cyclam ring, simultaneously promoting deprotonation of the amido groups.[26] It is seen that the incorporation of the second Cu$^{II}$ ion is more disfavored than is expected on statistical bases ($\Delta\log k_{stat} = \log 4 = 0.6$), showing mutual influence between rings. However, this seems to be due to the repulsion between the facing negatively charged oxygen atoms bound to each ring, rather than to interactions between the encircled metal centers. Mutual effects between the two rings settled in their definitive coordinative arrangements are expected to be small. The difference of the electrode potentials for the stepwise Cu$^{II}$/Cu$^{III}$ oxidation processes involving the dimetallic bisdioxocyclamato complex $[Cu_2(L^2)]$ (0.07 V, when corrected for the statistical term) must be considered small, if one takes into account that repulsive effects between metal centers are now involving tripositive cations.

In conclusion, double-ring macrocyclic complexes of the type described here present two proximate metal center that are able to release (or receive, provided that some coordinative features of the chambers and/or the cations are appropriately changed) a pair of electrons nearly at the same potential (*in a single step*). We believe that this situation may present some advantages in the assistance of many important two-electron redox processes, compared to the case for mononuclear analogues. This advantage should become larger and larger if the concentration of the metal complex is progressively reduced (e.g. to a *catalytic* level).

**Registry No.** **2**, 84507-37-9; **3**, 632-56-4; **4**, 4741-99-5; IV, 88524-90-7; V, 84493-40-3.

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[26] Equation 18 is the difference of eq 12 and 17, reported in Table II.

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# Adduct Formation and Electrochemistry of a Unipositive Nickel(II) Macrocycle, $[Ni(cyclops)]^+$

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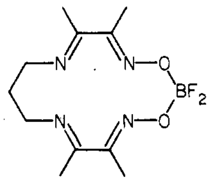
A series of diamagnetic five-coordinate square-pyramidal adducts of Ni(cyclops)$^+$ have been synthesized and characterized with the axial ligands NCS$^-$, I$^-$, pyridine, and *N*-benzylimidazole. Two binuclear ligand-bridged complexes of formula $[Ni_2(cyclops)_2X]ClO_4$ have also been isolated, where X = I$^-$, N$_3^-$. Formation constants for mononuclear 1:1 adduct formation have been measured both spectrophotometrically and electrochemically. The redox chemistry of the parent Ni(cyclops)ClO$_4$ has been reinvestigated. The cyclic voltammogram in CH$_3$CN exhibits two reversible one-electron reductions for which the potentials are concentration dependent. This is explained by the existence of a rapid dimerization equilibrium for the first reduced species, $2Ni(cyclops) \rightleftharpoons Ni_2(cyclops)_2$, for which $K_d = 5900 \pm 200$.

## Introduction

Recent work with copper(II) complexes of the anionic macrocycle 1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenate, hereafter abbreviated as cyclops (**1**), has shown that this macrocycle possesses unusual coordination properties related in part to its ring flexibility and uninegative charge.[2-5] The most extensively investigated system containing cyclops has been its complexes with copper. A series of interesting square-pyramidal Cu(cyclops)$^+$ adducts have been reported.[6] These display very strong axial ligand coordination wherein the copper(II) is pulled out of the tetraaza plane by as much as 0.58 Å—an unprecedented out-of-plane displacement for copper(II).[7] The redox chemistry of Cu(cyclops)$^+$ has proven even more unusual. Stable square-pyramidal copper(I) adducts have been isolated, and the carbon monoxide adduct exhibits strong Cu–CO bonding with the metal displaced 0.96 Å from the tetraaza plane.[8]



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Since our initial work, others have synthesized related copper(II) macrocyclic systems capable of forming square-pyramidal adducts.[9,10] These reports also have focused upon the interesting metal–axial ligand interactions and the structural and spectroscopic consequences.

