

202. *The Absorption Spectrum of Solid Anhydrous Cobalt Chloride.*

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As the result of a study of the absorption spectra of a number of cobalt pigments obtained by replacing other metallic atoms by cobalt in compounds of known crystal structure, the theory was advanced (Hill and Howell, *Phil. Mag.*, 1924, **48**, 833) that the colour of the cobaltous compounds, both in the solid state and in solution, is determined by the number of atoms or groups surrounding the cobalt atom : with four, the colour is blue ; with six, it is red.

Strong evidence for the correctness of this view has been forthcoming from the subsequent determination of the crystal structure of some cobaltous compounds and of other compounds from which cobalt pigments have been derived (see *Ann. Reports*, 1927, **24**, 288) ; from the change in density and viscosity (Howell, J., 1927, 158), refractive index

and surface tension (*idem, ibid.*, p. 2039), and electrical conductivity (*idem, ibid.*, p. 2843) accompanying the change of colour of aqueous cobalt chloride solution on addition of hydrochloric acid; from the spectroscopic study of the change of colour of aqueous cobalt chloride solution on addition of hydrochloric acid (Howell and Jackson, *Proc. Roy. Soc.*, 1933, *A*, **142**, 587), of magnesium chloride (*idem, J.*, 1936, 1268), or of potassium thiocyanate (*idem, this vol.*, p. 621); and from the change in physical properties (Howell, *J.*, 1929, 162) and in the absorption spectrum (Howell and Jackson, *Proc. Roy. Soc.*, 1936, *A*, **155**, 33) of aqueous solutions of cobalt chloride and hydrochloric acid with change of temperature.

There has appeared, however, one important fact in apparent opposition to the simple colour rule. It was shown (Ferrari, Celeri, and Giorgi, *Rend. R. Accad. Lincei*, 1929, **9**, 782), from *X*-ray examination by the powder method, that the chlorides of cobalt, cadmium, magnesium, iron, and nickel are all isomorphous. Subsequently, *X*-ray examination of a single crystal of cadmium chloride (Pauling and Hoard, *Z. Krist.*, 1930, **74**, 546) established that its crystal structure is of the layer type with each cadmium ion within a group of six chlorine ions. It follows that anhydrous cobalt chloride has the same type of structure.

The characteristics of salts possessing a layer structure are generally intermediate between those having a molecular and those having an ionic lattice. The layer structure of anhydrous cobalt chloride therefore explains its comparatively ready volatility and its solubility in organic solvents; also the fact that on sublimation it forms fine leaflets.

Since anhydrous cobalt chloride is blue, however, the fact that each cobalt ion lies between six chlorine ions is apparently not in harmony with the colour rule. In view of this exceptional behaviour, Professor W. L. Bragg, F.R.S., kindly consented to an *X*-ray examination in his laboratories of anhydrous cobalt chloride itself.

The salt was prepared by dehydrating Kahlbaum's pure hexahydrate (free from iron and nickel) in a current of dry hydrogen chloride. The caked mass was re-ground and re-heated in the stream of gas. This was repeated to obtain a fine powder, which was then filled whilst still hot into thin-walled Lindemann or Röntgen glass tubes, which were quickly sealed off.

The *X*-ray examination (Grime and Santos, *Z. Krist.*, 1934, **88**, 136) confirmed that at atmospheric temperature the crystal structure is of the layer type. The layer order is: Cl, Co, Cl; Cl, Co, Cl, etc.; and each cobalt ion lies between six chlorine ions.

Now it is known that on cooling in liquid air, anhydrous cobalt chloride turns red. The crystal structure was therefore also examined at the temperature of liquid air and was found to be indistinguishable from that at atmospheric temperature. Under these conditions, therefore, the salt conforms to the simple colour rule.

The change in colour without apparent change in the crystal structure demanded further investigation, and it was therefore deemed of interest to examine the (optical) absorption spectrum of solid anhydrous cobalt chloride. It will be shown in the sequel that the absorption spectrum is compounded of that typical of the cobalt atom in association with four chlorine atoms (colour: blue) and of that typical of its association with six groups (colour: red). The compound is essentially red and the change from red to blue with increasing temperature is discussed.

EXPERIMENTAL.

