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Synthesis and Characterization of Polymeric Complexes of Cobalt(II) with Chloro Substituted 2-Hydroxyacetophenone Oximes

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SUMMARY

The polymeric complexes of cobalt (II) with 5-chloro 2-hydroxyacetophenone oxime and 3,5- dichloro-2-hydroxyacetophenone oxime were synthesised and characterized by elemental analysis, magnetic measurements and spectral studies.

INTRODUCTION

In continuation of the earlier work (Lal et al. 1977) on the complexes of substituted 2- hydroxyacetophenone oxime, the results of polymeric complexes of cobalt (II) with 5-chloro-2-hydroxyacetophenone oxime (CHAO) and 3,5-dichloro-2-hydroxyacetophenone oxime (DCHAO) are reported here.

EXPERIMENTAL

The reagents CHAO and DCHAO were synthesised (Vogel 1972) and their ethanolic solution was used. The solution of $CoCl_2 . 6H_2O$ (B.D.H., AnalaR) was prepared in double distilled water.

A Varian V-4502-12 EPR spectrophotometer was used for ESR spectra. All other apparatus were used as reported earlier (Lal et al. 1977).

To a aqueous solution of cobalt chloride (50 ml, 0.02 M) ethanolic solution of CHAO was added with constant stirring. The pH of the solution was raised to 8.5, a pinkish precipitate appeared which was extracted into

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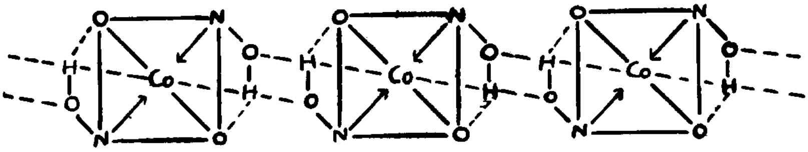
chloroform. On crystallization dark brown coloured complex was obtained. A similar procedure was adopted with DCHAO.

The complexes were analysed for the elements by usual methods, and found (%) Co-13 . 68, N-6.64 Cl-16.65; calculated (%) Co-13.76, N-6.54 Cl - 16.59 for $(CoC_{16}H_{14}N_2O_4Cl_2)_x$ and found (%) Co -11.74, N- 5.70 Cl-28.66; calculated (%) Co-11.85, N-5.63 Cl-28.58 for $(CoC_{16}H_{12}N_2O_4Cl_4)_x$.

RESULTS AND DISCUSSION

The magnetic moment (1.93 B.M.) of the complexes favour low spin O_h geometry (Figgis & Lewis 1964). It is apparent, therefore that the treatment with chloroform causes an increase in the coordination number 4 to 6. Since the conversion of the monomeric form to polymeric form does not involve any change in composition, thus attainment of hexa- coordination appears to be through the participation of the coordinatively unsaturated oxygen atom of the oximino group as shown in the figure.



The value of g was calculated from ESR spectra of the complexes and found to be 2.060 and 2.063 for CHAO and DCHAO complexes of cobalt (II). The effect of proposed molecular association would be the interaction of the ligands on the axial sites. This may move the dz^2 orbital above and dyz orbital leading to the ground state (Schmidt et al. 1967) $(dxy\ dyz\ dxz)^6\ (dz^2)^1$. EPR parameters obtained are in confirmity with such an arrangement.

In the electronic spectra of the complexes d-d bands could not be observed. Only two charge transfer bands at 31200 cm^{-1} and 25000 cm^{-1} appeared in each case.

I.R. spectra of the ligands and the complexes have been studied. The strong bands (values in cm^{-1}). at -3370 and -1400 are assigned to intra molecular hydrogen bonded OH and OH (Oximino group) (Bellamy 1964). These bands appear at -3300 and - 1415 in the complexes. The strong bands at 1580 and 1240 are assigned to C=N and N-O (Ramaswamy et al. 1967, Blinc et al.1958) in the ligands which shift to 1520 and 1220 in the complexes. The new bands appearing in the 430-35 and 480-90 region may be assigned to M-N and M-O respectively (Adams 1967).

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