Absorption Spectra of Salicylaldehyde-ethylenediimine and Related Compounds.

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Introduction. One of the authors(1) (T.T.) has reported on a number of inner complexes of *o*-hydroxybenzaldehyde and *o*-hydroxybenzaldimine series. With the aim of throwing light upon the subject, the author(2) has measured the absorption spectra of salicylaldehyde-ethylenediimine-cobalt and determined its steric configuration by applying the trans-diacido-theory(3)(4) of the third absorption bands of coordination compounds. On the other hand, the other of the authors(5)(6) (R.T.) has been studying absorption spectra of coordination compounds and has come to a conclusion that every chemical linkage might be regarded as coordinate combination or its extreme case and, therefore, the results obtained for absorption spectra of coordination compounds may be widely applied to various inorganic compounds. This conclusion may be further extended even to organic compounds. In other words, entire absorption spectrum of a compound, inorganic or organic, may be regarded generally as a complicated superposition of spectra of a number of coordination groups, each atom in the compound being taken as a coordination center. And to all of these centers may be applied the theory of absorption spectra of coordination compounds.

For the purpose of acquiring further informations of the above-mentioned inner complex, the authors measured the absorption spectra of benzaldehyde-ethylenediimine (dibenzylidene-ethylenediamine), *o*-methoxybenzaldehyde-ethylenediimine, salicylaldehyde-ethylenediimine and *o*-hydroxyacetophenone-ethylenediimine and tried to explain, from the viewpoint of coordination chemistry, these absorption spectra and that of the inner complex as well.

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(1) P. Pfeiffer, E. Breith, E. Lübbe, and T. Tsumaki, *Ann.*, **503** (1933', 84.

(2) T. Tsumaki, this Bulletin, **13** (1938), 252; *J. Chem. Soc. Japan*, **58** (1937), 1288.

(3) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.

(4) R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 586.

(5) R. Tsuchida, this Bulletin, **13** (1938), 388.

(6) R. Tsuchida, this Bulletin, **13** (1938), 436.

Experimental. Benzaldehyde-ethylenediimine and *o*-methoxybenzaldehyde-ethylenediimine were prepared by the methods of Mason.(7) The molar extinction coefficients $\varepsilon (I = I_0 \times 10^{-\varepsilon c d})$ were measured. The solvent: ethyl alcohol. The concentration: 0.001 mol/l. The thickness of layer: 0.02–15.0 cm.

Salicylaldehyde-ethylenediimine and *o*-hydroxyacetophenone-ethylenediimine were prepared by the method of Mason(8) and that of one of the present authors(9) (T.T.) respectively. The absorption spectra were measured. The solvent: ethyl alcohol. The concentration: 0.0001 mol/l. The thickness of layer: 0.02–15.0 cm. The absorption curves are shown in Fig. 1.

Discussion of the Results. Prior to the discussion on the organic compounds in question, it will be more convenient to describe briefly the main features of the absorption spectra of coordination compounds. An absorption spectrum of a coordination compound generally consists of the first, the second and the third band, accompanied by a few special bands. The first band is due to electron transitions in the unsaturated transition shell of the central ion and is, therefore, one of the most remarkable characteristics of transition elements. The second band is the most general feature of coordination compounds and is due to a kind of incomplete dissociation of a ligand, i.e., a coordinated ion or molecule. It has been found(6) that the frequency of the second band gives the true measure of the strength of the coordinate link. The third band is attributed to a kind of neutralization between the central cation and a ligand anion and appears only when two or more anions are coordinated in trans-positions referring to the coordination center. Those bands which are not proper to the coordination center in question but are attributed to ligands themselves, are defined as special bands. A special band, however, is originally a certain numbered band referred to its own center. It is further known(10) that coordinate combination of a ligand has a bathochromic and hypochromic effect on the absorption bands proper to the ligand. In other words, a special band due to a ligand is less absorptive and has longer wave-length than the corresponding band of the ligand in free state.

Now benzaldehyde-ethylenediimine (I) shows one band at $\nu = 121 \times 10^{13}$ sec.$^{-1}$ *o*-Methoxybenzaldehyde-ethylenediimine (II) has two bands at

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(7) A. T. Mason, *Ber.*, **20** (1887), 270, 272.

(8) A. T. Mason, *ibid.*, 271.

(9) P. Pfeiffer, E. Breith, E. Lübbe, and T. Tsumaki, *Ann.*, **503** (1933), 127.

(10) R. Tsuchida and M. Kobayashi, this Bulletin, **13** (1938), 471.