Little has been reported for the analogous nickel(II) system. Uhlig and Friedrich[11] first synthesized the precursor Ni(II) macrocycle in which H is substituted for BF$_2$. Also reported were the diamagnetic square-pyramidal adducts with I$^-$, Br$^-$, and SCN$^-$. Subsequently both Rose[12] and Gagné[5] prepared Ni(cyclops)$^+$ complexes with the latter focusing upon the redox properties of Ni(cyclops)$^+$ and the CO adducts of Ni(cyclops).

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[1] (a) Drexel University. (b) Western Washington University.

[2] Wicholas, M.; Addison, A. W.; Lau, L. K.-M. *Abstr. Pap.–Am. Chem. Soc.* **1977**, *173rd*, INOR 183.

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The present work is concerned with the chemistry of Ni(cyclops)$^+$, its square-pyramidal adducts, and the parallelisms that exist with the chemistry of Cu(cyclops)$^+$. The electrochemistry of Ni(cyclops)$^+$ has also been reinvestigated, and the concentration dependence of the two reduction processes is noted and explained.

## Experimental Section

**Physical Measurements.** Electronic spectra were recorded on a Cary 14 or Coleman 46 spectrophotometer using thermostated cells. ESR spectra were obtained on a Varian E-3 X-band spectrometer. Cyclic voltammetry was performed in deaerated solutions under argon at 24.0 ± 0.5 °C at a stationary mercury-coated gold amalgam disk electrode. Voltammograms were recorded on an X-Y recorder. The potentiostat was a PAR 173 with a PAR 176 *i*/*E* converter.

Solvents for electrochemistry were distilled under dinitrogen ($CH_3NO_2$), under dinitrogen over $P_4O_{10}$ ($CH_3CN$), or under vacuum over $CaH_2$ (*N*,*N*-dimethylformamide, DMF). The supporting electrolyte (0.2 M) was G. F. Smith polarographic grade tetraethylammonium perchlorate, recrystallized from water and dried in vacuo over $P_4O_{10}$.

*N*-Benzylimidazole (*N*-BzIm), from Aldrich Chemical Co., was recrystallized from cyclohexane and dried in vacuo before use. Both Ni(cyclops)$ClO_4$ and Ni(cyclops)$PF_6$ were prepared as described previously.[2,5,12]

All other reagents were used as obtained from commercial sources. Elemental analyses were obtained from Canadian Microanalytical Service, Vancouver, B.C., Canada and MICANAL, Tucson, AZ.

**Ni(cyclops)NCS.** To a hot solution of 100 mg of Ni(cyclops)$ClO_4$ in 10 mL of $CH_3OH$ was added NaNCS (91 mg, 5 equiv). Heating was continued until the NaNCS crystals dissolved completely. After the red solution was cooled in a freezer for 24 h, dark red needles appeared. These were filtered off, washed with ice-cold methanol, air-dried, and desiccated over BaO; yield 45 mg. Anal. Calcd for $C_{12}H_{18}BF_2N_5NiO_2S$: C, 35.7; H, 4.5; N, 17.3. Found: C, 35.7; H, 4.7; N, 17.1.

**Ni(cyclops)I.** This was prepared by the same method as for the $NCS^-$ adduct; however, a large excess of $(C_4H_9)_4NI$ (1.0 g) was used per 100 mg of Ni(cyclops)$ClO_4$ to preclude formation of the binuclear iodide complex. After the deep burgundy solution was cooled for 48 h and isolated as above, the yield was 45 mg of lustrous blue-black needles. Anal. Calcd for $C_{11}H_{18}BF_2IN_4NiO_2$: C, 28.0; H, 3.8; N, 11.9; I, 26.8. Found: C, 28.2; H, 3.9; N, 11.6; I, 27.1.

**[Ni(cyclops)($C_5H_5N$)]$ClO_4$.** This was prepared by the same method as the $NCS^-$ adduct using 1 mL of pyridine/100 mg of Ni(cyclops)$ClO_4$ dissolved in 8 mL of methanol. Approximately 50 mg of purple crystals was isolated. Anal. Calcd for $C_{16}H_{23}BClF_2N_5NiO_6$: C, 36.6; H, 4.4; N, 13.3. Found: C, 36.9; H, 4.3; N, 13.4.

