Electronic Absorption Spectra of Tris(2,2′-bipyridine)- and Tris(1,10-phenanthroline) Complexes of Vanadium(II) and Chromium(II)

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Electronic absorption spectra of tris(2,2′-bipyridine) complexes of vanadium(II) and chromium(II) were measured. When methyl groups are introduced into the coordinating bipyridine, (d, d^*) transitions in the central metal, (π, π^*) transitions in the coordinating ligand, and "metal to ligand" charge-transfer transitions show their respective characteristic shifts. Thus the visible and near-infrared bands of tris(2,2′-bipyridine) complexes of vanadium(II) and chromium(II) are assigned to "metal to ligand" charge-transfer transitions as well as the visible bands of tris(2,2′-bipyridine)iron(II). A comparison between the corresponding bands of tris(2,2′-bipyridine) complexes and tris(1,10-phenathroline) complexes also verifies the assignment.

Transition metal complexes of 2,2′-bipyridine, 1,10-phenanthroline and their derivatives are one of the best studied group of metal complexes.[1] The complexes of a divalent cation of the first transition-metals such as manganese(II), cobalt(II), nickel(II), copper(II), or zinc(II) give rise to feeble colors in the solid state and in solutions.[2–6] Formation of the tris complexes of divalent iron, however, gives intense red coloration which permits an effective amplification of iron signal in the colorimetry.[7] The electronic absorption spectra of the divalent complexes have been established on the basis of considerable experimental and theoretical work. Strong absorption bands in the ultraviolet region are assigend to (π, π^*) transitions of the coordinating ligands.[2–6,8,9] The absorption bands of the coordinating ligand are slightly shifted in position and also changed in intensityf or a possible conformational change upon chelation and for inductive and/or mesomeric perturbation by the central metal ion. The feebly colored complexes of manganese(II), cobalt(II), nickel(II), or copper(II) show weak absorption bands arising from (d, d^*) transitions in the visible and near-infrared regions.[2–6] On the other hand, the deeply colored iron complexes show intense absorption bands in the visible region. The intense absorption bands are assigned to "metal to ligand" charge-transfer transitions. An electron in a molecular orbital primarily localized on a $d\pi$ orbital of the central iron is promoted to one of the antibonding π molecular orbitals distributed over the coordinating ligands.[9,10] Similar visible bands observed in the corresponding ruthenium(II) complexes were also assigned to "metal to ligand" charge-transfer transitions.[6,11]

Tris(bipyridine)- and tris(phenanthroline) complexes of divalent vanadium and chromium are known to be deeply colored. Some of their intense absorption bands were observed in the visible and near-infrared region.[12] The observed absorption bands were as intense as those of the iron(II) complexes. So far, however, assignment of the electronic absorption spectra of these complexes has never been established on the basis of sufficient experimental evidences. In this paper, we present the electronic absorption spectra of tris(2,2′-bipyridine), tris(4,4′-dimethyl-2,2′-bipyridine) and tris(5,5′-dimethyl-2,2′-bipyridine), and also tris(1,10-phenanthroline) complexes of vanadium(II) and chromium(II). On the basis of the observed evidences, the visible and near-infrared bands of the vanadium(II) and chromium(II) complexes will be assigned to "metal to ligand" charge-transfer transitions.

Experimental

Materials. By means of Sasse's method, 2,2′-bipyridine and its 4,4′-dimethyl- and 5,5′-dimethyl derivatives were prepared (Fig. 1).[13,14] Commercially available 1,10-phenanthroline of analytical reagent grade made by Tokyo Kasei Co., Ltd. was used without further purification. 2,2′-Bipyridine and its 4,4′-dimethyl- and 5,5′-dimethyl derivatives and 1,10-phenanthroline are abbreviated to bipy, 4dmbip, 5dmbip, and phen, respectively.

Tris(2,2′-bipyridine)vanadium(II), -chromium(II), -iron(II), and -nickel(II) perchlorates, and tris(1,10-phenanthroline)chromium(II), -iron(II), and -nickel(II) perchlorates were prepared by the methods given in the literature.[15–20]

Since vanadium(II) and chromium(II) ions are very sensitive to oxygen in the air, all the preparations were carried out in an oxygen-free dry nitrogen atmosphere. The

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[1] W. R. McWhinnie and J. D. Miller, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 12, ed. by H. J. Emeléus and A. G. Sharpe, Academic Press, New York (1969), p. 135.

