

Fig. 1.—The system  $\text{Na}_2\text{CrO}_4$ – $\text{NaClO}_3$ – $\text{H}_2\text{O}$  at 19 and 50°.

only the hexahydrate at 19°. The isothermally invariant points for equilibrium, at each of these two temperatures, between the two adjacent hydrates in the ternary system were not determined.

The identity of the solid phases as reported is based on graphical and algebraic extrapolation of tie-lines. For the case of sodium chlorate as solid phase these tie-lines extrapolate to 100% sodium chlorate with an average absolute error, for all three isotherms, of 0.16%, calculated as % water. For the sodium chromate phases, the average error of extrapolation to the theoretical percentage of sodium chromate in the respective hydrates, is 0.11%, calculated as % sodium chlorate. There is consequently no indication, within the experimental error, of any solid solution formation between the equilibrium phases of the system.

### Summary

Solubility determinations are reported for the ternary system sodium chromate–sodium chlorate–water at 19, 25 and 50°. No evidence is found for any compound formation or solid solution between the two salts in this temperature range.

NEW YORK, N. Y.

RECEIVED AUGUST 6, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

## Absorption Spectra of Some Double Salts Containing Cobaltous Chloride\*

BY MELVIN L. SCHULTZ AND ERNEST F. LILEK

The blue color of solutions containing cobaltous chloride and hydrochloric acid or certain other chlorides in large excess has been shown by ion migration experiments<sup>1</sup> to be due to an anion of which cobalt is a constituent. It has been suggested frequently,<sup>2</sup> on the basis of indirect physico-chemical evidence, that this ion may be represented as  $\text{CoCl}_4^{--}$ .

The absorption spectra of solutions containing the ion in question have been observed, the most accurate measurements being those of Brode,<sup>3</sup> Brode and Morton,<sup>4</sup> and Kiss and Gerendas.<sup>5</sup>

\* Presented before the Division of Physical and Inorganic Chemistry at the Buffalo meeting of the American Chemical Society, September, 1942.

(1) F. G. Donnan and H. Bassett, *J. Chem. Soc.*, **81**, 939 (1902).

(2) See "Gmelins Handbuch der anorganischen Chemie, System-Nummer 58, Kobalt, Teil A," Verlag Chemie G. m. b. H., Berlin, 8 aufl., 1932, p. 490 for a summary of the work done before 1932. W. Feitknecht, *Helv. Chim. Acta*, **20**, 659 (1937), has summarized the more recent results and has presented a critical discussion of the relationship between color and constitution for a number of cobaltous compounds.

(3) W. R. Brode, *Proc. Roy. Soc. (London)*, **118A**, 286 (1928).

(4) W. R. Brode and R. A. Morton, *ibid.*, **120A**, 21 (1928).

(5) A. v. Kiss and M. Gerendas, *Z. physik. Chem.*, **180A**, 117 (1937).

The spectrum consists of many relatively narrow bands extending from the near infra-red through the visible into the ultraviolet. In the present paper, the results of the comparison of the portion of this spectrum lying within the visible region with spectra of several blue double salts containing cobaltous chloride are reported.

The structure of one of these double salts,  $\text{Cs}_3\text{CoCl}_6$ , has been determined by X-ray diffraction measurements.<sup>6</sup> These experiments have shown that in the crystal there exists an approximately regular tetrahedral arrangement of four chloride ions about each cobalt ion, the cobalt-chlorine distance being 2.34 Å. The fifth chloride ion is separated from the cobalt ion by a much greater distance, about 6.0 Å. The absorption spectrum responsible for the blue color of this crystal may be ascribed to the presence of the tetrahedral  $\text{CoCl}_4^{--}$  group.

