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Electronic Absorption Spectra of the Alkali Metal Complexes with Bipyridine

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Electronic absorption spectra of the alkali metal complexes with 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine or 5,5′-dimethyl-2,2′-bipyridine have been observed in tetrahydrofuran solutions. Each spectrum has four major bands in the near infrared, visible and near ultraviolet regions, and is essentially due to the π–π^* transitions in the negative ion (extra π electron trapping state) of bipyridine or its dimethyl derivatives coordinating to a metal ion. The band about 18000 cm^{-1} is the most sensitive to the metal ion species involved and assigned to a transition with the polarization parallel to the short axis of the bipyridine molecule. Each absorption band of the bipyrdine negative ion shows characteristic spectral shift upon CH_3-substitutions in its peripheral positions. This CH_3-substitution effect on the absorption spectra of bipyridine negative ion is quite different from that of complexes including neutral bipyridines and gives a basis of the criterion to determine whether the coordinating bipyridine in a certain bipyridine complex do exist in negative ion (π electron trapping state) or not.

Alkali metals (M) react with 2,2′-bipyridine (bipy) in tetrahydrofuran (THF), dioxane, liquid ammonia and others, forming two kinds of complexes, M_2(bipy) and M(bipy). They have been isolated as various types of crystals with some solvent molecules.[1] Some studies have been done by measuring magnetic susceptibility[2] and electron spin resonance[3-6] in the solid state and the solution, but nothing has been reported on their electronic absorption spectra in detail.[*1] In this paper electronic absorption spectra of the 1:1 complexes of alkali metals such as lithium, sodium and potassium with 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine (4dmbip) or 5,5′-dimethyl-2,2′-bipyridine (5dmbip) in tetrahydrofuran solutions are reported.

These complexes are of reddish violet and Na-complexes, for example, show spectra given in Fig. 1. Since Li- and K-complexes also give absorption curves similar to those of Na-complexes, whole curves need not be presented, and only four major absorption maxima are tabulated in Table 1. These bands, except those near 18000 cm^{-1}, are virtually invariant in their positions with the change of metal ion species. ESR studies[5,6] have shown that the alkali metal complex is rather an ion-pair formed by a metal ion, M^+, and a negative ion, bipy$^-$, an unpaired electron being predominantly delocalized in the antibonding π^* molecular orbitals of bipyridine but partly transferred to the atomic orbitals of metal ion. These lead to an assignment of the absorption bands to the π–π^* transitions in the coordinating bipyridine negative ion.

The spectral shift of the 18000 cm^{-1} band upon metal subsitution is small but is not out of resolution. Figure 2 shows the relation between the band positions and ionic radii (r) of the metal ions,[*2] where $R+r$ is the distance from the center of the metal ion to the center of bipyridine molecule. If bipy$^-$ acts as a bidentate ligand which coordinates to a metal ion through two nitrogen atoms, the π–π^* transitions may be polarized parallel to either the long axis or the short axis of bipyridine molecule. Since the latter axis passes through the metal ion, the electronic transitions polarized parallel to this are expected to be more sensitive to a positive charge on the metal ion than those

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[*1] Absorption curve of Na(bipy) has been reported by C. Mahon and W. L. Reynolds: *Inorg. Chem.*, **6**, 1927 (1967).

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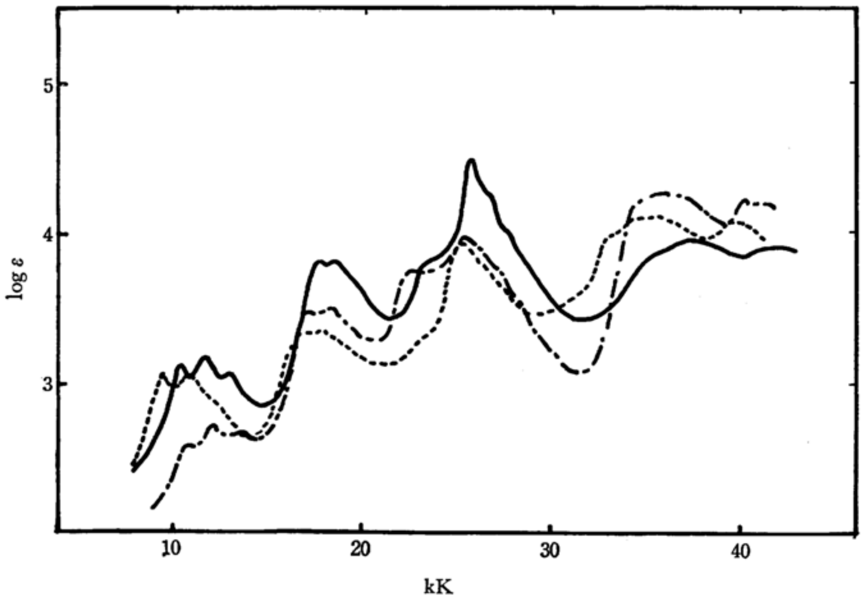

Fig. 1. Electronic absorption spectra in THF solutions.
——: Na(bipy), —·—: Na(4dmbip), - - -: Na(5dmbip)

Table 1. Absorption maxima of the complexes
(Absorption maxima are given in 10^3 cm^{-1} or kK and intensities, log ε in parentheses.)

