Complexes Coordinated by 2,2′-Bipyridine Negative Ion. II. Sodium 2,2′-Bipyridinetetracarbonylchromium, -molybdenum, and -wolfram

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Bipyridinetetracarbonylchromium, -molybdenum and -wolfram and their related complexes were reduced with sodium metal in tetrahydrofuran. Some products in the first stage of reduction were isolated. On the basis of the electronic absorption spectrum and the electron spin resonance, the complex formed in the reduction was concluded to be a complex coordinated by mononegative ion of bipyridine. Metal $d\sigma$ orbital in the complex is still higher than bipyridine π^* orbital, even if it is fairly lowered by a positive charge arising from the "metal to carbonyl" back-donation. Trapped electrons in the bipyridine π^* orbital are, however, readily transferred into $d\sigma$ orbital depending upon molecular environment. This gives rise to the formation of a pentacoordinate complex or complex dimer evolving carbon monoxide.

Coordinating bipyridine captures electrons when a bipyridine complex of less electron-acceptable metal is reduced by strong reducing reagents such as sodium metal. Bipyridine, with its strong σ-donating and π-accepting powers, gives a strong ligand-field to the central metal and a sufficient energy gap between $d\sigma$ and $d\pi$ orbitals. When a tris-bipyridine complex of metal with vacancies in $d\pi$ shell is reduced, electrons furnished by the reducing reagent are captured by the central metal ion. However, a tris-bipyridine complex of metal with no vacancy in $d\pi$ shell should capture electrons either in metal $d\sigma$ orbitals or in the vacant antibonding π molecular orbitals of the coordinating bipyridine. In the higher oxidation states, transition metal ions with $d\sigma$ electrons can exist in various stable coordination complexes.[1] In the lower oxidation states, however, electrons trapped in $d\sigma$ orbitals give rise to a dissociation of the coordinating ligand. Unless some electrostatic attraction between metal and ligand is present as in the higher oxidation states, $d\sigma$ electrons in the antibonding orbital of coordination binding destabilize the coordination binding. Although it shows a trend to form $[Co(bipy)_2]^+$, $[Co(bipy)_3]^+$ can trap two electrons in the metal $d\sigma$ orbitals (bipyridine is abbreviated to bipy).[2] On the contrary, however, $[Mn(bipy)_3]$ and $[Fe(bipy)_3]$ showed an evidence of coordinating bipyridine negative ion.[3] When a vacant antibonding π molecular orbital of the coordinating bipyridine is sufficiently lower than $d\sigma$ orbital of the central metal, electrons furnished upon reduction should be trapped by the coordinating bipyridines.

Porphyrin and phthalocyanine are as highly σ-donating and π-accepting as bipyridine and trap electrons in the conjugated system when the metal complexes are reduced.[4] Such coordinating negative ions have been obtained only for the conjugated nitrogen bases.

In the case of metal carbonyls, sufficient migration of $d\pi$ electron into the antibonding π molecular orbital of coordinating carbon monoxides makes the central metal more positive and therefore more σ-acceptable. Even so, reduction of the metal carbonyls with closed $d\pi$ shell gives rise to a reduction of coordination number or a formation of dimer with metal-metal bond or with carbonyl bridgings. As a matter of fact, a metal carbonyl with d^8 exists in a pentacoordinate structure as in $[Mn(CO)_5]^-$ or $[Cr(CO)_5]^{2-}$,[5] while the one with d^7, in a dimer structure as in $[Mn_2(CO)_{10}]$ or $[Cr_2(CO)_{10}]^{2-}$.[6] Central metal atom in a stable compound has an electronic configuration of the rare gases. It is required by Sidgwick's rule that no open shell exists in a stable structure. However, some monomeric metal carbonyls with open shell have in recent years been successfully prepared. An open shell metal carbonyl $[V(CO)_6]$ was prepared by oxidation of a closed shell metal carbonyl $[V(CO)_6]^-$.[7] In this case, however, a hole exists in a $d\pi$ orbital. Recently we succeeded in the isolation of the first stage reduction product of $[Cr(CO)_4(bipy)]$.[8] If an electron was trapped by the central metal, evolution of carbon monoxide should be expected. In fact, the evolution of carbon monoxide was observed during the second or further stage. As is seen in the formation of $[Cr_2(CO)_{10}]^{2-}$, an electron-capture at the central metal results in a dimer formation. However, in the first stage of reduction, a monomeric open shell species $[Cr(CO)_4(bipy)]^-$ was formed. Thus an electron given by sodium metal was predominantly localized on the coordinating bipyridine. In this paper, we will present a unified study on chromium-, molybdenum-, and wolfram carbonyls with coordinating negative ion of 2,2′-bipyridine.

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Experimental

Materials. 2,2'-bipyridine (bipy) and its 4,4'-dimethyl- (4dmbip) and 5,5'-dimethyl- (5dmbip) derivatives were prepared by the method of Sasse and Whittle.[9] Hexacarbonylmolybdenum $[\mathrm{Mo(CO)_6}]$ and hexacarbonylwolfram $[\mathrm{W(CO)_6}]$ were of reagent grade (Pressure Chem. Co., Penn., U. S. A.) and were used without further purification. All other reagents and solvents were commercially available. Tetrahydrofuran (THF) used for solvent was dehydrated by KOH, refluxed on CuCl, carefully distilled under nitrogen atmosphere and a trace of water was removed by $\mathrm{LiAlH_4}$.

Preparation of Compounds. $[\mathrm{Mo(CO)_4bipy}]$ was prepared by the method of Stiddard.[10] Dimethyl substituted bipyridine complexes also were prepared by the same method. $[\mathrm{Mo(CO)_4bipy}]$: Hexacarbonylmolybdenum (1.4 g) and bipyridine (0.8 g) were refluxed in toluene (50 m*l*) for 1.5 hr under oxygen-free, dry nitrogen atmosphere. After cooling, reddish orange needle crystals were collected, washed with petroleum ether (60 m*l*) and dried *in vacuo*.