**[Ni(cyclops)(*N*-BzIm)]$PF_6$.** To a solution of Ni(cyclops)$PF_6$ (0.5 g) in MeOH (25 mL) was added *N*-BzIm (0.5 g); the solution was immediately heated to boiling and filtered (charcoal). The product (0.35 g), which separated as deep red-orange crystals, was filtered off and dried in vacuo over $P_4O_{10}$. Anal. Calcd for $C_{21}H_{28}BF_8N_6NiO_2P$: C, 38.9; H, 4.35; N, 13.0. Found: C, 39.2; H, 4.40; N, 13.2.

**[$Ni_2$(cyclops)$_2$I]$ClO_4$.** This was prepared by the same method as used for the mononuclear complex with 126 mg of $(C_4H_9)_4NI$ (1.5 equiv)/102 mg of Ni(cyclops)$ClO_4$. After the mixture was cooled in the freezer for 24 h, the lustrous burgundy crystals were isolated as before; yield 81 mg. Anal. Calcd for $C_{22}H_{36}B_2ClF_4IN_8Ni_2O_8$: C, 28.8; H, 4.0; N, 12.2; I, 13.8. Found: C, 28.7; H, 3.8; N, 12.5; I, 14.2.

**[$Ni_2$(cyclops)$_2N_3$]$ClO_4$.** To a hot solution of 110 mg of Ni(cyclops)$ClO_4$ in 6 mL of methanol was added $NaN_3$ (15.5 mg, 1.5 equiv). Heating was continued until the volume was reduced to approximately 4 mL. After the blood red solution was cooled in a freezer for 24 h, dark red crystals appeared and were isolated as above; yield 58 mg. Anal. Calcd for $C_{22}H_{36}B_2ClF_4N_{11}Ni_2O_8$: C, 31.7; H, 4.4; N, 18.5. Found: C, 31.9; H, 4.6; N, 18.3.

## Results and Discussion

Four mononuclear and two binuclear adducts of Ni(cyclops)$^+$ have been prepared and characterized. The mononuclear adducts Ni(cyclops)X and [Ni(cyclops)L]$^+$ (X = $NCS^-$, $I^-$; L = pyridine, *N*-benzylimidazole) are isolated from the reaction of excess ligand with a methanol solution of Ni(cyclops)$^+$. By analogy with the previously studied Cu(cyclops)$^+$, all are expected to be of square-pyramidal geometry, and this has been verified for Ni(cyclops)I by single-crystal X-ray diffraction.[13] Also, all Ni(cyclops)$^+$ adducts are diamagnetic. This is consistent with the high ligand field strength of cyclops due to its imine functions,[12] which makes the existence of adducts having an $S = 1$ ground state improbable.

Table I. Visible-Region Electronic Spectra of Iodide Adducts of Ni(cyclops)$^+$

| compd | medium | λ, nm (ε) |
|---|---|---|
| Ni(cyclops)I | Nujol | 544 |
| | | 495 (sh) |
| | $CHCl_3$ | 545 (1880) |
| | | 492 (sh) |
| [$Ni_2$(cyclops)$_2$I]$ClO_4$ | Nujol | 612 |
| | | 551 (sh) |
| | $CH_3NO_2$ | 530 |
| | | 438 (sh) |

One difference between Ni(cyclops)$^+$ and the previously studied Cu(cyclops)$^+$ is that the former has a lower affinity for forming square-pyramidal adducts. This is first evident from the difficulty in preparing Ni(II) adducts. For example, with a neutral base such as pyridine, the square-pyramidal adduct can be isolated only by addition of a large excess of pyridine. With imidazole or 1-methylimidazole products could not be isolated. With other weak donors such as $C(CN)_3^-$ or dimethyl sulfoxide, no reaction is apparent.

