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The Electrochemical Behavior of the Low-valent Transititon-metal Complexes. I. Nickel-2,2′-Dipyridyl Complexes.

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The electrochemical behavior of zero-valent nickel-2,2′-dipyridyl complexes ($Ni(dipy)_2$, $Ni(CH_2CHCN)_2$-(dipy), and $Ni(NCCHCHCN)_2(dipy)$) was examined in a hexamethylphosphoric triamide solution by polarographic and ESR measurements. In the polarography, these complexes were first reduced at a very anodic potential ($E_{1/2}$: about −0.6——0.8 V *vs.* Ag wire). At this reduction step, the anion radical of the complex was observed for all the complexes by means of ESR analysis. The spectra of the anion radicals and their *g*-values suggested the localization of an unpaired electron on the ligand side. The addition of 2,2′-dipyridyl to the solution increased the height of the second wave, the half-wave potential of which was also more anodic than that of free 2,2′-dipyridyl, and the anion radical of 2,2′-dipyridyl was observed at this reduction step. It was concluded that the dianion species formed at the second reduction step dissociated to give the 2,2′-dipyridyl anion radical, and that the anion radical of the complex was reproduced in the presence of excess 2,2′-dipyridyl.

2,2′-Dipyridyl, with a fairly cathodic reduction potential, are comparable to that of naphthalene,[1] easily coordinates to the transition metal of a high oxidation state as a strong donor. On the other hand, dipyridyl has an acceptor level, as well as a donor level, so as to make it possible to coordinate to the low-valent transition metal.

It seemed that it would be interesting to perform a study of the electrochemical behavior of low-valent transition-metal complexes in relation to the evaluation of the charge distribution on the complexes of lower oxidation state, and the stability of the reduced complex. In basic and polar media, transition-metal complexes of lower oxidation states, such as the anion radical or the dianion species, are expected to exist fairly stably. Hexamethylphosphoric triamide (HMPT), with a large basicity, has been reported to have a potential ability to solvate the alkali metals and anion radicals of aromatic compounds.[2] Therefore, HMPT is an appropriate solvent for the electrochemical study of low-valent transition-metal complexes. The present authors made a study of the electrochemical behavior of zero-valent nickel-dipyridyl complexes in the HMPT solution and found interesting phenomena using polarographic and ESR techniques.

Experimental

Materials. The examined complexes were bis(2,2′-dipyridyl)nickel, bis(acrylonitrile)(2,2′-dipyridyl)nickel, and bis(fumaronitrile)(2,2′-dipyridyl)nickel. The bis(2,2′-dipyridyl)nickel was obtained by de-ethylation from diethyldipyridylnickel in the presence of 2,2′-dipyridyl, which had itself been prepared by the reduction of nickel acetylacetonate with diethylaluminum mono ethoxide in the presence of excess dipyridyl in tetrahydrofuran.[3] After the solution had stood for a long time following the reduction, a dark green complex of bis(2,2′-dipyridyl)nickel precipitated from the solution.

Bis(acrylonitrile)nickel was prepared by the reaction of acrylonitrile with nickel tetracarbonyl in tetrahydrofuran.[4] This complex was treated with excess 2,2′-dipyridyl in ether, refluxing for several hours gave reddish-brown bis(acrylonitrile)(2,2′-dipyridyl)nickel.

The bis(fumaronitrile)(2,2′-dipyridyl)nickel (dark brown) was prepared similarly. 2,2′-Dipyridyl was purified by the sublimation of the reagent, followed by recrystallization from *n*-hexane. Acrylonitrile was fractionally distilled after drying calcium chloride.

Fumaronitrile was recrystallized from ether-hexane.

Tetra-*n*-butylammonium perchlorate was obtained by adding hydroperchloric acid to aqueous tetra-*n*-butylammonium bromide, and it was recrystallized from hot water three times after washing with cold water. HMPT was refluxed over calcium hydride for several hours and was then fractionally

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[1] B. J. Tabner and J. R. Yandle, *J. Chem. Soc.*, *A*, **1968**, 381.

[2] H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Amer. Chem. Soc.*, **89**, 186 (1967); *ibid.*, 91, 4191 (1969); M. Fontanille and P. Sigwalt, *C. R. hebd. Seances Acad. Sci.*, *Ser. C*, **263**, 316 (1966); S. Boileau and P. Sigwalt, *ibid.*, *C*, **262**, 1135 (1966); J. P. Pascault and J. Gole, *ibid.*, *C*, **264**, 115 (1967).

