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Electrochemical Studies on Metal-Metal Interactions in Bismacrocyclic Ni(II) Complexes

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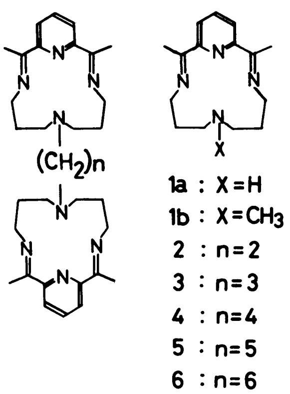
Synopsis. Studies on five Ni(II) complexes, i.e., 7,7′-*polymethylene*bis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene]dinickel(II) perchlorates with *polymethylene* bridges of 2—6-C length, by cyclic voltammetry and differential pulse polarography, have revealed that the half-wave potentials of the $[Ni^{II}Ni^{II}]/[Ni^{II}Ni^{III}]$ and $[Ni^{II}Ni^{III}]/[Ni^{III}Ni^{III}]$ couples are not changed among the hexa- to tetramethylene derivatives but shifted toward the positive side in the following order: tetramethylene<trimethylene<ethylene derivative. These results are explainable in terms of the electrostatic repulsion due to these two metal ions.

Binuclear metal complexes with bis(tetraazamacrocycle) linked by a polymethylene or a carbon–carbon bridge have been used for studies on metal-metal interactions.[1—10] For example, Murase et al.[4] investigated bismacrocyclic Cu(II) complexes with **2**—**6**[11] by ESR spectroscopy and found effects of polymethylene length on antiferromagnetic interaction. Metal-metal interactions of Ni(II) complexes with ligands bis(cyclam)[1,10] and bis(isocyclam)[8] were studied by electrochemical methods and attributed to an electrostatic repulsion between two cations located close to each other. A limited number of Ni(II) complexes bridged by a carbon–carbon bond,[1,10] ethylene,[8] or *p*-xylylene[8], have been investigated. Ligands **2**—**6** seem to have the following advantages: 1) the length of the polymethylene bridge can be varied without causing any structural change in the tetraaza moieties; 2) observed metal-metal interactions are free from the delocalization of the two macrocycles. The author, therefore, has performed electrochemical studies on the series of Ni(II) complexes with **1a**, **1b**, and **2**—**6**.



The oxidation of the Ni(II) complexes with **1a**, **1b**, and **2**—**6** in acetonitrile was studied. Figure 1 shows cyclic voltammograms (CVs) and differential pulse polarograms (DPs). Both the electrochemical measurements apparently reveal that the facility of the oxidation is affected by the bridge length of ligand. All the Ni(II) complexes with **4**, **5**, and **6** show CVs in which one anodic and one cathodic peak appear with a ratio i_{pa}/i_{pc} of almost unity. Their respective DPs show one nearly symmetrical peak. Similar results were obtained in the case of monomacrocyclic Ni(II) complexes with **1a** and **1b**. The Ni(II) complexes with **2** and **3** give quite different CVs and DPs. The CV of $[Ni^{II}{}_2(\mathbf{3})]^{4+}$ has two shoulders each near the anodic and near the cathodic peak. The CV of $[Ni^{II}{}_2(\mathbf{2})]^{4+}$ has two anodic peaks at 1.25 and 1.35 V and two cathodic ones at 1.22 and 1.32 V. In the DP of $[Ni^{II}{}_2(\mathbf{3})]^{4+}$ one broad peak is observed; its half-width is larger than those of the Ni(II) complexes with **1a**, **1b**, and **4**—**6** (See Table 1). The DP of $[Ni^{II}{}_2(\mathbf{2})]^{4+}$ has two distinct peaks (1.30_0 and 1.23_5 V) with nearly equal intensities. These results indicate that the Ni(II) complexes having short bridges are oxidized stepwise at distinctly different potentials according to the consecutive reaction

$$[Ni^{II}Ni^{II}]^{4+} \xrightleftharpoons{-e} [Ni^{II}Ni^{III}]^{5+} \xrightleftharpoons{-e} [Ni^{III}Ni^{III}]^{6+}. \qquad (1)$$

Table 1 lists electrochemical data evaluated from the DPs. The values of $E_{1/2}{}^1$ ($[Ni^{II}Ni^{II}]/[Ni^{II}Ni^{III}]$) of

