Kelvin equation to the present systems is justified. We may conclude, therefore, that in the systems investigated capillary condensation is superimposed on multilayer adsorption. This concept is implied in the BDDT theory, though they preferred to designate it as "additional energy."

Acknowledgment.—The authors wish to acknowledge their indebtedness to Dr. Ying Fu of this Laboratory for his valuable assistance in the development of the work of this paper.

Summary

1. The adsorption isotherms over the entire pressure range for di-ethylamine, *n*-butylamine, and di-*n*-butylamine on silica gel have been determined at 25°. These isotherms were found to be unusual in that within the relative pressure ranges of 0 to 0.01 and about 0.5 to 0.8 the rates of increasing adsorption with pressure were very great. The completion of the monolayers occurred at the very low relative pressure of about 0.01.

2. The three-constant BET equation was found to be applicable in the approximate relative pressure range of 0.002–0.4. The constant *n* was found to be less than 3 in all cases. A tentative interpretation of the constant *n* has been proposed and applied to the data.

3. Highly concordant values for the capillary radius of the gel were obtained by the application of the Kelvin equation, indicating that to account for the experimental data capillary condensation must be taken into consideration in addition to the chemi- and to multilayer adsorptions.

ANN ARBOR, MICHIGAN RECEIVED JULY 14, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Absorption Spectra of Some Cobalt(III) Coördination Compounds

BY FRED BASOLO

There is at present no general method completely reliable for the determination of configuration of ions of the type [Ma_4b_2], [Ma_4bc], [$M(AA)_2b_2$] and [$M(AA)_2bc$][1] in solution. The work of Shibata[2] suggests that this can be accomplished by means of absorption spectra when b and c are negative ligands. Very recently[3] it has been shown that rotatory dispersion curves may be used to reveal the configuration of such ions in which the AA groups are optically active.

That geometric isomers of certain metallic complexes exhibit distinctly different colors has long been known.[4] It has likewise often been stated that the *cis* compounds are more highly colored than the *trans*, but the exceptions to this rule are so numerous that it is without value. These observations do suggest however that there may be some correlation between the configurations of these ions and their absorption spectra. To establish whether this is true and to define the differences existing between such geometric isomers, a number of spectra were determined in neutral or acid water solutions or in methanol–water solutions. The compounds studied were of known configuration with groups b and c being either neutral or negative.

Experimental

Spectral Measurements.—All measurements were made with a Beckman model DU spectrophotometer in silica cells having a 1 cm. light path. Extinction coefficients were calculated from the familiar equation

$$\epsilon = 1/cd \log_{10} (I_0/I)$$

Measurements were made at room temperature and a total operation time of approximately two hours was required. The complete spectrum was obtained from 625 to 220 mμ.

Compounds.—The compounds studied were prepared by the procedures described in the literature[5] and purified either by recrystallization or reprecipitation by the addition of ethanol–ether to a concentrated aqueous solution of the salt. All of the compounds were analyzed for either halogen or nitrogen. A few of the compounds used were kindly supplied by Professor John C. Bailar, Jr.

Solutions.—Distilled water and reagent grade methanol were used as solvents. The molar concentration of the solutions varied from 3×10^{-2} to 1×10^{-5}. The acid aqueous solutions were prepared from a stock solution of dilute acid so that in all cases blanks were the same sample of solvent used for dissolving the compound studied. The methanol solutions were prepared by the immediate transfer of an aliquot of a concentrated aqueous solution to absolute methanol. This methanol solution was used in the longer wave length regions and subsequent dilutions were made with absolute alcohol. The blanks were obtained by starting with the same amount of water as the aliquot of concentrated solution and carrying out the same dilutions with methanol. These solutions varied from 95–99% methanol by volume.

Results.—The data obtained are summarized in Table I and the more pertinent results are shown in Figs. 1 to 6. It is evident from these absorption curves that the isomeric ions do have different spectra; however, in some cases this difference is only very slight. It is further evident that this difference is shown either by a shift in the absorption maximum to other wave lengths or by a change of intensity or by both.

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(1) The following abbreviations are used: a, b and c = monodentate groups; AA = bidentate groups.