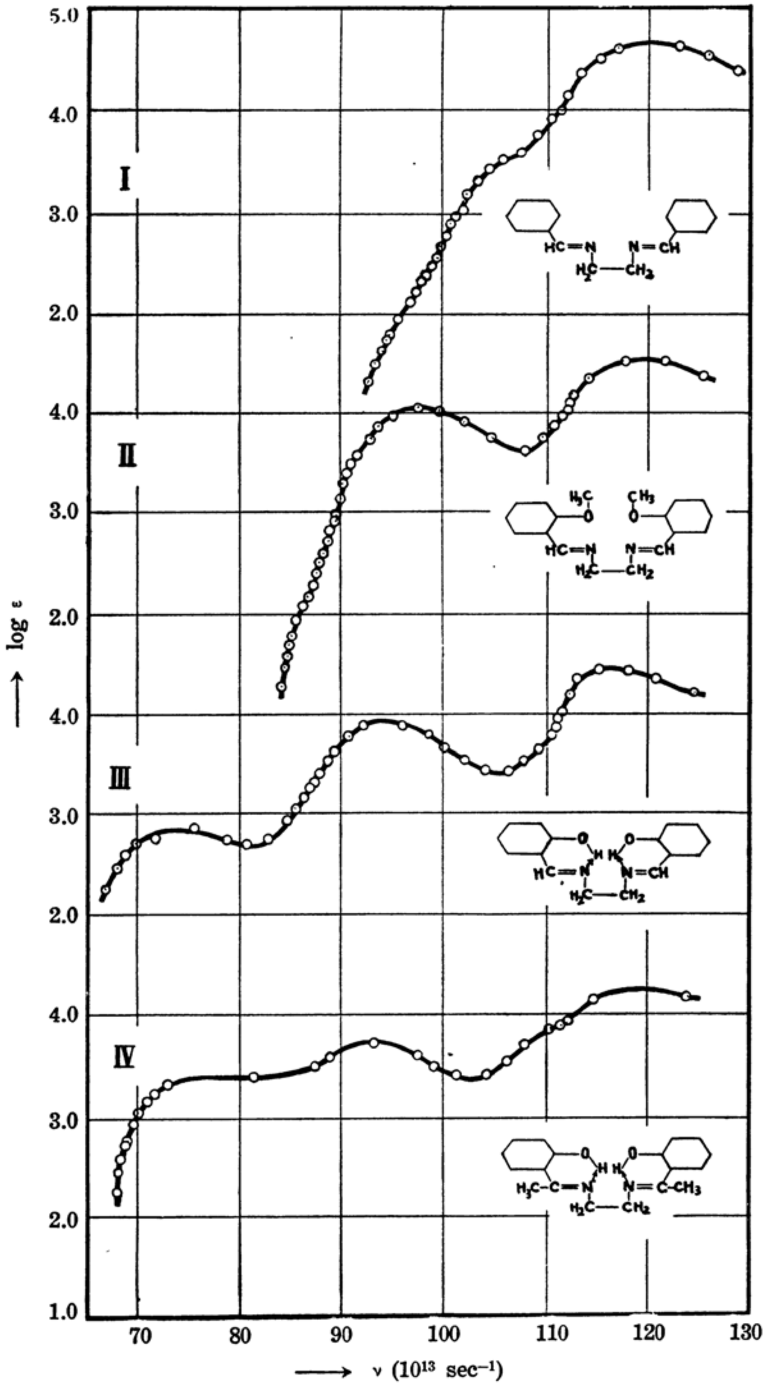
I
II
III
IV
5.0
4.0
3.0
2.0
1.0
→ log ε
70
80
90
100
110
120
130
→ ν (10¹³ sec⁻¹)
HC=N N=CH
H₂C—CH₂
H₃C CH₃
O O
H₃C-C=N N=C-CH₃

Fig. 1.

