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Complexes Coordinated by 2,2′-Bipyridine Negative Ion. I. Synthesis of Sodium 2,2′-Bipyridinetetracarbonylchromium

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Bipyridinetetracarbonylchromium was reduced by sodium metal in tetrahydrofuran. The first stage product of the reduction which showed a spectrum similar to that of sodium bipyridine (Na^+bipy^-) was isolated. The complex was identified as $Na[Cr(CO)_4bipy]$ by elementary analysis. On the basis of the electronic absorption spectrum and the electron spin resonance, the complex formed in the reduction was concluded to be complex coordinated by mononegative ion of bipyridine and should be named sodium 2,2′-bipyridine(1−)-tetracarbonylchromium(0).

An electronic configuration of the rare gas is required for the central metal atom in a stable compound of a transition metal in the lower oxidation state. Sidgwick's rule states that no open-shell exists in a stable compound. This rule has been found to be satisfied in various systems including organic and organometallic species. In the higher oxidation state, however, the transition metal ions with open *d* electron shell can exist in various stable coordination complexes. Even in an essentially ionic complex charge delocalization effect is crucial in coordination binding. However, the unpaired electron existing in the complex has been detected mainly on the central metal orbitals by physical measurements such as ESR.

For the past decade, tris-bipyridine complexes in the lower oxidation states have been prepared[1] and their electronic structures have been studied.[2–4] These compounds, even if in the lower oxidation states, can exist with open shell electronic configurations.[1] Monomeric tris-bipyridine complexes of the lower oxidation states are stabilized partly by chelate effect and partly by back-donation due to a higher π acceptability of the coordinating bipyridine. Migration of $d\pi$ electron into the antibonding π molecular orbital of the coordinating bipyridine makes the central metal more positive and therefore more σ-acceptable.

Some monomeric metal carbonyls of open shell electronic configuration have recently been succesfully prepared. An open shell metal carbonyl $[V(CO)_6]$ was obtained by oxidation of a closed shell metal carbonyl, $[V(CO)_6]^-$.[5] Oxidation or reduction of closed shell metal carbonyl is expected to give an open shell structure. However, in many cases it forms a dimer with carbonyl groups bridging or with metal-metal bonds.

In this paper, we present the synthesis of a new type of metal carbonyl with coordinating negative ion of 2,2′-bipyridine.

Experimental

Materials. 2,2′-Bipyridine (bipy) and its 4,4′-dimethyl (4dmbip) and 5,5′-dimethyl (5dmbip) derivatives were synthesized by the method of Sasse and Whittle.[6] Hexacarbonylchromium $Cr(CO)_6$ was of reagent grade (Strem Chemical Incorporated, Mass. U.S.A.) and was used without further purification. All other reagents and solvents were commercially available. Tetrahydrofuran (THF) used for solvent was purified by careful distillation over cuprous acetate, and a trace of water was removed by $LiAlH_4$.

Preparation of Compounds. $Cr(CO)_4$bipy was prepared by the method of Stiddard.[7] Dimethyl substituted bipyridine complexes also were prepared by the same method. $Cr(CO)_4$4dmbip: Hexacarbonylchromium (1.1 g) and 4dmbip (0.95 g) were refluxed in toluene (50 ml) for 2 hr under oxygen-free, dry nitrogen atmosphere. Unreacted hexacarbonylchromium sublimed from the reaction vessel into the reflux condensers in the course of reaction. After cooling, deep reddish orange crystals (0.5 g) were collected, washed with light petroleum (60 m*l*) and dried *in vacuo*. The yields were not so high since hexacarbonylchromium sublimed during the reaction.

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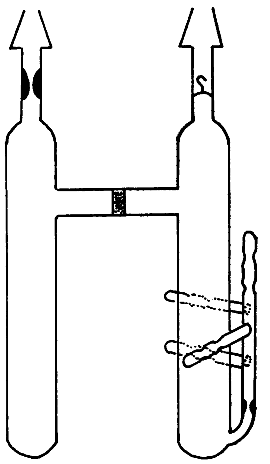

Fig. 1. Apparatus for reduction.

$Cr(CO)_4bipy$ Found: Cr, 16.5%. Calcd for $Cr(CO)_4$-bipy: Cr, 16.2%.

$Cr(CO)_4$4dmbip Found: Cr, 15.1%. Calcd for $Cr(CO)_4$4dmbip: Cr, 14.9%.

$Cr(CO)_4$5dmbip Found: Cr, 14.9%. Calcd for $Cr(CO)_4$5dmbip: Cr, 14.9%.

