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Magnetic and Spectral Investigations of Some Mixed Ligand Complexes of Bis(thioformohydroxamato) Cobalt(II)

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ABSTRACT

Mixed ligand complexes of bis(thioformohydroxamato) cobalt(II) with 1,10-phenanthroline and 2,2-bipyridyl have been synthesized, and their magnetic and spectral characteristics are reported.

INTRODUCTION

A survey of the literature reveals that a fair amount of work has been recently published emphasizing the characteristics of binary complexes of thiohydroxamic acids [1-5]. However, little work appears to have been carried out on the mixed complexes of these compounds. The present article describes the syntheses and magnetic and spectral behavior of mixed ligand complexes of diaquo-bis(thioformohydroxamato) cobalt(II) with, 1,10-phenanthroline or 2,2-bipyridyl.

EXPERIMENTAL

A solution of cobalt chloride 6 hydrate (0.01 mol) in ethanol-water was added to a solution of sodium thioformohydroxamate (0.02 mol) with constant stirring. The mixture was then refluxed for 4 h and the volume was reduced to 10 mL under reduced pressure. The separated Co(II) complex was filtered, washed with water, and dried in vacuo.

A stoichiometric amount of 1,10-phenanthroline or 2,2-bipyridyl, dissolved in minimum volume of ethanol, was added to the corresponding solution of bis(thioformohydroxamato) Co(II) in ethanol. The resulting solution was refluxed for an hour in nitrogen atmosphere. The crystalline solid separated out was filtered, washed with water, and dried in vacuo. The purity of complex was established by elemental analysis. Analytical data agreed with the composition of the complex within the limits of experimental errors.

The electronic spectra were measured on Carl Zeiss VSU-2 Spectrophotometer in ethanol. The IR spectra of the complexes were recorded on a Perkin-Elmer grating spectrophotometer. The magnetic measurements were carried out on Gouy magnetic balance at 300 ± 1 K.

RESULTS AND DISCUSSION

Three d-d transitions [6] are observed in the ground state of divalent cobalt: $4T_{1g}(F) \rightarrow 4T_{2g}$, $4T_{1g}(F) \rightarrow 4A_{2g}$, and $4T_{1g}(F) \rightarrow 4T_{1g}(P)$. These transitions are denoted by γ_1, γ_2 and γ_3, respectively. Under present investigations, the γ_3 band in these low spin Co(II) complexes occurs in the region 21,696-20,474 cm^{-1} as a shoulder, the band γ_2 occurs in the region 17,648-17,456 cm^{-1}, and the band γ_1 lies between the range of 8,820-8,534 cm^{-1}. The electronic spectral patterns of these chelates are found to be similar to those of the octahedral hexaquo cobalt(II) ions, thereby suggesting an octahedral stereochemistry for these low spin Co(II) complexes. The value for the Racah interelectronic repulsion parameter (B) and the crystal field splitting energy (10 Dq) have been computed following a strong field coupling scheme [7] (Table 1). The lower value of the nephelauxetic ratio β in mixed ligand chelates as compared to their parent complex, shows that there is an increase in the covalency on complexation.

TABLE 1. Calculated Values for Parameter B, 10 Dq (in cm^{-1}), β, and Magnetic Moment (in B.M.)

Complex	B	10 Dq	β	μ_{eff}
$Co(TFH)_2(H_2O)_2$	572.4	12826	0.49	1.75
$Co(TFH)_2(Bpy)$	447.6	11312	0.38	1.72
$Co(TFH)_2(Phen)$	396.3	11288	0.42	1.69

The values of magnetic moments (μ_{eff}) for the complexes lie between 1.69-1.75 B.M., close to the spin only moment value of 1.73 B.M. It clearly indicates the stereochemistry as a low spin-octahedral having one unpaired electron [8, 9].

The infrared spectrum of the parent complex $Co(TFH)_2(H_2O)_2$ has confirmed the presence of coordinated water molecules due to the presence of a band at 3410 cm^{-1}. The IR spectra of mixed ligand complexes do not show absorption in this region, which is indicative of the absence of water molecule. Hence these complexes are anhydrous.

The vibrations due to coordinated thioformohydroxamic acid, γ(OH), γ(C=S), γ(N–O), and γ(M–N), have been found to occur in the region 3120-3080, 1110-1080, 935-905, and 510-500 cm^{-1}, respectively. Since certain absorptions in both the coordinated ligands [viz., thioformohydroxamic acid and second ligand (1,10-phenanthroline or 2,2-bipyridyl)] are observed in the same region, it is difficult to assign particular absorption bands in detail. However, it has been observed that the bands of both the ligands of the complex are modified on chelation, clearly indicating their coordination to the metal atom.

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