[2] K. Yamazaki, H. Yokoi, and K. Sone, *Nippon Kagaku Zasshi*, **69**, 137 (1948).

[3] C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

[4] H. Ito, *Nippon Kagaku Zasshi*, **77**, 1399 (1956).

[5] A. Kiss and J. Császár, *Acta Chim. Acad. Sci. Hung.*, **38**, 405, 421 (1963).

[6] R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 865 (1966).

[7] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1959), p. 537.

[8] H. L. Schläfer, *Z. Phys. Chem. (N. F.)*, **8**, 373 (1956).

[9] I. Hanazaki and S. Nagakura, *Inorg. Chem.*, **8**, 648 (1969).

[10] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 166 (1957).

[11] W. W. Brandt and G. F. Smith, *Anal. Chem.*, **21**, 1313 (1949).

[12] E. König and S. Herzog, *J. Inorg. Nucl. Chem.*, **32**, 585, 601 (1970).

[13] W. H. F. Sasse, *J. Chem. Soc.*, **1956**, 618.

[14] W. H. F. Sasse and C. P. Whittle, *ibid.*, **1961**, 1347.

[15] S. Herzog, *Z. Anorg. Allgem. Chem.*, **294**, 155 (1958).

[16] G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1954), p. 1021.

[17] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, **1952**, 3570.

[18] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, **1931**, 2213; F. M. Jaeger and J. A. van Dÿk, *Z. Anorg. Chem.*, **227**, 273 (1936).

[19] S. Herzog, *Chem. Tech.*, **8**, 544 (1956).

[20] F. Blau, *Monatsh. Chem.*, **19**, 669 (1898); P. Pfeiffer and Fr. Tappermann, *Z. Anorg. Chem.*, **215**, 273 (1938).

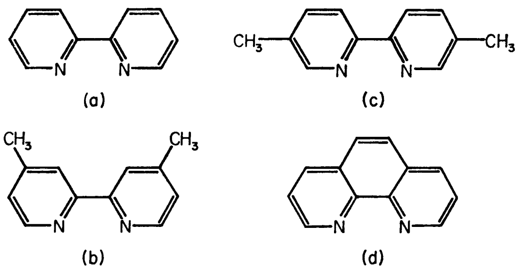

Fig. 1. Ligands.

(a) 2,2′-bipyridine (bipy)
(b) 4,4′-dimethyl-2,2′-bipyridine (4dmbip)
(c) 5,5′-dimethyl-2,2′-bipyridine (5dmbip)
(d) 1,10-phenanthroline (phen)

solvent used for the preparation should be thoroughly freed from oxygen.

Tris(4,4′-dimethyl-2,2′-bipyridine)vanadium(II) diperchlorate, [V(4dmbip)$_3$](ClO$_4$)$_2$. One gram of 4,4′-dimethyl-2,2′-bipyridine was dissolved in a mixture of 25 m*l* of methanol, 3 m*l* of 2N hydrochloric acid and 50 m*l* of water. To this solution was added 2 m*l* of 1M solution of vanadium(II) sulfate prepared by electrolytic reduction of oxovanadium(IV) sulfate.[22] When the complex was formed, the solution turned dark blue-green. It was stirred for several hours, and then mixed with a solution of 0.5 g of ammonium perchlorate in 20 m*l* of water. After standing for 3 hr, dark blue-green crystals were collected by filtration, washed twice with water and once with methanol, and dried over calcium chloride *in vacuo*.

Found: V, 6.1%. Calcd for [V(4dmbip)$_3$](ClO$_4$)$_2$: V, 6.35%.

Tris(5,5′-dimethyl-2,2′-bipyridine)vanadium(II) diperchlorate, [V(5dmbip)$_3$](ClO$_4$)$_2$. In a mixture of 25 m*l* of methanol and 20 m*l* of water, 2.7 g of 5,5′-dimethyl-2,2′-bipyridine was dissolved and then 6.0 m*l* of 1M solution of vanadium(II) sulfate was added. The solution turned dark blue-green. After it was stirred for several hours, a solution of 1.5 g of ammonium perchlorate in 15 m*l* of water was added to the colored solution. After standing for 24 hr, the dark blue-green precipitate was collected by filtration, washed with water and dried over calcium chloride *in vacuo*.