(2) Shibata, *J. Coll. Sci. Imp. Univ. Tokyo*, 37 (1915).

(3) O'Brien, McReynolds and Bailar, THIS JOURNAL, **70**, 749 (1948).

(4) Jörgensen, *J. prakt. Chem.*, **39**, 16 (1889).

(5) The literature references for the preparation of these compounds are given in Table I.

TABLE I

ABSORPTION MAXIMA OF SOME COBALT(III) GEOMETRIC ISOMERS

Compound	Configuration	Solvent	$\lambda_{max.}$, mμ	log ε	$\lambda_{max.}$, mμ	log ε	$\lambda_{max.}$, mμ	log ε	$\lambda_{max.}$, mμ	log ε
$[Co(NH_3)_4(NO_2)_2]Cl$[6]	*cis*	MeOH–H_2O	238	4.19	327	3.63	448	2.24		
	trans	MeOH–H_2O	255	4.19	356	3.72	440	2.40		
$[Co\,en_2(NO_2)_2]NO_3$[7]	*cis*	MeOH–H_2O	240	4.22	325	3.70	438	2.34		
	trans	MeOH–H_2O	250	4.09	347	3.62	433	2.34		
$[Co\,pn_2(NO_2)_2]Cl$[8]	*trans*	MeOH–H_2O	250	4.10	340	3.48	435	2.25		
$[Co\,en_2Cl_2]Cl$[9]	*cis*	MeOH–H_2O	240^a	4.28	390^a	1.89	530	1.88		
	trans	MeOH–H_2O	252	4.31	385	1.64	450	1.40	625	1.54
$[Co\,pn_2Cl_2]Cl$[10]	*trans*	MeOH–H_2O	255	4.03	380^a	1.62	450	1.41	610	1.53
$[Co\,en_2ClSCN]SCN$[11]	*cis*	MeOH–H_2O	300^a	3.28	510	2.30				
	trans	MeOH–H_2O	335	3.40	520	2.24				
$[Co\,en_2(SCN)_2]SCN$[12]	*cis*	MeOH–H_2O	335	3.53	520	2.54				
	trans	MeOH–H_2O	335	3.51	515	2.56				
$[Co\,en_2ClNO_2]Cl$[13]	*cis*	MeOH–H_2O	337	3.26	465	1.96				
$[Co\,en_2ClNO_2]NO_3$	*trans*	MeOH–H_2O	245	4.19	340	3.14	466	1.91		
$[Co\,en_2NH_3Cl]S_2O_6$[11]	*cis*	MeOH–H_2O	360	1.90	512	1.87				
	trans	MeOH–H_2O	355^a	1.65	407^a	1.61				
$[Co\,en_2NH_3OH]Br_2$[11]	*cis*	Water	360	1.90	495	1.92				
	trans	Water	365	1.90	495	1.94				
$[Co\,en_2H_2OOH]Br_2$[14]	*cis* or *trans*	Water	367	1.90	512	1.86				
$[Co\,en_2(NH_3)_2]Cl_3$[15]	*cis*	Water	338	1.55	470	1.52				
$[Co\,en_2(NH_3)_2]_2(S_2O_6)_3$[15]	*trans*	Water	338	1.78	470	1.81				
$[Co\,pn_2(NH_3)_2]Cl_3$[2]	*trans*	Water	338	1.86	470	1.90				
$[Co\,en_2NH_3H_2O]Br_3$[11]	*cis*	Water *p*H 0.7	340	1.86	485	1.79				
	trans	Water *p*H 0.7	345	1.81	485	1.83				
$[Co\,en_2(H_2O)_2]Br_3$[16]	*cis*	Water *p*H 0.7	355	1.82	495	1.85				
	trans	Water *p*H 0.7	355^a	2.03	497	1.65				
$[Co\,enNH_3SCN](SCN)_2$[11]	*cis*	MeOH–H_2O	323	3.30	500	2.47				
	trans	MeOH–H_2O	332	3.55	510	2.56				

These absorption bands are broad and diffuse, indicating perhaps an overlapping of two or more bands.

