

X-RAY K-ABSORPTION EDGES OF COBALT IN TWO RECENTLY PREPARED CHELATES

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ABSTRACT

K-absorption edges of cobalt in two chelates, *viz.*, Co (II) bis S-ethyl 1-amidino 2-thiourea and Co (III) isonitroso acetylacetonate have been recorded photographically. The results have been discussed in the light of available magnetic measurements and favour a tetragonal structure for the first and an octahedral one for the second chelate.

INTRODUCTION

X-RAY absorption spectroscopy is one of the interesting ways to study the nature of the chemical bond. The transition elements Cr to Zn form a large number of compounds of several types and hence present a wide field for study. Beeman *et al.* [Beeman and Friedman (1939), Beeman and Bearden (1942), Hanson and Beeman (1949) and Mitchell and Beeman (1952)] have shown that the structure of the X-ray absorption edges of these elements is decided to a very large extent by the immediate surroundings of the atom or ion in question. More recent work in this direction is due to Kauer (Kauer, 1956), Böke (Böke, 1957) and Collet (Collet, 1959), who attempted to correlate their results with magnetic measurements.

The present communication describes the results for two recently prepared* chelates of cobalt, *viz.*, Co (II) bis S-ethyl 1-amidino 2-thiourea and Co (III) isonitroso acetylacetonate.

EXPERIMENTAL

A bent crystal transmission spectrograph using a mica sheet oriented to reflect from ($\bar{2}01$) planes and curved cylindrically to a radius of 40 cm.

* These compounds have been prepared by Prof. B. C. Haldar, Chemistry Department, Institute of Science, Bombay, and were made available to the authors by his kind courtesy.

was used for recording the spectra. The plates used were of the type Kodak B-10.

The resolution of the instrument was tested by recording the Mo K $\beta_{1,2}$ doublet in the second order which has a separation of 0.571 x.u. The doublet was seen clearly resolved on the photographic plate. This value of the doublet separation has been taken from the latest Tables of X-ray Wavelengths (Bearden, 1964). The earlier reported value is 0.565 x.u. (Cauchois and Hulubei, 1947).

A Machlett OEG-60 tungsten tube run by an Enraf Diffractis FG unit served as an X-ray source. Since this is a sealed tube, the problem of recording the absorption edges and the reference lines on the same plate was solved as follows.

Figures 1a and 1b describe schematically the attachments that were constructed. Figure 1a shows the X-ray tube in the vertical position. This arrangement was used for recording the reference lines in fluorescence. X-rays coming out of the Be window (W) are incident on the sample (X) kept on an aluminium base housed in a lead case which in turn is screwed to the tube. The divergence of the beam is 60° which is preferred for fluorescence work. The rectangular slot (Y) is the exit for the fluorescence radiation which falls on the crystal mounted in the crystal holder C. The pointer (P) reads a scale (S) provided on the top of the crystal holder. This ensures the reproducibility of the beam direction to within a degree with respect to the crystal surface.

Figure 1b shows the tube in the horizontal position. This arrangement was used to record the absorption spectra. The crystal now lies farther away from the tube and to restrict the beam divergence it is necessary to use a collimator. As shown in the figure a thick aluminium tube (A) has been fitted in a cylindrical lead case (L). The movable tube (B) has a rectangular slot and can be pushed right up to the crystal holder, ensuring a well collimated beam. A pointer similar to P in Fig. 1a was provided in this arrangement for reproducibility of the beam direction.

The tube was kept horizontal for recording absorption edges and vertical for reference lines. The reference lines were: Yttrium K $\alpha_{1,2}$ 872.12 and 831.32 x.u. and Zirconium K $\alpha_{1,2}$ 784.3 and 788.51 x.u. The Co K-edge has a wavelength of λ 1604.6 x.u. and falls in between the above lines if the latter are recorded in the second order. The dispersion as given by these lines is 12 x.u./mm. for the Co K-edge in the first order. The sample for exciting fluorescence was a mixture of the oxides of yttrium and zirconium

pressed in a mylar packet. For fluorescence excitation the tube was run at 50 KV. and 25 mA. and an exposure of one hour was enough to record the lines with sufficient intensity.

