

## NOTES

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

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

The chelating behaviour of thiohydroxamic acids has extensively been studied and reported from our laboratories.<sup>1-3</sup> Survey of the literature reveals that solution studies of binary chelates of thiohydroxamic acids, have been undertaken by different workers due to the wide biocidal activities of thiohydroxamic acids. However, little work appears to have been carried out on the mixed complexes of these compounds. The present communication describes the synthesis, magnetic and spectral behaviour of mixed ligand complexes of diaquo-bis (thioacetohydroxamato) cobalt(II) with 1, 10-phenanthroline (Phen) and 2, 2'-bipyridyl (Bipy).

A solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.01 mole) in ethanol-water was added to a solution of sodium thioacetohydroxamate (0.02 mole) with constant stirring. This mixture was then refluxed for 4 hrs. and the volume was reduced to 10 ml. under reduced pressure. The separated cobalt(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 (thioacetohydroxamato) cobalt(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.

Three d-d transitions<sup>4</sup> are observed in the ground state of divalent cobalt:  $4\text{T}_{1g}(\text{F}) \rightarrow 4\text{T}_{2g}$ ,  $4\text{T}_{1g}(\text{F}) \rightarrow 4\text{A}_{2g}$  and  $4\text{T}_{1g}(\text{F}) \rightarrow 4\text{T}_{1g}(\text{P})$ . These transitions are denoted by  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  respectively. Under present investigations, the  $\nu_3$  band in these low spin cobalt(II) complexes occurs

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in the region 20,974–19,886  $\text{cm}^{-1}$  as a shoulder, the band  $\nu_2$  occurs in the region 18,132–17,984  $\text{cm}^{-1}$ , and the band  $\nu_1$  lies between the range of 8546–8288  $\text{cm}^{-1}$ . 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 cobalt(II) complexes. The value for Racah interelectronic repulsion parameter (B) and the crystal field splitting energy (10 Dq) have been computed following a strong field coupling scheme<sup>4</sup> (Table 1). The lower value of nephelauxetic ratio  $\beta$  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 OF PARAMETERS B, 10 Dq (in  $\text{cm}^{-1}$ ),  
 $\beta$  AND MAGNETIC MOMENT (B. M.)

Complex	B	10 Dq	$\beta$	$\mu_{\text{eff}}$
$\text{Co}(\text{TAH})_2(\text{H}_2\text{O})_2$	604.6	13282	0.53	1.84
$\text{Co}(\text{TAH})_2(\text{Bipy})_2$	562.3	12064	0.44	1.76
$\text{Co}(\text{TAH})_2(\text{Phen})_2$	438.6	11986	0.38	1.70

The values of magnetic moment ( $\mu_{\text{eff}}$ ) for the complexes lie between 1.70–1.84 B.M., close to the spin only moment value of 1.75 B.M. It clearly indicates the stereochemistry as a low spin-octahedral having one unpaired electron<sup>5-7</sup>.

The infrared spectrum of the parent complex  $\text{Co}(\text{TAH})_2(\text{H}_2\text{O})_2$  has confirmed the presence of coordinated water molecules due to the presence of a band at 3390  $\text{cm}^{-1}$ . The IR spectra of mixed ligand complexes do not show absorption in this region, which is indicative of the absence of water molecules. Hence these complexes are anhydrous. The vibrations due to coordinated thiohydroxamic acid,  $\nu(\text{OH})$ ,  $\nu(\text{C-S})$ ,  $\nu(\text{N-O})$  and  $\nu(\text{M-N})$  have been found to occur in the region 3200–3160, 1125–1090, 970–955 and 490–475  $\text{cm}^{-1}$ , respectively. Since certain absorptions in both the coordinated ligand viz. thioacetohydroxamic 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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