Discussion

The absorption spectra of all complexes containing one or more negative ligands was determined in methanol–water solutions. This was found to be necessary because of the rather rapid rate of aquation of some of these complex ions.[16] Dichlorobis-(ethylenediamine)cobalt(III) chloride, which in water is almost entirely changed to the chloroaquo in one hour, remains virtually unchanged in methanol–water (99%) for a period of several weeks.

There is reason to believe that the absorption spectra of these geometric isomers might differ in some regular fashion, thus permitting their configuration to be deduced on the basis of spectral differences. It has already been mentioned that the *cis* isomers are reportedly more highly colored than the *trans*. The examination of Figs. 1–6 reveals that this is not correct, for the extinction coefficients of the stereoisomers vary in a random manner. Likewise it has been demonstrated numerous times[17] that ligands *trans* to a negative group are more labile than groups opposite neutral ligands. This observation, often referred to as the "*Trans Effect*," has been fairly well correlated[18] on the basis of the polarization of the central atom. This suggests that the *trans* isomer of a bis-(ethylenediamine) or tetrammine complex would possess a more labile group (be less stable chemically) than the *cis* salt. Tsuchida[19] has shown that the position of the second absorption band can be taken as a qualitative measure of stability; the more stable complex will absorb in the shorter wave length region. It therefore should follow that the second absorption band of a *cis* isomer be shifted slightly toward the shorter wave length as compared to that of the *trans* complex. Figures 1 and 2 clearly show that this is true and further illustrate that a similar shift occurs with the third[20] absorption band. It is

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(6) Biltz and Biltz, "Laboratory Methods of Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1909, pp. 178–179.

(7) Werner and Humphrey, *Ber.*, **34**, 1726 (1901).

(8) Watts, "Dissertation," Zurich, Switzerland, 1912.

(9) Werner and Fröhlich, *Ber.*, **40**, 2225 (1907).

(10) Werner, *Ann.*, **386**, 1 (1912).

(11) Werner and Bräunlich, *Z. anorg. Chem.*, **22**, 127 (1899).

(12) Werner and Gerb, *Ber.*, **34**, 1739 (1901).

(13) Werner, *ibid.*, **40**, 272 (1907).

(14) Werner, *Ann.*, **351**, 65 (1907).

(15) Werner, *Ber.*, **40**, 262 (1907).

(16) Mathieu, *Bull. soc. chim.*, **3**, 2152 (1936).

(17) Chernyaev, *Ann. inst. platine*, **4**, 243 (1926); Bailar and Peppard, THIS JOURNAL, **62**, 105 (1940).

(18) Grunberg, *Acta. Physicochim. U. S. S. R.*, **3**, 573 (1935).

(19) Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388, 436 (1938).

(20) This nomenclature has been used by previous investigators to designate approximate wave lengths as follows: first band = visible; second band = long ultraviolet; third band = short ultraviolet.

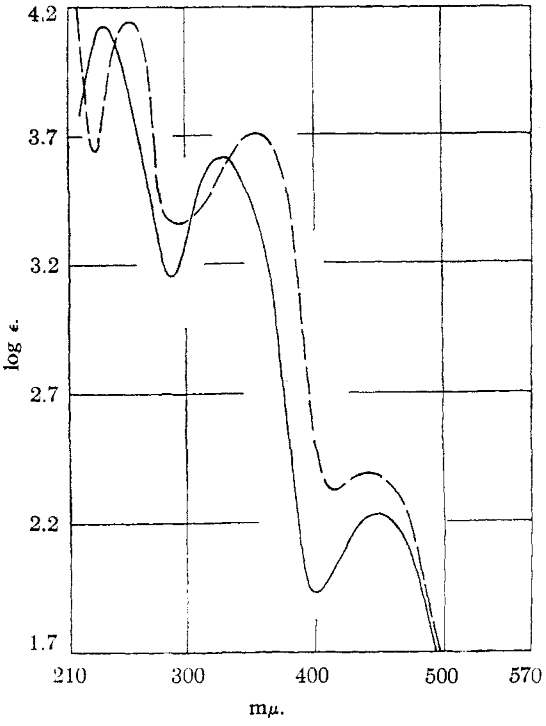

Fig. 1.—Absorption spectra of dinitrotetramminecobalt(III) salts in methanol–water solution: — *cis*-[Co $(NH_3)_4(NO_2)_2$]Cl; — — *trans*-[Co $(NH_3)_4(NO_2)_2$]Cl.