Found: V, 6.0%. Calcd for [V(5dmbip)$_3$](ClO$_4$)$_2$: V, 6.35%.

Tris(1,10-phenanthroline)vanadium(II) diperchlorate, [V(phen)$_3$](ClO$_4$)$_2$. 0.6 g of vanadium(II) sulfate hydrate was dissolved in 50 m*l* of water, and then 1.3 g of 1,10-phenanthroline previously dissolved in a small amount of methanol was added.[22] The solution turned dark blue. After it was stirred for several hours, the solution was added a mixture of 0.5 g sodium perchlorate hydrate and 0.3 m*l* of 70% perchloric acid in a small amount of water. The dark blue fine crystal thus formed was collected, washed several times with water and dried *in vacuo*.

Found: V, 6.4%. Calcd for [V(phen)$_3$](ClO$_4$)$_2$: V, 6.46%.

Tris(4,4′-dimethyl-2,2′-bipyridine) chromium(II) diperchlorate, [Cr(4dmbip)$_3$](ClO$_4$)$_2$. 0.5 g of chromium(II) acetate was dissolved in a mixture of 1.0 m*l* of 6N hydrochloric acid and 50 m*l* of water. To this was added 1.2 g of 4,4′-dimethyl-2,2′-bipyridine dissolved in a mixture of 0.1 m*l* of 6N hydrochloric acid and 100 m*l* of water. The dark brown solution was then thoroughly stirred, and to this was added 1 g of sodium perchlorate dissolved in a small amount of water. Black precipitate thus obtained was collected by filtration, washed several times with water and dried *in vacuo*.

Found: Cr, 6.3%. Calcd for [Cr(4dmbip)$_3$](ClO$_4$)$_2$: Cr, 6.47%.

Tris(5,5′-dimethyl-2,2′-bipyridine)chromium(II) diperchlorate, [Cr(5dmbip)$_3$](ClO$_4$)$_2$. The procedure was the same as that for tris(4,4′-dimethyl-2,2′-bipyridine)chromium(II) diperchlorate.

Found: Cr, 6.3%. Calcd for [Cr(5dmbip)$_3$](ClO$_4$)$_2$: Cr, 6.47%.

Measurements of Electronic Absorption Spectra. Electronic absorption spectra were taken on a Beckman spectrophotometer Model DU and a Shimadzu automatic recording spectrophotometer Model MPS-50. Quartz cuvettes of 1 and 10 mm optical path were used. Cylindrical cells of 100 mm path with quartz windows were used for measurements of weak (*d*, *d**) bands.

Since the vanadium(II) and chromium(II) complexes in the solid state are fairly stable against oxidation, the samples were weighed in the usual way in a dried atmosphere. The sample thus weighed was sealed in a vessel with a branch attached to an optical cuvette previously saturated with dry nitrogen. The vessel was connected through a ground joint to a vacuum line and evacuated. The procedure was carried out as quickly as possible.

Methanol was used as a solvent. The methanol was thoroughly degassed by successive freeze-thaw pumping cycles and transferred by distillation into the vessel. After the vessel was sealed off from the vacuum line, the sample was allowed to dissolve in methanol. Both procedure and apparatus were described in detail in a previous paper.[23]

Results and Discussion

Electronic absorption spectra of vanadium(II), chromium(II), iron(II), and nickel(II) complexes of 2,2′-bipyridine and its 4,4′-dimethyl- and 5,5′-dimethyl derivatives and of 1,10-phenanthroline are shown in Figs. 2—6.

Two intense absorption bands were observed in the ultraviolet region. They are assigned to (π, π^*) transitions within the molecular orbitals of the coordinating ligand. The lowest transitions of free bipyri-

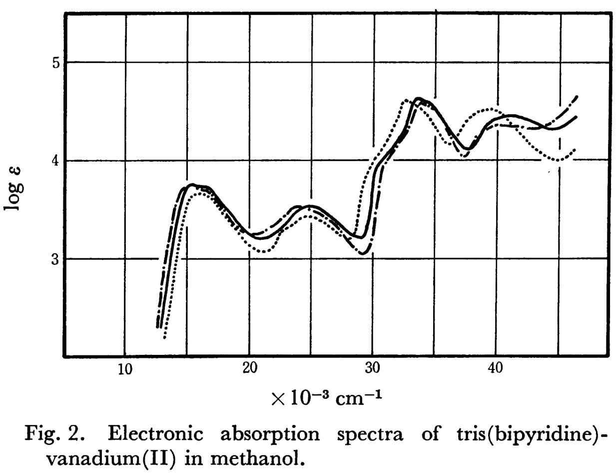

Fig. 2. Electronic absorption spectra of tris(bipyridine)-vanadium(II) in methanol.