Li(bipy)	Na(bipy)	K(bipy)	Na(4dmbip)	Na(5dmbip)
10.6	10.5 (3.13)	10.4 (3.42)	11.1 (2.6)	9.5 (3.06)
12.0	12.0 (3.19)	11.9 (3.48)	12.4 (2.7)	10.9 (3.07)
13.0	13.3 (3.06)	13.2 (3.36)	13.7 (2.7)	12.3 (2.90)*
18.2	17.8 (3.81)	17.6 (3.97)	17.1 (3.5)	17.0 (3.35)
19.2	18.8 (3.79)	18.7 (3.97)	18.3 (3.5)	17.9 (3.36)
	23.7 (3.80)*		22.5 (3.8)*	23.0 (3.25)*
26.0	25.9 (4.47)	25.8 (4.58)	25.4 (4.0)	25.3 (3.94)
	37.4 (3.94)	37.7 (3.91)	35.5 (4.3)	35.5 (4.08)

* shoulder

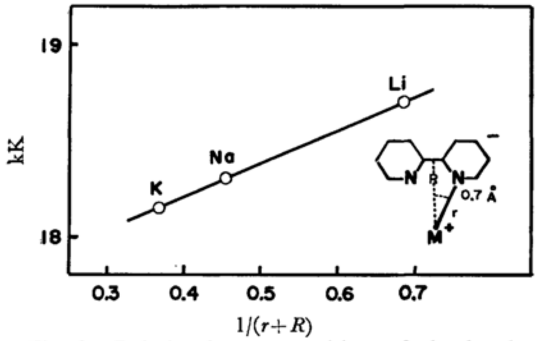

Fig. 2. Relation between positions of the bands near 18000 cm^{-1} and ionic radii of alkali metal ions.[*1]
Li, Na and K denote Li(bipy), Na(bipy), and K(bipy), respectively.

polarized perpendicular to this axis. The facts that the 18000 cm^{-1} band is the most sensitive to the metal ion species and its position is proportional to $1/(r+R)$, seem to be interpreted as followes. Spectral shift due to an electrostatic interaction between a positive charge on the metal ion, Ze and the transition dipole moment μ is approximately given by

$$\delta\varepsilon=\frac{Ze\mu}{(r+R)}\cos\theta\left[1+\frac{l^2}{8(r+R)^2}(5\cos^2\theta-3)+\cdots\right],$$

for $r+R>(1/2)l$, where θ is an angle between the transition dipole moment and the straight line connecting both centeres of the ligand and the metal ion, and l is the real dimension of the transition dipole. If the transtion moment orients perpendicular to the ligand-metal line, the electrostatic spectral shift seems to be very small, since $\cos\theta=0$, and $\delta\varepsilon=0$. The transition moment in the direction of the line gives relatively large electrostatic shift, since $\cos\theta=1$, and $\delta\varepsilon$ is maximum. The 18000 cm^{-1} band is caused by a π-π^* transition polarized toward the metal ion, while the others insensitive to the metal substitution are polarized perpendicular to the 18000 cm^{-1} transition.

The whole absorption curve of Na(bipy) does not change its shape so much upon CH_3-substitutions at 4 and 4′ or 5 and 5′ positions of the conjugated system. However, each band does change its position and intensity in a characteristic way of each wave number region. This is known by Fig. 1. The lowest wave number bands, for example, are shifted to the higher wave number in the order 5dmbip < bipy < 4dmbip, while the second lowest ones near 18000 cm^{-1} are in the order 5dmbip < 4dmbip < bipy. Therefore the effects of the CH_3-substitutions on the conjugated system can not be explained in terms of simple rules, whithout knowing the actual electronic structure of each energy state. The CH_3-substitution, a very weak perturbation to the π electron system, however, is reasonably expected not to give a drastic change in the whole π electronic structure but only to change slightly the energy scheme of the molecular orbitals. Experimental rules of the spectral behaviors observed upon the CH_3-substitutions in the bipyridine negative ion, rather weakly binding to the metal ion, are expected to be held even in fairly strong coordination to the metal ion with higher oxidation number than one, unless the coordination enhances drastically π electron delocalization between the coordinating negative ion and the metal ion or gives rise to a crucial electron transfer from negative ion to the metal ion.

