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 $sp^3d^2$.

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. 1 a. In Fig. 1 b 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.
RESULTS AND DISCUSSION

A. Valency.—It is well known that the position of the K absorption edge of an element in any compound depends upon its valency in the compound.\(^1\) Boehm, Faessler and Rittmayer\(^6\) have recently determined the valency of cobalt in vitamin B\(_{12}\) by measuring the position of the K absorption edge and have reported that cobalt is trivalent in vitamin B\(_{12}\). We have applied this method to study the change in valency of cobalt in its T.M.A. complex.

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FIGS. 1 \(a\) and 1 \(b\) show the front view and the end view respectively of the absorption cell. \(D\) is the stainless steel sheet, \(C\), the celluloid film and \(S\), the solution. \(B\) is a screw on the shield of the X-ray tube which supports the absorption cell through the hole \(B\). The solution is poured in the cell through the opening \(A\).

In addition to the discontinuity in this complex, we have measured the positions of the cobalt K absorption discontinuity in several compounds in which valencies are well established. All these spectra were recorded on films and measurements were made by means of a comparator. The reference lines used were \(L_{a1}\) and \(L_{a2}\) and \(L_{l}\) of tungsten, their wavelengths being taken from the Tables of Cauchois and Hulubei.\(^7\) Table I shows our measurements on the K absorption discontinuity in cobalt metal and in several divalent and trivalent cobalt compounds. The maximum possible error in these measurements is found to be \(\pm 0.04\) X.U. We have also given in this table for comparison the measurement of the K absorption edge of metallic cobalt as given in the Tables of Cauchois and Hulubei, which agrees very well with our value.

It will be seen from Table I that the average shift of the absorption edge for divalent cobalt compounds is about 2.2 X.U. with respect to the absorption edge of metallic cobalt. For trivalent compounds the average shift is ...
### Table I

<table>
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<tr>
<th>Absorber</th>
<th>Wavelength in X.U.</th>
<th>Δλ</th>
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<tbody>
<tr>
<td>Co (Metal)</td>
<td>1604.87</td>
<td>..</td>
</tr>
<tr>
<td>(Cauchois and Hulubei)</td>
<td>1604.8</td>
<td>..</td>
</tr>
<tr>
<td>Co (Metal) (Authors)</td>
<td>1604.8</td>
<td>..</td>
</tr>
<tr>
<td>Valency CoSO₄·7H₂O</td>
<td>1602.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Two CoCl₂·6H₂O</td>
<td>1602.5</td>
<td>2.3</td>
</tr>
<tr>
<td>CoCO₃</td>
<td>1602.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Co(NO₃)₂·6H₂O</td>
<td>1602.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Valency [Co (NH₃)₆]Cl₃</td>
<td>1601.2</td>
<td>3.6</td>
</tr>
<tr>
<td>Three Na₂[Co (NO₂)₆]</td>
<td>1601.5</td>
<td>3.3</td>
</tr>
<tr>
<td>Co₂O₈</td>
<td>1601.1</td>
<td>3.7</td>
</tr>
<tr>
<td>T.M.A. complex of cobalt (freshly prepared)</td>
<td>1602.3</td>
<td>2.5</td>
</tr>
<tr>
<td>T.M.A. complex of cobalt (after keeping it in air for more than 24 hours)</td>
<td>1601.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

About 3.5 X.U. The observed shift in the case of freshly prepared T.M.A. complex is 2.5 X.U. and for the complex when kept in air for about 24 hours is 3.4 X.U. These shifts can also be seen in the spectra reproduced in Fig. 2. Figure 2 a shows the spectra taken on the same photographic plate in cobalt metal and in the freshly prepared complex. Figure 2 b shows the spectra taken in the same way in freshly prepared complex and in the complex kept in air for more than 24 hours. It might thus be concluded that the valency of cobalt in freshly prepared complex is 2 and changes to 3 when it is kept in air for more than 24 hours.