If this same complex is present in other crystals or in solution the absorption spectra ought to re-

(6) H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 359 (1935).

semble one another closely. It need not be expected, however, that the positions and relative intensities of corresponding absorption bands be identical. For the crystals, differences in the identity of the surrounding ions and differences in their arrangement about the  $\text{CoCl}_4^{--}$  complex would be expected to give rise to differences in the spectra. The absorption bands for the solution should be more diffuse than those for the crystals with fewer details of structure resolved because of the less regular arrangement of neighbors about the complex ions and because of the effect of thermal agitation upon the arrangement. Any change in the binding energy between cobalt and chlorine for the complex in solution as compared with the crystal might produce shifts in the positions of the absorption bands. If, however, the complex responsible for the absorption, either in solution or in a crystal other than  $\text{Cs}_3\text{CoCl}_5$ , has a different composition or structure the absorption spectrum should be qualitatively different. From the results of measurements by Brode<sup>7</sup> it may be inferred that the blue color of solutions of cobalt chloride in various solvents is not always due to the same complex since the spectra of such solutions do show characteristic differences in their structure.

We have found that the absorption spectra of crystals of  $\text{Cs}_3\text{CoCl}_5$ ,  $\text{Cs}_2\text{CoCl}_4$ ,  $(\text{PyH})_2\text{CoCl}_4$ ,  $(\text{QuH})_2\text{CoCl}_4$  and  $(\text{QuH})_2\text{CoCl}_4 \cdot \text{H}_2\text{O}$ , in which PyH represents the pyridinium ion and QuH the quinolinium ion, are nearly identical. Furthermore, there is a close correspondence between these spectra and the spectrum of the hydrochloric acid solution of cobalt chloride. It may be concluded, therefore, that in these crystals and in the blue aqueous cobalt chloride solutions containing large excess of chloride ion the characteristic color is due to a tetrahedral  $\text{CoCl}_4^{--}$  complex ion.

### Experimental

The spectra were photographed using a Hilger constant deviation wave length spectrometer, fitted with a camera of 30 cm. focal length, and Eastman Spectroscopic Plates types IV B, IV F and 144 N. The linear dispersion at 4500 Å. was about 50 Å. per mm. An image of the source, an automobile headlight bulb operated from a small motor generator, was focused on the crystal. An image of the illuminated crystal was then focused on the spectrograph slit which was set at a width of about 0.02 mm. Exposure times varied from a few seconds to about nine hours.

The double salts used were prepared by methods de-

scribed in the literature.<sup>8</sup> The composition of each was confirmed by determination of chloride. Single crystals up to about 2 mm. in thickness were used in photographing the weak absorption bands. For the more intense bands the material was powdered and pressed between microscope slides whose surfaces had been ground with fine carborundum. With  $(\text{PyH})_2\text{CoCl}_4$  and  $(\text{QuH})_2\text{CoCl}_4 \cdot \text{H}_2\text{O}$  large single crystals could not be obtained. In order to photograph the weak bands of these two substances relatively thick layers of the powdered material were used which made long exposure times necessary.

The wave lengths of the bands were determined by first spotting visually on the plates the centers of the bands and by then determining the positions of the spots with respect to the comparison spectrum using a measuring microscope. For each band, with the exception of a few which were very weak, the value reported is the mean of at least five independent measurements. The average deviation, from the chosen value, of the individual measurements on a given band varied from about 1.5 Å. in the blue to about 6 Å. in the far red. The relative intensities of the bands were estimated visually from the plates and are expressed on a scale of 0-10. Since the absorption bands observed were rather sharp with clearly defined edges the band widths were estimated roughly by spotting, on the plates, the band edges. The values reported for the widths have been rounded off to the nearest 10  $\text{cm}^{-1}$ .

### Results and Discussion

The wave numbers, calculated from the measured wave lengths, of the band centers for the five double salts studied are listed in Table I together with the band widths and estimated intensities. These data are plotted in Fig. 1, in which the vertical lines represent the positions of the band centers and the heights of the lines represent the relative intensities. The only marked differences among these spectra occur in the group of weak bands lying between 19,200  $\text{cm}^{-1}$  and 20,300  $\text{cm}^{-1}$ . The remaining bands appear in all the spectra with nearly the same positions and relative intensities. Evidently, the energy levels characteristic of the complex ion are not very sensitive to changes in the surroundings.