$[\mathrm{Mo(CO)_4bipy}]$ (reddish orange) Found: Mo, 26.8%. Calcd for $[\mathrm{Mo(CO)_4bipy}]$: Mo, 26.3%.

$[\mathrm{Mo(CO)_44dmbip}]$ (reddish orange) Found: Mo, 24.9%. Calcd for $[\mathrm{Mo(CO)_44dmbip}]$: Mo, 24.5%.

$[\mathrm{Mo(CO)_45dmbip}]$ (yellow) Found: Mo, 24.5%. Calcd for $[\mathrm{Mo(CO)_45dmbip}]$: Mo, 24.5%.

Preparation of $[\mathrm{Mo(CO)_3P(C_6H_5)_3bipy}]$. $[\mathrm{Mo(CO)_4bipy}]$ (0.182 g) and $[\mathrm{P(C_6H_5)_3}]$ ($[\mathrm{P(C_6H_5)_3}]$ is abbreviated to $\mathrm{P\phi_3}$) (0.184 g) were refluxed in benzene for 5 hr. After cooling, violet needle crystals precipitated were collected by filtration, washed with petroleum ether and dried *in vacuo*.

$[\mathrm{Mo(CO)_3P\phi_3bipy}]$ (violet needle) Found: Mo, 16.0%. Calcd for $[\mathrm{Mo(CO)_3P\phi_3bipy}]$: Mo, 16.0%.

$[\mathrm{Mo(CO)_3P\phi_34dmbip}]$ (red purple) Found: Mo, 15.7%. Calcd for $[\mathrm{Mo(CO)_3P\phi_34dmbip}]$: Mo, 15.3%.

$[\mathrm{Mo(CO_3)P\phi_35dmbip}]$ (red purple) Found: Mo, 15.0%. Calcd for $[\mathrm{Mo(CO)_3P\phi_35dmbip}]$: Mo, 15.3%.

$[\mathrm{W(CO)_4bipy}]$ was prepared in xylene instead of toluene by the same method as for molybdenum complexes.[10]

$[\mathrm{W(CO)_4bipy}]$ (red purple) Found: W, 40.7%. Calcd for $[\mathrm{W(CO)_4bipy}]$: W, 40.7%.

Preparation of $[\mathrm{Cr(CO)_4bipy}]$, $[\mathrm{Cr(CO)_44dmbip}]$ and $[\mathrm{Cr(CO)_45dmbip}]$ were given elsewhere.[8]

Reduction of $[M(CO)_4L]$. $\mathrm{Na[Mo(CO)_4L]}$, where L denotes bipy, 4dmbip, or 5dmbip, were prepared by reduction with sodium metal in an apparatus (Fig. 1) in a high vacuum by a similar method as for the preparation of $\mathrm{Na[Cr(CO)_4L]}$.[8,11]

$\mathrm{Na[Mo(CO)_4bipy]}$ Found: Mo, 25.5%. Calcd for $\mathrm{Na[Mo(CO)_4bipy]}$: Mo, 24.8%.

$\mathrm{Na[Mo(CO)_44dmbip]}$ Found: Mo, 22.9%. Calcd for $\mathrm{Na[Mo(CO)_44dmbip]}$: Mo, 23.1%.

$\mathrm{Na[Mo(CO)_45dmbip]}$ Found: Mo, 22.5%. Calcd for $\mathrm{Na[Mo(CO)_45dmbip]}$: Mo, 23.1%.

Electronic Absorption Spectra. Absorption spectra were taken on a Shimadzu automatic recording spectrophotometer Model MPS-50. Measurements of the spectra of air-sensitive compounds were described in a previous paper.[11]

Electron Spin Resonance. ESR spectra in THF solution were measured at room temperature using a Japan Electron Optics Laboratory spectrometer Model JES-3BSX. The g-value was determined with the aid of the standard sample of $\mathrm{Mn^{2+}}$ ion.

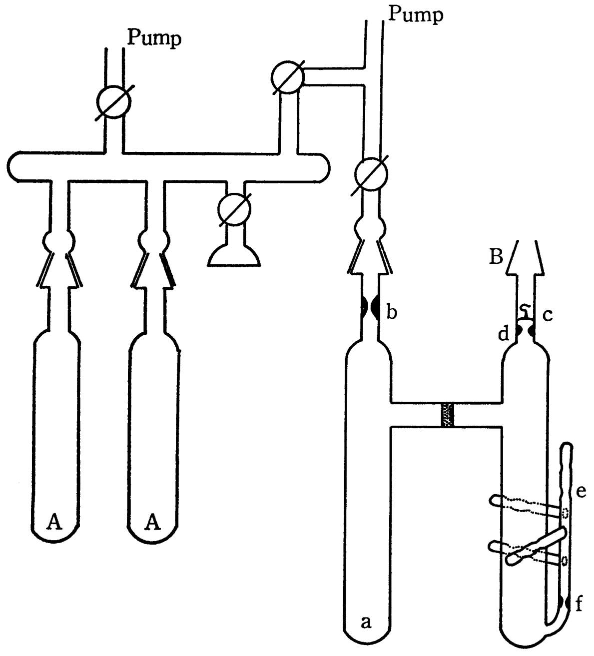

Fig. 1. Apparatus for reduction.
After $[\mathrm{M(CO)_4L}]$ was placed at a with a slight excess of sodium metal, the apparatus was evacuated up to 10^{-3} mmHg. Dried THF at A, after being thoroughly degassed, was transferred to a by distillation, a being cooled with liquid nitrogen. After being sealed off at b, the THF solution was shaken for about 10 hr and then filtrated. The apparatus was joined with a vacuum line at B. The solvent of the filtrate was then removed by distillation into the vacuum system and the residue was dried *in vacuo*. After being sealed off at d, the product was collected in e and then a branch of sample tubes was sealed off at f. The sample should be stored *in vacuo* and in a dark place.