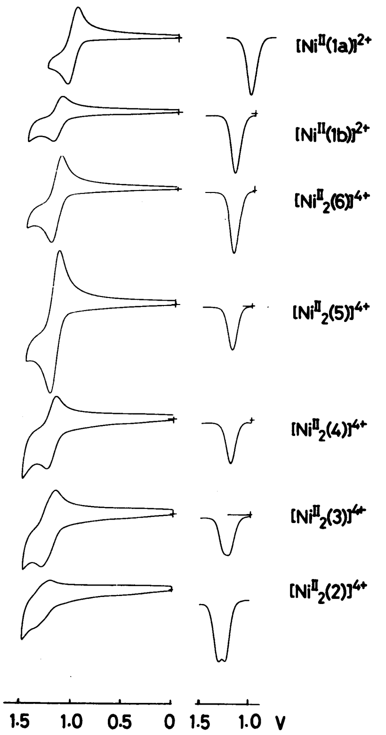


Fig. 1. Cyclic voltammograms (scan rate: 100 mV s^{-1}) and the respective differential pulse polarograms (scan rate: 1 mV s^{-1}; pulse amplitude: 10 mV) in acetonitrile. V vs. Ag-Ag$^+$ (0.01 mol dm^{-3} $AgNO_3$). Glassy carbon electrode.[18] T=25 °C.

Table 1. Data of Differential Pulse Polarography[a)]

Complex	E_p/V	Half-width/mV	$E_{1/2}$/mV[b)]	$E_{1/2}{}^1$ or $E_{1/2}{}^2$/V[b)]
$[Ni^{II}(\mathbf{1a})]^{2+}$	1.03_8	10_5		1.04_3
$[Ni^{II}(\mathbf{1b})]^{2+}$	1.19_0	10_6		1.19_5
$[Ni^{II}_2(\mathbf{6})]^{4+}$	1.20_2	10_7	4_9	1.18_3 1.23_2
$[Ni^{II}_2(\mathbf{5})]^{4+}$	1.20_5	10_7	4_9	1.18_5 1.23_4
$[Ni^{II}_2(\mathbf{4})]^{4+}$	1.20_5	10_7	4_9	1.18_5 1.23_4
$[Ni^{II}_2(\mathbf{3})]^{4+}$	1.23_7	15_1	7_5	1.21_5 1.28_0
$[Ni^{II}_2(\mathbf{2})]^{4+}$	1.23_5 1.30_0	17_2	$8_9(8_7)$	1.22_9 1.31_7

a) In acetonitrile, vs. Ag-Ag$^+$ (0.01 mol dm^{-3} AgNO$_3$), T=25 °C, and I=0.1 (Et$_4$NClO$_4$). b) Evaluated from half-width data by the method of Ref. 14. The value in parentheses was evaluated from E_p data.

the Ni(II) complexes with **4**—**6**, independent of bridge length, are very close to that of $[Ni^{II}(\mathbf{1b})]^{2+}$.[12)] The $E_{1/2}{}^1$ values shift toward the positive side in the sequence of ligands: **2**>**3**>**4**. A similar but more pronounced trend is observed with the second oxidation step, $E_{1/2}{}^2$ ($[Ni^{II}Ni^{III}]/[Ni^{III}Ni^{III}]$). On a theoretical ground, consecutive oxidation of two equivalent and independent metal centers involves a potential separation, $\Delta E_{1/2}=E_{1/2}{}^2-E_{1/2}{}^1$, of 36 mV.[13,14)] Thus, the larger value (49 mV) is observed with the Ni(II) complexes with **4**—**6**. More remarkable differences are found with $[Ni^{II}_2(\mathbf{2})]^{4+}$ (89 mV) and $[Ni^{II}_2(\mathbf{3})]^{4+}$ (75 mV). These results are reasonable because the electrostatic repulsion due to two metal ions undoubtedly increases with decrease in their distance.[15)] Furthermore, the more pronounced effects observed for the second oxidation step as well as $\Delta E_{1/2}$ are acceptable, since the electrostatic repulsion due to two Ni(III) ions should be larger than that due to Ni(II) and Ni(III), which is in turn larger than that due to two Ni(II) ions.

Thus, all the data obtained show that the metal–metal interaction of the bismacrocyclic Ni(II) complexes is affected by the bridge length; the interaction is increased in the following sequence of ligands **2**>**3**>**4**=**5**=**6**. The crucial bridge length for the interaction lies between tri- and tetramethylene; to our best knowledge, such a finding is unprecedented in the literature.