——: [V(bipy)$_3$]$^{2+}$
—·—·: [V(4dmbip)$_3$]$^{2+}$
------: [V(5dmbip)$_3$]$^{2+}$

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21) G. B. Kauffman and L. T. Takahashi, "Inorganic Syntheses," Vol. 8, (1966), p. 227.

22) M. Kranz, "Inorganic Syntheses," Vol. 7 (1963), p. 94.

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

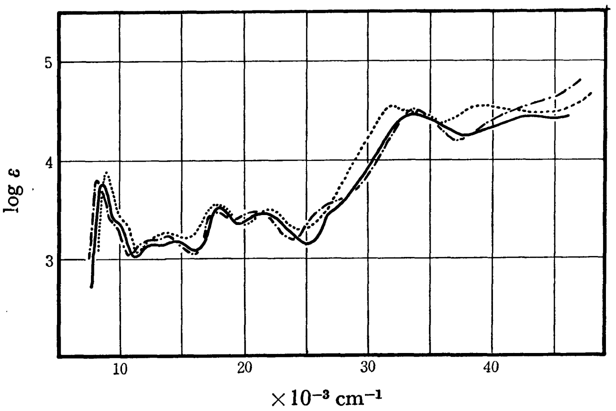

Fig. 3. Electronic absorption spectra of tris(bipyridine)-chromium(II) in methanol.
——: $[Cr(bipy)_3]^{2+}$
—·—: $[Cr(4dmbip)_3]^{2+}$
······: $[Cr(5dmbip)_3]^{2+}$

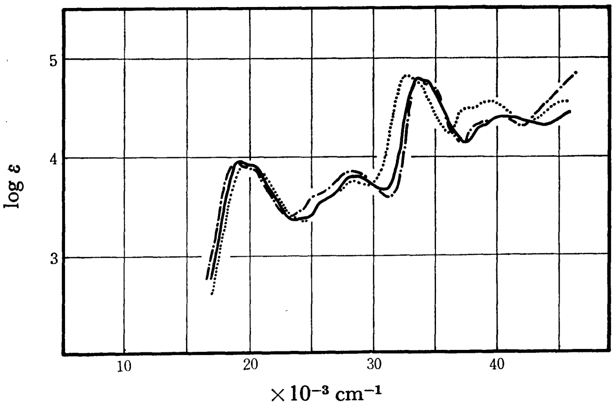

Fig. 4. Electronic absorption spectra of tris(bipyridine)-iron(II) in methanol.
——: $[Fe(bipy)_3]^{2+}$
—·—: $[Fe(4dmbip)_3]^{2+}$
······: $[Fe(5dmbip)_3]^{2+}$

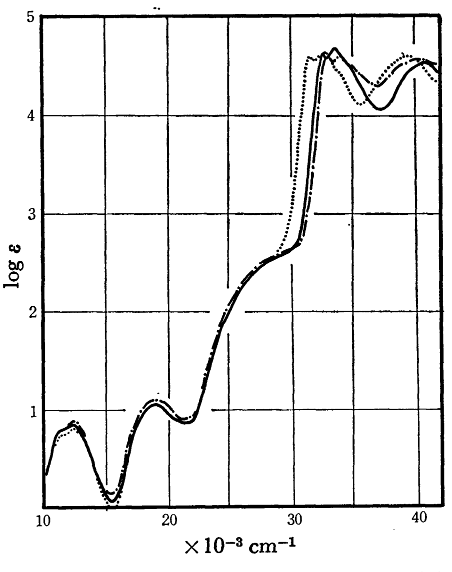

Fig. 5. Electronic absorption spectra of tris(bipyridine)-nickel(II) in methanol.
——: $[Ni(bipy)_3]^{2+}$
—·—: $[Ni(4dmbip)_3]^{2+}$
······: $[Ni(5dmbip)_3]^{2+}$