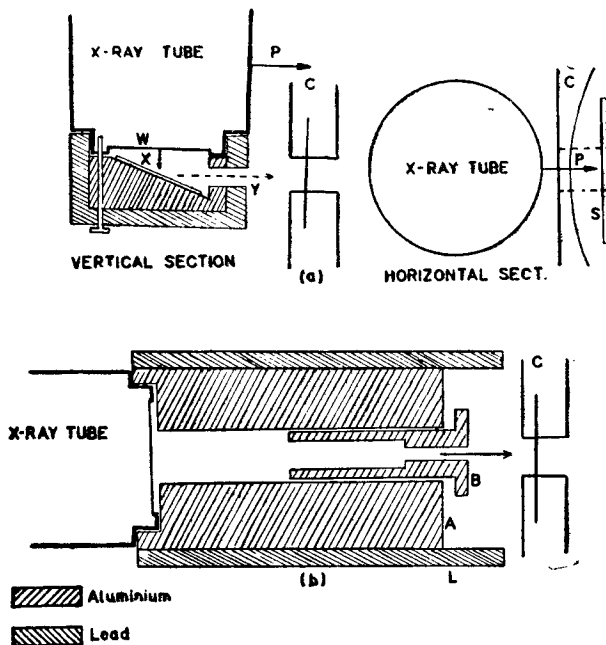


FIG. 1. Attachments for recording (a) reference lines in fluorescence, (b) absorption spectra.

Absorbers were prepared in the form of screens and kept between the crystal and the plate. Powdered compounds were pressed between two thin mylar sheets. For Co (II) compound the distribution 34 mg./cm.^2 and for Co (III) compound 40 mg./cm.^2 were used. Both of these distributions offer nearly 6 mg./cm.^2 of the cobalt element to the incident X-rays and produce maximum contrast in the absorption spectra. The tube was run at 12 kV. and 30 mA. Each absorption spectrum required nearly 33 hours of exposure.

A Moll microphotometer was used to record the variation in the blackening of spectrograms. The magnification used was 50. Such microphotograms of several plates having varying times of exposure were taken. Finally all the curves so obtained for a compound were superposed and the features common to all were regarded as reproducible variations in the intensity. The curves so obtained do not represent the absolute variation of the transmitted intensity. However, it is known (Lemasson, 1949) that if one

redraws the true absorption curves there is a negligible change in the position of the X-ray absorption edge when compared to the direct microphotometer tracings and lies well within a fraction of an electron volt. Therefore conclusions drawn on the basis of the direct microphotometer records are not likely to be affected in an appreciable way.

RESULTS AND DISCUSSION

Figure 2 shows the microphotometer tracings of K-absorption edge of cobalt in metal powder and the two chelates. Transmitted intensity has been shown as a function of energy. As usual, the first slope of the metal edge has been chosen as the zero of the energy scale. The metal edge has a shape which is in agreement with the one obtained by the earlier workers (Beeman and Friedman, 1939 and Böke, 1957) who used a double crystal spectrometer in their investigations and plotted directly the μ -curve. Thus the intensity minima in our curves correspond to the absorption maxima in theirs. The conventional wavelength of the edge with unresolved features is 1604.6 x.u. and has been shown by a dashed line. The first slope of the edge is interpreted as $1s \rightarrow 3d$ transition in the metallic state. The results for the edges in metal and in the two compounds have been collected in Table I.

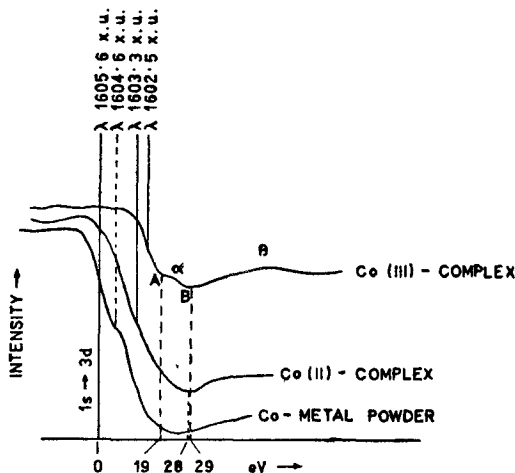


FIG. 2. Microphotometer records of the Co K-edge in metal powder and the two chelates.