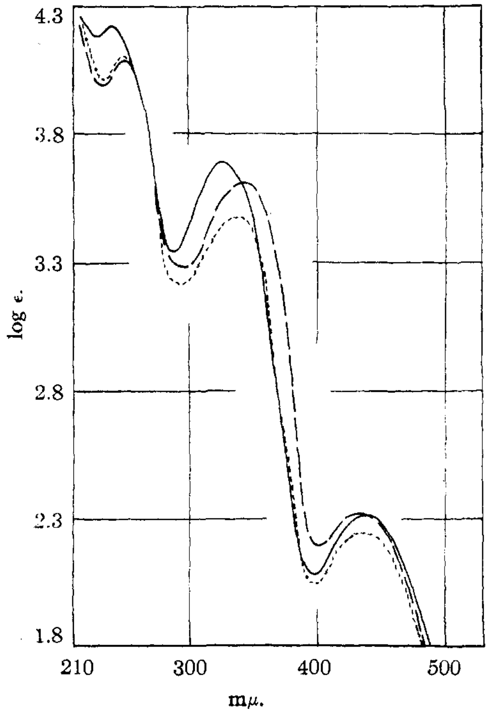

Fig. 2.—Absorption spectra of dinitrotetramminecobalt(III) salts in methanol–water solution: — *cis* [Co $en_2(NO_2)_2$]NO_3; — — *trans* [Co $en_2(NO_2)_2$]NO_3; - - - - *trans* [Co $pn_2(NO_2)_2$]Cl.

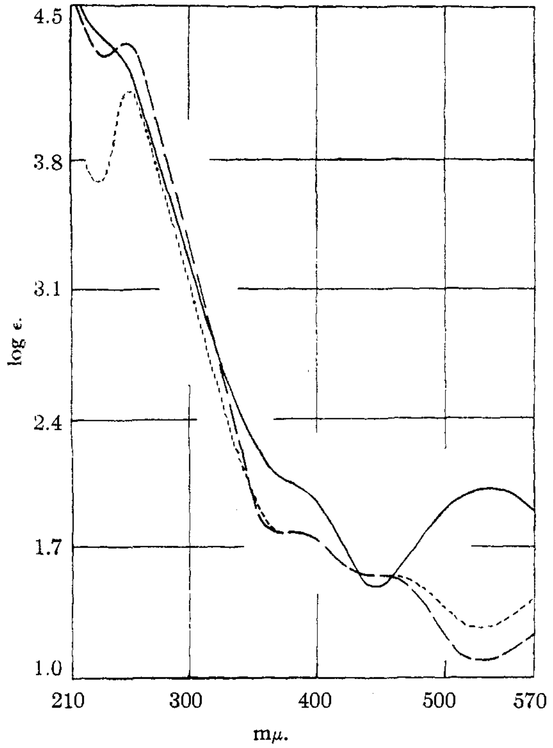

Fig. 3.—Absorption spectra of dichlorotetramminecobalt(III) salts in methanol–water solution: — *cis* [Co en_2Cl_2]Cl; — — *trans* [Co en_2Cl_2]Cl; *trans* [Co pn_2-Cl_2]Cl.

likewise seen that the distinct bands in Fig. 3 differ in such a manner that the absorption bands of the *trans* compound are at the longer wave length regions. In all of the other cases studied there is no measurable difference in the band positions. This would seem to indicate that whenever the stability differences of stereoisomers are sufficiently large to cause a shift in the absorption band positions, then the one that absorbs at the shorter wave length is the *cis* isomer.