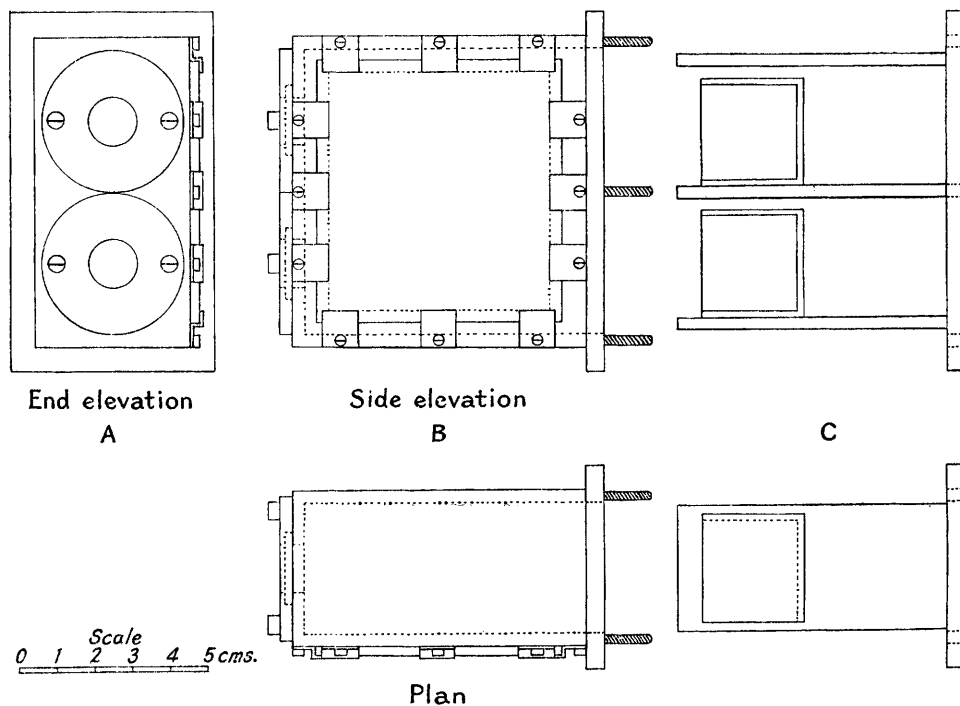
All measurements were made with the Hilger-Nutting spectrophotometer used in the previous investigations. Since all the experiments had to be made with scattered light, the standard lamp-housing and the tube supports provided on the instrument were removed.

Anhydrous cobalt chloride is extremely deliquescent; arrangements therefore had to be made for keeping the specimen under examination in a perfectly dry atmosphere. A cell (Fig. 1) made of brass and blackened all over was provided with a square window at one side (B) to receive the incident light. One end (A) was provided with two circular windows exactly similar to those of the photometer box of the instrument, and the cell was fixed so that the two pairs corresponded exactly. The other end of the cell was closed by a plate (C) fastened by bolts to the flanged end with an air-tight washer between. This plate carried at right angles three metal strips running the length of the cell, and between these were fixed two cube-shaped cardboard boxes; of each of these, one side (facing the square window) was missing for reception of the

incident light, and another (facing the circular windows) for exit of the scattered light at right angles. The other four faces were covered on the inside with the material used as substratum for the blank and with the same coated with anhydrous cobalt chloride for the other beam. Small glass vessels filled with phosphoric oxide were also carried on the strips to maintain a dry atmosphere, and a thermometer was fixed through the end-plate to give the temperature during an observation. The absorption spectrum of a specimen kept in the cell for three days was unchanged over this period.

When filter-paper (or similar material) was used as substratum, a rectangular sheet (4 in. \times 2.5 in.) was evenly impregnated with a suitable volume (1.5 c.c.) of aqueous cobalt chloride solution of known concentration. By using solutions of different concentrations, different known

FIG. 1.



amounts of cobalt chloride were taken for examination (see the next paper). The sheet was then carefully air-dried over a flame. With the aid of a templet, a piece of the right shape for covering the inside of the cardboard box was cut out. In this way a constant area was also ensured for the comparison of the relative intensities of absorption with different amounts of cobalt chloride. After the coated paper and the blank had been fixed in the boxes, these were placed between the strips attached to the back of the cell, and the whole was heated in an air oven at 120–125° for $\frac{1}{2}$ hour to ensure complete dehydration. Whilst still hot, the whole fitting was assembled with the remaining part of the cell.

The method used with other materials as substratum, *e.g.*, sintered Jena glass, was similar except that four squares of the material were cut and assembled in metal frames. Impregnation with cobalt chloride solution was done *in situ*.

The source of illumination was a 500 c. p. lamp, housed in an asbestos box with a square tube leading to the window of the cell. Considerable heating occurred, and measurement of the absorption spectrum was delayed until equilibrium was established, when the temperature remained constant at $60^\circ \pm 1^\circ$.