[3] T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Amer. Chem. Soc.*, **88**, 5198 (1966).

[4] G. N. Schrauzer, *ibid.*, **81**, 5310 (1959); **82**, 1008 (1960).

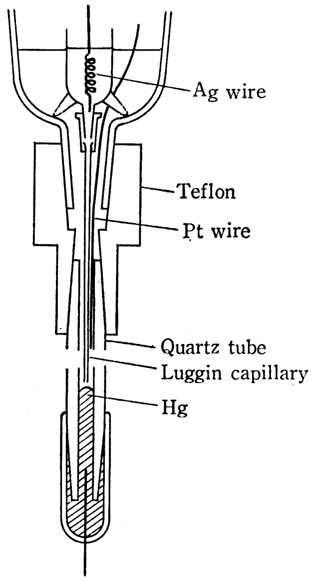

Fig. 1. Electrolytic cell for ESR measurement.

distilled under reduced nitrogen pressure.

Apparatus and Procedure. The polarographic analysis was performed using an H-type cell with a side arm to enable the insertion of an Ag-wire reference electrode.

The cathode was a dropping mercury electrode. The concentration of the complexes was generally 5.0×10^{-3} mol/*l*, while that of tetra-*n*-butylammonium perchlorate was 2.0×10^{-1} mol/*l*. The polarograph used was a Yanagimoto Model PB-105. For the ESR analysis, a electrolytic cell as is shown in Fig. 1 was used. The silver wire used as the reference electrode was dipped into a solution in a small reservoir equipped with a Luggin capillary, whose tip was set near the mercury surface to conduct the controlled potential electrolysis. A platinum wire was used as an anode, it was set about 3 cm from the mercury surface. The complex solution had the same composition as that used for the polaroghaphic analysis. The ESR spectra were recorded using a JEOL Model JS-3BS-X spectrometer. The electronic spectra of the complex in the HMPT solution were recorded using a Shimadzu MPS-50L spectrophotometer. The complexes to be examined were all air-sensitive, so the preparation and measurement of the complex solutions were performed under nitrogen purified by activated copper.

Results and Disscusion

Polarographic Results on the Complexes. The complexes were stable to only a small degree in solvents, such as acetonitrile, tetrahydrofuran, or ethyleneglycol dimethylether, but they were readily soluble in HMPT, giving strongly colored solutions, as is indicated in Table 1.

TABLE 1. THE COLOR OF NICKEL-DIPYRIDYL COMPLEXES

Complex	Solid state	HMPT solution (λ_{max} in mμ)
$Ni(dipy)_2$	dark green	dark green (680)
$Ni(AN)_2(dipy)$	reddish-brown	dark reddish-brown (570, 430, 340)
$Ni(FN)_2(dipy)$	dark brown	dark red (520)

AN: acrylonitrile FN: fumaronitrile

TABLE 2. POLAROGRAPHIC RESULTS ON THE COMPLEXES IN HMPT

Compound	Half-wave potential $-E$ V *vs.* Ag wire	Wave height ratio
$Ni(dipy)_2$	0.73 1.00 1.25 1.60 2.05 (67.0) (73.1)[a]	1.0 : 0.9 : 0.5 : 0.4 : 3.5
$Ni(AN)_2(dipy)$	0.67 1.32 1.94 (65.7) (115.0)	1.0 : 0.9 : 0.1
$Ni(FN)_2(dipy)$	0.87 1.68 2.25 (80.1) (93.7)	1.0 : 1.0 : 0.2
$Ni(AN)_2$	1.74	
$Ni(FN)_2$	1.93	
dipyridyl	2.37 2.80	1.0 : 0.7

a) Values in the parenthesis are the slope of the waves in the log-plott analysis.

Concentration of the compound	5×10^{-3} mol/*l*
$(C_4H_9)_4NClO_4$ concentration	2×10^{-1} mol/*l*

The complexes were stable in HMPT, the color of which did not change over a week under nitrogen.

The polarographic results are shown in Table 2. The first wave of three complexes lie in the range of -0.6—-0.8 V *vs.* Ag wire, which is far anodic than the first reduction wave of dipyridyl and also more anodic than those of acrylonitrile and fumaronitrile. For comparison, bis(acrylonitrile)nickel and bis(fumaronitrile)nickel were also examined. They were reduced at about -1.7—-1.9 V, indicating that the species to be reduced at -0.6—-0.8 V contained dipyridyl in the molecule, at least in the cases of nitrile-containing complexes. The stability of π-coordinated acrylonitrile or fumaronitrile in neutral complexes was affirmed by the CN stretching in the IR spectra of the solid complex, its HMPT solution, and the free nitrile in HMPT. The first reduction step was fairly reversible for $Ni(dipy)_2$ and $Ni(AN)_2(dipy)$.

