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Electronic Absorption Spectra of Zero-Valent* Tris-(2,2′-bipyridine) Metal Complexes

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Electronic absorption spectra of zero-valent tris(2,2′-bipyridine) metal complexes of the first transition metals from titanium to cobalt have been studied. These spectra give a criterion to determine whether the central metal atom or the ligand is trapping the electrons furnished by reducing reagents upon syntheses of the complexes, if the absorption spectra of the coordinating negative ions are fairly free from the influence of the configuration interactions by the "ligand-metal" charge transfer excited states and/or by the "metal-ligand" ones. The vanadium complex is concluded as a complex of the metal atom in zero oxidation state and neutral bipyridine molecules, where the 'metal-ligand' charge transfer bands are observed. The iron- and the manganese-complexes are ionic complexes of the metal ion in a non-zero oxidation state and the negative ions of bipyridine, where the (π–π^*) absorption bands of coordinating bipyridine negative ion are observed. On the basis of their spectral character, the complexes of the other transition metals might be assigned to be a hybrid of the two typical electron traps given above.

Stabilization of complexes with a metal of lower oxidation states, $Cr(CO)_6$ for example, is well interpreted as due to the strong pi-bondings between the metal atom and the ligand molecules. The former acts as a $d\pi$ electron donor while the latter as acceptors by use of vacant anti-bonding pi-molecular orbitals of lower energy.1) It is well known that 2,2′-bipyridine (bipy) is one of the ligands which stabilize the lower oxidation states of metals. Recently a large number of tris-bipyridine metal complexes of lower valency have been prepared by Herzog and his coworkers, and others.2) We showed evidence of pi-bonding between the central metal atom and the ligand in the tris-bipyridine metal (II) complexes and also in the trisphenanthroline ones.3) It might be expected that the lower the oxidation state, the more stable the pi-bonding. Although the essential role of pi-bonding in the stabilization of lower oxidation states of metals in such complexes as zero-valent bipyridine complexes should be appreciably important as was pointed out by Orgel and Jϕrgensen,4,5) the existence of an isostructural zero-valent aluminum complexes, which is described as a complex of Al^{3+} coordinated by bipyridine negative ions, namely $[Al(III)(bipy^-)_3]$, should not be overlooked, even if there exists a crucial pi-electron delocalization effect between Al^{3+} and the coordinating bipyridine negative ions.

Electron trapping seems to happen mainly in the central metal atom in the case of comparatively stable lower valency complexes of the first transition metals, *e.g.* $[Cr(I)(bipy)_3]^+$. However, the existence of coordinating negative ion, or electron trapping ligand, seems to be possible even in the first transition metal complexes depending upon the electron trapping powers of the central metal atom and the ligands.

Since bipyridine is a strong σ-donating ligand, the positive charge of the central metal ion, even in an essentially ionic complex, is almost neutralized with σ-electron charge donated by the nitrogens of the coordinating bipyridine. However, since what we discuss here is not the charge distribution of the σ-bonds in the zero-valent com-

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[*1] In this paper, the term "valency" stands for a net charge (electrovalency) of the complex as a whole. Therefore "zero-valent" means that no net charge is accompanied by the complex. The term "oxidation state" or "oxidation number" stands for a degree of electron detachment of the central metal or a formal charge of the central metal.

1) E. W. Abel, *Quart. Rev.* London, **17**, 133 (1963).

2) a) S. Herzog and R. Taube, *Z. Anorg. Allg. Chem.*, **306**, 160 (1960). b) S. Herzog, *ibid.*, **294**, 155 (1958). c) S. Herzog and W. Schön, *ibid.*, **297**, 323 (1958). d) F. Hein and S. Herzog, *ibid.*, **267**, 337 (1952). e) G. M. Waind and B. Martin, *J. Inorg. Nucl. Chem.*, **8**, 551 (1958).

3) I. Fujita, T. Yazaki, Y. Torii and H. Kobayashi, to be published.

4) L. E. Orgel, "An Introduction To Transition-Metal Chemistry," Second Ed., Methuen & Co., Ltd, London (1966), p. 150.

5) C. K. Jϕrgensen, "Inorganic Complexes," Academic Press, London (1963), p. 75.

plexes but the majority trapping of the extra electrons furnished by reducing reagents upon synthesis of the zero-valent complexes, the notations such as $[Al(III)(bipy^-)_3]^0$ or $[Al(0)(bipy)_3]^0$, roughly show majority population of the molecular orbital trapping the extra electrons but not anything about the degree of σ-electroneutrality.

