defined as $\lambda^2[1 + \lambda^2 + 4\lambda\Delta(2 + 2\Delta^2)^{-1/2}]^{-1}$ given in Table II.

TABLE II

	λ	Ionic character, %	$(1/e)(\partial\mu/\partial r)$
HF	1.325	44.7	0.8686
HCl	0.7319	22.0	.6750
HBr	.7169	21.3	.6002
HI	.5868	17.2	.4307

Both the ionic character and $\partial\mu/\partial r$ decrease in the same direction. The magnitudes of the ionic characters are not too unreasonable. The $\partial\mu/\partial r$ values are larger than the experimental values, but one notes qualitative agreement. The values for HCl and HBr are of the same order of magnitude and the HI value is less than either of the former. The ratio of the values from HCl to HI is about 1:0.9:0.6 while the experimental ratio is about 1:0.6:0.4.

In view of the approximation used and the qualitative agreement obtained, one may conclude that the sign of the experimental $\partial\mu/\partial r$ is positive. This choice of sign is in agreement with the results of Smith and Eyring,[5] but not with those of Hammer and Rollefson,[6] Warhurst[7] or Bell and Coop.[8,9]

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[5] R. P. Smith and H. Eyring, THIS JOURNAL, **73**, 5512 (1951).

[6] C. F. Hammer and R. Rollefson, "Symposium on Molecular Structure and Spectroscopy," Ohio State University, Columbus, Ohio, June 12, 1951.

[7] E. Warhurst, *Trans. Faraday Soc.*, **45**, 461 (1949).

[8] R. P. Bell and I. E. Coop, *ibid.*, **34**, 209 (1938).

[9] NOTE ADDED IN PROOF.—Herman, Silverman and Wallis, Am. Phys. Soc. meeting, New York, Jan. 28, 1954, have concluded, from a study of infrared vibration-rotation line intensities in HCl, that μ and $\partial\mu/\partial r$ have the same sign.

The Absorption Spectrum of Cs_2CoCl_4 at Liquid Nitrogen Temperatures

BY LEONARD I. KATZIN

RECEIVED FEBRUARY 8, 1954

In continuation of earlier reported work on reflection spectra,[1] it has been possible to obtain absorption spectra for Cs_2CoCl_4 in the solid state, both at room temperature and at liquid nitrogen temperatures, under transmission conditions of good resolution. This makes it possible better to compare the spectrum of the $CoCl_4^=$ group, which has been crystallographically identified in the solid material,[2] and the spectrum of what has always been assumed to be this group, found in appropriate "blue" Co(II) solutions. The previous attempts to obtain similar spectra of solids containing the cobaltous halide complex grouping[3] have not been such as to allow any detailed description of the spectrum to be made.

Experimental

A recrystallized, dry sample of Cs_2CoCl_4, prepared originally by crystallization from water of a $CsCl-CoCl_2$ mixture,[1] was finely ground, and a small portion was reground with a large amount of KBr. A portion of this mixture was further diluted with KBr, and transparent discs of the two mixtures were prepared by published techniques.[4-6] For observation, the discs were mounted in a special evacuated cell which allowed refrigeration with liquid nitrogen.[7] Observations were made, both at room temperature and at liquid nitrogen temperature, with the aid of the Cary recording spectrophotometer. Observations were made at room temperature alone of solutions of cobaltous chloride in concentrated HCl, for comparison with the absorption of the solid preparations. The results are shown in Figs. 1–3.

Grateful acknowledgement is made of the loan of apparatus and of assistance in preparation of the solid samples by Dieter Gruen, and of assistance in obtaining the traces by Peter Pringsheim and James C. Hindman.