For the experiments at higher temperatures, the metal cell was replaced by a cylindrical tube of clear silica glass, which was wound with nichrome wire and heavily lagged by means of an asbestos case filled with kieselguhr. An opening was left in the winding and lagging corresponding to the square window of the metal cell. One end of the tube was closed with a plane plate

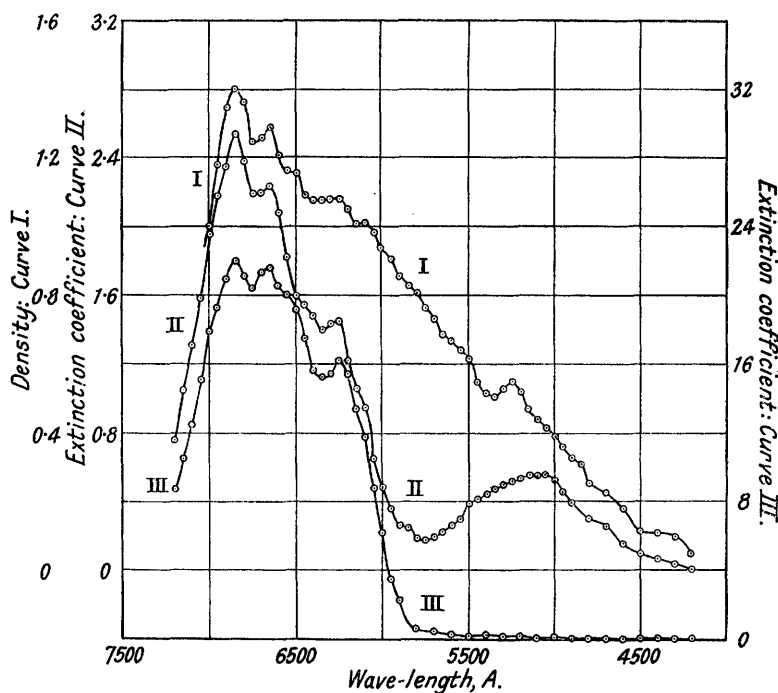
(also of clear silica glass and sealed on) which was covered with asbestos sheet having two small circular holes corresponding to those on the photometer box. The other end of the tube was flanged; this was fitted with a metal end-plate which was bolted to a metal ring bearing against the other side of the flange. The end-plate carried a metal frame bearing the coated box and blank as with the metal cell.

The resistance wire was heated with current from the mains, and a bank of lamps as external resistance enabled any temperature up to 400° to be maintained to within about 2° for the duration of a measurement of the absorption spectrum.

DISCUSSION.

Solid Anhydrous Cobalt Chloride on Cellulose.—The absorption spectrum of solid anhydrous cobalt chloride deposited on filter-paper, by impregnating the paper with aqueous cobalt chloride solution and then dehydrating it in the manner already described, is shown in Fig. 2. The form of the curve is independent of the amount of solid deposited; the intensi-

FIG. 2.



Curve I. Solid anhydrous cobalt chloride.
 Curve II. Cobalt chloride in 6.75*N*-aqueous HCl solution.
 Curve III. Cobalt chloride in 13.1*N*-aqueous HCl solution.

ties of all the bands, however, increase correspondingly with increasing deposition of cobalt chloride in the manner discussed in the following paper. There are also reproduced for comparison the absorption spectrum of the solution of cobalt chloride in moderately concentrated (6.75*N*) aqueous hydrochloric acid, which is partly blue, and of that in very concentrated (13.1*N*) aqueous hydrochloric acid, which is wholly blue.

It is seen that the initial portion of the absorption spectrum of solid anhydrous cobalt chloride is precisely similar to that of cobalt chloride in aqueous hydrochloric acid solution; the same bands are clearly defined in both: the two principal bands at 6850 Å. and 6650 Å., the two subsidiary bands at 6250 Å. and 6100 Å., and also the less pronounced band at 6500 Å. These bands which are so much more intense than the others account for the blue colour of anhydrous cobalt chloride. It has been shown that, with cobalt chloride in

aqueous hydrochloric acid solution, these bands are due to the complex $[\text{CoCl}_4]''$, and therefore there must be in the solid anhydrous salt also an association between the cobalt ion and four chlorine ions. This is discussed below.

The absorption of cobalt chloride in very concentrated aqueous hydrochloric acid solution falls to practically zero at 5800 A. and remains negligible up to the limit of the visible spectrum. That of solid anhydrous cobalt chloride, however, continues to be appreciable and exhibits a well-defined band at 5250 A.