Analysis of ESR spectra and electronic absorption spectra give a means to determine whether the central metal atom or the ligands trap electrons. For this purpose, however, only effective magnetic moments have been measured and optical spectrum has been reported in only a few cases.[6)] As far as the zero-valent complexes are concerned, only the spectrum of the iron complex[7)] and the ESR of the vanadium complex[8)] have been published.

In this paper, the electronic absorption spectra of the zero-valent tris-bipyridine complexes of the first transition metals from Ti to Co are presented, and the actual oxidation states of the central metals are discussed based on their absorption spectra.

Experimental

The tris-bipyridine complexes such as $[Ti(bipy)_3]$, $[V(bipy)_3]$, $[Cr(bipy)_3]$, $[Mn(bipy)_3]$, $[Fe(bipy)_3]$, and $[Co(bipy)_3]$ were prepared by the method of Herzog *et al.*[2a–2d, 9–11)] The compounds were identified by elementary analysis of metal.

Tris(4,4′-dimethylbipyridine)vanadium was prepared in 50% methanol solution by the reduction of $[V(4dmbip)_3](ClO_4)_2$[3)] with magnesium powder and purified by extraction with tetrahydrofuran (THF) or benzene. The compound was a blue-violet crystalline substance. Found: V, 8.31%. Calcd for $[V(4dmbip)_3]$: V, 8.44%.

Tris(5,5′-dimethylbipyridine) vanadium was prepared in 60% methanol solution by the reduction of $[V(5dmbip)_3](ClO_4)_2$[3)] with magnesium powder and purified by extraction with THF. The compound was a blue-violet crystalline substance and less soluble in organic solvents than $[V(4dmbip)_3]$ and $[V(bipy)_3]$. Found: V, 8.11%. Calcd for $[V(5dmbip)_3]$: V, 8.44%.

Measurement of electronic absorption spectra. Sample solutions for spectral measurement were prepared by the method described in a previous paper.[12)] Electronic absorption spectra were measured in quartz cells with light path of 0.1 cm and 1 cm, using a Shimadzu multipurpose recording spectrophotometer model MPS-50.

Results and Discussion

The electronic absorption spectra of the zero-valent tris-bipyridine complexes are given in Figs. 1—3. The general feature of their absorption spectra in the near infrared region is very diffuse and intense. Intense absorption appears in a lower wave number region than those observed for the corresponding tris-bipyridine complexes of divalent metal ions. These diffuse and intense bands might be assigned to the "metal to ligand" charge transfer bands fairly strongly red-shifted by the central metal atom M(0) with smaller ionization potential, whereas this type of charge transfer bands are usually observed in the visible region

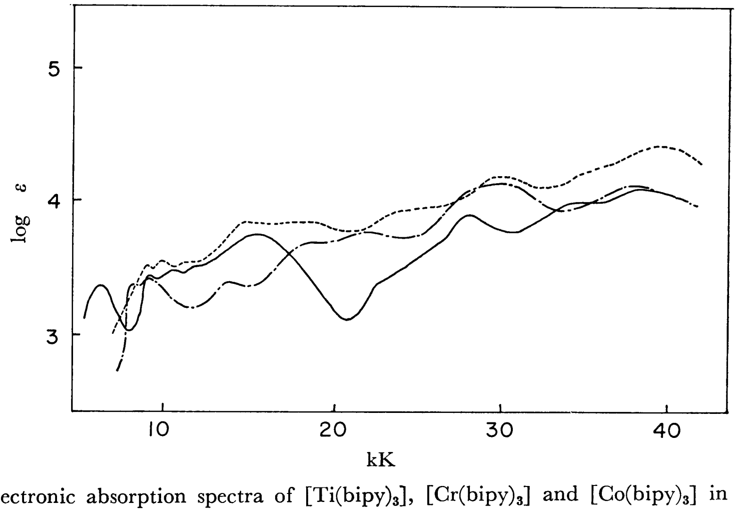

Fig. 1. Electronic absorption spectra of $[Ti(bipy)_3]$, $[Cr(bipy)_3]$ and $[Co(bipy)_3]$ in THF solution
——: Ti complex, —-—: Cr complex, ----: Co complex

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6) S. Herzog, E. König and H. L. Schläfer, Proc. VII Int. Conf. on Coordination Chemistry, Stockholm (1962), p. 21.

7) F. S. Hall and W. L. Reynolds, *Inorg. Chem.*, **5**, 931 (1966).

8) E. König, *Z. Naturforsch.*, **19a**, 1139 (1964).

9) S. Herzog and M. Schmidt, *Z. Chem.*, **2**, 24 (1962).

10) S. Herzog and H. Prakel, *ibid.*, **5**, 469 (1965).