Discussion

In Fig. 1 are shown three curves for different concentrations of cobaltous chloride in concentrated HCl. The relative intensities of the strong absorption around 690 mμ and of the weaker peaks below 610 mμ are seen by comparing the heights of the 533 mμ absorption in the three curves. The fourth curve, to show the difference of the "red" absorption, is for cobaltous nitrate in water. The essential features of the chloride absorption do not differ significantly from similar figures which have been published by earlier workers.[8-10]

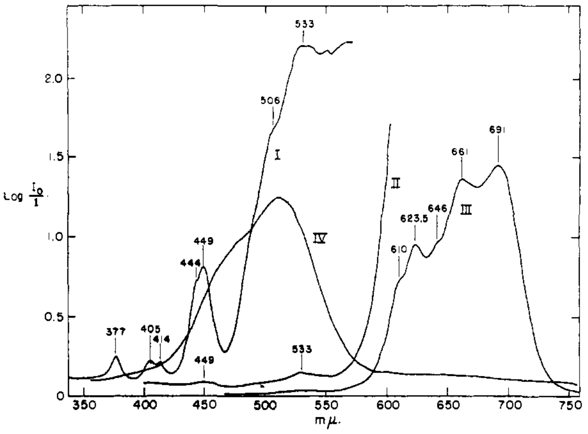

Fig. 1.—Absorption spectra of cobalt solutions. Curves I, II, III, successively lower concentrations of cobaltous chloride in concentrated HCl. Curve IV, cobaltous nitrate in water, to show characteristic difference of "red" cobalt absorption.

The solid preparations of Cs_2CoCl_4 at liquid nitrogen temperatures show peaks greatly sharpened, and slightly shifted to lower wave lengths, compared to the same material at room temperature (not shown). Resolution of groups of peaks, such as the one around 450 mμ, is thereby greatly improved. The most definite difference from the spectrum of the HCl solution is in the relative heights of the components of the main absorption peak between 600 and 700 mμ. Though the effect

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[1] L. I. Katzin and E. Gebert, THIS JOURNAL, **75**, 2830 (1953).

[2] Stanley Siegel, private communication.

[3] M. L. Schultz and E. F. Lilek, THIS JOURNAL, **64**, 2748 (1942); M. L. Schultz, *ibid.*, **71**, 1288 (1949).

[4] M. M. Stimson and M. J. O'Donell, *ibid.*, **74**, 1805 (1952).

[5] U. Schiedt and H. Reinwein, *Z. Natursforsch.*, **7b**, 270 (1952).

[6] U. Schiedt, *ibid.*, **8b**, 66 (1953).

[7] R. Casler, P. Pringsheim and P. Yuster, *J. Chem. Phys.*, **18**, 887 (1950).

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

[9] W. R. Brode and R. A. Morton, *ibid.*, **A120**, 21 (1928).

[10] A. V. Kiss and M. Gerendas, *Z. physik. Chem.*, **180**, 117 (1937).