Co (II) bis S-ethyl l-amidino 2-thiourea: The absorption edge in this compound lies at 1603.3 x.u. and is shifted by 11 eV on the higher energy side of the metal edge. The edge does not show any pronounced structure

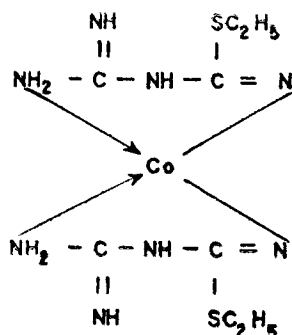
but has a wide dip at 28 eV. This wide dip is a feature common to almost all the complex compounds that contain sulphur in their ligands.

TABLE I

K-absorption edges of cobalt in metal powder and the two compounds

| Substance | λ x.u. | ν/R | $\Delta\nu/R$ | Δ eV. |
|-------------------------|----------------|---------|---------------|--------------|
| Co-Metal powder | 1605.6 | 567.56 | .. | .. |
| Co (II) compound | 1603.3 | 568.37 | 0.81 | 11 \pm 1 |
| Co (III) compound | 1602.5 | 568.66 | 1.10 | 15 \pm 1 |

The compound is paramagnetic and has a susceptibility 2.1.* The proposed structure is as follows:



The magnetic susceptibility indicates that the structure could be either square planer or tetragonal with the hybridisations dsp^2 and $d^2 sp^3$ respectively. The former structure favours a $1s \rightarrow 4p$ transition but the latter forbids it.

Böke (1957) has calculated the $4p$ and $5p$ levels for Co^{++} ion. According to his calculation the $5p$ level should lie 27 eV above the $3d$. This suggests that our dip could be interpreted as a $1s \rightarrow 5p$ absorption transition. These observations therefore favour the tetragonal structure since it forbids $1s \rightarrow 4p$ transition. It may be mentioned that 27 eV is the value for free Co^{++} ion. According to Böke, $5p$ level should be lowered in a complex due to effective decrease in the charge of the central ion. The possibility*† of back donation

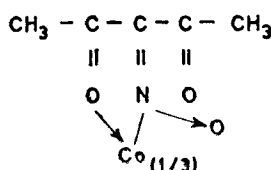
* Private communication from Prof. Haldar.

*† Suggested by Prof. B. C. Haldar.

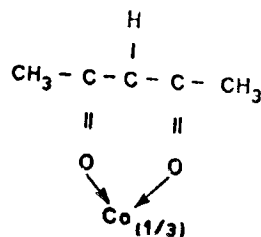
by sulphur is however not ruled out which would bring $5p$ level in Co^{++} back to its original position.

Co (III) isonitroso acetylacetonate: This compound is diamagnetic. Co (III) is "a well-known case being diamagnetic in strong field octahedral complex". (Lewis and Wilkins, 1960). The configuration for the diamagnetic state is t^6_{2g} and hence the shell is full. The $d^2 sp^3$ octahedral hybridisation completely fills the $4s$ and $4p$ apart from the cobalt d shell.

The K-absorption edge in this compound has a wavelength 1602.5 x.u. and is shifted by 15 eV on the higher energy side of the metal edge. The curve also shows an extended structure A, α , B and β . A and B are absorption maxima and lie at 19 and 29 eV respectively. These data are similar to those obtained by Böke for Co (III) acetylacetonate: Edge shift = 13 eV and two absorption maxima at 77 and 30 eV . Böke has interpreted these maxima as $1s \rightarrow 5p$ and $1s \rightarrow 6p$ transitions. A comparison of the structures of the two compounds is shown below:



Co (III) isonitroso acetylacetonate.



Co (III) acetylacetonate

Thus our observed maxima can also be understood as $1s \rightarrow 5p$ and $1s \rightarrow 6p$ transitions and they favour the compound to have an octahedral structure.

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