11) S. Herzog, R. Klausch and J. Lantos, *ibid.*, **4**, 150 (1964).

12) Y. Torii, T. Yazaki, Y. Kaizu, S. Murasato and H. Kobayashi, This Bulletin, **42**, 2264 (1969).

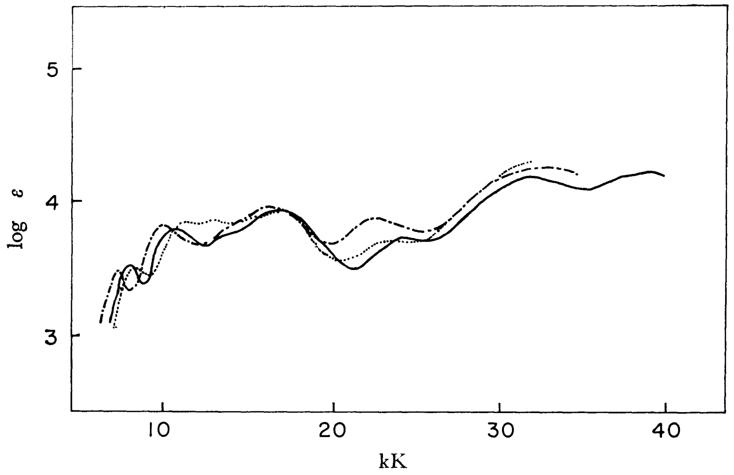

Fig. 2. Electronic absorption spectra of the V-compounds in THF solution
——: [V(bipy)$_3$], – – –: [V(4 dmbip)$_3$], ----: [V(5 dmbip)$_3$]

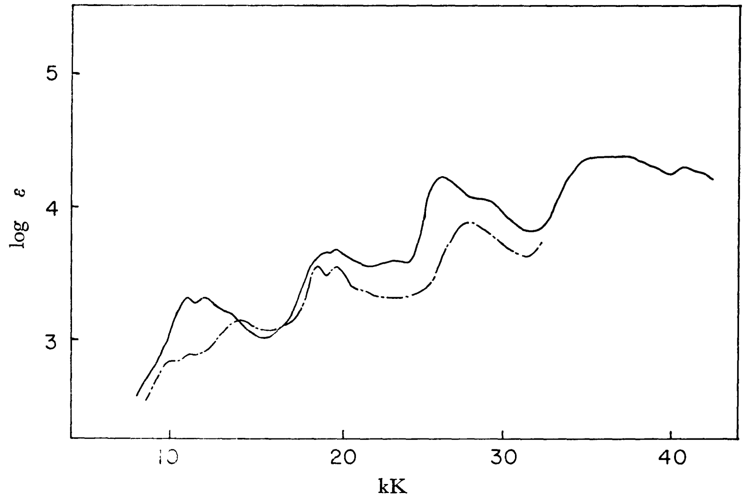

Fig. 3. Electronic Absorption spectra of [Mn(bipy)$_3$] and [Fe(bipy)$_3$] in THF solution. The intensity of the iron complex is in arbitrary scale ——: Mn complex, – – –: Fe complex

for the corresponding tris-bipyridine complexes of such metal ions as V(II), Cr(II) and Fe(II).3) The assignment is based on the assumption that the oxidation number of the central metals is zero, in other words the central metal atom captures electrons given by reducing reagents. On the other hand, tris(bipyridine)aluminum complex is interpreted by an approximate charge distribution such as $[\mathrm{Al(III)(bipy^{-})_3}]$,13) since it shows an absorption spectrum very close to that observed for sodium bipyridinate and also gives ESR spectrum with a free spin g-value of 2.0037. An aluminum cation is coordinated by three bipyridine negative ions rather than an aluminum atom of zero-oxidation number is coordinated by ordinary bipyridine molecules, even if pi-electron delocalization effects between the central metal and the coordinating bipyridine are appreciable. It has also been reported for Na[Fe(bipy)$_3$] to show similar properties.14) In this case, the actual oxidation state of the central ion is not minus one but much more positive and the ligands are trapping a sufficient part of pi-electrons. Since these complexes are made of bipyridine negative ions coordinating to an ionic metal species, the absorption bands which appear in the near infrared region could be assigned to the $(\pi$–$\pi^*)$ transitions of the coordinating bipyridine negative ion rather than the charge transfer bands mentioned above. Actually they give rise to a very similar feature to

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13) Y. Torii, S. Murasato, Y. Kaizu and H. Kobayashi, to be published.