Experimental

Materials. Monomacrocyclic Ni(II) complexes **1a** and **1b** were prepared according to the method described by Karn and Busch.[16)] Bismacrocyclic Ni(II) complexes were synthesized by a method similar to that reported by Murase et al.[4)]

Physical data of new compounds are given below together with some comments.

$[Ni^{II}_2(\mathbf{2})](ClO_4)_4$: A crude product was purified by column chromatography with ion-exchange resin (SP-Sephadex C-25) and 0.6 mol dm^{-3} NaCl as the eluant. The counter ion of the complex thus purified was replaced with perchlorate by the conventional method. Found: C, 36.28; H, 4.30; N, 10.27; Ni, 10.44%. Calcd for $C_{32}H_{46}N_8Ni_2Cl_4O_{16}$: C, 36.33; H, 4.38; N, 10.59; Ni, 11.09%. IR (Nujol): 1630 (C=N) and 1580 cm^{-1} (py); ^{13}C NMR (CF$_3$COOD, TMS) δ=17.8 (q), 25.2 (t), 41.9 (t), 51.7 (t), 55.6 (t), 127.8 (d), 145.1 (d), 156.7 (s), and 181.0 (s).

$[Ni^{II}_2(\mathbf{2})]Cl_4$: MS (FAB) m/z 764 ([M−Cl+H]$^+$), 729 ([M−2Cl+H]$^+$) and 693 ([M−3Cl+H]$^+$).

$[Ni^{II}_2(\mathbf{5})](ClO_4)_4\cdot 2H_2O$: Found: C, 36.86; H, 4.60; N, 9.68%. Calcd for $C_{35}H_{52}N_8Ni_2Cl_4O_{16}\cdot 2H_2O$: C, 37.00; H, 4.97; N, 9.86%. IR (Nujol): 1628 (C=N) and 1583 cm^{-1} (py); ^{13}C NMR (CF$_3$COOD, TMS) δ=17.5 (q), 20.1 (t), 24.2 (t), 25.8 (t), 51.6 (t), 52.3 (t), 55.2 (t), 127.7 (d), 146.1 (d), 156.2 (s), and 181.2 (s).

$[Ni^{II}_2(\mathbf{6})](ClO_4)_4\cdot H_2O$: Found: C, 38.04; H, 4.83; N, 9.94%. Calcd for $C_{36}H_{54}N_8Ni_2Cl_4O_{16}\cdot H_2O$: C, 38.19; H, 4.99; N, 9.90%. IR (Nujol): 1635 (C=N) and 1580 cm^{-1} (py); ^{13}C NMR (CF$_3$COOD, TMS) δ=17.3 (q), 19.7 (t), 24.0 (t), 27.6 (t), 51.3 (2t), 54.9 (t), 127.8 (d), 145.8 (d), 156.4 (s), and 181.2 (s).

The isolation of the Ni(II) complex perchlorates with **3** and **4** was also confirmed by elemental analysis, IR, and ^{13}C NMR.

Measurements: Electrochemical measurements were performed according to the same method as described in our previous paper.[17)] The concentration of the Ni(II) complexes was ca. 1×10^{-3} mol dm^{-3}. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as the supporting electrolyte.

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11) Ligand abbreviations: 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (**1a**), 2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17), 2,11,13,15-pentaene (**1b**), and 7,7′-*polymethylene*bis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11, 13,15-pentaene], where *polymethylene* is ethylene (**2**), trimethylene (**3**), tetramethylene (**4**), pentamethylene (**5**), or hexamethylene (**6**).

12) The $E_{1/2}{}^1$ values of $[\mathrm{Ni^{II}}(\mathbf{1b})]^{2+}$ and the bismacrocyclic Ni(II) complexes are more positive than that of $[\mathrm{Ni^{II}}(\mathbf{1a})]^{2+}$, which indicates that the Ni(II) complex with one tertially nitrogen atom is more resistant to oxidation than that with one secondary nitrogen atom.

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15) The molecular model suggests that the approximate distance between the two Ni(II) ions in $[\mathrm{Ni^{II}}_2(\mathbf{n})]^{4+}$ is 7.1 (**n**=**2**), 8.1 (**3**), 9.3 (**4**), 10.5 (**5**), or 12.0 Å (**6**), if the two rings are positioned as far as possible.

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