

## COBALT K X-RAY ABSORPTION SPECTRUM IN PINK AND BLUE SOLUTIONS OF COBALT (II) CHLORIDE

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Van Nordstrand (1960a, b) has recently reported a large number of  $K$  absorption curves of transition metal ions in different types of compounds. He classifies these curves in four categories (see Sinha and Mande, 1963 for details). Of these, the type IV curves, that is the curves for the transition metal ions with tetrahedral surroundings, alone show the splitting of the principal absorption edge. Sinha and Mande (1963) have explained this splitting of the absorption discontinuity on the basis of the ligand field theory. It appears, that the tetrahedrally surrounded metal ion gives a very characteristic X-ray absorption spectrum. In this note we report the shape of the  $K$  X-ray absorption discontinuity of cobalt in pink and blue solutions of cobalt chloride.

A Cauchois type bent crystal X-ray spectrograph of diameter 40 cms, designed and constructed in our workshop, was used in this investigation. A well tried crystal of mica was used as analyser. The spectra were photographed using the (100) and (201) reflections of mica. A Philips sealed X-ray tube with tungsten target was employed. It was operated at 20KV, the current ranging from 20ma to 30 ma. Exposure times varied from 12 to 30 hours on Agfa ultraviolet plates. Microphotometer records of the plates were obtained with magnification 50 on a Moll microphotometer. The absorption cell containing the solution of cobalt chloride 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. The proper thickness of the absorbing solution was attained by placing the solution between two very thin films of celluloid separated by a stainless steel sheet of requisite thickness. Deep blue solutions were obtained by adding excess of concentrated HCl to the pink solutions.

The forms of Co  $K$  absorption edge in pink and blue solutions of  $\text{CoCl}_2$  respectively are shown in figures 1 and 2. These forms have been obtained from several microphotometer records taken in turn from several plates obtained under varying conditions of exposure. It is seen that these curves resemble very well with type I and type IV spectra respectively obtained by Van Nordstrand. However, it should be noted that the curves given by Van Nordstrand are absorption coefficient versus energy curves, where as our curves show the variation of transmitted intensity with energy. It will be seen that Fig. 1 shows a single  $K$

discontinuity while Fig. 2 shows the splitting of the principal absorption edge into two successive components  $K_1$  and  $K_2$ . Both discontinuities show secondary fine structure near the absorption edge on the high energy side. However, for the blue solution, the curve somewhat flattens after the maximum of the secondary structure.

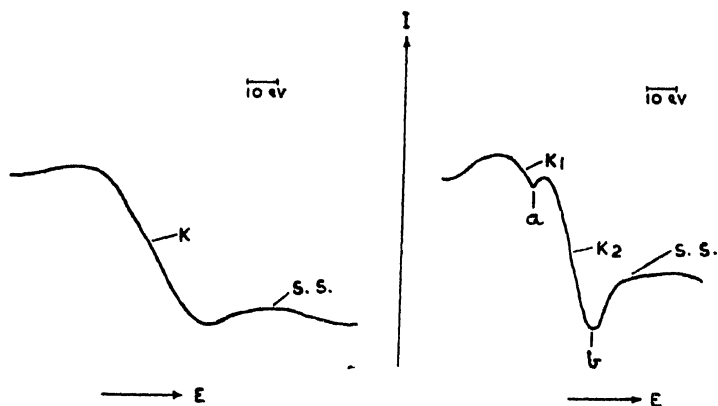


Fig. 1

Fig. 2

Figures 1 and 2 show the form of the Co K absorption edge in pink and blue solutions respectively of cobaltchloride. The markings S. S. stand for secondary structure.

The K absorption curves for the pink and blue solutions of cobalt chloride obtained in this investigation are characteristic of the transition metal ion associated with an octahedral co-ordination in the common salts and the ion associated with a tetrahedral configuration respectively. Hence we conclude that in the pink solution the  $\text{Co}^{++}$  ion is octahedrally surrounded and in the blue solution the coordination is a tetrahedral one. In the general interpretation given by Sinha and Mande, the minima at the markings 'a' and 'b' in Fig. 2 represent the X-ray absorption transitions  $1s \rightarrow 4p$  and  $1s \rightarrow p$  limit. The empty  $4p$  orbital of the  $\text{Co}^{++}$  ion is localised only in the tetrahedral configuration, thus making possible the  $1s \rightarrow 4p$  transition.

These results also establish that although in the solution state the lattice structure breaks down, the individual octahedral and tetrahedral units around the cobalt ion retain their identity. This work thus supports the assumptions made by Mookherji (1962) about the nature of the crystal fields in his recent magnetic studies of these solutions.

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