Results and Discussion

The spectral change of the reduction process of $[\mathrm{Cr(CO)_4bipy}]$ with sodium metal is shown in Fig. 2. During the first stage of reduction, the spectrum gently changed with the isosbestic points from that of the starting material $[\mathrm{Cr(CO)_4bipy}]$ to the one shown as (a) in Fig. 2. After that, the curve changed to the spectrum (b), the isosbestic points being shifted. This indicates that the reduction proceeds stepwise. Two steps, at least, are involved in the process. In a previous paper we reported on the isolation of the first stage reduction product of $[\mathrm{Cr(CO)_4bipy}]$.[8] The spectrum of the isolated $\mathrm{Na[Cr(CO)_4bipy]}$ is shown in Fig. 3. It coincides with the spectrum (a).

A similar stepwise spectral change was observed in the reduction processes of $[\mathrm{Mo(CO)_4L}]$, $[\mathrm{W(CO)_4L}]$, and $[\mathrm{Mo(CO)_3P\phi_3L}]$ (L: bipy, 4dmbip, 5dmbip) with sodium metal. As a matter of fact, the first reduction product $\mathrm{Na[Mo(CO)_4L]}$ (L: bipy, 4dmbip, 5dmbip) could be isolated. Absorption spectra of $\mathrm{Na[Mo(CO)_4L]}$ are shown in Fig. 4. Absorption spectra of the first stage reduction product were obtained for $\mathrm{Na[Mo(CO)_3P\phi_3L]}$ and $\mathrm{Na[W(CO)_4L]}$

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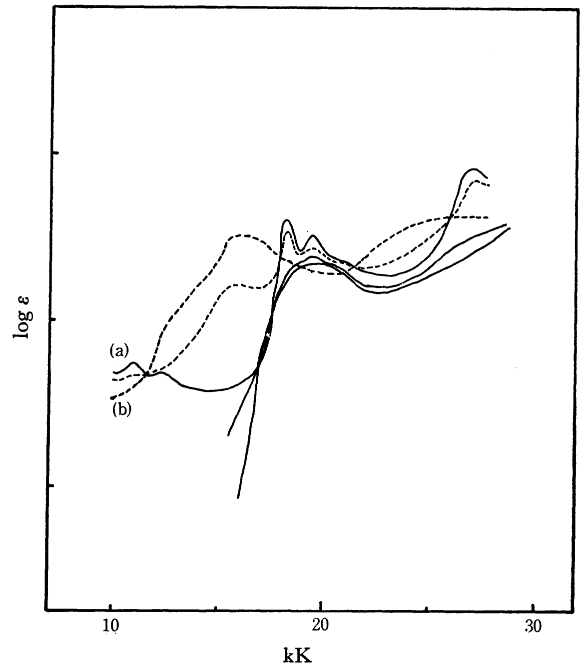

Fig. 2. Spectral changes in the reduction process of [Cr(CO)$_4$bipy] with sodium metal in THF.
——: first stage reduction which forms complex (a)
----: second stage reduction which forms complex (b)

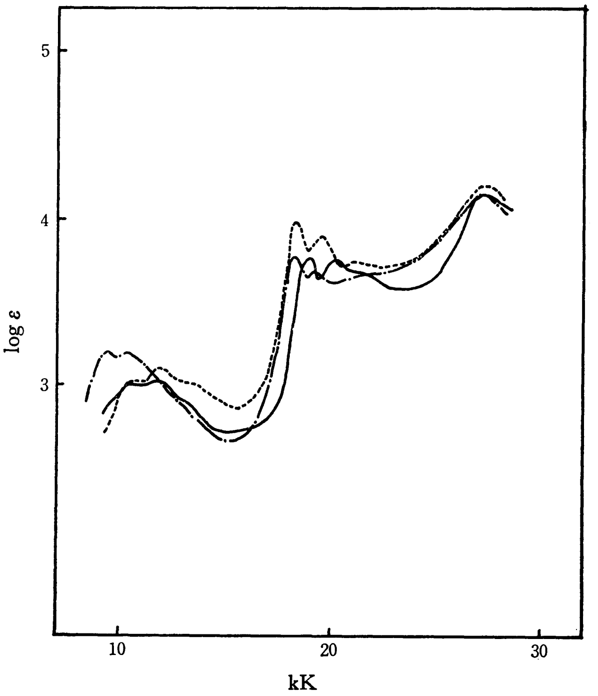

Fig. 4. Electronic absorption spectra of Na[Mo(CO)$_4$L] in THF.
——: L: bipy, ----: L: 4dmbip, —·—·: L: 5dmbip

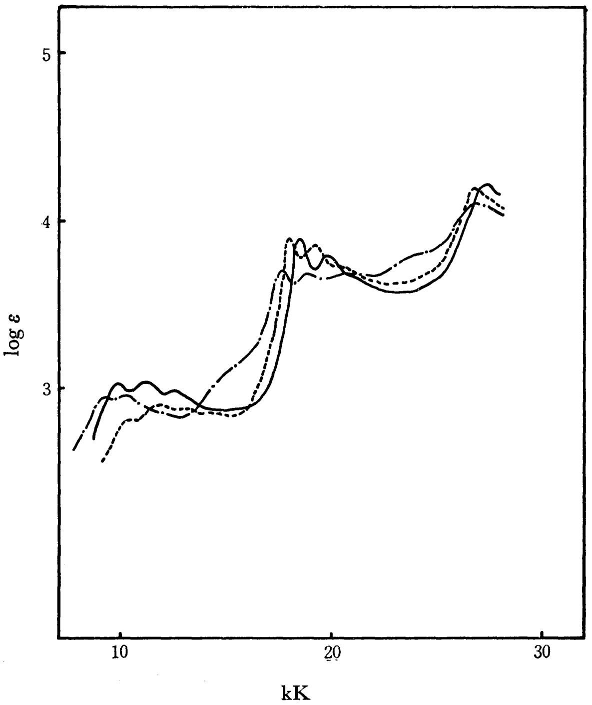

Fig. 3. Electronic absorption spectra of Na[Cr(CO)$_4$L] in THF.
——: L: bipy, ----: L: 4dmbip, —·—·: L: 5dmbip

