

The Structure and Colour of Anhydrous Cobalt Chloride, $CoCl_2$, at Room and very Low Temperatures.

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(With 1 figure.)

1. In a series of papers O. R. Howell has sought to establish a connection between the colours of the cobaltous compounds and the corresponding environment of the cobalt atom. In the first paper, Hill and Howell (1) gave a summary of earlier work and theories and, after an examination of the optical absorption spectra of certain cobaltous compounds and their relationship with data at that time available from crystal structure, suggested that in the blue compounds the cobalt atom is associated with four other atoms or groups whilst in the red compounds the cobalt atom is associated with six atoms or groups.

Since the publication of that paper a good deal of new data both of a chemical and physical nature has accumulated. In the case of solutions the evidence as to the nature of the grouping about the cobalt atom has been mainly drawn from a study of optical absorption spectra along with experiments on densities and viscosities (2), refractive indices and surface tensions (3), and electrical conductivities (4) of aqueous solutions of $CoCl_2$ and HCl of varying concentrations. In the solid state — which interests us here — the evidence is drawn from a study of the optical absorption spectra and crystal structure of certain well known pigments. These pigments are formed when divalent cobalt replaces the metal atoms in certain colourless crystalline compounds. When the crystal structure is known one obtains at once in a very satisfactory manner direct information of the environment of the cobalt atom.

In Table I we give a short list of cobalt pigments already examined. In the first column is given the name of the pigment. In the second is given the colourless compound from which the pigment is derived by

replacing certain metal atoms by cobalt. In the fourth column is given the colour of the pigment as seen by eye. Actually the pink and red compounds show identical absorption bands in the red part of the spectrum whilst the green and blue compounds have identical bands in the blue. It will be seen from the table that the colour and association rule quoted above is satisfied.

Table I.

Pigment	Original Compound	Atomic grouping about cobalt	Colour of Pigment
Cobalt Blue (<i>Mg, Co</i>) <i>Al</i> ₂ <i>O</i> ₄	Spinel	Four oxygen atoms about each cobalt atom	Blue
Cobalt Pink (<i>Mg, Co</i>) <i>O</i>	<i>MgO</i> (rocksalt structure)	Six oxygen atoms about each <i>Co</i> atom	Pink
Cobalt Green (<i>Co, Zn</i>) <i>O</i>	<i>ZnO</i>	Four oxygen atoms about each <i>Co</i> atom	Green (with optical absorption band in blue)
Cobalt Oxide		Six oxygen atoms about each <i>Co</i> atom	Red
Orthosilicate Blue (<i>Zn, Co</i>) ₂ <i>SiO</i> ₄	Willemite (<i>Zn</i> ₂ <i>SiO</i> ₄)	Four oxygen atoms about each <i>Co</i> atom	Blue
Orthosilicate red (<i>Mg, Co</i>) ₂ <i>SiO</i> ₄	Olivine (<i>Mg</i> ₂ <i>SiO</i> ₄)	Six oxygen atoms about each <i>Co</i> atom	Red
Cobalt fluoride (<i>CoF</i> ₂) (Rutile type)		Six fluorine atoms about each <i>Co</i> atom	Red

2. In 1930 H. Bassett (5) discussed at length this problem of the colour of cobaltous salts and strongly disagreed with Howell's conclusions. Bassett's arguments were based on chemical considerations. For example, he proposed for the red compound *CoCl*₂*HgCl*₂·4*H*₂*O* the coordination formula [*Co*(*H*₂*O*)₄]²⁺ [*HgCl*₄]²⁻ giving a coordination of four molecules about the cobalt atom. One would however satisfy the colour rule if one could write the formula [*CoCl*₂·4*H*₂*O*] [*HgCl*₂]. Since this compound is solid at room temperatures a successful X-ray examination of the crystal structure would determine the correct formula and thus supply evidence for or against the rule. Unfortunately the substance is not ideal for such a test, for, apart from its highly hygroscopic character, the crystal symmetry is low and the presence of the heavy cobalt and mercury atoms makes the location of the water molecules and chlorine atoms unusually difficult. However, Bassett's objections to

the applicability of the colour rule did not seem to us so strong as evidence from another source relating to the structure of anhydrous cobalt chloride, $CoCl_2$.