As with the Cu(cyclops)$^+$ system, binuclear ligand-bridged complexes of formula [$Ni_2$(cyclops)$_2$X]$ClO_4$ (X = $N_3^-$, $I^-$) have been isolated by reaction of Ni(cyclops)$^+$ with 1.5 equiv of anion in $CH_3OH$. These complexes precipitated presumably because of the lesser solubility of binuclear complex vs. mononuclear adduct.[15] For the iodide system, only by addition of a 12-fold excess of iodide in $CH_3OH$ could monomeric Ni(cyclops)I be induced to precipitate. The monomeric azide has never been isolated. However easy it is to prepare these binuclear complexes in the solid state, they revert to mononuclear species when dissolved in nonaqueous solvent. This can be illustrated by the electronic spectra of mononuclear and binuclear iodide complexes listed in Table I. In $CHCl_3$, Ni(cyclops)I clearly remains undissociated. In contrast [$Ni_2$(cyclops)$_2$I]$ClO_4$, which is insoluble in $CHCl_3$, yields a spectrum when dissolved in $CH_3NO_2$ similar to that of the mononuclear iodide. Undoubtedly the forces favoring bridging are weak, and only because of their relative insolubility in $CH_3OH$ are these binuclear complexes at all isolated.

The extent of metal–axial ligand interaction and its structural consequences are the issues of most interest for these nickel(II) and copper(II) adducts. In the latter case, the results of five single-crystal X-ray structure determinations by Anderson[7] show that the copper(II) is displaced from the macrocycle $N_4$ plane by 0.18–0.58 Å, depending upon the nature of the axial ligand. For the square-pyramidal, low-spin nickel(II) adducts of this study, smaller displacements are expected because the $d_{x^2-y^2}$ orbital is vacant. This has been confirmed for Ni(cyclops)I, where the metal displacement is 0.15 Å less than that for Cu(cyclops)I.[13]

We had previously proposed that the observed spectrochemical series for axial binding to Cu(cyclops)$^+$ is related to the strength of the Cu(II)–axial ligand bond. The ordering

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(13) Anderson, O. P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1194.

(14) Bencini, A.; Gatteschi, D.; Zanchini, C.; Wicholas, M. *Inorg. Chim. Acta* **1981**, *49*, 1.

(15) Addison, A. W.; Landee, C. P.; Willett, R. D.; Wicholas, M. *Inorg. Chem.* **1980**, *19*, 1921.

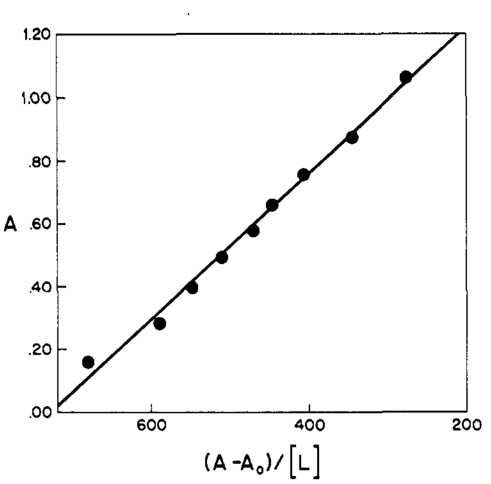

**Figure 1.** Plot of the absorbance, $A$, vs. the function $(A - A_0)/[L]$ for Ni(cyclops)ClO$_4$ + I$^-$ in CH$_3$CN at 23 °C ($I$ = 0.1 M ((C$_4$H$_9$)$_4$NClO$_4$)).

Table II. Formation Constants for Ni(cyclops)$^+$ Adducts in CH$_3$CN

| addend | $K$ | $T$, °C | addend | $K$ | $T$, °C |
|---|---|---|---|---|---|
| I$^-$ | 434 ± 17 | 23 | $N$-BzIm | 29.3 ± 0.8 ($K_1$) | 24 |
| Br$^-$ | 649 ± 15 | 23 | | 9.1 ± 0.3 ($K_2$) | |

of axial ligands in terms of relative crystal field contribution is H$_2$O < pyridine < I$^-$ ~ Br$^-$ < Cl$^-$ < NCS$^-$ << CN$^-$ ~ NCO$^-$. This trend may also be followed for Ni(cyclops)$^+$, but spectral verification is more difficult because strong charge-transfer absorptions obscure part of the visible spectrum and this complex tends to form 2:1 (ligand:Ni) adducts with neutral donors (vide infra).

