

Monoazo 金屬錯鹽의 吸收 Spectra 와 그 構造

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Absorption Spectra and the Structure of Metalized Monoazo Complexes*

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Abstract

UV absorption spectra of some metalized monoazo complexes have been measured, and the structure of the complexes is discussed based on the spectra. A compressed octahedron is proposed as the geometrical structure of the complexes.

要 約

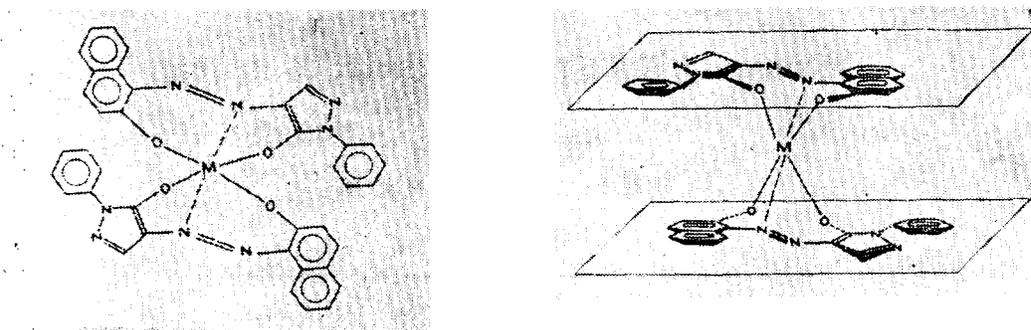
몇가지 monoazo-金屬錯鹽들의 UV 吸收 spectra 를 測定하여 이것을 基礎로하여 그 金屬錯鹽들의 構造를 論하였다. 옆으로 찌그러진 八面體모양의 幾何學的構造를 提案하였다.

In the previous paper⁽¹⁾ concerned with the formation of metallized monoazo complexes, it was pointed out that the metallic complexes are a kind of chelate compound. This speculation was based upon the fact that the formation requires the presence of hydroxyl groups at ortho positions with respect to the azo group in the molecule. This paper is concerned with the structure of the complexes, based upon their UV absorption spectra. The presumable structures upon a thought are as follows. Structure 1 is a coplanar, that is the two molecules of an azo-compound and a transition metal are on the same plane in structure 1, whereas two planes of the two azo-compounds are

laid symmetrically up and down, and a metal is placed at the center of the symmetry like the structure of ferrocene in structure 2.

According to the spectroscopic consideration of ligand field theory of organic complexes containing transition metals,⁽²⁾ it has been known that energy due to d electrons of a transition metal is degenerated by the centrosymmetric force field when the element is isolated as an ion. However, since energy due to the d electrons and ligands splits to various levels when the elements being a part of complex, the most likely to be of importance are $t_{2g} \rightarrow e_g^*$ and $t_{1g} \rightarrow e_g^*$. The first transition generally appears in the region

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of near infrared or visible range as a broad and weak band. On the other hand, the second transition is observed at ultraviolet range as the so-called charge transfer band, whose intensity is known to be significantly strong. It can be seen from Figure 1 that

spectra of nonmetalized 1-(1'-azo-2'-hydroxy-5'-nitrophenyl)-2-naphthol-6-sulfonic acid (4) and its metallized complexes (4-Cr, 4-Cu and 4-Co) have three major bands, respectively.

