of summation; his results check the specific heat of Johnston and Davis to 0.002 cal./deg. and the other functions to 0.001 or better.

Acknowledgment.—The author is very grateful to both Professor D. M. Dennison and Dr. O. K. Rice, each of whom independently corrected an error in the quantum weights for carbon dioxide.

Summary

1. The free energy, heat content and specific heat of nitrous oxide have been calculated up to 1500°K.

2. The heat content and specific heat of carbon dioxide have been computed to 1000°K. and the free energy to 1500°K.; less accurate estimates have been made up to 3500°K. The equilibrium constants for the water-gas and producer-gas reactions have been tabulated from 300 to 3000°K., and that for the dissociation of carbon dioxide to 3500°K.

PITTSBURGH, PA. RECEIVED APRIL 4, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

The Absorption Spectra of Cobalt Compounds. V. The Cobalt–Ethylenediamine–Halogen Complexes

BY MAURICE L. ERNSBERGER AND WALLACE R. BRODE

In a continuation and extension of previously reported work[1] on compounds of the type $(CoEn_2X_2)X$, this paper presents the absorption spectra of a series of halogen substituted derivatives and the effect on the absorption caused by a change in the halogen substituent. Some of these compounds described have not been previously prepared or had their absorption spectra recorded, and in the case of some of the compounds with recorded absorption spectra, the data available were not satisfactory.

The compounds were prepared according to the methods used by Werner.[2] They react slowly with water and this vitiates to some extent the accuracy of the absorption spectra measurements. By dissolving the compounds in the least possible amount of water and diluting to the desired concentrations with alcohol, solutions were obtained in which the reaction with water was retarded sufficiently to make reliable measurements possible.

The spectra were measured in the visible region by means of a Bausch and Lomb spectrophotometer. In the ultraviolet region measurements were made with a Bausch and Lomb quartz spectrograph using as a light source an underwater spark between tungsten electrodes.[3] The Hilger rotating sectorphotometer system was used.

TABLE I

RESULTS OF BAND ANALYSES OF THE ABSORPTION SPECTRA OF SALTS OF THE TYPE $(CoEn_2X_2)X$

Compound	Mean frequency difference	Multiple number	Bands Observed	Bands Calculated	Difference
1,6-$(COEn_2F_2)NO_3$[a]	51.4	10	515	514	− 1
		13	660	668	+ 8
		16	835	823	−12
1,6-$(CoEn_2Cl_2)Cl$	48.5	10	484	485	− 1
		13	635	631	− 4
		16	775	776	+ 1
1,6-$(CoEn_2ClBr)NO_3$	47.0	10	470	470	0
		13	620	611	− 9
(Fig. 1)		16		752	
		(18)	825	822	(−3)[b]
		19		894	
1,6-$(CoEn_2Br_2)Br$	45.6	10	456	456	0
		13	600	593	− 7
		16	740	730	−10
		(18)	820	(821)	+ 1
		19	860	867	+ 7
		22	1010	1003	− 7
1,6-$(CoEn_2I_2)I$	44.8	10	448	448	0
		13		583	
(Fig. 2)		16	720	717	− 3
		19	850	852	+ 2
		22	990	986	− 4
1,2-$(CoEn_2F_2)F$[a]	84.7	7	605	593	−12
		10	835	847	+12
1,2-$(CoEn_2Cl_2)Cl$	79.7	7	558	558	0
		10	800	797	− 3
1,2-$(CoEn_2ClBr)Br$	78.7	7	551	551	0
		10	790	787	− 3
1,2-$(CoEn_2Br_2)Br$	77.9	7	545	545	0
		10	780	779	− 1

[a] Values taken from Gordienko.[1a] [b] Approximate.

The compound 1,6-$(CoEn_2I_2)I$ was prepared from $(CoEn_2CO_3)I$. Solid $(CoEn_2CO_3)I$ was treated with concentrated hydriodic acid (44%)

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(1) (a) Seibt, Dissertation, Zurich, 1913, p. 53; Gmelin's "Handbuch der anorganischen Chemie," Berlin, 1930, Vol. 58-B, p. 228; (b) Lifschitz, *Z. physik. Chem.*, **105**, 33 (1923).

(2) Werner, *Ann.*, **386**, 1–272 (1912).

(3) Brode, *Bur. Standards J. Research*, **47**, 504–507 (1929).

and the brown solution evaporated just to dryness on the steam-bath. Bright green crystals of 1,6-($CoEn_2I_2$)I were obtained. The compound decomposed on the addition of water and slowly on standing in air. It dissolved incompletely in absolute alcohol to give a green solution, leaving a residue of unknown composition. Since it did not all dissolve, the concentrations of the solutions were not known.