For $Ni(FN)_2(dipy)$, the first step was less reversible than the former two. The electron to be transfered was supposed to be one from the slope of the reduction wave for all three complexes. The complexes were, therefore, considered to be reduced to form the anion radical.

At this reduction step, no color change was apparent except in $Ni(AN)_2(dipy)$ under prolonged reduction. In the case of $Ni(AN)_2(dipy)$, the solution turned a deep red from a dark reddish-brown as a result of one-electron transfer.

The 1 : 1 ratio of the heights of the first and the second waves in all the dipyridyl complexes indicates a one-electron transfer in the second wave as well as in the first, though the second wave is less reversible than the first. It has previously been reported that nickel complexes containing *o*-mercaptoaniline or thiobenzoylhydrazine readily undergo one-electron transfer steps to give mono- and dianions.[5]

The bis(dipyridyl)nickel showed three more reduction waves with comparatively large wave heights, so a reduction state farther than the dianion may be expected. Tris(2,2'-dipyridyl)chromium has previously been reported to be reduced to the hexa-anion stage,

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[5] R. H. Holm, A. L. Balch, A. Davisdon, A. H. Maki, and T. E. Berry, *ibid.*, **89**, 2866 (1967).

$Ca_3[Cr(dipy)_3] \cdot 7NH_3$.⁶⁾

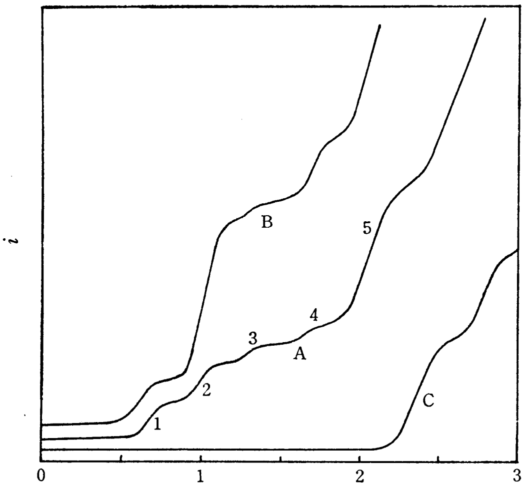
For nitrile-containing complexes, the steps after the second are very small in height.

Since HMPT with a donor- and an acceptor-level can also coordinate to a low-valent transition metal, it is probable that coordinated dipyridyl is replaced by HMPT to lower the effective concentration of dipyridyl complexes below the calculated value. In the case of violet-colored bis(dipyridyl)iron, its HMPT solution slowly turned to brown from violet, and this color change was suppressed by the addition of more than 10-fold molar amount of dipyridyl to the complex solution.⁷⁾ The addition of dipyridyl to the nickel-dipyridyl complex solution, did not affect the height and potential of the first step.

This indicates that HMPT does not replace the coordinated dipyridyl of the examined neutral nickel-dipyridyl complexes.

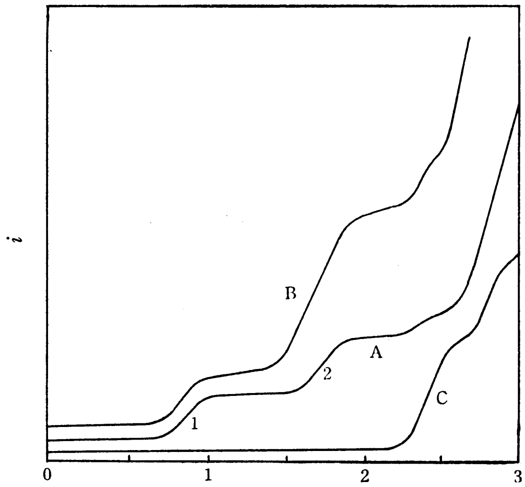
The second wave increased in height upon the addition of dipyridyl, though the half-wave potential of this step scarcely changed in three complexes. Some steps after the second were also affected. The effect of the addition of dipyridyl is shown in Figs. 2 and 3 for $Ni(dipy)_2$ and $Ni(FN)_2(dipy)$. In the case of $Ni(dipy)_2$, dipyridyl addition increased the height of the second, fourth, and fifth waves, the third being left unchanged. Further, the waves became less reversible as their height was increased by dipyridyl addition. In Table 3, the change in the slope of the second wave is shown for $Ni(dipy)_2$. The change in the height and reversibility of the second wave suggests that added dipyridyl takes part in this reduction step and that its rate of coordination to the metal is slow.