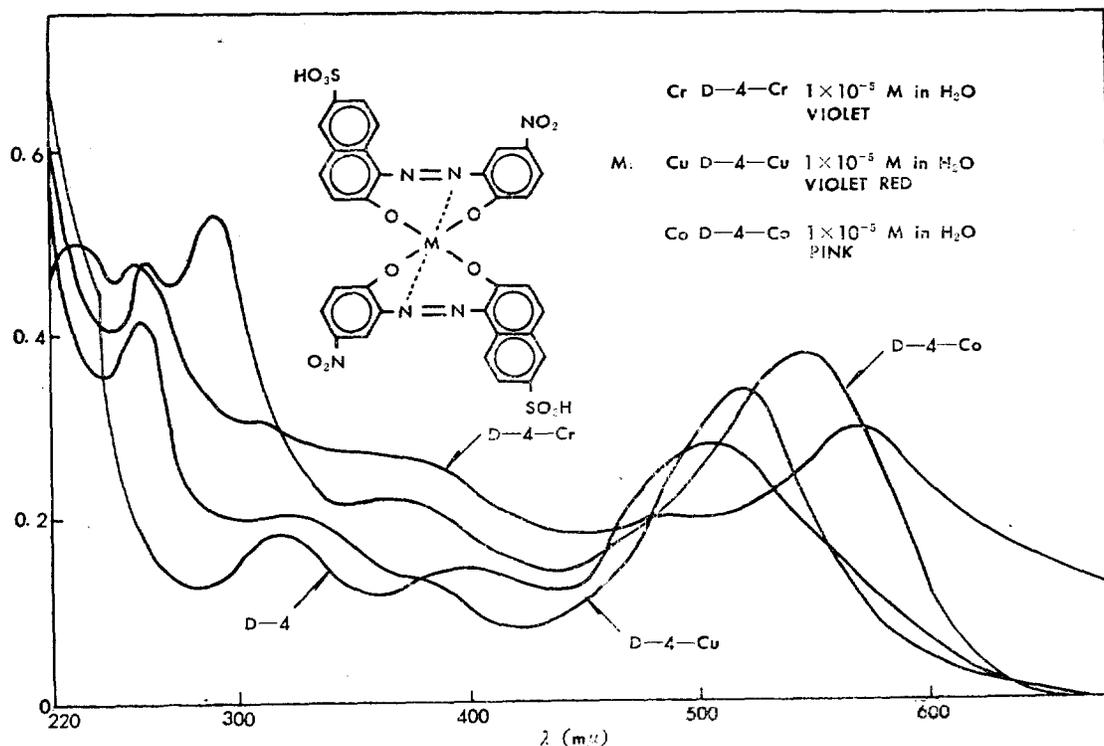


Figure 1.-UV Spectra of 1-(1'-Azo-2'-hydroxy-5'-nitrophenyl)-2-naphthol-6-sulfonic acid and its metallized complexes (Cr, Cu, Co).

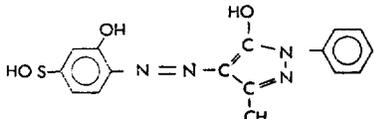
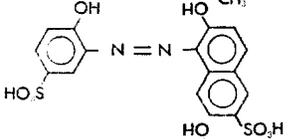
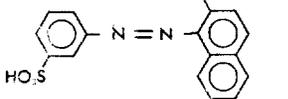
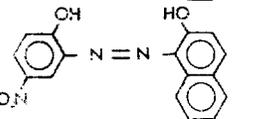
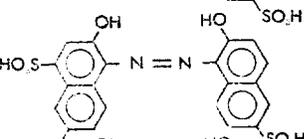
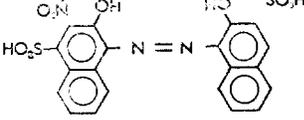
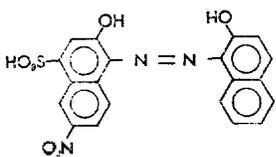
The first bands appear below 300 $m\mu$ and the second bands appear between 300 and 400 $m\mu$. Finally the third bands are observed in the region of 500 $m\mu$. The first bands are obviously due to phenyl rings in

the molecule ($'B2u \leftarrow 'Alg$).⁽⁵⁾ The bands in the region of 300-400 and 500 $m\mu$ are most likely due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition,^{(2),(4),(5)} respectively. These bands hardly refer to $t_{2g} \rightarrow e_g^*$ and