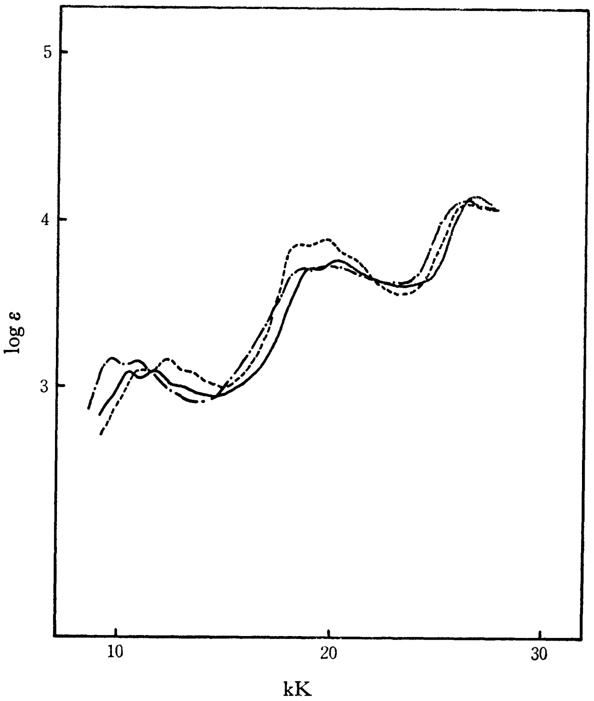

Fig. 5. Electronic absorption spectra of Na[Mo(CO)$_3$Pϕ_3L] in THF.
——: L: bipy, ----: L: 4dmbip, —·—·: L: 5dmbip

(Figs. 5 and 6), although they were not intended to isolate.

Three intense characteristic absorption bands were observed from near-infrared to ultraviolet region. These bands are slightly shifted with a variety of central metals. The second band at about 20,000 cm^{-1} is blue-shifted in the order Cr$<$Mo$\leq$W. Dimethyl substitutions in the coordinating bipyridine give rise to a blue-shift in the first band in the order 5dmbip$<$bipy$\leq$4dmbip and a blue-shift in the second band in the order 5dmbip$\leq$4dmbip$<$bipy, regardless of the central metal species.

ESR spectra of the first stage reduction product of [Cr(CO)$_4$L] (L: bipy, 4dmbip, 5dmbip) and [Mo-

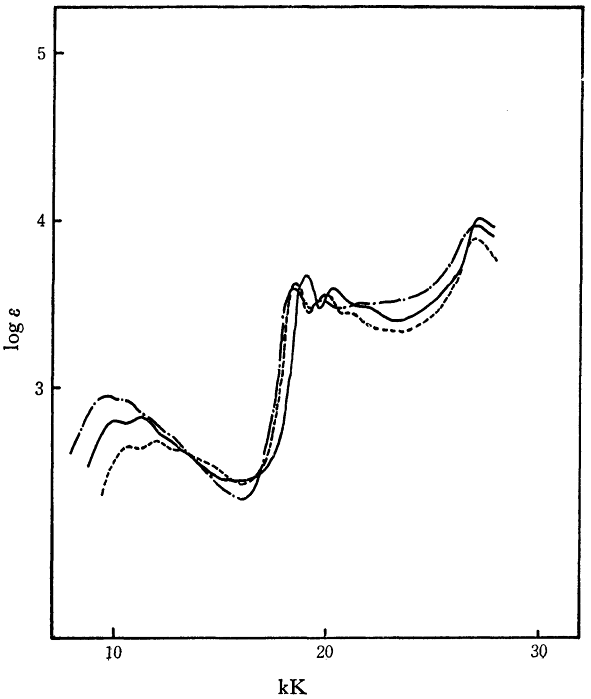

Fig. 6. Electronic absorption spectra of Na[W(CO)$_4$L] in THF.
——: L: bipy, ----: L: 4dmbip, —·—·: L: 5dmbip

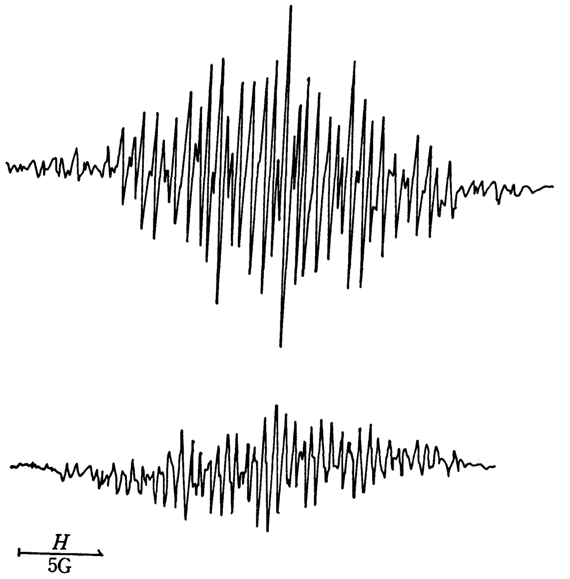

Fig. 7. ESR spectra of Na[Cr(CO)$_4$bipy] and K bipy in THF at room temperature.
upper: Na[Cr(CO)$_4$bipy], lower: K bipy