98×10^{13} sec.$^{-1}$ and 120×10^{13} sec.$^{-1}$, of which the latter is a special band proper to benzaldehyde-ethylenediimine (I), as can be seen from its frequency and extinction coefficients. The band at 98×10^{13} sec.$^{-1}$, accordingly, is attributed to CH_3O group. Salicylaldehyde-ethylenediimine (III) shows three bands at 75×10^{13} sec.$^{-1}$, 95×10^{13} sec.$^{-1}$ and 117×10^{13} sec.$^{-1}$ Both the absorption bands of the methoxy-derivative (II) are retained in this compound. The bathochromic and hypochromic effect on these special bands is remarkable: the frequencies of the special bands in salicylaldehyde-ethylenediimine (III) are 95×10^{13} sec.$^{-1}$ and 117×10^{13} sec.$^{-1}$ and the corresponding extinction coefficients are $\log^{-1} 3.9$ and $\log^{-1} 4.4$, whereas those of the absorption bands of methoxy-derivative (II) are 98×10^{13} sec.$^{-1}$, 120×10^{13} sec.$^{-1}$, $\log^{-1} 4.1$ and $\log^{-1} 4.5$ respectively. This fact as well as the band at 75×10^{13} sec.$^{-1}$ indicates that salicylaldehyde-ethylenediimine (III) has another absorption center which could not be found in its methoxy-derivative (II). The band at 75×10^{13} sec.$^{-1}$ is also found in the absorption spectrum of *o*-hydroxyacetophenone-ethylenediimine (IV), whose bands are at 75×10^{13} sec.$^{-1}$, 94×10^{13} sec.$^{-1}$ and 119×10^{13} sec.$^{-1}$, the corresponding extinction coefficients being $\log^{-1} 3.4$, $\log^{-1} 3.8$ and $\log^{-1} 4.3$. Of these the latter two are the special bands of the same origins as those of salicylaldehyde-ethylenediimine (III). The longest-waved band is seen only in the compounds (III and IV) containing OH group, but not in those (I and II) lacking the group. The band is, therefore, characteristic of the OH group, or rather of H in the group, as we have already distinguished the bands due to the absorbing center of O in the compounds (II, III and IV) which have either OH or OCH_3. In order to give rise to a band, the hydrogen atom should be a coordination center. Thus the band at 75×10^{13} sec.$^{-1}$ is attributed to the hydrogen bridge formed between the hydroxyl-group and the nitrogen atom. Then the band should be regarded as the second band of the absorbing center, $O—H \leftarrow N$. Whereas Hilbert, Hendricks, Wulf, and Liddel(11) have supposed the existence of a hydrogen bond in a hydroxyl-compound, e.g., nitrophenol, by the absence of the hydroxyl-absorption band in the infrared region (6000 to 7500 cm.$^{-1}$), the present authors have now shown a hydrogen bond by the presence of a coordination band in the ultra-violet region.

The absorption bands of the compounds are summarized in Table 1 where the bands due to the same origin are shown in the same vertical column. Thus the bands under [a] are those which are common to all

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(11) G. E. Hilbert, O. R. Wulf, S. B. Hendricks, and U. Liddel, *J. Am. Chem. Soc.*, **58** (1936), 548.

the compounds containing benzaldehyde-ethylenediimine, and those under [b] are attributed to the absorbing unit whose center is O. The bands under [c] are those due to the hydrogen bridge between the hydroxyl-group and the nitrogen atom.

Table 1.

	Compounds	[c]		[b]		[a]	
		$\nu(10^{13})$	log ε	$\nu(10^{13})$	log ε	$\nu(10^{13})$	o g
I	Benzaldehyde-ethylenediimine					121	4.7
II	*o*-Methoxybenzaldehyde-ethylenediimine			98	4.1	120	4.5
III	Salicylaldehyde-ethylenediimine	75	2.9	95	3.9	117	4.4
IV	*o*-Hydroxyacetophenone-ethylenediimine	75	3.4	94	3.8	119	4.3

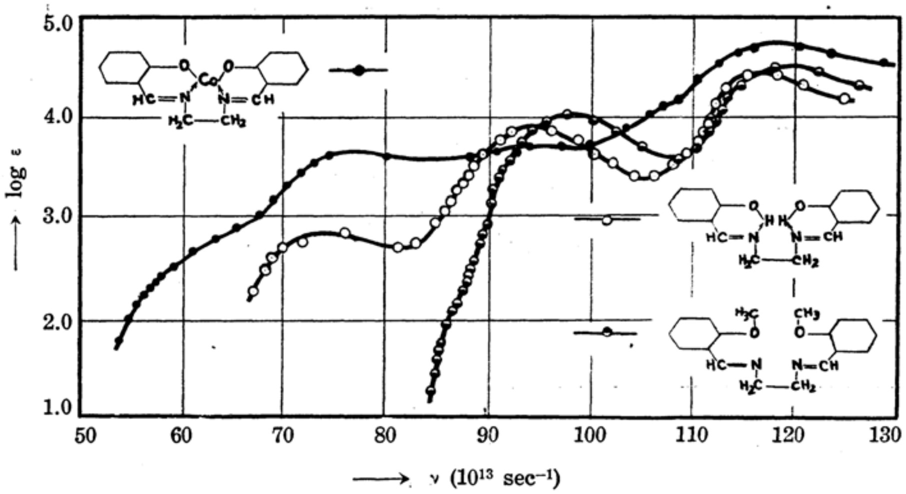


Fig. 2.