$t_{1u} \rightarrow e_g$ transitions based on the ligand field theory, because intensities of the bands ranged at 300-400 and 500m μ are in contrast with those anticipated intensities of charge transfer and $t_{2g} \rightarrow e_g^*$ transition bands. Absorption maxima of nonmetalized azo-compounds and their metallic complexes concerned in this study are summarized in Table I. It should be noted that the $n \rightarrow \pi^*$ bands of the complexes showed

bathochromic shift without exception, although the $\pi \rightarrow \pi^*$ transition bands showed hypso-bathochromic shifts. Thus, the two major bands of the metalized complexes do not seem likely to be due to the formation of chelate between central metal and four oxygen atoms of bond hydroxyl groups in a complex molecule, but rather likely due to the depression or elevation of transition energy levels.

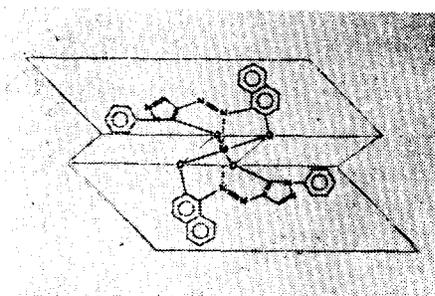
Table I UV Absorption Maxima of Some Hydroxy Monoazo-Compounds and Their Metallic Complexes

No.	Compds.	M. Free	max(m μ)		
			Cr	Cu	Co
1.		325	340	355	320
		468	530	508	470
2.		310	420(W)	disa.	315
		492	550	520	504
3.		315(W)	308	310, 400	300, 395
		480	488	500	520
4.		300, 400(W)	380(b)	325(W)	292, 375(b)
		500	566	520	546
5.		286(W)	300(W)	290(W, b)	300(W)
		528	602	570	572
6.		330(W)	340(W)	354(W)	440(W)
		530	620	556	576
7.		300(b, W)	310(b)	315(W)	312(W)
		530	615	560	564

This means that these complexes are not formed by only four ionic bonds between central metal and anionic oxygen atoms. Consequently, the above speculation indicates that the central metal and either π electrons in azo group, or lone pair electrons on nitrogen atoms might participate in the formation of

complexes. This, in turn, suggests that π electrons or lone pair electrons in azo group of two molecules of azo-compounds from opposite sides might function as two ligands directing to the center metal. This is a case to which the perturbation of molecular orbital theory and ligand field theory could be applied.⁽⁶⁾

Thus, structures 1 and 2 are not likely to be the structure of the complexes. And the structure of 1:2 metalized monoazo complexes is proposed as structure 3.



Since both of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands are influenced by the presence of central metal, it is hardly decided which electrons among π and lone pair electrons participate predominantly in the formation of the complexes. However, one thing can be clearly concluded; that is, the structure of the complexes can not be perfect octahedron. If the azo group were placed at the two opposite corners of a regular octahedron, maintaining the coplanarity of azo-compound itself, the structure would become the same as structure 2, a kind of ferrocene type. However, the fact that orthohydroxy groups are chelated with the central metal and keep a coplanarity with azo group at the same time clearly rules out the possibility of the perfect octahedral structure. And it is also obvious that a coplane consisting of the central metal and the four oxygen atoms must be angled with a coplane of an azocompound at some point between 0 and 90 degrees. If the angle were 0 degrees, the bond

between metal and the oxygen atom would not be formed. On the other hand, if the angle were 90 degrees or more, the bond between the metal and the π electrons or lone pair electrons in azo-group would be destroyed.

Experimental

The formation of complexes in the present study has been described in the previous paper.⁽¹⁾ The measurement of UV absorption spectra was carried out by a Shimadzu Model QR-50 spectrophotometer. The solvent used was aqueous alcohol and the concentration was mostly between 10^{-4} and 5×10^{-5} mole.

Acknowledgment.

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