(CO)$_4$bipy] are shown in Figs. 7—10. ESR spectra of bipyridine negative ions, K bipy, K 4dmbip, K 5dmbip and also Na 4dmbip are shown in Fig. 7 and Figs. 11—13. Observed *g*-value and line widths are summarized in Table 1. ESR spectrum of Na[Cr(CO)$_4$bipy] is similar to that of K bipy. In the case of K bipy, the binding between K$^+$ and bipy$^-$ is essentially ionic and the trapped electron in bipy$^-$ has a very poor population on K$^+$. The ESR spectrum of K bipy does not show a hyperfine structure due to the nuclear spin of potassium ion. The ESR spectrum of Na bipy, however, clearly shows a hyperfine structure due to the nuclear spin of sodium ion (Fig. 13). This phenomenon has been generally observed in

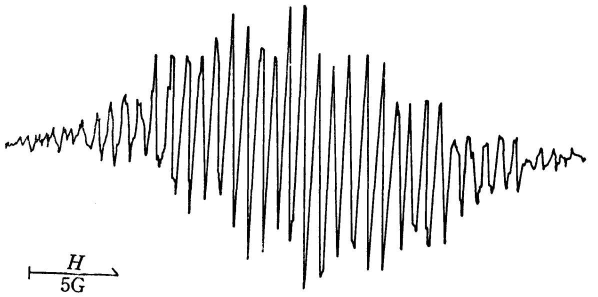

Fig. 8. ESR spectrum of Na[Cr(CO)$_4$4dmbip] in THF at room tempertaure.

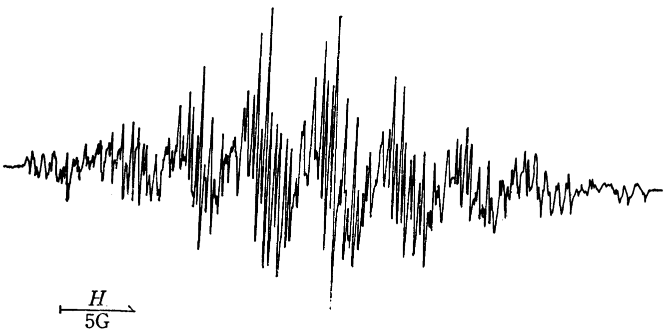

Fig. 9. ESR spectrum of Na[Cr(CO)$_4$5dmbip] in THF at room temperature.

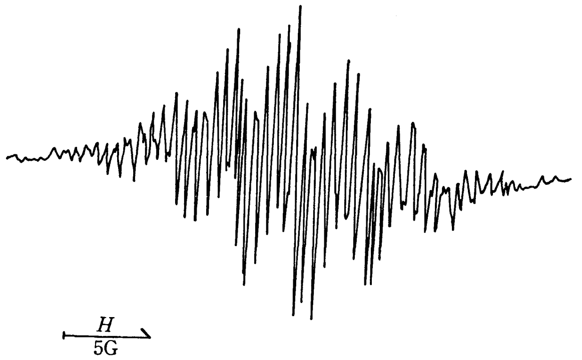

Fig. 10. ESR spectrum of Na[Mo(CO)$_4$bipy] in THF at room temperature.

TABLE 1. *g*-VALUE AND LINE WIDTH

	g-value	line width
Na[Cr(CO)$_4$bipy]	2.0023	14.5G
Na[Cr(CO)$_4$4dmbip]	2.0019	17.1G
Na[Cr(CO)$_4$5dmbip]	2.0004	15.6G
Na[Mo(CO)$_4$bipy]	2.0021	12.7G
Na[W(CO)$_4$bipy]	2.0031	12.6G
K bipy	2.0026	12.0G
K 4dmbip	2.0024	11.6G
K 5dmbip	2.0025	14.0G

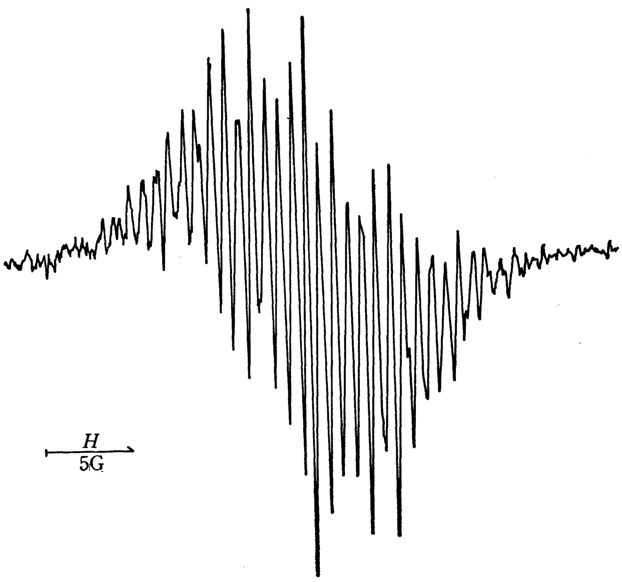

Fig. 11. ESR spectrum of K 4dmbip in THF at room temperature.

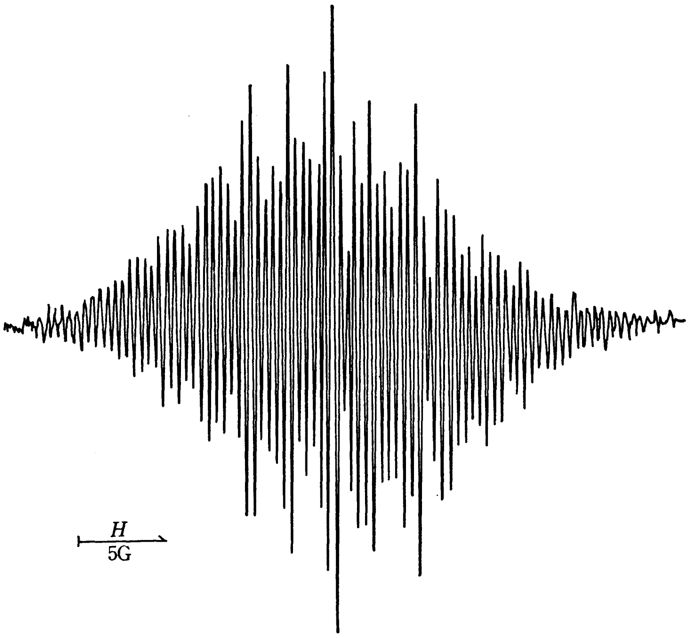

Fig. 12. ESR spectum of K 5dmbip in THF at room temperature.

various aromatic negative ions.[12] Thus ESR spectra of the negative ions obtained by reduction with potassium metal are regarded as those of the respective free negative ions. $Na[Cr(CO)_4bipy]$ does not show any hyperfine structure due to either sodium or chromium. An unpaired electron in an antibonding π orbital of bipyridine can not strongly interact with the closed $d\pi$ shell of chromium and also does not migrate over the outer sodium ion.