14) C. Mahon and W. L. Reynolds, *Inorg. Chem.*, **6**, 1927 (1967).

that of the bipyridine ion in alkaline salts. Among the formally zero-valent compounds of the first transition metals, $[Fe(bipy)_3]$ and $[Mn(bipy)_3]$ show a similar spectrum to that of (Na^+bipy^-) (Fig. 3). The iron complex is not so stable in solvents and decomposes so easily to Fe metal and bipyridine that $\log \varepsilon$ could not be quantitatively determined. The spectrum in the ultraviolet region could not be given because of superposing absorption bands due to the bipyridine set free in the solution (Fig. 3).

We might conclude that the Fe- and the Mn-compounds are regarded as ionic complexes of metal cation and bipyridine negative ion, $bipy^-$. The actual, but not formal, oxidation states of the central metals of these complexes could not be zero. However, molecular orbital calculations and direct experimental determinations are desirable. The Ti-, V-, Cr- and Co-compounds show another type of absorption spectra different from those for the Fe- and Mn-compounds. König interpreted his ESR spectra of the V-compound on the basis of a remarkable difference between the optical spectra observed for the V-compound and (Na^+bipy^-), assuming that trapped electrons are localized at the central metal and can not be delocalized around the ligands. Such a difference, however remarkable, does not always give a criterion when the $(\pi-\pi^*)$ transition bands of the coordinating negative ion are drastically changed by a superposition and/or a mixing of "metal to ligand" or "ligand to metal" charge transfer bands.

In a previous paper, it was shown that small perturbations such as introduction of CH_3 group to the ligand, namely introduction of two methyl groups to the bipyridine in 4 dmbip and 5 dmbip, for example, show quite opposite spectral shifts for the "metal-ligand" charge transfer bands and the $(\pi-\pi^*)$ transition bands of the coordinating negative ion at the lowest wave number region.[12] The charge transfer bands shift to the lower wave number in the order, 5 dmbip, bipy, 4 dmbip, while the $(\pi-\pi^*)$ transitions of the bipyridine negative ions at the lowest wave number shift to the higher wave number in the order, 5 dmbip, bipy, 4 dmbip, which is similar to the usual $(\pi-\pi^*)$ transitions of the bipyridines. As is shown in Fig. 2, the absorption band at the lowest wavenumber of the V-compounds shifts towards the lower wavenumber in the order, 5 dmbip, bipy, 4 dmbip. This small perturbation technique gives the criterion that the lowest wave number band of the V-compounds is due not to a $(\pi-\pi^*)$ transition but to a "metal-ligand" charge transfer transition. This rejects the possibility of a coordinating negative ion in the case of the V-compound. We conclude that the vanadium traps electrons and is in zero oxidation state.

The Ti-compound shows a similar absorption spectrum to that of the V-compound at the near infrared and visible regions (Fig. 1). In the ultraviolet region, however, the spectra of the compounds are not identical. The absorption bands at the adjacent region of 30000 cm^{-1} are due to the $(\pi-\pi^*)$ transition of the coordinated bipyridine. In the case of the tris-bipyridine compounds of metal(II), or metal(III), the total shift of these absorption bands ranges over several hundred wavenumbers varying with the central metal ion among the first transition metals. On the contrary, the corresponding absorption bands of the Ti-compound are observed to shift several thousand wave numbers in a comparison with the V-compound (Figs. 1 and 2): Although the $(\pi-\pi^*)$ transition of the coordinating bipyridine changes very much in the Ti-compound, the fact that the absorption bands at the lowest wave number appear in the region lower than 10000 cm^{-1} and resemble that of the V-compound makes us conclude that the Ti-compound consists of neutral bipyridine but not negative ions. In the zero-valent complex discussed in the paper, the electron delocalization between the central metal $d\pi$-orbitals and the ligand antibonding molecular orbitals should be appreciable even in the ground state. Since the antibonding pi-orbitals of the coordinating bipyridine is donated $d\pi$-electron by the central metal through so-called back-donation, the $(\pi-\pi^*)$ transitions of the coordinating bipyridine should be much modified. This type of large pi-interactions between the metal $d\pi$-orbitals and the ligand antibonding pi-orbitals can explain not only the spectral behavior of the coordinating bipyridine but also the diamagnetism of the Ti-compound.[2a] As Fig. 1 shows, the Cr- and the Co-compounds give visible and near infrared spectra similar to those observed for the Ti-compound and the V-compound, while in the ultraviolet region, they are different from those observed for the V-compound.

Zero-valent tris-bipyridine compounds of the first transition metals can be formally classified on the basis of spectral criterion of the electronic structure: The V-compound is a complex of the metal of zero oxidation state and neutral ligands, while the Fe- and Mn-compounds are ionic complexes of the metal of non-zero oxidation state and negative ion ligands. The others seem to be in between.