Reductions of $Cr(CO)_4L$. $Na[Cr(CO)_4L]$, where L is bipy, 4dmbip or 5dmbip, was prepared by reduction with sodium metal in the apparatus shown in Fig. 1 in a high vacuum using the method described in a previous paper.[8] $Na[Cr(CO)_4$4dmbip]: A mixture of $Cr(CO)_4$4dmbipy and a little excess amount of sodium metal in 15 m*l* of dried THF was shaken for 10 hr. After the solution was filtrated, the solvent was removed by distillation into a liquid-nitrogen cooling trap jointed to the vacuum system, the product was collected and dried *in vacuo*.

$Na[Cr(CO)_4bipy]$ Found: Cr, 15.4%. Calcd for $Na[Cr(CO)_4bipy]$: Cr, 15.2%.

$Na[Cr(CO)_4$4dmbip] Found: Cr, 13.9%. Calcd for $Na[Cr(CO)_4$4dmbip]: Cr, 14.0%.

$Na[Cr(CO)_4$5dmbip] Found: Cr, 14.4%. Calcd for $Na[Cr(CO)_4$5dmbip]: Cr, 14.0%.

Electronic Absorption Spectra. Measurements of the electronic absorption spectra of air-sensitive compounds were described in a previous paper.[8] Spectra were measured using a Shimadzu automatic recording spectrophotometer Model MPS-50.

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

Results and Discussion

Until quite recently no electronic absorption and electron spin resonance (ESR) studies had been carried out on complexes such as $[Al(bipy)_3]$, $[Mn(bipy)_3]$[4] or $Na[Fe(bipy)_3]$.[3] However, it has been recognized since a few years ago that the complexes, at least, $[Al(bipy)_3]$ should consist of a metal cation and bipyridine negative ions.[9] The low-valent tris-bipyridine complexes show a spectrum similar to that of bipyridine negative ion and an ESR spectrum of the free electron *g*-value (2.003).[4,10] The tris-bipyridine complexes are concluded to consist of bipyridine negative ions and a metal cation.

When zero-valent bipyridinetetracarbonylchromium was reduced by sodium metal in THF, the absorption spectrum of the solution changed stepwise and showed that there were two or more stages in the reduction. To obtain a complex coordinated by bipyridine negative ion, we tried to isolate a complex formed at the first stage of reduction.

The electronic absorption spectra of the bipyridine complexes isolated in this work are shown in Fig. 2. In such a low oxidation state, an extra electron donated by a reducing reagents in the preparation should be delocalized over the whole complex. However, partial localization of the trapped electron in some part of the complex has been reported.[4] The electronic absorption spectra, at least, of tris-bipyridine complexes have been reported to give a criterion on the major location of the trapped electron.[4] When the trapped electron is mainly localized on the coordinating bipyridine, it does not show charge transfer bands characteristic to the electron trapping by the central metal but a spectrum similar to that of the bipyridine negative ion. As shown in Fig. 2, the

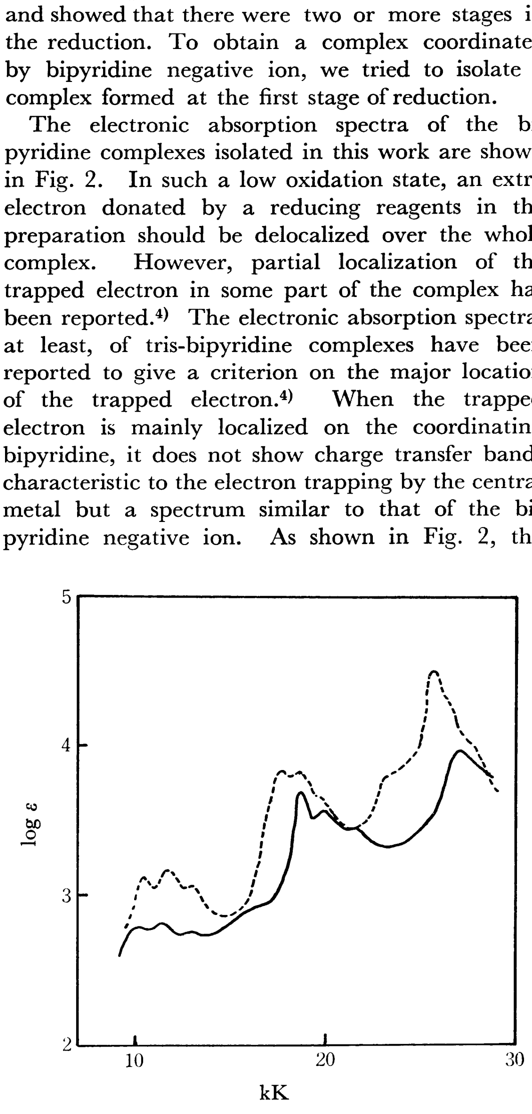

Fig. 2. Electronic absorption spectra in THF.
——: $Na[Cr(CO)_4bipy]$, ----: Na bipy

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[8] Y. Torii, T. Yazaki, Y. Kaizu, M. Murasato and H. Kobayashi, This Bulletin, **42**, 2290 (1969).