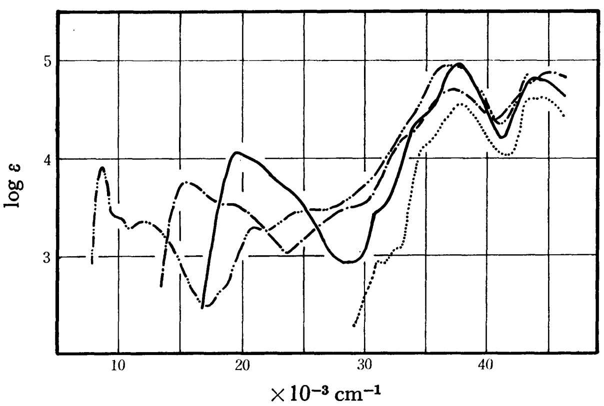

Fig. 6. Electronic absorption spectra of tris(phenanthroline) complexes of vanadium(II), chromium(II), and iron(II) in methanol.
—·—: $[V(phen)_3]^{2+}$
—··—: $[Cr(phen)_3]^{2+}$
——: $[Fe(phen)_3]^{2+}$
······: phenanthroline

dine which are assigned to (π, π^*) transitions are shifted by such a weak perturbation as methyl substitutions (Fig. 7). The lowest wave number band of the bipyridine is shifted to higher wave number in the order 5dmbip < bipy < 4dmbip. The ordering is preserved in the lowest (π, π^*) transition of the coordinating bipyridines. A conformational change of two pyridine rings in bipyridine on the chelate formation is expected to change the (π, π^*) transition. However, such an effect, at least to the lowest excited states, was estimated to be negligibly small by theoretical calculation. The lowest (π, π^*) transition of the bipyridines coordinating to Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) was observed around 33000 cm^{-1}, whereas the corresponding band of free bipyridine was observed at 35000 cm^{-1}. This shift might be attributed to a spectral shift arising from an excitation coupling between three bipyridines in a tris complex. However, the exciton interaction predicts another direction of the spectral shift. The coordinat-

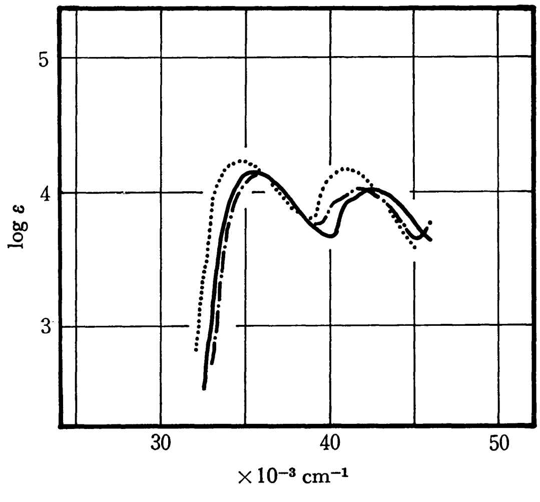

Fig. 7. Electronic absorption spectra of bipyridine.
——: 2,2′-bipyridine
—·—: 4,4′-dimethyl-2-2′-bipyridine
······: 5,5′-dimethyl-2,2′-bipyridine

ing bipyridine is polarized partially by an electrostatic interaction due to the residual positive charge on the central metal ion and partially by σ donation of the coordinating nitrogens. Such a polarization, however, gives rise to a slight red-shift. The lowest wave number band is shifted to lower wave number in the order Fe(II) < Mn(II) ~ Zn(II) < Co(II) ~ Ni(II) < Cu(II). Although the observed shift is within several hundred wave numbers, it is almost parallel to the natural order of complex stability except for Fe(II).[24]

Since iron(II) in the diamagnetic state is highly π-donating, π electronic system of the bipyridine coordinating to the iron can not be described in terms of a simple electronic polarization as in the complexes of less π-donating metal ions such as Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). The vanadium(II) and chromium(II) complexes show absorption bands corresponding to those of the coordinating bipyridine at almost the same position as in the iron(II) complexes. Since V(II), Cr(II) as well as Fe(II) are less π electron-attractive, the coordinating ligand should accept migration of π electron into the vacant molecular orbitals. The lowest excited states of the coordinating bipyridine in such a complex should be described in terms of a configuration admixture of "metal to ligand" charge-transfer excited states and coupled (π, π^*) excited states of three coordinating bipyridines.