![Fig. 3. Shows the form of the Co K absorption edge in T.M.A. complex of cobalt (after keeping it in air for more than 24 hours). The markings S.S. stand for secondary structure.](image-url)
This study thus confirms the polarographic results of Kapoor and Nigam on the change of valency in this complex.

**B. Co-ordination.**—Several microphotometer records of the Co K absorption spectra in trivalent T.M.A. complex were obtained. One of the representative microphotometer traces is shown in Fig. 3. This curve is characteristic of a transition metal ion with octahedral surroundings. We therefore conclude that this complex has an octahedral co-ordination. The change of valency of cobalt in this complex may thus be attributed on the basis of the ligand field theory to the transfer of an electron from \( e_g \) orbital.

It might be mentioned here that the monotonic nature of the absorption curve is not due to poor resolution of the spectroscopic technique. With a similar technique and under similar experimental conditions the authors have resolved K absorption discontinuities into two components \( K_1 \) and \( K_2 \) in tetrahedrally co-ordinated compounds and complexes, such as in cobalt chloride and in anhydrous cobalt oxinate.

**C. Magnetic properties and electronic structure.**—According to Mathur and Nigam the magnetic moment of the trivalent complex is 5.49 B.M. These authors believe that this value is rather high to explain satisfactorily the structure of this complex.

The electronic configuration of Co\(^{3+}\) ion is \( 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^5 \), its ground state being \(^9\)D. Because of the high value of the magnetic moment the field due to the ligands surrounding the central cobalt ion must be considered to be weak. Hence the orbital diagram of Co\(^{3+}\) in octahedral surrounding can be represented as

\[
\begin{array}{c|c|c}
3d & s & p \\
\hline
\uparrow & \uparrow & \uparrow \\
\hline
\end{array}
\]

The magnetic anomaly of this complex can be explained if we use the following formula for the magnetic moment

\[
\mu_{\text{eff.}}^2 = \beta^2 g_{\text{eff.}}^2 S (S + 1).
\]

Taking the value of the magnetic moment as 5.49 obtained by Mathur and Nigam and using the value of \( S = 2 \) (from the orbital diagram), we get \( g_{\text{eff.}} = 2.242 \). As is well known from ligand field theory, such changes in \( g \) value arise from the fact that we are not dealing with pure \( d \) orbitals and that we
should take into account spin-orbit coupling effects. It would be interesting to verify this value of $g_{zz}$ from electron paramagnetic resonance experiments.

Mathur and Nigam have pointed out that for an octahedral structure, two hybridizations $d^2sp^3$ and $sp^3d^2$ are possible. The first appears to be impossible as in such a case the magnetic moment would be zero. Hence $sp^3d^2$ hybridization might be expected in this complex. An alternative way to look at this is the molecular orbital approach. Only the ligand $p_x$ orbitals take part strongly in the bonding and antibonding admixtures. Thus we take eighteen electrons in all, 12 from the ligands and 6 valence electrons from the Co$^{3+}$ ion, which are to be distributed in the molecular orbitals. The molecular orbitals in increasing order of energy are $a_{1g}$, $t_{1u}$, $e_g$ (bonding), $t_{2g}$ (non-bonding) and $e_g^*$. $a_{1g}$, $t_{1u}$ (antibonding). Hence the electronic configuration in this complex can be described as $a_{1g}^2t_{1u}^6e_g^4t_{2g}^4e_g^*$. This picture is consistent with $s = 2$ as shown in the orbital diagram.

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<th>Author(s)</th>
<th>Reference Information</th>
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FIG. 2

COBALT METAL

T.M.A. COMPLEX OF COBALT FRESHLY PREPARED

W L\_1, L\_2

CoK\_abs.

W L\_p

T.M.A. COMPLEX OF COBALT FRESHLY PREPARED

T.M.A. COMPLEX OF COBALT KEPT IN AIR FOR 24 HOURS

x 4