3. In 1929 Ferrari, Celeri and Giorgi (6) suggested from a study of powder photographs that the chlorides of *Cd*, *Co*, *Mg*, *Ni* and *Fe* were isomorphous. Later, Pauling and Hoard (7) using a single crystal determined the structure of cadmium chloride. This structure which is simple and interesting is of the layer type and bears a strong resemblance to the well known layer structure of cadmium iodide CdI_2 . In both crystals the negative ions are arranged in closest packing and in both crystals the cadmium atoms are found within groups of six anions. It follows that if $CoCl_2$ is truly isomorphous with $CdCl_2$ the cobalt atom must also be associated with six chlorine ions — a fact contrary to Howell's expectation since the compound is blue in colour. In view of its apparent critical importance we thought it worth while to investigate directly the structure of $CoCl_2$.

4. The compound was specially prepared for us by Dr. O. R. Howell to whom we express our best thanks. Satisfactory crystals not being available we were obliged to rely on the X-ray powder method. The substance in the form of a very fine powder, blue in colour, was sealed in thin-walled Lindemann or Röntgen glass tubing (diameter about 0.4 mm) since the slightest trace of moisture changed at once the composition and colour of the compound. X-ray photographs were taken with both nickel and copper anticathodes. The photographs obtained were good except for the relatively heavy background — due to the general radiation scattered by the cobalt — which made the estimation of intensities difficult. The measurements were corrected for the thickness and absorbing power of the powder specimen by the methods described by Bradley and Jay (8). Since these corrections were of importance a preliminary examination of powdered cadmium chloride was made for control purposes.

The results for Nickel radiation are collected in Table II. They are in agreement with the proposal that $CoCl_2$ and $CdCl_2$ are isomorphous. In calculating the intensities for column 4 use was made of atomic f curves based on the Thomas model for Caesium. In column 3 lines which are practically superposed in the photographs are bracketed together and the sum of the numbers given will therefore correspond to the intensity expressed in the fourth column.

Table II.

Indices	$\sin \theta$ (NiK_{α} radiation)	Calculated Intensity (arbitrary units)	Observed Intensity	Indices	$\sin \theta$ (NiK_{α} radiation)	Calculated Intensity (arbitrary units)	Observed Intensity
(211)	0.3298	403	v. s.	(2 $\bar{1}$ 0)	0.7152	13	} v. w.
(221)	.3593	49	v. w.	(554)	.7173	0	
(333)	.4273	5	} v. w.	(442)	.7187	0	absent
(322)	.4281	14		(21 $\bar{1}$)	.7200	0	absent
(332)	.4659	53		(543)	.7369	16	} s.
(1 $\bar{1}$ 0)	.4672	53	v. s.	(310)	.7386	58	
(210)	.4885	22	w.	(533)	.7508	7	} v. v. w.
(11 $\bar{1}$)	.5416	9	v. v. w.	(320)	.7520	13	
(433)	.5461	1	absent	(421)	.7872	15	v. v. w.
(321)	.5472	3	absent	(655)	.8062	17	} v. s.
(200)	.5478	1	absent	(431)	.8086	63	
(444)	.5698	12	} m.	(2 $\bar{1}$ 1)	.8092	32	
(220)	.5719	37		(553)	.8198	8	} v. w.
(443)	.5878	8	} v. w.	(22 $\bar{1}$)	.8216	8	
(311)	.5894	8		(300)	.8216	8	} v. w.
(432)	.6332	14	} v. w.	(654)	.8518	18	
(331)	.6337	7		(644)	.8562	0	} absent
(422)	.6598	30	w.	(532)	.8572	0	
(544)	.6736	7	absent	(330)	.8579	0	
(555)	.7122	2	absent	(411)	.8579	0	

The unit cell is rhombohedral with

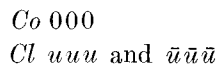
$$a = 6 \cdot 16 \text{ \AA} \quad \alpha = 33^{\circ} 26'$$

giving for the corresponding hexagonal cell

$$a = 3 \cdot 545 \text{ \AA} \quad c = 17 \cdot 44 \text{ \AA}$$

and therefore the unusually large ratio for c/a of 4.92.

There is one molecule of cobalt chloride in the rhombohedral cell and the probable Space Groups are C_{3v}^5 , D_3^7 and D_{3d}^5 . The parameters for the atoms which satisfy these three Space groups are



The value found for u is 0.25.