In this respect solid anhydrous cobalt chloride differs from all the blue cobalt pigments which have been examined (Hill and Howell, *loc. cit.*). The absorption of all the pigments falls rapidly with decreasing wave-length from about 5400 A.; none shows an absorption band at 5250 A. On the other hand, all the red pigments and solutions have a well-defined band between 5300 A. and 5100 A. That this band must be attributed to the red form of anhydrous cobalt chloride is further demonstrated by the fact (see below) that with increasing temperature its intensity decreases whilst that of the bands of the blue form increases, exactly as for the solutions already examined which are partly blue and partly red at a given temperature. Moreover, it is seen that there is a considerable difference in intensity between the two principal bands (6850 A. and 6650 A.) with solid cobalt chloride as with partly blue and partly red solutions (compare the curve for 6.75*N*-hydrochloric acid), whereas with wholly blue solutions the difference is very small (compare the curve for 13.1*N*-acid).

The band of the red form is not due to partial hydration of the salt, since the measurements were made with every precaution against this possibility; moreover, the same band is found (see below) at temperatures above that at which the salt is definitely wholly anhydrous. It is therefore evident that solid anhydrous cobalt chloride is simultaneously blue and red, indicating an association of the cobalt ion with both four and six chlorine ions.

Comparison of the absorption spectrum of solid anhydrous cobalt chloride with that of cobalt chloride in 6.75*N*-aqueous hydrochloric acid solution (Fig. 2) shows that the curves are remarkably similar. If the difference in the absorption at each wave-length be plotted, it is found that the only essential difference between the two curves is that the band at 5850 A. is much more pronounced for the former than for the latter. Marked absorption in this part of the spectrum is characteristic of all the cobalt pigments (see Hill and Howell, *loc. cit.*; see also the curves for solid cobalt chloride in Fig. 3) but is lacking in the blue solutions.

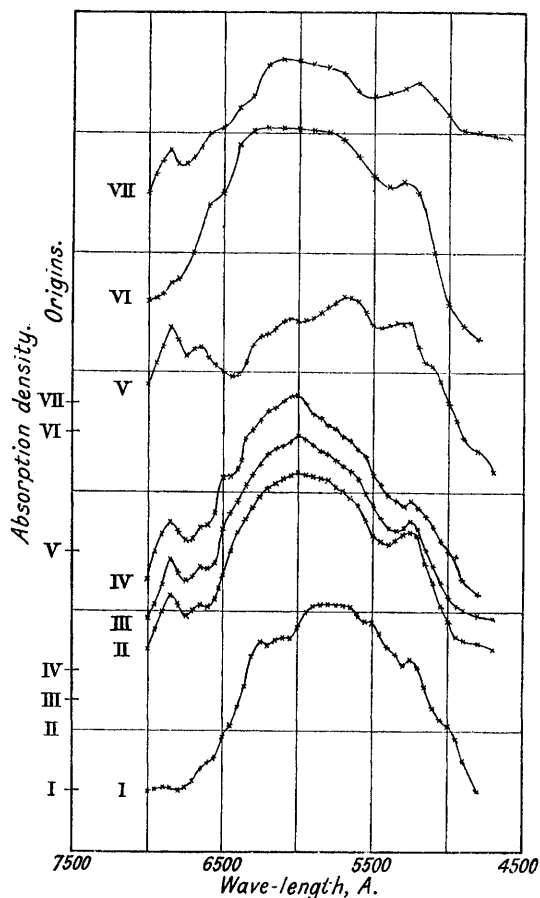
It has been shown that, with cobalt chloride in 6.75*N*-aqueous hydrochloric acid solution, the amount of the blue form is quite small; the extinction coefficient for the first principal band (6850 A.) is only 2.54 as against 22.0 in the wholly blue solution, so the fraction of the cobalt present as the blue form is only 0.115. It is unfortunately not possible to make a similar direct comparison for solid cobalt chloride, because this cannot be converted to the wholly blue form. Some estimate can be made, however, by comparing the intensity of the band of the red form with that of the chief principal band of the blue form in the two instances; the values are, respectively, 0.56 and 2.54 for the solution and 0.55 and 1.4 for the solid. How far the intensity of the band of the red form of solid cobalt chloride is affected by the enhanced absorption of the band at 5850 A. is unknown. The effect is probably small, since with all the blue cobalt pigments, which do not give a band at 5250 A., the absorption falls rapidly from 5400 A. The amount of the blue form present in solid anhydrous cobalt chloride at the working temperature (60°) is therefore probably considerably smaller than in the aqueous solution of cobalt chloride in 6.75*N*-hydrochloric acid at 20°, *i.e.*, less than one-tenth of the whole.