The absorption curve for the solution of cobalt chloride in concentrated hydrochloric acid is plotted also in Fig. 1 with wave numbers as abscissas and  $\log \epsilon$  as ordinates. This curve was constructed from the data of Brode<sup>3</sup> and Brode and Morton.<sup>4</sup> The similarity between the curve for the solution and the spectra of the crystals is apparent. Each consists of four regions of absorption: a group of intense bands in the red, a group of smaller intensity in the green and yellow and two groups of weak bands in the blue. The

(8) H. W. Foote, *Am. J. Sci.*, **13**, 158 (1927); E. G. V. Percival and W. Wardlaw, *J. Chem. Soc.*, 1505 (1929).

(7) W. R. Brode, *THIS JOURNAL*, **53**, 2457 (1931).

TABLE I  
 ABSORPTION BANDS OF COBALT CHLORIDE DOUBLE SALTS

$\text{Cs}_2\text{CoCl}_6$			$\text{Cs}_2\text{CoCl}_4$			$(\text{PyH})_2\text{CoCl}_4$			$(\text{QuH})_2\text{CoCl}_4$			$(\text{QuH})_2\text{CoCl}_4 \cdot \text{H}_2\text{O}$		
$\nu$ , cm. <sup>-1</sup>	Width, cm. <sup>-1</sup>	Int.	$\nu$ , cm. <sup>-1</sup>	Width, cm. <sup>-1</sup>	Int.	$\nu$ , cm. <sup>-1</sup>	Width, cm. <sup>-1</sup>	Int.	$\nu$ , cm. <sup>-1</sup>	Width, cm. <sup>-1</sup>	Int.	$\nu$ , cm. <sup>-1</sup>	Width, cm. <sup>-1</sup>	Int.
14258	200	10	14258	230	10	14299	290	10	14242	220	10	14269	310	10
15021	190	10	14988	220	10	15000	180	10	15000	220	10	15036	220	10
15403	130	8	15393	130	9	15524	170	8	15496	180	8	15496	140	8
15783	140	9	15803	140	10	15881	210	9	15811	230	9	15868	220	9
16238	110	9	16242	120	9	16311	140	8	16281	160	8	16314	170	8
16583	90	8	16570	180	8	16725	140	7	16698	140	7	16681	100	7
17262	200	4	17198	170	3	17308	150	4	17227	120	3	17246	120	4
17703	180	2	17635	150	2	17698	120	3	17698	120	2	17684	90	3
18073	90	3	18072	140	3	18066	130	4	18067	170	3	18053	130	4
18642	180	6	18600	120	6	18623	180	5	18621	140	5	18606	110	5
18872	160	6	18837	120	6	18915	130	6	18897	190	6	18867	160	6
19273	130	1				19305	180	4				19258	100	2
19659	160	2	19559	180	5	19684	170	2	19667	220	3	19647	180	3
20153	340	1				20284	350	1	20320	270	2	20243	260	1
21909	110	4	21889	180	2	21918	170	4	21896	160	2	21876	170	2
22155	100	5	22143	130	5	22210	200	3	22152	160	2	22148	140	3
22410	140	4	22444	160	4	22498	180	3	22462	120	3	22446	120	3
22843	160	0	22832	170	0	22856	100	0	22800	120	1	22765	110	1
24044	100	1	24040	110	2	24026	110	2	24018	100	0	23996	120	0
24510	110	2	24497	120	1	24489	90	1	24462	130	0	24442	140	0

number of components, six, of the group in the red is the same for the solution and for the crystals although the bands in solution are somewhat more diffuse. The remaining groups of bands show less structure in the spectrum of the solution than in the spectra of the crystals. For these

groups, however, the curve for the solution follows approximately the envelope of the bands for the crystals if slight shifts in the positions of some of the groups are made. This comparison indicates that the differences between the two spectra are due principally to the effects of thermal agitation in solution. Therefore, the conclusion that the same complex is responsible for the absorption by the solution and by the crystals may be drawn.