It has been pointed out by Shibata[2] that in addition to the two absorption bands always observed in cobalt(III) ammines, certain of these compounds have an additional band in the shorter ultraviolet region. A much more extensive study has been made by Tsuchida[21] who concludes that any two negative ligands, when in a *trans*-position to each other, give rise to a third absorption band at approximately 250 mμ; whenever they occupy a *cis*-position, the third band is absent. Mention was made earlier[22] of preliminary studies which indicated that this third band was likewise present in the shorter ultraviolet region for certain compounds containing adjacent negative ligands. Figures 1 and 2 show clearly that this is true while Fig. 3 reveals only a diffuse third band for *cis*-[Co en_2Cl_2]Cl. That the third absorption band is not always present for compounds having nega-

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[21] Tsuchida, *Bull. Chem. Soc. Japan*, **11**, 785 (1936).

[22] Basolo, THIS JOURNAL, **70**, 2634 (1948).

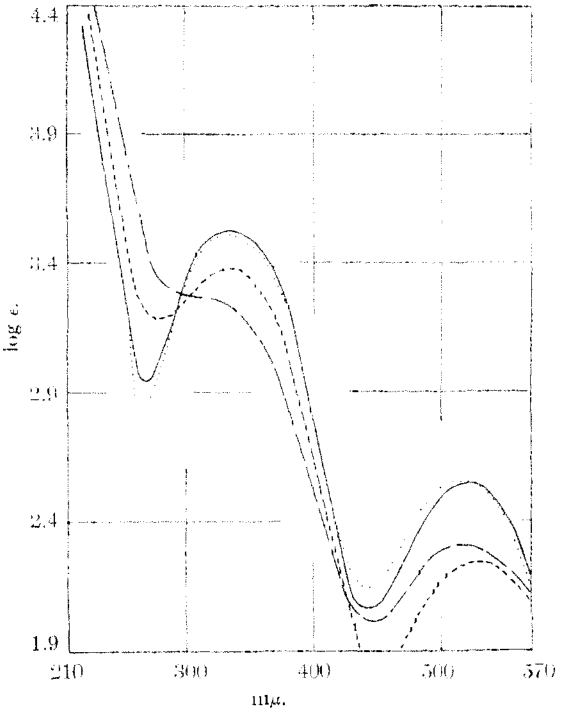

Fig. 4.—Absorption spectra of dithiocyanato and chlorothiocyanatobis-(ethylenediamine)-cobalt(III) salts in methanol–water solution: —— *cis*-[Co en$_2$(SCN)$_2$]SCN; ...... *trans*-[Co en$_2$(SCN)$_2$]SCN; — — *cis*-[Co en$_2$Cl-SCN]SCN; ------ *trans*-[Co en$_2$Cl(SCN)$_2$]SCN.

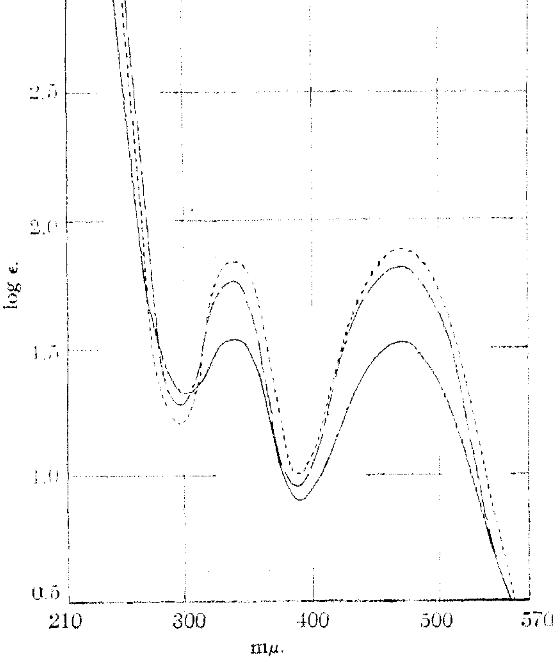

Fig. 5.—Absorption spectra of hexamminecobalt(III) salts in water solution: — *cis*-[Co en$_2$(NH$_3$)$_2$]Cl$_3$; - - - *trans*-[Co en$_2$(NH$_3$)$_2$]$_2$(S$_2$O$_6$)$_3$ - - - - *trans*-[Co pn$_2$(NH$_3$)$_2$]Cl$_3$.

