# The Electrochemical Behavior of BR₂-linked Bis(glyoximato)nickel(II) Complexes in a Nonaqueous Solvent

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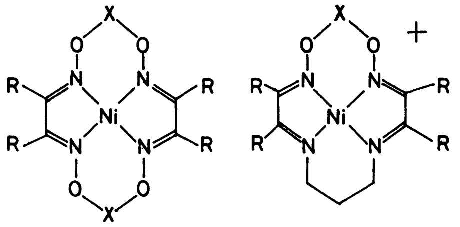
**Synopsis.** Nickel(II) complexes with dioximers replaced by $BF_2$ and $B(C_2H_5)_2$ groups for bridging by the hydrogen atom were investigated by electrochemical methods. The nickel(II) complexes exhibited two distinct one-electron reduction waves in *N,N*-dimethylformamide. It was found that the electron-withdrawing effect of the replaced group is exerted on the electronic states of the nickel(II) complexes.

The nickel(II) complexes of $BF_2$- or $B(Et)_2$- linked dioximers (Fig. 1) were synthesized and characterized by Schrauzer[1] and Gagnè.[2] Schrauzer concluded that these substituents exert no effect on the ligand field around the nickel(II) ion. One of the present authors (Y. N.) reported on the effects of $BF_2$- and $B(Et)_2$-substitution for bridging by the hydrogen atom in the Co(II), Ni(II), and Cu(II) complexes with some oximate ligands.[3] The $BF_2$-substitution caused a red-shift of the d-d band, increased the $g_{/\!/}$-value for copper(II) complexes, and caused a positive shift of the polarographic half-wave potential of nickel(II) complexes. These results suggested that the electrochemical method is useful in investigating the electronic state of the nickel(II) complexes.

The present report deals with the electrochemical behavior of nickel(II) complexes with $BF_2$- or $B(Et)_2$-substituted macrocyclic ligands, as is shown in Fig. 1.



$R = CH_3$: $Ni(dmgX)_2$ $R = CH_3$: $Ni(tnomX)^+$
$R = C_6H_5$: $Ni(dpgX)_2$ $X = H, BF_2$ and $B(Et)_2$

Fig. 1. Structures and abbreviations of the complexes in this study.

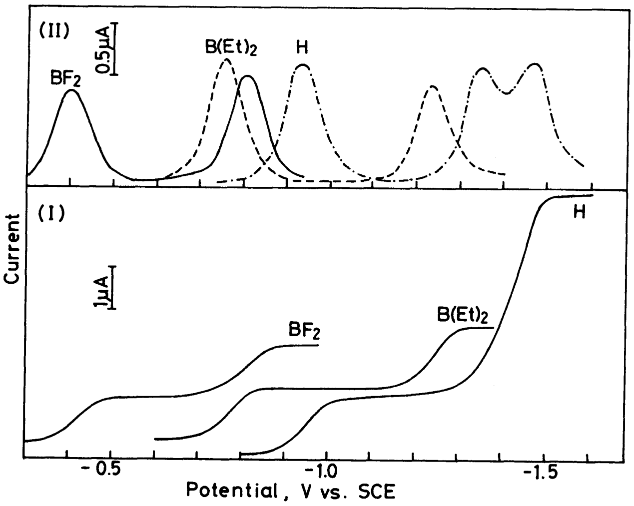


Fig. 2. Current-sampled dc polarograms(I) and differential pulse polarograms(II) of 0.5 mM $Ni(dpgX)_2$ in DMF.

## Experimental

*Synthesis of the Complexes.* The complexes were prepared according to the method reported previously.[3]

*Electrochemical Measurements.* All the measurements were carried out in an 0.1 M tetraethylammonium perchlorate (TEAP) solution (1 M=1 mol dm$^{-3}$) of *N,N*-dimethylformamide (DMF) at 25±0.1 °C. A Fuso Model 312 polarograph and a DME (or HMDE) were employed for the polarographic and cyclic voltammetric measurements, respectively. The reference electrode was an SCE with a salt bridge.[4] Controlled-potential electrolysis was performed at a mercury pool under stirring. The other apparatus was the same as that described previously.[4]

## Results and Discussion

Some typical current-sampled dc polarograms for the $Ni(dpgX)_2$ complexes in DMF are shown in Fig. 2. For $Ni(dmgX)_2$, the same current-sampled dc polarograms were obtained in DMF. Each complex gives a two-stepped reduction wave. The heights of the first and second waves were almost the same except in the $Ni(dmgH)_2$ and $Ni(dpgH)_2$ systems. The height of the second wave for these two systems was larger than that of the first wave. On the other hand, the second wave for the $Ni(tnomX)^+$ system split into two waves.

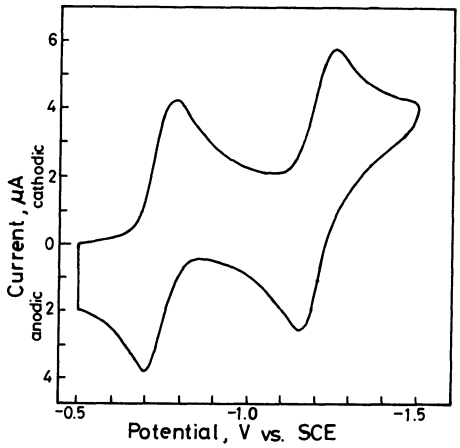


Fig. 3. Cyclic voltammogram of 0.5 mM Ni{dpgB(Et)₂}₂ in DMF at HMDE, scan rate 200 mV/sec.