We have attempted to determine on a limited basis whether the above ordering is valid for Ni(cyclops)$^+$ by measurement of formation constants for its 1:1 adducts. It is particularly important to confirm whether a neutral nitrogen base donor is less strongly coordinated to Ni(II) than a halide ion, as is found for copper(II). Formation constants for the 1:1 I$^-$ and Br$^-$ adducts were evaluated spectrophotometrically via the relationship[16] $A = A_\infty + K^{-1}(A_0 - A)/[L]$, where $A_0$ is the absorbance for Ni(cyclops)$^+$ and $A_\infty$ is the absorbance of Ni(cyclops)L. Absorbances, $A$, were measured for a series of acetonitrile solutions of constant ionic strength having a fixed concentration of Ni(cyclops)$^+$ and varying concentration of L. Reiterative computation gave the best values of $A_\infty$, [L], and $K$. The linear plot of $A$ vs. $(A_0 - A)/[L]$ with slope = $1/K$ is illustrated for the I$^-$ system in Figure 1, and the results are reported in Table II.

In both cases the existence of isobestic points was first verified. No evidence for dimer formation or 2:1 adduct formation was discerned in the concentration ranges used.

The interaction of Ni(cyclops)$^+$ with nitrogen bases is more complex due to formation of both 1:1 and 2:1 adducts. The latter are paramagnetic, and their presence can be verified by the proton NMR line broadening resulting when excess base such as pyridine is added to a solution of Ni(cyclops)ClO$_4$. Without accurate knowledge of the extinction coefficients of both 1:1 and 2:1 adducts, formation constants cannot readily be determined spectrophotometrically.

For such systems formation constants can be obtained electrochemically with use of cyclic voltammetry. This technique, as discussed previously,[5,6] has been applied here to monitor the interaction between Ni(cyclops)$^+$ and the nitrogen donor $N$-benzylimidazole, a stronger $\sigma$-donor base than either imidazole or pyridine. In this method the shift in the first reduction potential, $\Delta E$, of Ni(cyclops)$^+$ is monitored as a function of added ligand. If only 1:1 adduct formation were significant, then a plot of $e^{-nF(\Delta E)/RT}$ vs. [L] would be linear, which is not the case here. Assuming Ni(cyclops)$^+$ forms both 1:1 and 2:1 adducts in the 2+ oxidation state, the respective $K$ values, $K_1$ and $K_2$, are given as

$$(e^{-nF(\Delta E)/RT} - 1)/[L] = K_1 + K_1K_2[L]$$

Reiterative calculations were done by computer to arrive at the best values for [L], $K_1$, and $K_2$. The plot of $(e^{-nF(\Delta E)/RT} - 1)/[L]$ vs. [L] for $N$-benzylimidazole is illustrated in Figure 2 and is linear as expected. The formation constants are listed in Table II.

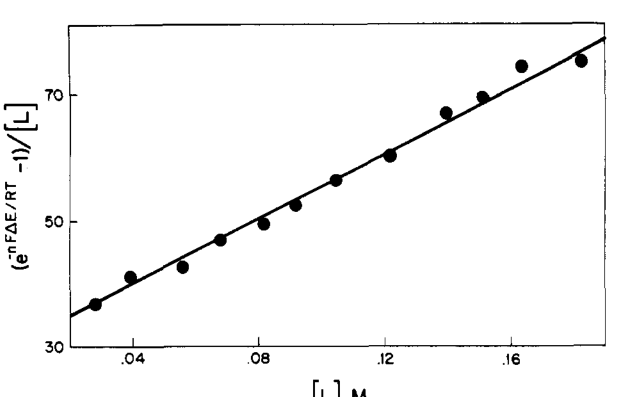

**Figure 2.** Plot of the function $(e^{-nF(\Delta E)/RT} - 1)/[L]$ vs. [L] for 1.13 mM Ni(cyclops)ClO$_4$ + $N$-BzIm in CH$_3$CN at 24 °C ($I$ = 0.1 M ((C$_2$H$_5$)$_4$NClO$_4$)).