Apparently the ESR of K bipy, K 4dmbips, and K 5dmbip differs a great deal each other (Figs. 7, 11—12). Thus many hyperfine structure lines are observed for K 5dmbip, but not so many for K 4dmbip. The hyperfine structure of the ESR of K bipy has been analysed.[13] A similation analysis predicted the highest spin density at 5 and 5′.[14] The highest spin density at the positions 5 and 5′ and lower spin density at 4 and 4′ can give an interpretation of the hyperfine structure due to the dimethyl substitutions. We have never succeeded in similations of the ESR of K 5dmbip and K 4dmbip, however, we can point out that a higher hyperfine constant of six protons of two methyl groups introduced at the positions 5 and 5′ gives a well-resolved hyperfine structure, while the hyperfine constant of 4,4′-dimethyl protons is so small that it just gives an apparent broad line. Actually K 4dmbip gives the simplest ESR spectrum. Another possible interpretation is that the hyperfine structure of K 5dmbip arises from potassium nuclear spin (I=3/2). As shown in Fig. 12, odd number peaks of hyperfine splitting are observed, while even number peaks are expected for I=3/2.

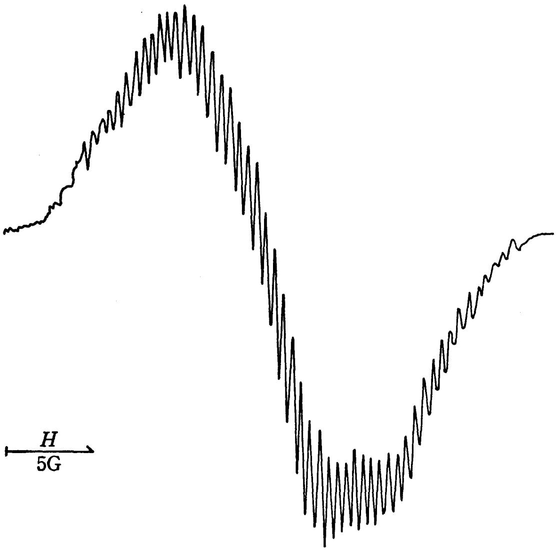

Fig. 13. ESR spectrum of Na 4dmbip in THF at room temperature.

The reduced bipyridine complexes show ESR spectra which actually coincide with those of the corresponding bipyridine negative ions prepared by reduction with potassium metal. Although the magnitude of the hyperfine splitting is, in fact, slightly changed, g-values in the reduced bipyridine complexes actually coincide with that of K bipy (Table 1). In the case of 5,5′-dimethyl bipyridine, however, hyperfine splitting in the reduced bipyridine complex is appreciably changed from that of the negative ion, and g-value of the complex (2.0004) is significantly smaller than the free-spin value, g=2.0023. This indicates that a small interaction between the closed $d\pi$ shell of chromium and the antibonding π orbital of bipyridine changes slightly the electron-trapping molecular orbital and thus spin density at the posi-

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[12] N. M. Atherton and S. I. Weissman, *J. Amer. Chem. Soc.*, **83**, 1330 (1961). K. Nakamura and Y. Deguchi, This Bulletin, **36**, 359 (1963).

[13] E. König and H. Fischer, *Z. Naturforsch.*, **17a**, 1063 (1962).

[14] J. S. Veiga, W. L. Reynolds, and J. R. Bolton, *J. Chem. Phys.*, **44**, 2214 (1966).

tions 5 and 5'. Although the spectra have never been reproduced by similation, the electronic structure of bipyridine in the reduced complex is concluded to be very close to that of bipyridine negative ion.

Three characteristic absorption bands of the reduced complexes correspond to respective three bands of bipyridine negative ions. Although these bands are slightly shifted for a variety of the central metal, spectral behavior of the complexes upon a weak perturbation such as dimethyl substitution corresponds to that of bipyridine negative ions regardless of the central metal. As previously reported, the second band at about 20,000 cm^{-1} of bipyridine negative ion is blue-shifted with increasing electrostatic potential due to the coordinating counter cation.[11] The second band of the complexes reported in this paper is blue-shifted in the order $Cr < Mo \leq W$. However, the fact that three characteristic bands of the complexes are changed in spectral intensity and position for the central metal and do not exactly coincide with the corresponding bands of bipyridine negative ion, indicates a binding effect of bipyridine negative ion and metal species. Although an evidence of the existence of bipyridine negative ion is also obtained from the observed *g*-value which is close to the free-spin value, ESR measurements in this particular case do not give a decisive direct evidence of the binding of bipyridine negative ion and metal species. If the coordinating bipyridine is set free upon reduction, the ESR spectrum should show a signal observed for Na bipy in THF. ESR spectrum does not show any hyperfine structure of sodium when [Mo(CO)$_4$bipy] is reduced with sodium metal in THF. This might be an evidence of the binding.