These systems were investigated by means of normal pulse polarography. Each system exhibited electrochemical behavior much like the current-sampled dc polarography. The relationship of the current ($i$, μA) of the normal pulse polarogram and the sampling time

Table 1. Polarographic data for 0.5 mM Ni(II) complexes

| Complex | $E_{1/2}$ | $i$ | Slope | $n$ | $E_{1/2}$ | $i$ | Slope | $n$ |
|---|---|---|---|---|---|---|---|---|
| | V *vs.* SCE | μA | mV | | V *vs.* SCE | μA | mV | |
| $Ni(dmgH)_2$[a] | −1.279 | 0.48 | 56 | | −1.608 | 1.56 | | |
| $Ni\{dmgB(Et)_2\}_2$ | −1.119 | 1.10 | 56 | 1.1 | −1.652 | 1.48 | 55 | |
| $Ni(dmgBF_2)_2$ | −0.729 | 1.15 | 67 | 1.1 | −1.225 | 1.48 | 55 | 2.1 |
| $Ni(dpgH)_2$ | −0.962 | 1.18 | 59 | 1.0 | −1.435 | 4.20 | | |
| $Ni\{dpgB(Et)_2\}_2$ | −0.771 | 0.98 | 53 | 1.1 | −1.228 | 1.23 | 53 | 2.0 |
| $Ni(dpgBF_2)_2$ | −0.442 | 0.94 | 53 | 1.1 | −0.830 | 1.08 | 65 | 2.1 |
| $Ni(tnomH)^+$ | −0.802 | 0.97 | 40 | 1.0 | −1.304 | 0.58 | 39 | |
| | | | | | −1.454 | 0.55 | 41 | |
| $Ni\{tnomB(Et)_2\}^+$ | −0.723 | 1.09 | 51 | 1.0 | −1.211 | 0.93 | 37 | |
| | | | | | −1.364 | 0.29 | 25 | 2.0 |
| $Ni(tnomBF_2)^+$ | −0.559 | 0.63 | 43 | | −0.970 | 0.73 | 45 | |
| | | | | | −1.146 | 0.40 | 50 | |

a) Measured at the concentration of the 0.3 mM Ni(II) complex.

($t$, s) was determined. There exists an obvious linear relationship between $i$ and $t^{-1\ 2}$. These facts indicate that each electrode reaction is diffusion-controlled.

Some typical differential pulse polarograms of $Ni(dpgX)_2$ in DMF are shown in Fig. 2. Two main peaks were observed on each differential pulse polarogram, and their shapes were found to be symmetrical. The differential pulse polarograms for $Ni(dmgH)_2$ and $Ni(dpgH)_2$ indicate that the second wave of the current-sampled dc polarogram contains two-reduction waves. Each second wave of the current-sampled dc polarogram was three times or more larger than the first wave. Therefore, the reduction at the second wave was assumed to correspond to the electron transfer to the metal and ligand in the complex.

A typical cyclic voltammogram of the $Ni\{dpgB(Et)_2\}_2$ in DMF is shown in Fig. 3. Two peaks were observed on the cathodic branch, and two peaks, on the anodic branch, suggesting reversible processes.

The results of constant potential electrolysis showed the consumption of one electron for each step to be as is summarized in Table 1.

The electrode reactions for the $Ni(dmgX)_2$ and $Ni(dpgX)_2$ systems were assumed to be as follows.

$$Ni^{II}L + e \rightleftharpoons Ni^{I}L \qquad (1)$$

$$Ni^{I}L + e \rightleftharpoons Ni^{0}L \qquad (2)$$

where L denotes $(dmgX)_2$ and $(dpgX)_2$.

For $Ni(tnomX)^+$, the same electrode reaction was assumed for the first wave, but the reciprocal slope of each wave was 37—50 mV. These values were assumed to suggest Ni–Ni metal intramolecular interaction. The same behavior has been observed in polynuclear metal complexes.[5]

A comparison of the half-wave potentials for the $Ni(dmgX)_2$, $Ni(dpgX)_2$, and $Ni(tnomX)^+$ systems is shown in Fig. 4. The order of the half-wave potentials is; $BF_2 > B(Et)_2 > H$. The Ni(II) complex with the $BF_2$-substituted group is more easily reduced compared with the other complexes; this is because of the electron-withdrawing effect of the $BF_2$ group. The electron-withdrawing effect of the $BF_2$ group in these complexes was observed, although Schrauzer suggested that the effect of $BF_2$ groups on the nickel(II) ion could not be observed in a spectrophotometric study.

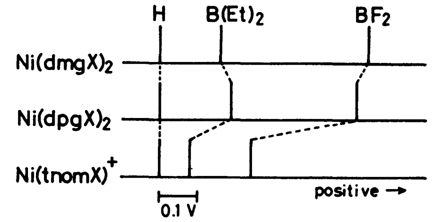


Fig. 4. Comparison of the half-wave potentials of each first wave as a criterion of that of Ni(II) complexes with hydrogen bridging.

The reduction potentials of $Ni(dpgX)_2$ are more positive than those of $Ni(dmgX)_2$. This fact may correspond to the weak electron-donating effect of the phenyl group.

On the other hand, the effect of a substituted group on the $Ni(tnomX)^+$ system is weak compared with those for $Ni(dmgX)_2$ and $Ni(dpgX)_2$. This is because of the structure of $Ni(tnomX)^+$, which has a closed ring and only one substituted group. However, the effect of Ni–Ni metal interaction on the half-wave potential should also be considered. This will be a subject for further study.

## References

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