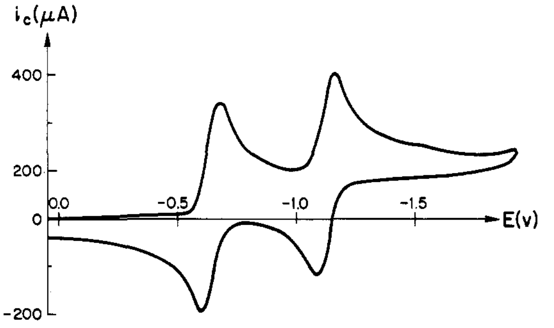

**Figure 3.** Cyclic voltammogram of 1.8 mM Ni(cyclops)ClO$_4$ in CH$_3$CN. Potential referred to SHE. $D\eta$ = 3.7 × $10^{-8}$ g cm/s$^2$.

The ordering of formation constants supports our earlier premise regarding interactions: viz., neutral bases form substantially weaker axial adducts than halides when coordinated to M(cyclops)$^+$. This consequently implies that ionic interactions are more important in axial adduct formation and that a halide ion is better suited than an imidazole ligand for this purpose.

Recent calculations concerning the complexes of the related macrocycle TIM[17] are consistent with the above conclusion. Maroney and Norman[18] completed SCF–X$\alpha$–SW calculations on simple models of square-planar Cu(TIM)$^{2+}$ and its square-pyramidal Cl$^-$ adduct. They have concluded that the Cu–Cl interaction is best described as being ionic.

**Electrochemistry of Ni(cyclops)$^+$.** The electrochemical behavior of Cu(cyclops)$^+$ has been extensively discussed,[2,6,8] and that of Ni(cyclops)$^+$ has been briefly alluded to by Gagné,[3,5] who investigated the Ni(II) → Ni(I) reduction of a series of nickel macrocycles.

A cyclic voltammogram of Ni(cyclops)$^+$ in CH$_3$CN shows two reversible one-electron reductions (Figure 3). Both re-

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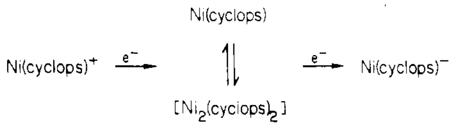
(16) Ewert, A.; Wannowius, K. J.; Elias, H. *Inorg. Chem.* **1978**, *17*, 1691.

(17) TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.

(18) Maroney, M. J.; Norman, J. G., private communication.

duction half-wave potentials are concentration dependent. Upon dilution $E_{1/2}(1)$, the first reduction potential, shifts anodically whereas $E_{1/2}(2)$ shifts cathodically. This behavior is consistent with the existence of a *rapid* monomer–dimer equilibrium in solution for the first reduced species:



The evidence for dimer formation is as follows. A 3.4 mM acetonitrile solution of Ni(cyclops)$^0$ shows no X-band ESR signal at 77 K. Since Ni(cyclops)$^0$ is known to be paramagnetic in a propylene carbonate glass at 100 K ($S = {}^1/_2$, $g_0 = 2.002$), it seems certain that virtually complete dimerization occurs in $CH_3CN$ solution. Furthermore, such dimerization in reduced Ni(II) species is not unprecedented. Both Holm[19] and Goedken[20] have isolated and characterized by single-crystal X-ray crystallography stable dimers of reduced, highly conjugated nickel(II) macrocycles wherein the monomer units are connected by a Ni–Ni bond. Prevailing thought is that these dimers contain Ni(II) (not Ni(I)) plus reduced macrocycle with the odd electron in a $\pi^*$ orbital. These dimers are further stabilized by weak $\pi$ bonding between the macrocyclic rings, which results in spin pairing of the odd electrons. The Ni–Ni bond can also be found in nonreduced Ni(II) species such as the related $Ni(dmgBF_2)_2$, which in the solid state is a dimer with a Ni–Ni bond distance of 3.207 Å.[21]

