text{CHB})\text{PA}$ in absolute alcohol in a stoichiometric 1 : 2 molar ratio (metal : ligand) for bivalent metal ions and 1 : 3 for Fe^{+3} . Precipitates were obtained by addition of sodium acetate. The complexes were washed with hot water and ethanol.

2.3 Elemental analyses

Carbon and hydrogen were microanalysed by Coleman carbon hydrogen analyzer.

2.4 Metal content in the complexes

Known amounts of the metal complexes were decomposed with AR conc. HCl, HNO_3 , HClO_4 and H_2SO_4 . The residue was cooled, dissolved in water and made up to a known volume in a volumetric flask. All the metal ions were determined by EDTA titration using appropriate indicator.

2.5 Physical measurements

Magnetic susceptibility of the complexes at room temperature was determined by Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. Molar susceptibilities were corrected for diamagnetism of the constituent elements using Pascal's constants. The IR spectra of ligand and complexes were recorded in the form of KBr pellet on UR-10 spectrophotometer in the range $3600\text{--}400\text{ cm}^{-1}$. Diffuse reflectance spectra in the solid state were obtained from a Beckman DU spectrophotometer using MgO as reference. TG data were obtained from an assembly capable of producing temperatures up to 800°C with a heating rate 10° min^{-1} .

3. Results and discussion

The important thermal, spectral and magnetic moment data of the complexes are summarised in table 1. The infrared spectra provide important information about the attachment of ligand to the metal ions. IR spectra of all the metal complexes show absorption characteristic of the asymmetric (at 1600 cm^{-1} as compared to 1670 cm^{-1} in free ligand) $\nu_{\text{as}}\text{COO}$ for coordinated carboxylate group attached to the aromatic ring (Mishra and Jha 1980). The broad band observed in the ligand due to phenolic --OH reduced from $2500\text{--}3600\text{ cm}^{-1}$ to $3300\text{--}3600\text{ cm}^{-1}$ in complexes indicating removal of hydrogen bonding (Garg *et al* 1971). The IR spectral studies thus suggest that aromatic carboxylic group hydrogen is replaced and the phenolic group remains in tact.

The analytical data agree with the general formula ML_2 (where M = bivalent metal ions) and ML_3 (where M = Fe(III)). TGA data show that the decomposition of the complexes starts at 200 (Cu), 250 (Ni), 260 (Co), 250 (Mn), 260 (Zn) and 220°C (Fe) and complete decomposition of the organic material takes place at $550\text{--}660^\circ\text{C}$ leaving a residue of the metal oxide. Nickel(II) complex shows 5.96% wt loss at 220°C corresponding to loss of two coordinated water molecules.

The magnetic moment of the copper compound is 2 BM which is very close to the spin only value of 1.73 BM expected for one unpaired electron. The excess of magnetic

Table 1. Thermal, spectral and magnetic moment data of the complexes.

Compound	Decomposition Temp (°C)	μ_{eff} (BM)	Energies	Transition	
δ (CHB) PA	220				
Cu [δ (CHB) PA] ₂	200	2.00	14285	${}^2B_{1g} \rightarrow {}^2B_{2g}$	
Ni [δ (CHB) PA · H ₂ O] ₂	250	2.71	8770	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	
			14290	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
			22222	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
Co [δ (CHB) PA] ₂	260	3.86	8000	${}^4A_2 \rightarrow {}^4T_1(F)$	
			16667	${}^4A_2 \rightarrow {}^4T_1(P)$	
Mn [δ (CHB) PA] ₂	250	4.42	20000	${}^6A_1 \rightarrow {}^4T_1(G)$	
				${}^6A_1 \rightarrow {}^4T_2(G)$	
				${}^6A_1 \rightarrow {}^4E_1, {}^4A_1(G)$	
Fe [δ (CHB) PA] ₃	220	4.84	20000	${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$	
				14285	${}^6A_{1g} \rightarrow {}^4T_{2g}$
				12500	${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$
Zn [δ (CHB) PA] ₂	260	Diamagnetic	—		

moment to spin only value (1.73 BM) might be due to orbital contribution (Baker *et al* 1966). The magnetic susceptibility data wants detailed examination because of the low values obtained in the case of Ni(II), Co(II), Mn(II) and Fe(III) complexes. Ni(II) complex shows a magnetic moment of 2.71 BM which is lower than the spin only value. This may be due to the octahedral distortion (Rastogi and Sharma 1974). Cobalt(II) complex exhibits magnetic moment of 3.86 BM which is lower than that expected for regular tetrahedral Co(II) complexes. The subnormal magnetic moment may be due to the covalent nature of the metal ligand bonds (Sengupta *et al* 1981). The room temperature magnetic moment of the Mn(II) complex is 4.42 BM which does not conform well with the spin only moment expected for the spin free configuration. The low value of magnetic moment may be due to aerial oxidation of Mn(II) \rightarrow Mn(III) during preparation. However, some workers explain this low magnetic moment on the basis of antiferromagnetic interaction between manganese(II) ions in solid state (Patel and Patil 1982). The effective moment of the Fe(III) complex is 4.84 BM which is quite lower than the spin only value of 5.92 BM for high spin d^5 system. Subnormal magnetic moment can be interpreted in terms of antiferromagnetic behaviour (Syamal and Kale 1980). In most cases the electronic spectrum of Cu(II) complex possesses only a single broad band, making the assignment of individual electronic transition difficult (Patel *et al* 1981). A broad band at 14285 cm^{-1} is observed which may be assigned to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition for square planar stereochemistry (Patel *et al* 1981). Nickel(II) complex shows bands at 8770 cm^{-1} (ν_1), 14290 cm^{-1} (ν_2) and 22222 cm^{-1} (ν_3) which may be assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions respectively for distorted octahedral stereochemistry (Lever 1968). The value of B (Racah inter-electronic repulsion parameter) was calculated using the method suggested by Konig (1971). The calculated values of B , β and CFSE are found to be 680 cm^{-1} , 0.629 and 30.08 kcal/mol respectively. The ratio ν_2/ν_1 (1.60) supports distortion in octahedral stereochemistry (Arora and Misra 1982). The reflectance spectrum of Co(II) complex under study shows two bands at 8000 and 16667 cm^{-1} assigned to ${}^4A_2 \rightarrow {}^4T_1(F)$ and ${}^4A_2 \rightarrow {}^4T_1(P)$ transitions respectively for tetrahedral

structure (Patel and Patil 1982). The transition energies ν_1 , ν_2 and ν_3 have been calculated using the known relation (Konig 1971). The values of B , β and $CFSE$ are found to be 895.8 cm^{-1} , 0.80 and 12.8 kcal/mole respectively. Manganese (II) complex exhibits a broad absorption band at 20000 cm^{-1} which may be assigned to the group of three lowest energy bands as ${}^6A_1 \rightarrow {}^4T_1(G)$, ${}^6A_1 \rightarrow {}^4T_2(G)$ and ${}^6A_1 \rightarrow {}^4E, {}^4A_1(G)$ for tetrahedral stereochemistry (Forster and Goodgame 1964). In Fe(III) complex three bands are observed at 20000 , 14285 and 12500 cm^{-1} attributable to ${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ transitions for octahedral stereochemistry (Srivastava *et al* 1974). The Zn(II) complex is diamagnetic and may have a tetrahedral structure.

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