When such a high π-donating power is attained as in V(II), Cr(II), or Fe(II), some "metal to ligand" charge-transfer excited states should be lower than (π, π^*) excited states. These charge-transfer transitions, however, should be very weak unless they can borrow their intensities from the allowed (π, π^*) transitions by a mixing due to the configuration interaction mentioned above. In fact, the vanadium(II) and chromium(II) complexes give rise to a series of superposing intense and diffuse absorption bands over the visible and near-infrared region (Figs. 2—3). These bands are assigned to charge-transfer transitions as well as those observed in the iron(II) complexes (Fig. 4). The fact that the charge-transfer transitions were observed indicates that mixing due to the configuration interaction takes place. The vanadium(II) complexes show a remarkable extra shoulder at 31600 cm^{-1} besides the corresponding band of the iron(II) complexes, while the chromium(II) complexes show a rather diffuse composite system of bands. In the case of the open-shell ions such as V(II) and Cr(II), not only singlet-singlet (π, π^*) excited states but also singlet-triplet (π, π^*) excited states can appreciably participate in the lowest excited states of the coordinating bipyridine.

As is shown in Fig. 2, the visible absorption spectrum of the vanadium(II) complexes indicates a characteristic of the allowed transition very similar both in shape and intensity to that of the iron(II) complexes except for the position which is shifted by about 4000 cm^{-1} to lower wave number. The visible absorption spectrum of the chromium complexes is rather complicated, but also shows a characteristic of the allowed transition as well (Fig. 3). The lowest wave number bands at *ca.* 20000 cm^{-1} of the iron(II) complexes are charge-transfer bands and are shifted to the higher wave number upon methyl substitutions in the order 4dmbip < bipy < 5dmbip. The ordering is the reverse of that observed in the lowest (π, π^*) transitions of the coordinating bipyridine. The band at 16000 cm^{-1} of the vanadium(II) complexes and that at 8500 cm^{-1} of the chromium(II) complexes show a similar spectral shift as observed in the charge-transfer band at 20000 cm^{-1} of the iron complexes. On the other hand, the band at 25000 cm^{-1} of the vanadium(II) complexes, that at 28000 cm^{-1} of the iron(II) complexes and that at 18000 cm^{-1} of the chromium(II) complexes are observed in the order 4dmbip < 5dmbip < bipy. This does not coincide with the ordering observed for either the lowest wave number charge-transfer transition or for the lowest (π, π^*) transition. The bands are assigned to charge-transfer transitions from a $d\pi$ orbital to a second antibonding π molecular orbital of the ligand. The band at 21500 cm^{-1} of the chromium complexes, however, contrary to the band at 18000 cm^{-1} shows a similar behavior upon methyl substitutions to that observed for the band at 8500 cm^{-1}. The molecular orbitals involved in both transitions are very similar.

Nickel(II) complexes give rise to two weak (d, d^*) bands of Laporte forbidden character in the visible region (Fig. 5). When the coordinating bipyridine is introduced methyl groups, "metal to ligand" charge-transfer bands in the vanadium(II), chromium(II), and iron(II) complexes are shifted, but not much the (d, d^*) transitions in the nickel(II) complexes. Energy of the first (d, d^*) transition, $^3T_2 \rightarrow {}^3A_2$, of an octahedral nickel(II) complex corresponds to the ligand-field splitting parameter, 10 Dq.[25] The fact that no shifts of the first band of the nickel(II) complexes were observed upon methyl substitutions indicates that σ donation of the ligand, hence the ligand-field splitting of the d orbitals, is not influenced by such a weak perturbation as introduced by methyl substitutions. This must be true in the (d, d^*) transitions of other metal ions.

The spectral shifts arising from dimethyl substitutions of tris(bipyridine) complexes are summarized in Fig. 8.

The coordinating phenanthroline gives rise to (π, π^*) transitions in the ultraviolet region. Absorption spectrum of the coordinating ligand preserves the band shape of free ligand and is slightly shifted to lower wave number in the order Fe(II) < V(II) < Cr(II) (Fig. 6).