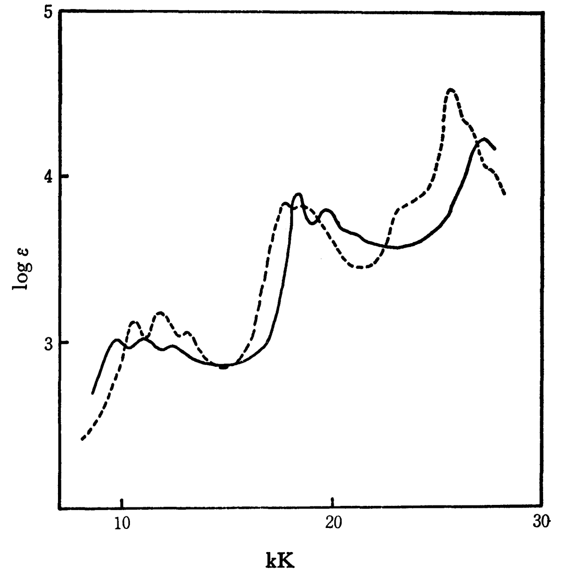


Fig. 14. Electronic absorption spectra of Na[Cr(CO)$_4$bipy] and Na bipy in THF.

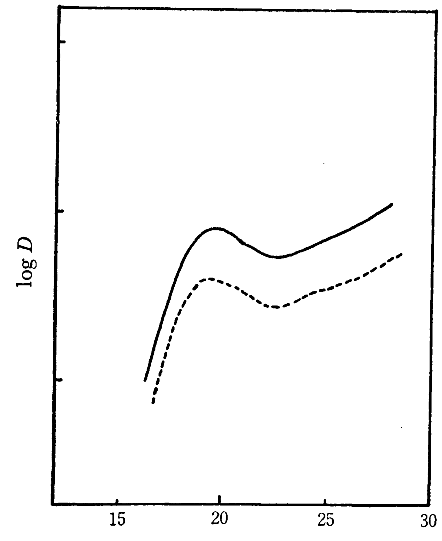


Fig. 15. " Metal to bipyridine " charge-transfer band of a complex formed by oxygen-oxidation of Na[Cr(CO)$_4$bipy] in THF. ----: [Cr(CO)$_4$bipy]

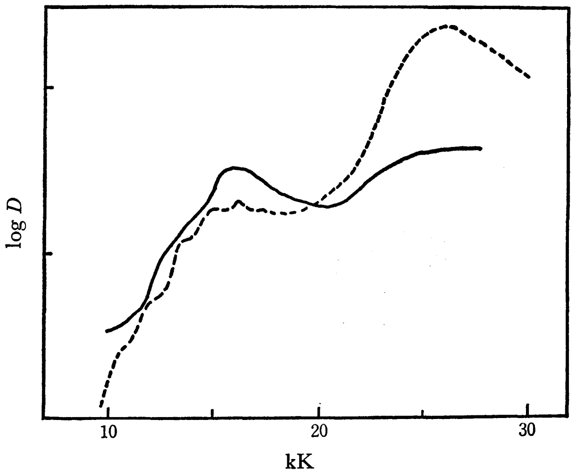
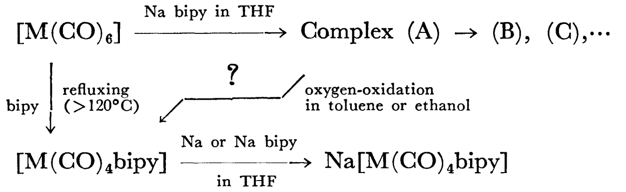


Fig. 16. Electronic absorption spectra of a complex formed in the second stage of reduction (——) and bipyridine dinegative ion, Li$_2$bipy (----).

When [Cr(CO)$_4$bipy] is reduced by Na bipy instead of sodium metal, absorption spectrum of the first stage reduction product ((a) in Fig. 2) is obtained. The absorption spectrum is observed with no contamination of that of Na bipy unless excess of Na bipy is added. This indicates that Na bipy is wasted to reduce the coordinating bipyridine in [Cr(CO)$_4$bipy]. The spectra of the reduced complex and bipyridine negative ion are similar but the difference can be detected (Fig. 14). When the reduced complex is oxidized by oxygen, it gives rise to a characteristic "metal to bipyridine" charge-transfer band in the visible region. From this, a complex formed upon the oxygen-oxidation should be a complex with certain coordinating bipyridine (Fig. 15). Since free bipyridine produced by oxygen-oxidation of free negative ion could not react with a metal carbonyl at room temperature, bipyridine negative ion should be binding to the central metal in the reduced complexes. The second stage complex (b) in Fig. 2 is obtained by reduction with sodium metal but not with Na bipy, a one-electron reducing reagent. However, the spectrum of complex (b) is different from that of bipyridine dinegative ion, Li_2bipy, and therefore a complex formed in the second stage could not be assigned to a complex coordinated by dinegative ion (Fig. 16). The first stage reduction product, complex (a), can be obtained even by one-electron donating Na bipy. Thus it is assigned to a one-electron trapping state.