In deducing the structure dimensional considerations alone help considerably. They suggest for example that the chlorine atoms are in cubic close packing and that the cobalt atoms are located in the available octahedral groups of chlorine atoms and not in the tetrahedral groups. The X-ray evidence confirms these suggestions and leads to an arrangement of octahedral groups enclosing metal atoms linked in

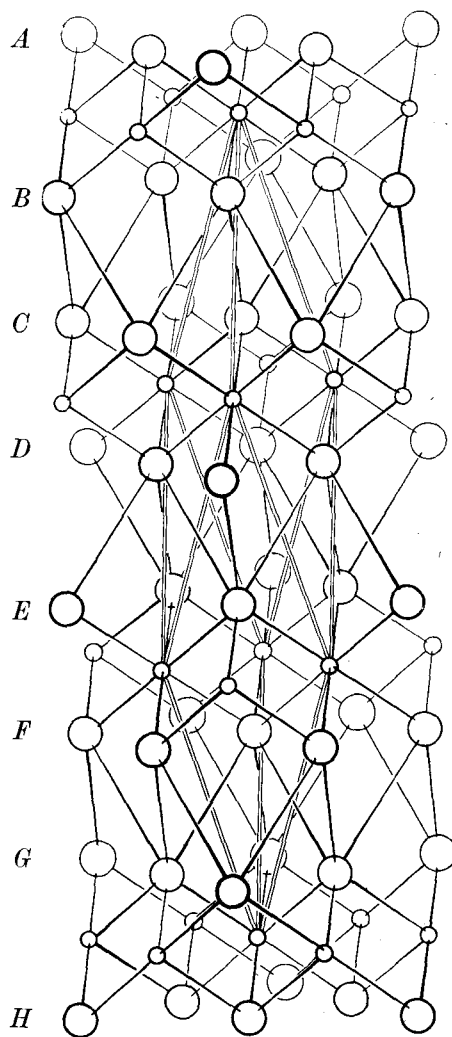


Fig. 1. Small circles represent cobalt atoms, large circles represent chlorine atoms. The unit cell is indicated by double lines.

cobalt atom whereas by the colour rule we should anticipate a four coordination we appear to have direct evidence invalidating the relation of colour and structure. On the other hand the structure is of rather special type (layer) and the striking evidence in Table I in favour of the relation can hardly be due to pure coincidence. It certainly seems necessary to introduce some modification into the simple rule originally proposed.

such manner that each chlorine atom is associated with three cobalt atoms and that a layer structure parallel to (111) is formed. The general character of the structure will be clear from fig. 1 which is based on one for $CdCl_2$ given in the Strukturbericht (9). If we letter successive identical sheets of closepacked chlorine atoms parallel to (111) $A, B, C, D, E, F, G, \dots$ we see that the sheets A and B are interleaved by a sheet of cobalt atoms to form a compound layer ($A-B$) of composition $CoCl_2$. The layers ($C-D$), ($E-F$) etc. are similarly constituted whilst the layers ($B-C$), ($D-E$) etc. contain no metal atoms. In the better known structure of cadmium iodide layers of CdI_2 identical in form with ($A-B$), ($C-D$) . . . exist but these are so superposed one upon the other that instead of the anions being arranged in cubic close packing and satisfying a rhombohedral translational group the anions are arranged in hexagonal close packing and the resulting unit cell is hexagonal.

Since the structure deduced for $CoCl_2$ requires a six coordinated

An examination of the optical absorption spectra of solid $CoCl_2$ is now being made by Howell to see whether there is a difference in this respect between $CoCl_2$ and those blue pigments which do satisfy the simple rule.

The colour and crystal structure of Cobalt chloride at the temperature of liquid air.

It is an interesting fact that if the sealed tubes of cobalt chloride used in the above experiments be dipped into liquid air the colour of the compound changes from blue to a somewhat dull pink. We have not investigated carefully the temperature at which the colour change occurs but it is certainly near that of liquid air.

We have examined by X-rays specimens of the compound at this low temperature in order to see whether the colour change is accompanied by a change in structure. The apparatus used was described in a recent number of the *Journal of Scientific Instruments* (10). It provides a simple and convenient method of taking X-ray photographs of crystal powders when maintained at the temperature of liquid air. On comparing a series of photographs for the same specimen when obtained at the two temperatures we were unable to detect any evidence of a change of structure. It follows that the number of chlorine atoms associated with each cobalt atom has remained the same although the colour has changed. It is desirable to examine carefully the optical absorption spectra of the compound at these two temperatures to see exactly in what particulars they differ. Indeed it would be interesting to follow the change, if any, in the absorption spectra as the temperature of cobalt chloride is raised from the temperature of liquid air to a very high temperature, and to correlate the results with those obtained by corresponding X-rays studies.

In conclusion we wish to thank Professor W. L. Bragg F. R. S. and Mr. J. West, under whose direction the work was carried out, for their interest and advice.

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