The visible absorption bands of $[\mathrm{Fe(phen)_2}]^{2+}$ are assigned to "metal to ligand" charge-transfer transitions as well as the visible bands of $[\mathrm{Fe(bipy)_3}]^{2+}$.[26] The band at 16000 cm^{-1} of $[\mathrm{V(phen)_3}]^{2+}$ corresponds to that at almost the same position as $[\mathrm{V(bipy)_3}]^{2+}$. As was observed in $[\mathrm{Cr(bipy)_3}]^{2+}$, the visible and near-infrared spectrum of $[\mathrm{Cr(phen)_3}]^{2+}$ is much more complicated than those of $[\mathrm{V(phen)_3}]^{2+}$ and $[\mathrm{Fe(phen)_3}]^{2+}$. However, a similar spectral corre-

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[24] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3192.

[25] J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press (1961), p. 286.

[26] T. Ito, N. Tanaka, I. Hanazaki, and S. Nagakura, This Bulletin, **42**, 702 (1969).

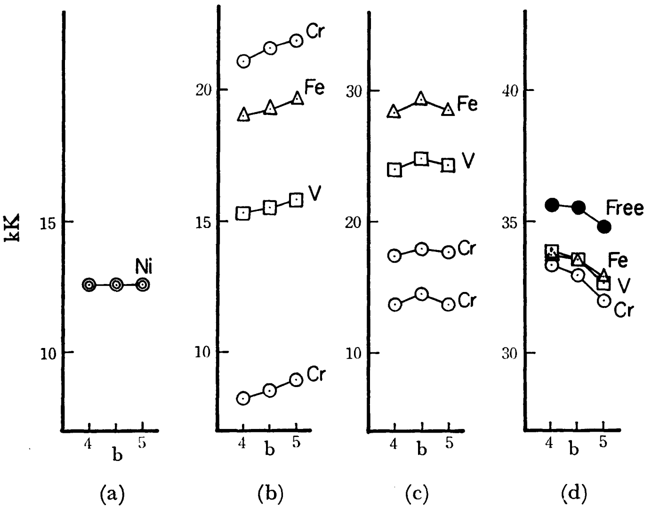

Fig. 8. Dimethyl substitution effects of the absorption spectra of tris(bipyridine) complexes.
(a) (d,d^*) transition
(b) the lowest charge-transfer transition (A charge-transfer band of the chromium(II) complexes at 21500 cm^{-1} shows a similar dimethyl substitution effect to that of the lowest charge-transfer transition.)
(c) the second charge-transfer transition
(d) (π,π^*) transition of the free and coordinating bipyridines
□: vanadium(II) complexes
○: chromium(II) complexes
△: iron(II) complexes
4: 4dmbip; b: bipy; 5: 5dmbip

spondence is observed between $[V(phen)_3]^{2+}$ and $[V(bipy)_3]^{2+}$, and also $[Cr(phen)_3]^{2+}$ and $[Cr(bipy)_3]^{2+}$. The absorption spectra of $[V(phen)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ in the visible and near-infrared region are assigned to "metal to ligand" charge-transfer transitions.

Transition energy of the lowest charge-transfer excitation should be proportional to a difference of the ionization potential of the metal $d\pi$ orbitals in complex and the electron affinity of the lowest vacant antibonding π orbitals in the coordinating ligand. Excitation energy of the charge-transfer band of tris(bipyridine) complexes, for example, varies primarily depending upon the $d\pi$ ionization potential of the central metals. Since the same argument holds for tris(phenanthroline) complexes as well, a linear relationship is expected between transition energies of the corresponding charge-transfer bands of tris(bipyridine) complexes and tris(phenanthroline) complexes. In fact, plots of the transition energies show an excellent linearity as seen in Fig. 9. This will very likely verify an assignment of "metal to ligand" charge-transfer transitions to the visible and near-infrared bands observed in the vanadium(II) and chromium(II) complexes.