In the presence of the complexes of 5×10^{-3} mol/*l*, the reduction waves with considerably cathodic potential could not be successfully observed because of the disturbance in the wave shapes. By decreasing the concentration of the complex, those waves were, however, observed in the case of $Ni(dipy)_2$, as is indicated in Fig. 4. The concentration of the complex was 3×10^{-4} mol/*l*, and that of added dipyridyl was 3×10^{-2} mol/*l*. The reduction wave of free dipyridyl was observed after the waves in which the complex was considered to take part. After a prolonged reduction (for



$-E$ *vs.* Ag wire

Fig. 2. Effect of dipyridyl addition on the reduction waves of $Ni(dipy)_2$ in HMPT.
A: $Ni(dipy)_2$
B: dipy: $Ni(dipy)_2$=3 : 1
C: free dipyridyl



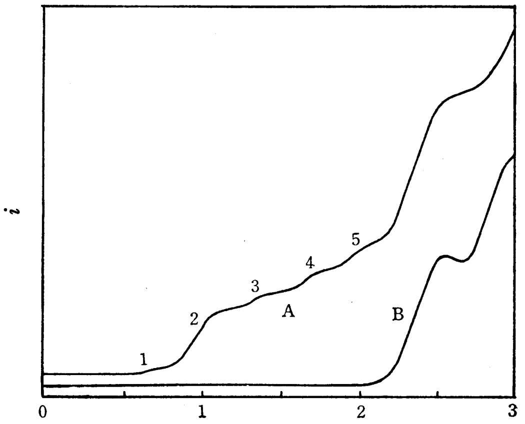
$-E$ *vs.* Ag wire

Fig. 3. Effect of dipyridyl addition on the reduction waves of $Ni(FN)_2(dipy)$ in HMPT.
A: $Ni(FN)_2(dipy)$
B: dipy: $Ni(FN)_2(dipy)$=3 : 1
C: free dipyridyl

TABLE 3. THE EFFECT OF DIPYRIDYL ADDITION ON THE SECOND REDUCTION WAVE OF $Ni(dipy)_2$

Molar ratio		Relative wave height	Slope[a] (mV)
dipy/$Ni(dipy)_2$	0	1.0	67.0
dipy/$Ni(dipy)_2$	3	2.3	81.2
dipy/$Ni(dipy)_2$	10	7.1	90.0

a) Values in the log-plott analysis.
$Ni(dipy)_2$, 5×10^{-3} mol/*l*; $(C_4H_9)_4NClO_4$, 2×10^{-1} mol/*l*.



$-E$ *vs.* Ag wire

Fig. 4. Polarogram of $Ni(dipy)_2$ in the presence of large excess of dipyridyl
A: $Ni(dipy)_2$+100-fold dipyridyl
B: polarogram after the reduction at about −2.0 V for 20 min

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6) S. Herzog, U. Grimm, and W. Waichenbauer, *Z. Chem.*, **7**, 355 (1967).

7) To be published in This Bulletin.

20 min) of this solution at about -2.0 V *vs.* Ag wire, the color of the solution (dark green) faded and the resulting polarogram showed only the reduction waves of dipyridyl. This result may be attributable to the unstability of the reduced species at -2.0 V in spite of the presence of a large excess of dipyridyl. As is shown in Figs. 2 and 4, the ratio of the second and fourth wave-heights in the polarogram of Ni(dipy)$_2$ is dependent on the concentrations of the complex and dipyridyl.

Fig. 5.

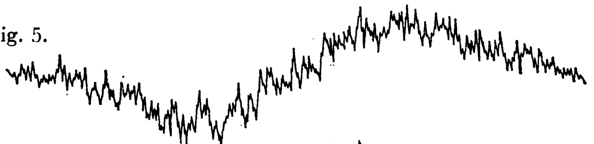

Fig. 6.