On the other hand, in some cases where the ligand is molecular bipyridine but not negative ion, electronic absorption bands with $\log\varepsilon \gtrsim 3$ have been frequently observed in the near infrared and visible regions. $[Cr^{II}(bipy)_3]^{2+}$ ion is an example of this case. These bands are to be approximately assigned to charge transfer transitions from the d orbitals of the central metal ion to the lowest vacant π^* orbitals of bipyridine molecules.[7] The CH_3-substitutions give quite different spectral effects on the metal-ligand charge transfer bands from effects on the π-π^* bands in the coordinating bipyridine negative ion. The lowest wave number bands near 9000 cm^{-1}, for example, are shifted to the higher wave number in the order 4dmbip < bipy < 5dmbip, which is reverse to the effect observed in the lowest wave number bands of the coordinating negative ion near 11000 cm^{-1}.

Tris bipyridine metal complexes with lower abnormal valency[1] such as $[M(bipy)_3]$, where M=Ti, V, Cr, Mn, Fe, Co or Al, may be divided into two extreme types; the one includes bipyridine molecules coordinating to a metal ion with abnormal oxidation number, and the other includes bipyridine negative ions coordinating to a metal ion with rather normal oxidation number, although electron delocalization possibly makes this distinction a little bit indistinguishable. They both show generally deep color and have absorption bands with $\log\varepsilon \gtrsim 3$ in the near infrared and visible regions. Their absorption curves are very complicated and apparently similar to each other, but by the use of the method of CH_3-substitutions described above, we can determine whether they include negative ion or not.[8]

Experimental

Materials. Na(bipy), Na(4dmbip), Na(5dmbip) and K(bipy) were prepared in the apparatus shown in Fig. 3. Equimolar metallic sodium and bipyridine or its dimethyl derivatives were placed at the part marked a in a branch of the H-tube, apparatus I. THF, which was used as a solvent, had been previously purified by the usual method and stored on $LiAlH_4$ in an atmosphere of nitrogen free from oxygen. A flask containing THF was connected to a vacuum system at the joint C. THF was distilled into the tube A or B from the storing flask, degassed under freezing to remove a trace of oxygen in the solvent, and distilled into the tube a. The H-tube was sealed off at the point d. All the procedures were carried out under vacuum. The tube was shaken. Bipyridine or its dimethyl derivatives were reduced by metal sodium in THF

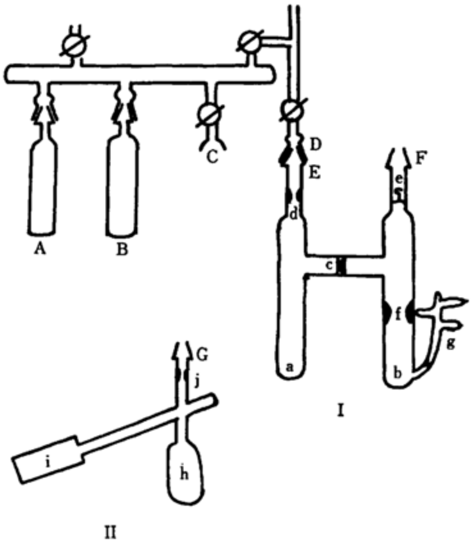

Fig. 3. Apparatus for the preparation of the materials (I) and of the sample solutions of absorption spectrum measurements (II).

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[7] I. Fujita, T. Yazaki, Y. Torii and H. Kobayashi, This Bulletin, to be published.

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and reddish violet solutions were obtained. The reduction was completed in about one day at room temperature. The solution was then filtrated through the glass filter c and the filtrate was collected in the tube b. Again the H-tube was connected with the vacuum system at the joint F. After the breakable seal e was broken, THF was completely distilled off and the tube was sealed off at the point f. Compounds thus obtained were stored in the tube g under vacuum. The tube g has several branches which are used to take a portion of material.

Li-complex was prepared by a method virtually identical with that described above, except for the use of apparatus II instead of the H-tube. The preparation was carried out in the flask h, and solution thus obtained were not evaporated to isolate crystalline substance but directly transferred to the quartz cell i for the measurement of its electronic absorption spectra.

Electronic Absorption Spectra. Sample solutions for spectral measurement were prepared with apparatus II connected to the vacuum system through the joints D and G. A capsule containing a small amount of the sample was placed in the quartz cell i and solvent THF was distilled directly into the flask h, in which the volume of the solvent was measured. The apparatus was then sealed off at the point j. The capsule was broken by a breaker, previously enclosed in the apparatus, in the flask h, and the compound was dissolved into the solvent. The amount of compound was estimated from the difference between weight of the unbroken capsule containing the compound and that of the capsule, taking into account the buoyancy correction for the unbroken capsule. The sample solution thus obtained in the flask h was transferred into the quartz cell i, the light path of which is 0.1 cm or 1 cm long, and electronic absorption spectra were measured using a Shimadzu multipurpose recording spectrophotometer model MPS-50.