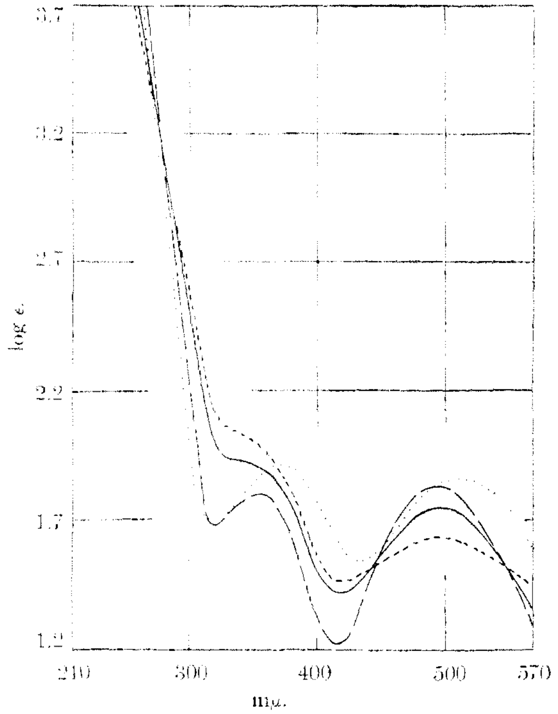

Fig. 6.—Absorption spectra for hydroxoaquo and diaquobis-(ethylenediamine)-cobalt(III) salts in water and dilute hydrobromic acid (pH 0.7) solutions, respectively: .... *cis* and *trans*-[Co en$_2$H$_2$OOH]Br$_2$; — — *cis*-[Co en$_2$-(H$_2$O)$_2$]Br$_3$; ---- *trans*-[Co en$_2$(H$_2$O)$_2$]Br$_3$; — *cis* and *trans*-[Co en$_2$H$_2$OOH]Br$_2$ allowed to stand in water for one hour, then acidified to pH 0.7 with hydrobromic acid.

tive groups in *trans*-positions is shown in Fig. 4. These observations suggest that the configuration of coördination compounds containing negative ligands cannot be conclusively deduced solely on the basis of the presence or absence of a third absorption band.[23] However, if the absorption spectra of both isomers are determined and reveal a third band in only one case then this would indicate that the salt which gives a third band has a *trans* configuration; the third band of the more stable *cis* complex presumably being shifted to such short wave lengths that it is not detected.

The absorption spectra of *cis* and *trans* [Co en$_2$-(SCN)$_2$]SCN (Fig. 4) reveal that in certain cases the absorption spectra of geometric isomers may be only slightly different. It can be seen in Fig. 6 that the spectra of *cis* and *trans* Co en$_2$H$_2$OOH Br$_2$ are identical within experimental error. This is disturbing because Werner[14] describes these isomers as having slightly different colors. These results may be interpreted as meaning that the *cis* and *trans* hydroxoaquo complex both readily rearrange to an equilibrium mixture of the two geometric forms. This interpretation has been shown to be correct. Dissolution of *cis* and *trans* [Co en$_2$H$_2$OOH]Br$_2$ in a dilute solution of hydro-

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[23] Tsuchida and Kobayashi, *Bull. Chem. Soc. Japan*, **12**, 83 (1937); Sueda, *ibid.*, **13**, 450 (1938).

bromic acid (*p*H 0.7) gives the diaquo complexes having different absorption spectra (Fig. 6). However, if the hydroxoaquo salts are dissolved in water and allowed to stand at room temperature for one hour before acidifying, the resulting diaquo complexes have the same absorption spectrum (Fig. 6). It should likewise be noted that this spectrum lies between those of *cis* and *trans* [Co en$_2$(H$_2$O)$_2$]Br$_3$ suggesting that it is an equilibrium mixture of these stereoisomers. These observations of the ease with which *cis* and *trans* [Co en$_2$H$_2$OOH]Br$_2$ rearrange in neutral or slightly alkaline solution as compared to the stability of *cis* and *trans* [Co en$_2$(H$_2$O)]Br$_3$ in strongly acid solutions is in accord with findings of Brüll.[24]

It might be expected that analogous compounds of the same configuration would have similar absorption spectra. That this is the case is seen in Figs. 2, 3 and 5. In every instance the propylenediamine complex of known configuration has an absorption spectrum which closely resembles that of the corresponding ethylenediamine salt of the same configuration.