A complex coordinated by bipyridine negative ion, Na[$M(CO)_4L^-$], could not be obtained by a direct reaction of [$M(CO)_6$] and Na bipy. When [$M(CO)_6$] was added with Na bipy in THF, evolution of carbon monoxide was followed by formation of a pale green complex (A). Complex (A) in the solid state was labile at room temperature even in a vacuum. It did not show any similar spectrum of Na[$M(CO)_4L$]. When the isolated solid sample of (A) was oxidized by washing with oxygen-containing toluene or ethanol under nitrogen atmosphere, it gives a very similar spectrum of [$M(CO)_4$bipy]. However, this may indicate the formation of a metal carbonyl complex with bipyridine other than [$M(CO)_4$bipy]. Since free bipyridine could not react with a metal carbonyl at room temperature, bipyridine is expected to enter into the coordination sphere during the reducing process but not the oxidizing process. During the first stage of reaction of [$M(CO)_6$] and Na bipy, reduction of [$M(CO)_6$] by Na bipy forms a reactive intermediate [$M(CO)_5$] evolving carbon monoxide and then, taking a bipyridine molecule, complex (A), probably a metal carbonyl dimer which includes bipyridine. When electrons are trapped in *dσ* orbital, hexacoordinate metal carbonyl gives rise to a pentacoordinate complex or a dimer complex with metal-metal bond or carbonyl bridgings. On the other hand, the first stage of reaction of [$M(CO)_4$bipy] and Na bipy is just electron-transfer reaction from bipyridine negative ion in Na bipy to the coordinating bipyridine in [$M(CO)_4$bipy]. Since the antibonding vacant *π* molecular orbital of bipyridine is lower than that of the coordinating carbon monoxide and also is lower than *dσ* orbital which is predominantly localized on the central metal atom, an electron given by Na bipy is trapped in the vacant *π* orbital of the coordinating bipyridine. The lowest charge-transfer transition in [$M(CO)_4$bipy] is of "metal to bipyridine" type but not of "metal to carbonyl." Recently we succeeded in the observation of luminescence of [$M(CO)_4$bipy]. The luminescence arises from not a *dσ-dπ* transition but a "bipyridine to metal" charge-transfer transition. As far as a sufficient difference of interelectronic terms does not reverse the order, these observations may indicate that the lowest vacant *π* molecular orbital of the coordinating bipyridine is the lowest vacant.



An electronic configuration of the rare gas is required for the central metal atom in a stable compound of transition metal in the lower oxidation state. No open shell exists in a stable compound. In various systems including organic and organometallic species, this rule is satisfied. Since *dσ* orbital is occupied in the case of d^7 and d^8 systems, the rule requires d^7 system to form a metal-metal bond with or without carbonyl bridgings ([$Mn_2(CO)_{10}$] and [$Cr_2(CO)_{10}$]$^{2-}$) and for d^8 system to decrease the coordination number ([$Mn(CO)_5$]$^-$ and [$Cr(CO)_5$]$^{2-}$). In the higher oxidation state, however, transition metal ions with open *d* shell exist in various stable coordination complexes. Trisbipyridine complexes, even if in the lower oxidation states, can exist in monomeric state with open shell electronic configurations. In the case of [$Co(bipy)_3$]$^+$, two electrons with parallel spins are trapped in *dσ* orbitals, though migration of *dπ* electron into the antibonding *π* molecular orbital is appreciable.[2] In the case of isoelectronic [$Fe(bipy)_3$], however, electrons are trapped in the coordinating bipyridine rather than in the *dσ* orbitals.[3] Electrostatic potential due to a positive charge on the central metal should play an important role to cause the difference. The observed maximum of the lowest (*π*, *π**) transition of coordinating bipyridine is a function of formal charge on the central metal. The bipyridine (*π*, *π**) transition of [$Cr(CO)_4$bipy] is observed at 33,400 cm^{-1} which is close to those observed in [$Cr(bipy)_3$]$^+$ and [$Co(bipy)_3$]$^+$. Since back-donation of metal *dπ* electrons towards the coordinating carbon monoxides is appreciable and thus the central metal becomes more positive, the coordinating bipyridine in [$Cr(CO)_4$bipy] is polarized as in [$Cr(bipy)_3$]$^+$ and [$Co(bipy)_3$]$^+$ (Fig. 17). Although +1 charge of the complex [$Cr(bipy)_3$]$^+$ or [$Co(bipy)_3$]$^+$ is delocalized over the whole

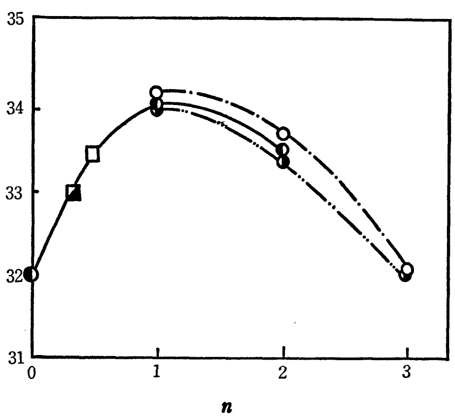


Fig. 17. Energy of the lowest (*π*, *π**) transition of the coordinating bipyridine *vs.* formal charge of tris-bipyridine complexes, *n* of [$M(bipy)_3$]$^{n+}$. The lowest (*π*, *π**) transition of the coordinating bipyridine in [$M(CO)_4$bipy] is numerically rather close to those of [$M(bipy)_3$]$^{2+}$. $P\phi_3$ is a stronger *σ* donor than CO and therefore a positive charge on Mo of [$Mo(CO)_3P\phi_3$bipy], for example, should be lower than that of [$Mo(CO)_4$bipy]. The lowest (*π*, *π**) transition of the coordinating bipyridine is red-shifted for the substitution of CO by $P\phi_3$. This indicates the transition energy of [$M(CO)_4$bipy] should be plotted in the region from $n=0$ to $n=1$ but not near $n=2$.

-◐-: vanadium compounds, -◑-: chromium compounds
-○-: cobalt compounds, □ : [$M(CO)_4$bipy]
◪ : [$M(CO)_3P\phi_3$bipy]

complex, electron affinity of the metal atom in such an environment is still higher than that of such a neutral complex as [Cr(CO)$_4$bipy]. In the former, metal *dσ* orbital is appreciably lower than bipyridine π^* orbital, while in the latter, metal *dσ* orbital is still higher than bipyridine π^* orbital, even though it is fairly lowered by a positive charge arising from the "metal to carbonyl" back-donation. Actually [Cr(CO)$_4$bipy] traps an electron in the bipyridine π^* orbital in the first stage of reduction, however, the trapped electron can be readily transfered into the *dσ* orbital. Another electron furnished in the second stage of reduction may occupy *dσ* orbital. When metal *dσ* orbital is occupied, a hexacoordinate complex turns out to be a pentacoordinate complex or a complex dimer evolving carbon monoxide.