Anhydrous cobalt chloride, however, appears blue to the eye because the intensity of absorption of cobalt in the blue form is far greater than that in the red; thus it has already been shown that the intensity of absorption of $[\text{CoCl}_4]''$ is 92.5 times that of $[\text{Co}(\text{H}_2\text{O})_6]''$. At the temperature of liquid air, the anhydrous salt is red to the eye and therefore wholly or almost wholly of the red form; since the cobalt ion is in association with six chlorine ions, the colour rule is thus satisfied.

Solid Anhydrous Cobalt Chloride on Other Supports and at Higher Temperatures.—Various materials were tried as supports for the solid cobalt chloride in order to find one suitable for examination of the spectrum at higher temperatures. The curves obtained with some of

these are given in Fig. 3. It is seen that the general form of the curve varies very greatly with the different supports; the absorption spectrum of the deposited solid is profoundly affected by the nature of the substratum. This effect merits further investigation. The

FIG. 3.



Solid anhydrous cobalt chloride on :

- I. Porous tile.
 - II. Sintered Jena glass, 70°.
 - III. " " " 145°.
 - IV. " " " 220°.
 - V. Ground glass. Deposited from alcoholic solution.
 - VI. Copper gauze. Magnesium oxide as blank.
 - VII. Lead sheet.
- Each ordinate division is 0.4. The "origin" of each curve is shown.

from the other two; nor was any difference in structure observed at atmospheric temperature from that at the temperature of liquid air. A very small change in the relative positions of the chlorine ions, however, would account for the observed change in colour, and more detailed investigation of the crystal layer might yield interesting information on this point.

SUMMARY.

1. The absorption spectrum of solid anhydrous cobalt chloride deposited on filter-paper is very similar to that of cobalt chloride in aqueous hydrochloric acid or magnesium chloride solution.

same bands are, however, still present but some are much more highly developed on some surfaces than on others. It is important that the band at 5250 Å. due to the red form is present in every instance.

The most suitable surface was sintered Jena glass. This was coated with anhydrous cobalt chloride and the absorption spectrum of the same specimen was measured at a series of temperatures in the manner already described. There was no attack of the glass by the salt over the range examined; after the measurements were complete, the whole of the deposit dissolved in water, leaving the glass as colourless as at first.

Curves of the absorption spectrum at three different temperatures are given in Fig. 3. It is seen that with increasing temperature the intensity of the bands of the blue form increases whilst that of the red form decreases. The effect is not large but is quite definite; taken in conjunction with the fact that cobalt chloride is red at the temperature of liquid air, it establishes that with increasing temperature there is a gradual transition from red to blue as for cobalt chloride in moderately concentrated aqueous hydrochloric acid or magnesium chloride solution.

The crystal structure of solid anhydrous cobalt chloride shows that the cobalt ion is centrally situated between six chlorine ions. The gradual change from red to blue with increasing temperature should be explained, according to the colour rule, by increasing association of the cobalt ion with four of the chlorine ions and corresponding decrease of its association with all six. There is, however, no indication that four of the six chlorine ions are differently disposed

2. The bands typical of the cobalt ion in association with four chlorine ions (colour : blue) and the band typical of its association with six groups (colour : red) are all present.

3. At the temperature of liquid air anhydrous cobalt chloride is red to the eye and therefore consists almost wholly of the red form.

4. At the ordinary temperature it is evident from a comparison of the intensity of the absorption bands of the solid with those of solutions of cobalt chloride in aqueous hydrochloric acid, that anhydrous cobalt chloride is still chiefly red. It appears blue to the eye because the intensity of a given amount of cobalt in the blue form is far greater than that in the red.

5. At higher temperatures the intensity of the bands of the blue form increases whilst that of the red form decreases, but even at 350° the red form still persists.

6. The essentially red character of anhydrous cobalt chloride is in accord with the colour rule, since its crystal structure shows that each cobalt ion is surrounded by six chlorine ions.

7. The gradual conversion from red to blue of solid anhydrous cobalt chloride with increasing temperature is exactly comparable with that of the salt in aqueous hydrochloric acid or magnesium chloride solution and should therefore be due to the same cause, *viz.*, increasing association of the cobalt ion with four of the chlorine ions.

8. The crystal structure (determined by the powder method) gives no indication of such change or of any difference in disposition of four of the six chlorine ions, but further investigation of the lattice layer would be of interest.

9. The absorption spectrum of solid anhydrous cobalt chloride deposited on various supports shows that the deposit is affected by the nature of the substratum. Different bands are enhanced by different surfaces.