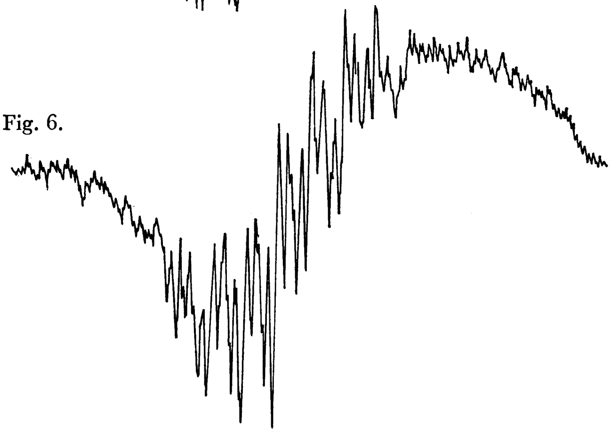

Fig. 5. ESR signal in the electrolysis of Ni(dipy)$_2$ at -0.8 V *vs.* Ag wire.

Fig. 6. ESR signal in the electrolysis of Ni(dipy)$_2$ at -1.1 V *vs.* Ag wire.

Fig. 7.

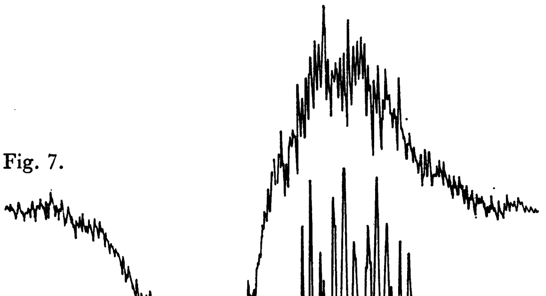

Fig. 8.

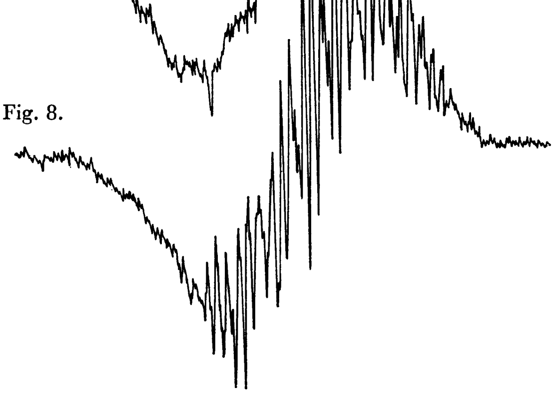

Fig. 7. ESR signal in the electrolysis of Ni(FN)$_2$(dipy) at -1.07 V.

Fig. 8. ESR signal in the electrolysis of Ni(FN)$_2$(dipy) at -1.7 V.

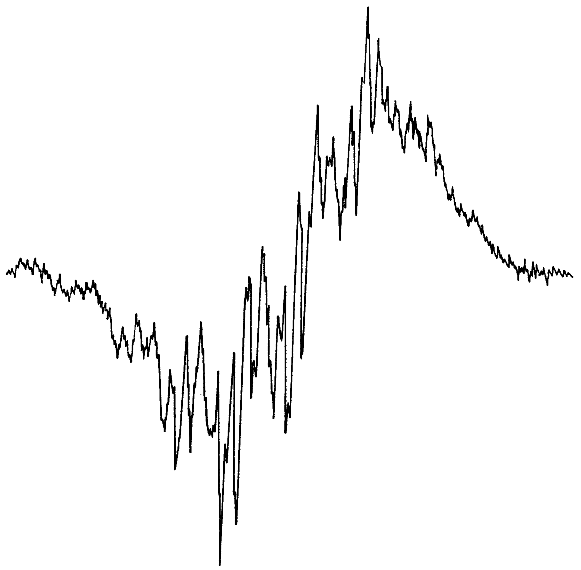

Fig. 9. ESR signal in the electrolysis of Ni(AN)$_2$(dipy) at -0.8 V.

ESR Measurements. In electrolysis at the potential sufficient cathodic to cause the first reduction step, the signal attributable to the anion radical of the complex was observed for all the nickel complexes, as is shown in Figs. 5, 7, and 9. The complexes before reduction, naturally, gave no ESR signal. Zero-valent nickel has a d^{10} configuration, so the unpaired electron of the complex anion radical seems to be mainly localized on the ligand side. For Ni(dipy)$_2$, no signal with a well-defined hyperfine structure could be obtained.

For Ni(AN)$_2$(dipy) and Ni(FN)$_2$(dipy), a comparatively well-defined structure was obtained. The spectra indicated the localization of the unpaired electron on the ligand side, compared with those obtained for the anion radicals of dipyridyl and dipyridyl metal carbonyl complexes.[8)]

The *g*-values of the complex anion radicals were as follows; Ni(dipy)$_2$, 2.0036; Ni(AN)$_2$(dipy), 2.0009; Ni(FN)$_2$(dipy), 2.0013 (dipyridyl, 2.0023). They were close to that of the dipyridyl anion radical. This also indicates the spin localization of the ligand side.