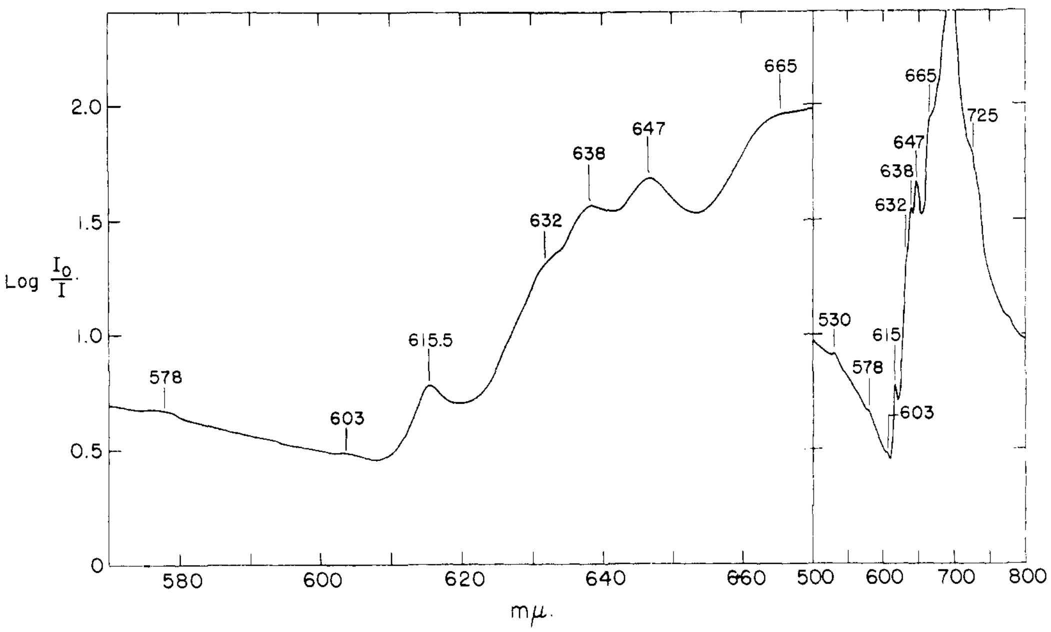

Fig. 2.—Absorption spectrum of Cs_2CoCl_4 dispersed in KBr ("thin" preparation) at liquid nitrogen temperatures, against arbitrary diaphragm air blank; condensed and spread wave length scale tracings, to show general features and resolution of peaks.

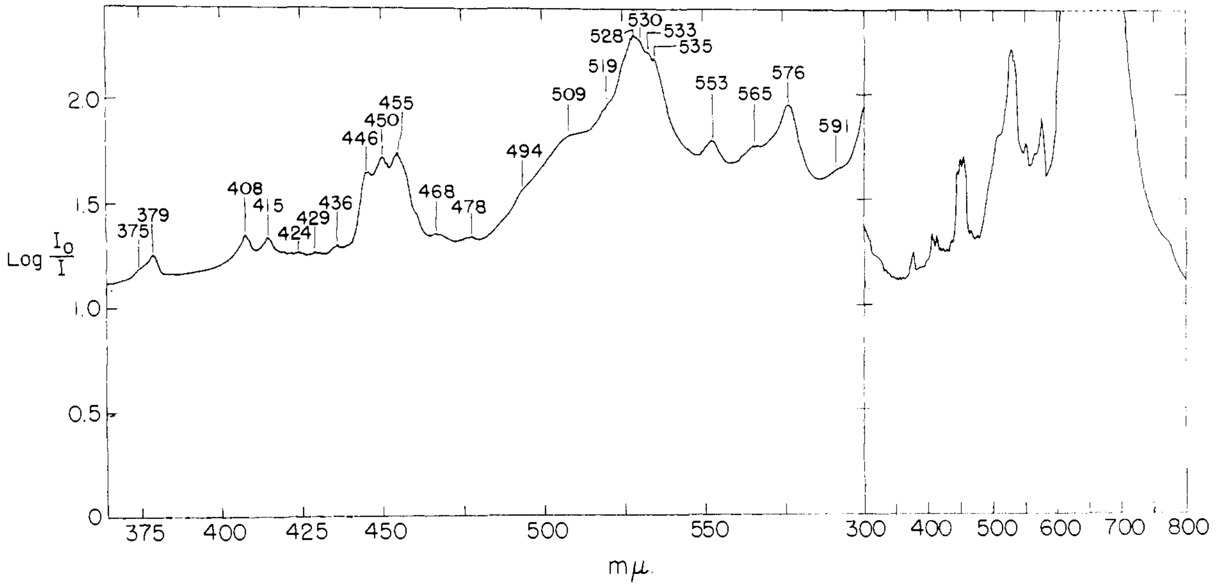

Fig. 3.—Absorption spectrum of Cs_2CoCl_4 dispersed in KBr ("thick" preparation) at liquid nitrogen temperatures, against equivalent KBr blank; condensed and spread wave length scale tracings, to show general features and resolution of peaks.

is exaggerated at low temperatures, even at room temperature the absorption at about 700 mμ dominates the shoulder at 675 mμ, and is about twice the absorption at 650 mμ. The room temperature spectrum resembles to a large extent the published curves for cobalt in HI solution.[8,9] In the solution (Fig. 1), the absorptions at 691 and 661 mμ are fairly well resolved, though there may be a hint of a peak at about 680 mμ[8-10] which does not show well in the tracing.

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Barium Iron Oxide Isomorphs of Hexagonal and Tetragonal $BaTiO_3$

BY W. W. MALINOFSKY AND H. KEDESDY

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Investigations of the formation of magnetic barium iron oxide led to the study of the reaction product obtained from a $2BaCO_3$–Fe_2O_3 powder mixture fired at 900° in oxygen. The composition of the barium iron oxide reaction product from this mixture should be close to $BaFeO_3$, analogous to $BaTiO_3$. A reaction product of that approximate composition was reported in an earlier investigation of