Brode<sup>3</sup> and Brode and Morton<sup>4</sup> have shown that their absorption curve for the solution may be analyzed into components each of which is a multiple of a frequency of 409 cm.<sup>-1</sup>. Although there are minor discrepancies between their data and those of Kiss and Gerendas,<sup>5</sup> the spectrum reported by the latter for these same solutions may be analyzed in the same fashion. The wave numbers,  $\nu$ , of the bands found, including those in the ultraviolet which were not studied by Brode and Morton, may be represented by an expression of the form

$$\nu = a + bn$$

in which  $a$  and  $b$  are constants and  $n$  is a running positive integer. The values of  $a$  and  $b$  which give the best fit between the calculated and experimental wave number values are found in Table II. The constant frequency difference, 416 cm.<sup>-1</sup>, is in approximate agreement with the value of Brode and Morton.

The absorption spectra of the crystals may be represented by similar expressions. The con-

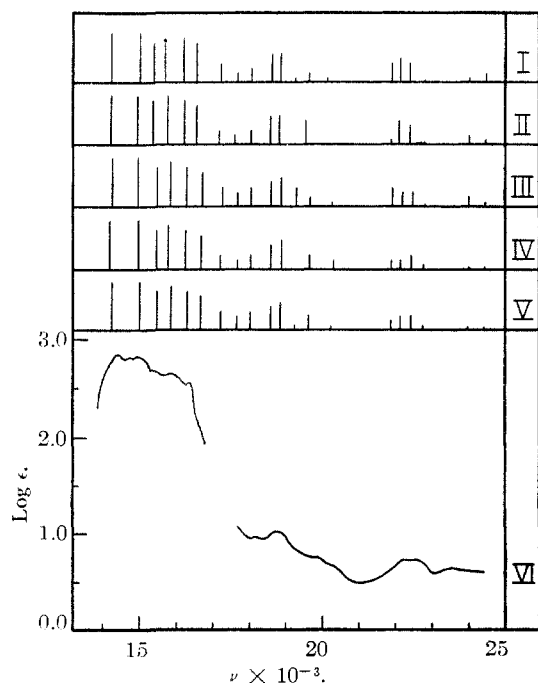


Fig. 1.—The absorption spectrum of  $\text{CoCl}_4^{2-}$  in: I,  $\text{Cs}_2\text{CoCl}_6$ ; II,  $\text{Cs}_2\text{CoCl}_4$ ; III,  $(\text{PyH})_2\text{CoCl}_4$ ; IV,  $(\text{QuH})_2\text{CoCl}_4$ ; V,  $(\text{QuH})_2\text{CoCl}_4 \cdot \text{H}_2\text{O}$ ; VI, cobalt chloride in hydrochloric acid (from data of Brode and Morton<sup>3,4</sup>).

TABLE II

	a, cm. <sup>-1</sup>	b, cm. <sup>-1</sup>	Av. dev., cm. <sup>-1</sup>
CoCl <sub>2</sub> in HCl <sup>a</sup>	14302	416	68
C <sub>5</sub> H <sub>5</sub> CoCl <sub>2</sub>	14225	393	57
C <sub>5</sub> H <sub>5</sub> CoCl <sub>4</sub>	14231	391	69
(PyH) <sub>2</sub> CoCl <sub>4</sub>	14304	390	73
(QuH) <sub>2</sub> CoCl <sub>4</sub>	14236	391	64
(QuH) <sub>2</sub> CoCl <sub>4</sub> ·H <sub>2</sub> O	14282	389	74

<sup>a</sup> Analysis based on the data of Kiss and Gerendas.<sup>5</sup>

stants, together with the average deviations between the calculated and experimental values of  $\nu$ , are listed in Table II. The latter are somewhat larger than the experimental uncertainties in the wave number values of the bands but are of the same order of magnitude. Since the bands are from 100 to 300 cm.<sup>-1</sup> in width, the deviation might be due, in part, to slight systematic errors in picking out the band maxima.

