X-RAY SPECTROSCOPIC STUDY OF THE THIOMALIC ACID COMPLEX OF COBALT

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ABSTRACT

The cobalt K absorption spectrum has been studied in thiomalic acid complex of cobalt using a bent crystal X-ray spectrograph. It has been observed that the position of the absorption discontinuity taken with the freshly prepared complex differs from that of the discontinuity obtained with the complex kept in air for about 24 hours. It has been shown that this shift of the absorption edge is due to the change in valency of cobalt in the complex. The shape of the absorption discontinuity has revealed that the complex has an octahedral structure with the hybridization $sp^3d^2$. On the molecular orbital theory the electronic configuration in this complex can be described as $a_{1g}^2t_{1u}^6e_g^4t_{2g}^4e_g^2$.

INTRODUCTION

It is well known that X-ray spectroscopy provides a powerful method of studying the electronic structure of transition metal complexes.\(^1\)-\(^3\)

Kapoor and Nigam\(^4\) have recently made some interesting studies on the thiomalic acid (T.M.A.) complex of cobalt. According to them, the cobalt (II) complex oxidises in air completely to cobalt (III) and the oxidised complex does not contain adsorbed oxygen. According to Mathur and Nigam,\(^5\) the magnetic susceptibility of this complex shows an anomalous magnetic behaviour of Co (III). With the above studies in view we thought it would be interesting to study the cobalt K absorption spectrum in this complex, specially in order to see if some light could be thrown on its electronic structure, which might explain its magnetic behaviour.

EXPERIMENTAL

A Philips sealed X-ray tube with tungsten target was employed as a source of white radiation. The tube was operated at 20 kV, the current ranging
from 10 to 15 ma. A Cauchois type bent crystal X-ray spectrograph of 40 cm. diameter, designed and constructed in the Central Workshop of the Poona University, was used in this investigation. The spectrograph was equipped with a well-tested mica crystal whose (100) reflecting planes were used to record the spectra. Several spectra were photographed on Ilford double-coated X-ray films under varying conditions of exposure. Some spectra were also taken on Agfa ultra-violet plates. Exposure times on plates increase by about 4 fold as compared to those on films. However, plates were found to be much more suitable for microphotometry. Exposure times varied from about 3–4 hours on films and 10–14 hours on plates. Microphotometer records of the plates were obtained with magnification 50 on a Moll microphotometer.

*Preparation of the complex.*—Molar solutions of T.M.A. and of cobalt sulphate were prepared by weighing. The complex was prepared following the method described by Mathur and Nigam by mixing the two solutions in the ratio Co : T.M.A. = 1 : 2, keeping the mixture at pH = 2.6. It was observed that the colour of the freshly prepared complex changed from pink to dark brown when it was kept in air for about 24 hours.

*Absorption cells.*—The preparation of absorption cells for obtaining absorption edges with good contrast is of prime importance and presents considerable difficulty in the work. In order to obtain the absorption spectra of substances in solution, it is essential to use a cell which will not be attacked by the solution and also at the same time will suitably transmit the radiation. The proper thickness of the absorbing solution was obtained by placing the solution between two very thin films of celluloid separated by a stainless steel sheet. It was found after some trial that the requisite thickness of the stainless steel sheet was 1 mm. A front view of the absorption cell is shown in Fig. 1a. In Fig. 1b is shown the end view of the cell.

Thin films of celluloid were obtained by dissolving celluloid in acetone and spreading the resulting viscous fluid over a well-levelled glass plate. It was found that the thin films of celluloid prepared by this method were stiff and transparent and were not attacked by the complex under investigation.

The absorption cell containing the solution of the complex was placed in front of the X-ray tube window and was supported by means of two screws provided on the shield of the X-ray tube.