Acknowledgment.—The author takes this opportunity to thank Professor John C. Bailar, Jr., for supplying some of the compounds that were studied and Professor Ralph G. Pearson for valuable suggestions in the interpretation of some of the absorption spectra.

Summary

The absorption spectra of several ions of the type [Ma$_4$b$_2$], [Ma$_4$bc], [M(AA)$_2$b$_2$] and [M(AA)$_2$bc] have been determined.

It has been shown that absorption spectra data can be applied to establish the configuration of geometric isomers whenever the position of the absorption maxima of the second and third bands are significantly shifted. It is likewise possible to determine the structure of a complex by comparing its spectrum to the spectra of analogous *cis* and *trans* salts.

The *cis* isomers of [Co(NH$_3$)$_4$(NO$_2$)$_2$]$^+$, [Co en$_2$(NO$_2$)$_2$]$^+$ and [Co en$_2$Cl$_2$]$^+$ have an absorption band at approximately 240 mμ. There is no absorption band at this short wave length for the stereoisomers of either [Co en$_2$ClSCN]$^+$ or [Co en$_2$(SCN)$_2$]$^+$.

cis and *trans*-[Co en$_2$H$_2$OOH]Br$_2$ rearrange rapidly in neutral or slightly alkaline solutions to yield an equilibrium mixture of the two isomers.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 3, 1950

[24] Brüll, *Compt. rend.*, **209**, 630 (1939).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1342]

The Vibrational Spectra of Tetrahydropyran and *p*-Dioxane[1]

BY STANLEY C. BURKET AND RICHARD M. BADGER

In the course of an investigation of the infrared spectra of the carbohydrates it was found that no really thoroughgoing attempts have been made to interpret the spectra of simpler compounds which have structural features in common with them, in particular with the pyranose sugars. The features which we have regarded to be particularly pertinent are (1) the oxygen-containing ring and (2) the presence of many hydroxyl groups attached to a ring. Both of these structural features are found to give rise to strong absorption in the region 8–10μ, which in hydrocarbons is usually relatively transparent, but in the carbohydrates is characteristically opaque.

Our major purpose in the present paper will be to identify the bands which arise from the stretching vibrations of the tetrahydropyran ring. While it is not expected that these bands will occur unshifted in sugar spectra, their identification may be expected to be of assistance in the discussion of sugar spectra. In the carbohydrates the hydrogens which are attached to carbons are predominantly tertiary and bands involving them may be expected to fall at somewhat higher frequencies than C–C or C–O stretchings (*e.g.*, see Rasmussen[1a]), but in tetrahydropyran and *p*-dioxane some of the hydrogen frequencies do lie in this spectral region so that we include a brief treatment of the methylene vibrations.

Our general procedure has been to start from the results of a normal coördinate analysis of cyclohexane by Lu, Beckett and Pitzer (to be published) as reported in an article by Beckett, Pitzer and Spitzer[2] and to extend these results to tetrahydropyran and *p*-dioxane. We have attempted to choose symmetry coördinates for cyclohexane which are probably a reasonable approximation of the normal coördinates and the ring vibrations have been regarded as a first approximation to those in tetrahydropyran and *p*-dioxane, while the approximate form of the hydrogen vibrations has been estimated by considering the effect of removing two or four hydrogens from cyclohexane. Rough relative intensities and activities were then estimated and the most reasonable possible assignments consist-

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[1] This paper is based on work supported by the Bureau of Ordnance, United States Navy, and done under contract with the Office of Naval Research, Contract N6-ori-102, Task Order VI.

[1a] R. S. Rasmussen, *J. Chem. Phys.*, **16**, 712 (1948).

[2] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).