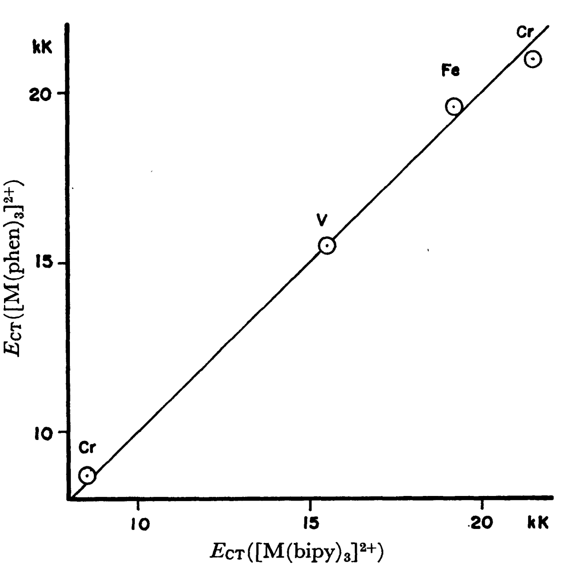

Fig. 9. Plots of the charge-transfer excitation energies of tris(1,10-phenanthroline) complexes, $E_{CT}([M(phen)_3]^{2+})$ *vs.* tris(2,2'-bipyridine) complexes, $E_{CT}([M(bipy)_3]^{2+})$.

Figure 9 reveals that the $d\pi$ ionization potential of the central metals is decreased in the order $Cr < V < Fe$. The ionization potential of M(II) in the ground state was experimentally estimated to be 29.31 eV for V(II), 30.95 eV for Cr(II) and 30.64 eV for Fe(II). When the ionization potential is estimated for the valence state, the values are obtained as follows: 29.5 eV for $V(II)(d\pi)^3$, 28.8 eV for $Cr(II)(d\pi)^4$, and 35.3 eV for $Fe(II)(d\pi)^6$.[27] The observed ordering of π-donating power of the central metals can be reproduced. However, a divalent cation in such a complex must be electroneutralized by σ-donation of the coordinating nitrogens and the values should be corrected for the electroneutrality. The ionization potentials were evaluated for the neutral species with the configuration d^ns^2,[28] where s^2 is assumed to be furnished by σ-donation of the coordinating nitrogens. The values thus obtained seem to be a rather realistic approximation and are, in fact, linear to the lowest charge-transfer transition energy of the respective complexes.

	$d\pi$ ionization potential	$E_{CT}([M(bipy)_3]^{2+})$	$E_{CT}([M(phen)_3]^{2+})$
$V(II)\sigma^2$ $(d\pi)^3s^2$	11.27 eV	1.92 eV	1.93 eV
$Cr(II)\sigma^2$ $(d\pi)^4s^2$	10.25 eV	1.05 eV	1.06 eV
$Fe(II)\sigma^2$ $(d\pi)^6s^2$	12.61 eV	2.38 eV	2.43 eV

In the case of Cr(II), however, there are two types of the lowest $d\pi$ ionization as follows:

$$\text{I}\quad (d\pi_1)^2(d\pi_2)(d\pi_3) \longrightarrow (d\pi_1)(d\pi_2)(d\pi_3) + e$$

$$\text{II}\quad (d\pi_1)^2(d\pi_2)(d\pi_3) \longrightarrow (\overline{d\pi_1})(d\pi_2)(d\pi_3) + e$$

In the process I an electron with β spin pairing in a $d\pi$ orbital is detached, while in the process II an electron with α spin is transferred. The difference in the inter-electronic electrostatic repulsion energy between the processes I and II is given in terms of Racah's parameters and estimated at 13000—15000 cm^{-1} by the empirical values of the central metal ion. There must be two types of the charge-transfer transition from chromium(II) to the lowest antibonding π orbitals of the coordinating ligands. In fact, as was shown in

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[27] J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press, (1961), p. 100.

[28] C.E. Moore, "Atomic Energy Levels," Vol. 1 and 2, National Bureau of Standards, Washington (1949, 1952).

Fig. 8, $[Cr(bipy)_3]^{2+}$ gives rise to a charge-transfer band at 21500 cm^{-1}, which shows a similar dimethyl substitution effect to that of the lowest charge-transfer band at 8500 cm^{-1}. The energy difference is 13000 cm^{-1}. For the other ligands, the observed energy differences are 12850 cm^{-1} for 4dmbip, 12800 cm^{-1} for 5dmbip and 12400 cm^{-1} for phen. These values indicate a reduction of Racah's parameters in the complexes due to the delocalization of $d\pi$ electrons over the ligands.