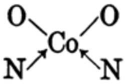
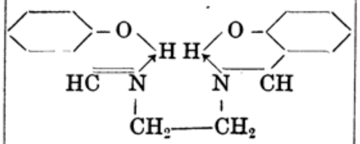
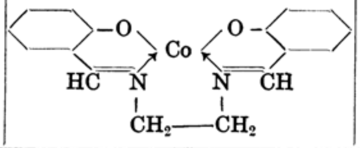
When salicylaldehyde-ethylenediimine (III) forms an inner complex with a metal ion, e.g., cobalt, the structure is quite similar to that of the original organic compound. The absorption spectrum of the inner complex⁽²⁾ is shown in Fig. 2 together with those of salicylaldehyde-ethylenediimine (III) and *o*-methoxybenzaldehyde-ethylenediimine (II). The inner complex has five bands, viz., ca. 60×10^{13} sec.$^{-1}$, 77×10^{13} sec.$^{-1}$, 93×10^{13} sec.$^{-1}$, ca. 110×10^{13} sec.$^{-1}$ and 118×10^{13} sec.$^{-1}$ For this inner complex the second band of the absorbing center,  , is expected instead of the band due to hydrogen bridge, O—H←N. The band at 77 × 10^{13} sec.$^{-1}$ is the second band or the coordination band of the cobaltous ion as center, whereas the coordination band of the hydrogen bridge in salicylaldehyde-ethylenediimine is at 75 × 10^{13} sec.$^{-1}$ It is, therefore, evident that the coordinate link of cobalt with salicylaldehyde-ethylenediimine is more stable(6) than that of hydrogen in the organic compound, and the method of preparing the inner complex(1) may thereby be explained.(6) The longest-waved band at ca. 60 × 10^{13} sec.$^{-1}$ is the first band due to the incomplete transition shell of the cobaltous ion. The one at 93 × 10^{13} sec.$^{-1}$ is a special band due to the same origin as those in the column [b] in Table 1: viz., a band attributed to an absorbing unit, whose coordination center is oxygen. The band at about 110 × 10^{13} sec.$^{-1}$ is also a special band which belongs to the same class as those in the column [a] in the table, i.e., a special band common to all the benzaldehyde-ethylenediimine derivatives. Fig. 2 shows that the two bands of *o*-methoxybenzaldehyde-ethylenediimine (II) undergo the bathochromic and hypochromic effect in salicylaldehyde-ethylenediimine (III) and its inner cobaltous complex (V). The last band of the inner complex at 118 × 10^{13} sec.$^{-1}$ can not be a special band, as the maximal extinction coefficient is much greater than that of *o*-methoxybenzaldehyde-ethylenediimine (II). It is, therefore, the third band which is attributed to the neutralization between the central cobaltous ion and the phenolate residue. In Table 2 the

Table 2.

	Coordination compounds	1st band		2nd band		Special bands				3rd band	
						[b]		[a]			
		ν_1 (10^{13})	log ε	ν_2 (10^{13})	log ε	ν(10^{13})	log ε	ν(10^{13})	log ε	ν_3 (10^{13})	log ε
III				75	2.9	95	3.9	117	4.4		
V		ca. 60	2.5	77	3.7	93	3.5	ca. 110	4.2	118	4.8

absorption spectra of salicylaldehyde-ethylenediimine and its inner cobaltous complex are compared.

Thus the third band of the inner complex has been confirmed and the asymmetric configuration of the compound which had been reported in the previous paper⁽²⁾ has thereby been corroborated.

Summary.

(1) Absorption spectra of benzaldehyde-ethylenediimine, *o*-methoxybenzaldehyde-ethylenediimine, salicylaldehyde-ethylenediimine and *o*-hydroxyacetophenone-ethylenediimine have been measured, and the structures of the spectra have been qualitatively explained by the theories of absorption spectra of coordination compounds.

(2) The longest-waved band of salicylaldehyde-ethylenediimine as well as of *o*-hydroxyacetophenone-ethylenediimine has been explained as due to intramolecular formation of a hydrogen bridge between the hydroxyl group and the nitrogen atom. In other words an absorption band of a hydrogen bond has been found in the near ultra-violet region.

(3) The absorption spectrum of salicylaldehyde-ethylenediimine-cobalt has been explained and the steric configuration of the inner complex has thereby been corroborated.

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