It was noted that the electrolysis at the second reduction step produced the anion radical of dipyridyl.

The intensity of this signal increased upon the addition of dipyridyl to the solution. The set potential was more anodic by 0.6—1.3 V than the half-wave potential of free dipyridyl. In Figs. 6 and 8, the signal attributable to the anion radical of dipyridyl is shown. This dipyridyl anion radical was stable in HMPT and was observed to be overlapped with another signal with an ill-defined structure. Without excess dipyridyl, the first anion radical-signal of the complex was again observed by shifting the set potential to the first reduction step, but the signal intensity was lower than before.

Taking into account the polarographic results at the second step, it was concluded that the dianion species of

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[8)] R. E. Dessy, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, **88**, 5112 (1966); R. E. Dessy, Intern. Symp. on the Synthetic and Mechanistic Aspects of Electro-organic Chemistry, 63 (1968).

the complex was formed by two one-electron transfer steps and that the dipyridyl anion radical was formed by the dissociation of this dianion species. To the authors' knowledge, this is the first time the dipyridyl anion radical has been formed at a far more anodic potential than the reduction potential of free dipyridyl in aprotic solvents.[9]

The polarographic results suggested the formation of the species with unpaired electron upon further reduction, for example, in the case of Ni(dipy)$_2$. Its ESR analysis was, however, impossible because of the presence of stable dipyridyl anion radical with a half-wave potential of about -2.8 V *vs.* Ag wire. This potential was more cathodic than the fifth reduction step in the polarography of Ni(dipy)$_2$. In the experiments with the complexes containing nitriles, the signal which corresponds to the anion radical of acrylonitrile or fumaronitrile was not detected. This suggests that π-coordinated acrylonitrile or fumaronitrile is stable in the complex dianion species.

The present authors also attempted the electrolysis of bis(dipyridyl)iron. The Fe(dipy)$_2$-HMPT solution was unstable and gave a disturbed polarogram, from which no clear-cut information was obtained, but the ESR analysis at the potential corresponding to the second step recorded the anion radical of dipyridyl. This potential was more anodic than the reduction potential of dipyridyl, too.

In the examined systems, the solvent HMPT was considered to have an important role. Its ability to solvate anions is greater than tetrahydrofuran or acetonitrile. The reduction potential to obtain the complex anion radical from Ni(dipy)$_2$ in HMPT was far anodic than that reported in acetonitrile.[10] The solvation mechanism of neutral complexes and derived complex anion radicals in HMPT is not yet clear and needs to be studied further.

The dissociation of dianion species produces a paramagnetic species containing a nickel atom, along with the formation of a dipyridyl anion radical, and the former coordinated by dipyridyl to reproduce complex anion radical species in the presence of excess dipyridyl.

Therefore, the degree of dissociation increases upon the addition of dipyridyl because of the difference in the stability between anion radicals and dianion species.

Were it not for the free dipyridyl in the solution, HMPT would coordinate to the above paramagnetic species.

The ill-defined signal in Figs. 6 and 8 may supposedly be ascribed to the complex anion radical and/or species derived from the previous paramagnetic species and HMPT.

As a mechanism of the electro-reduction of nickel-dipyridyl complexes, the following mechanism was proposed, for example, in the case of Ni(dipy)$_2$.

1st step

$$\mathrm{Ni(dipy)_2 + e^- \rightleftharpoons [Ni(dipy)_2]^-}$$

2nd step

$$\mathrm{[Ni(dipy)_2]^- + e^- \rightleftharpoons [Ni(dipy)]^{2-}}$$

$$\mathrm{[Ni(dipy)_2]^{2-} \rightleftharpoons [Ni(dipy)]^- + [dipy]^-}$$

$$\mathrm{[Ni(dipy)]^- + dipy \rightleftharpoons [Ni(dipy)_2]^-}$$

$$\mathrm{[Ni(dipy)]^- + HMPT \rightleftharpoons [Ni(dipy)(HMPT)]^-}$$

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[9] N. Maki, T. Hirano, and S. Musha, This Bulletin, **36**, 756 (1963).

[10] N. Tanaka and Y. Sato, *Inorg. Nucl. Chem. Letters*, **4**, 487 (1968).