In view of these regularities, following a suggestion made recently by one of us<sup>9</sup> for several other complex ions, these spectra may be interpreted as having originated in electronic transitions for which vibrational structure characteristic of the CoCl<sub>4</sub><sup>2-</sup> complex ion is developed. It may be noted that the average frequency for the complex in solution, 413 cm.<sup>-1</sup>, differs by 22 cm.<sup>-1</sup> from the average value of the crystals, 391 cm.<sup>-1</sup>. Since the frequencies of the normal vibrations of the complex depend on the force constant of the cobalt-chlorine bond and since the frequency found here is probably that of the totally symmetric vibration, the existence of this difference indicates that the binding energy of the complex ion in the crystal is smaller than in solution.

(9) M. L. Schultz, *J. Chem. Phys.*, **10**, 194 (1942).

Although each observed band in the spectra of the crystals (and in the solution as well) is represented by an integral value of  $n$ , not all values of  $n$  represent observed bands. This, together with the somewhat unsatisfactory fit of the group of bands at 22,000 cm.<sup>-1</sup> into the suggested analysis, indicates that this analysis is too simple. Probably several electronic transitions, each with its associated vibrational structure, occur. With the data at present available, no reliable energy level diagram can be constructed. It is the intention in this Laboratory to study the spectra of these crystals at low temperatures in order to obtain information which might permit the construction of such a diagram and also in order to study in more detail the effect of the environment upon the spectrum.

### Summary

1. The absorption spectra of crystals of two cesium cobaltous chlorides, dipyridinium cobaltous chloride, diquinolinium cobaltous chloride and diquinolinium cobaltous chloride monohydrate have been measured.

2. Comparison of the spectra of these crystals with the spectrum of the solution of cobaltous chloride in concentrated hydrochloric acid shows that the same complex ion, CoCl<sub>4</sub><sup>2-</sup>, is present in all.

3. A tentative analysis of the spectra of the crystals has been made. This analysis suggests that the spectra may be considered to originate in coupled electronic-vibrational transitions.

CHICAGO, ILLINOIS

RECEIVED JULY 27, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

## Some Boron Trifluoride Catalyzed Alkylations of Halobenzenes<sup>1</sup>

BY G. F. HENNION AND V. R. PIERONEK

### Introduction

Previous work in this Laboratory has shown that boron trifluoride, in the presence of a strong dehydrating agent such as phosphoric anhydride or sulfuric acid, is an excellent catalyst for the alkylation of benzene<sup>2</sup> and its homologs<sup>3</sup> with alcohols. This method was extended in the present work to the halobenzenes.

In many respects boron trifluoride has been found superior to aluminum chloride for these alkylations. With aluminum chloride there may be considerable halogen migration to produce benzene, dihalobenzene and alkylbenzene as well as the desired alkylhalobenzene.<sup>4,5</sup> Furthermore, the aluminum chloride methods result in both meta and para substitution,<sup>6,7</sup> thus giving an

(1) Paper XXVII on organic reactions with boron trifluoride; XXXVI delayed in press; XXV, *THIS JOURNAL*, **63**, 2603 (1941).

(2) Toussaint and Hennion, *ibid.*, **62**, 1145 (1940).

(3) Welsh and Hennion, *ibid.*, **63**, 2603 (1941).

(4) Dumreicher, *Ber.*, **15**, 1866 (1882).

(5) Berry and Reid, *THIS JOURNAL*, **49**, 3146 (1927).

(6) Tsukervanik, *J. Gen. Chem. (U. S. S. R.)*, **8**, 1512 (1938); *C. A.*, **33**, 4587 (1939).

(7) Dreisbach, Britton and Perkins, U. S. Patent 2,193,760 (1940).