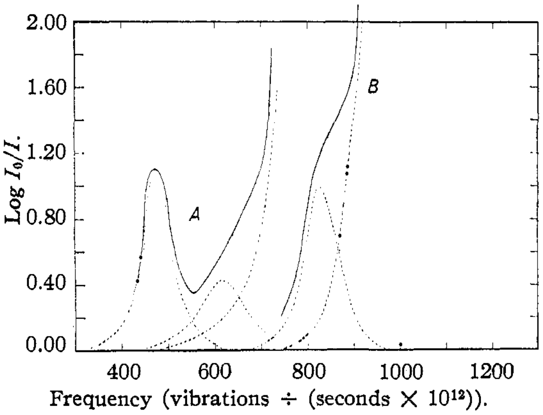

Fig. 1.—The absorption spectrum of 1,6-($CoEn_2ClBr$)NO_3 in alcohol: (A) concn. = 3.36 g. per liter. (0.01 *N*); cell thickness = 1.0 cm.; (B) concn. = 0.68 g. per liter (0.002 *N*); cell thickness = 1.0 cm. Band analysis shown by dotted curves.

Anal. Required for ($CoEn_2I_2$)I: Co, 10.53; I, 68.3. Found: Co, 10.2, 9.77, 9.95; I, 70.4.

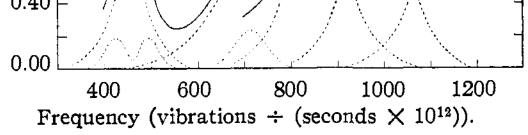

Fig. 2.—The absorption spectrum of 1,6-($CoEn_2I_2$)I in alcohol; concn. of B = $^1/_2$ A; cell thickness = 1.0 cm. Band analysis shown by dotted curves.

All the compounds included in Table I were prepared and their absorption spectra measured, with the exception of the 1,6- and 1,2-difluoro compounds, the data for which were taken from the work of Gordienko. The absorption spectra of both the 1,6- and 1,2-series of compounds have been analyzed graphically into component bands indicated by dotted lines on the graphs, according to the method described by Brode.[4] The bands were found to fit into definite frequency series for which mean frequency differences and band numbers have been calculated (Table I). These results show certain regularities in the absorption spectra of this series of compounds. Replacement of a halogen substituent by a heavier halogen atom causes a corresponding decrease in the frequencies at which absorption bands occur, *i. e.*, it causes a shift of the bands toward the red. Figure 3 shows the mean frequency differences for the absorption bands of the various complex cations of the 1,6 series plotted against the total atomic weight of the halogen substituents. Evidence for the idea that the absorption bands are due to a vibratory system including the halogen substituents as an essential part of the chromophore is shown by the following facts: (1) a calculation of band numbers and frequency differences can be made on the basis of a fundamental frequency difference; (2) the absorption bands for the different cation complexes have the same band numbers; (3) an increase in the weight of the halogen substituents causes a decrease in the mean frequency difference of the absorption bands.

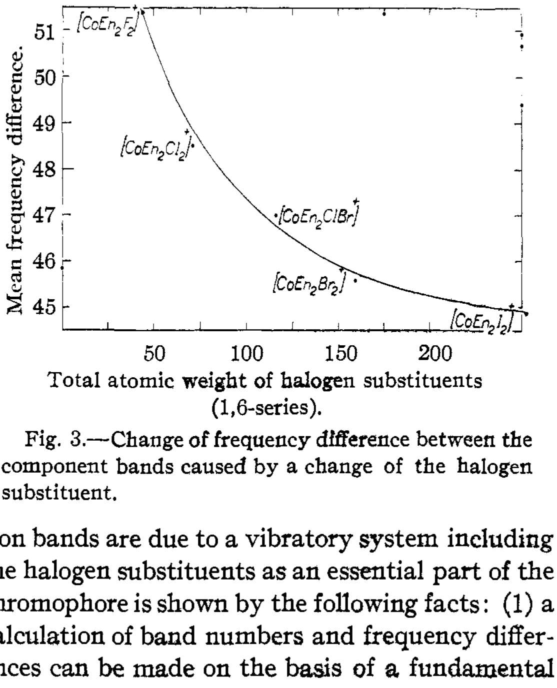

Fig. 3.—Change of frequency difference between the component bands caused by a change of the halogen substituent.

Summary

1. Compounds of the type ($CoEn_2X_2$)X, where X is halogen, have been prepared and their absorption spectra studied and analyzed. A regular decrease in mean frequency difference corresponding to increase in the weight of the substituents was found.

COLUMBUS, OHIO RECEIVED APRIL 14, 1934

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[4] Brode, *Proc. Roy. Soc.* (London), **A118**, 286–296 (1928).