[9] L. E. Orgel "An Introduction To Transition-Metal Chemistry," Second Ed., Methuen Co. Ltd., London (1966), p. 150; C. K. Jørgensen "Inorganic Complexes" Academic Press, London (1963), p. 75.

[10] Y. Torii, M. Murasato and Y. Kaizu, *Nippon Kagaku Zasshi*, **91**, 549 (1970).

complex reported here gave a spectrum similar to that of the mononegative ion of bipyridine in Na bipy. However, they did not coincide in details. The exact position of the absorption peak at about 19000 cm^{-1} of the complex was slightly shifted to the higher wavenumber. This tendency was observed for the other two complexes, $Na[Cr(CO)_4$-4dmbip] and $Na[Cr(CO)_4$5dmbip], and also in the case of zero-valent tris-bipyridine aluminum complex.[10] For such a small perturbation as introduced by two methyl groups, the absorption peak at about 19000 cm^{-1} of the bipyridine negative ion was blue-shifted in the order 5dmbip, 4dmbip and bipy.[8] When the extra electron was trapped by the central metal, the metal-ligand charge transfer bands found in the visible region showed a quite different behavior for the methyl substitutions. The absorption peaks at about 19000 cm^{-1} of $Na[Cr(CO)_4$-5dmbip], $Na[Cr(CO)_4$4dmbip] and $Na[Cr(CO)_4$-bipy] show the negative ion type of spectral shift. These findings on the electronic absorption spectra suggest that the bipyridine attached to the central chromium is not a neutral molecule but a negative ion. The ESR spectrum of $Na[Cr(CO)_4bipy]$ in Fig. 3 gives a *g*-value close to that of a free electron ($g=2.0025$) and a well-dispersed hyperfine structure. The hyperfine constants in the coordinating bipyridine negative ion were not so different from those of K bipy, even if the negative ion was strongly attached to the central chromium. 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^+. As a matter of fact, the ESR spectrum of K bipy does not show the hyperfine structure due to the nuclear spin of potassium ion.[11] The ESR spectrum of Na bipy clearly shows the hyperfine structure due to the nuclear spin of sodium ion,[11] whereas in the case of $Na[Cr(CO)_4bipy]$, it does not show any hyperfine structure due to either sodium or chromium. This is explained by the fact that an unpaired electron in an antibonding π orbital of bipyridine can not strongly interact with the closed shell $d\pi$ electron of the chromium and does not migrate over the outer sodium ion.

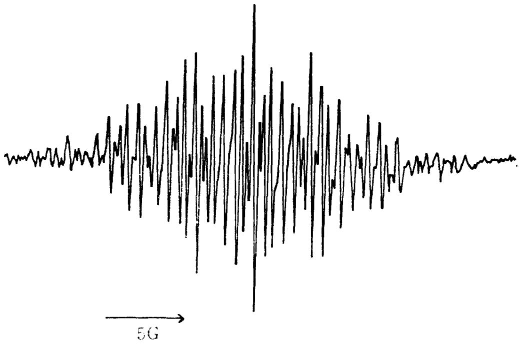

Fig. 3. The ESR spectrum of $Na[Cr(CO)_4bipy]$ in THF at room temperature.

All of the complexes reported here are extremely soluble in polar organic solvents such as THF. They are very sensitive to oxygen and moisture in the air and are readily oxidized to the corresponding zero-valent complexes.

These observations and chemical analyses give sufficient evidence to conclude that the complexes synthesized in this work are the kind coordinated by bipyridine negative ion.

The sum of the numbers of the valence electrons in the central chromium and the σ electrons contributed by the ligands is the number of electrons in Kr atom. The paramagnetic character of the complex $Na[Cr(CO)_4bipy]$ was identified by ESR, though, it still satisfies Sidgwick's rule as mentioned above. Since the complex is made of zero-valent chromium atom, four carbon monoxides and a bipyridine negative ion, the compound should be named sodium 2,2′-bipyridine(1−)tetracarbonylchromium(0).

The authors are indebted to Professor M. Nakahara, St. Paul's University for his advice concerning nomenclature.

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11) E. König and H. Fischer, *Z. Naturforsch.*, **17a**, 1063 (1962); J. S. Veiga, W. L. Reynolds and J. R. Bolton, *J. Chem. Phys.*, **44**, 2214 (1966).