It is possible to derive the value of $K_{\text{dimer}}$ for 2Ni(cyclops)$^0$ $\rightleftharpoons$ $[Ni(cyclops)]_2$ from the dependence of the first reduction potential upon the concentration of bulk Ni(cyclops)$^+$ in solution. With use of the Nernst equation and mass balance relationships it can be shown for the first reduction process that $E = E_{1/2}(1) + (RT/nF \ln ([\text{Ni(cyclops)}^+]/[\text{Ni(cyclops)}]) + RT/nF \ln (1 + 2K_d[\text{Ni(cyclops)}])^{-1}$, where $E$ is the applied potential at any point in the reduction process for a Ni(cyclops)$^+$ solution of specified concentration and $E_{1/2}(1)$ is the half-wave potential for this first reduction. If $E_0(1)$ is then defined as the first reduction potential in the limit of *infinite dilution*,[22] then

$$E_0(1) = E_{1/2}(1) + \frac{RT}{nF} \ln (1 + 2K_d[\text{Ni(cyclops)}])^{-1}$$

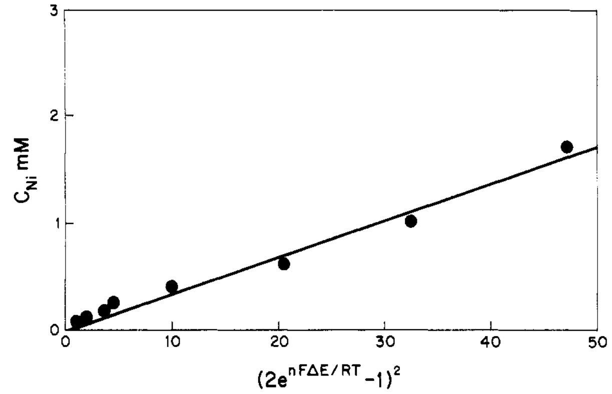


**Figure 4.** Plot of $C_{Ni}$ vs. the function $(2e^{nF(\Delta E_1)/RT} - 1)^2$ for Ni(cyclops)$ClO_4$ in $CH_3CN$ at 24 °C.

This can be expressed as a function of $C_{Ni}$, the bulk concentration of Ni(cyclops)$^+$ before electroreduction. Substitution yields

$$[2 \exp(nF(\Delta E_1)/RT) - 1]^2 = 1 + 4K_dC_{Ni}$$

where $\Delta E_1 = E_{1/2}(1) - E_0(1)$.

A plot of $[2 \exp(nF(\Delta E_1)/RT) - 1]^2$ vs. $C_{Ni}$ for a series of Ni(cyclops)$^+$ solutions at 24 °C over a 100-fold concentration range is illustrated in Figure 4. Linear regression analysis gives $K_d = 5900 \pm 200$. This large value is consistent with the EPR-silent behavior of reduced Ni(cyclops)$^+$ in $CH_3CN$ at 77 K. For example, a 0.01 M Ni(cyclops)$^+$ solution should be approximately 90% dimer at 24 °C if $K_d = 5900$. If $\Delta H^\circ < 0$ for the dimerization, as one might expect, then the system should be completely diamagnetic at 77 K.

No investigation was made of the second reduction process, which corresponds to the generation of a formally Ni(0) macrocycle. Further, a corresponding plot of $[2 \exp(nF{\cdot}(\Delta E_2)/RT) - 1]^2$ vs. $C_{Ni}$ is not linear.

**Acknowledgment.** This work was supported by Drexel University and a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, to M.W.

**Registry No.** Ni(cyclops)Br, 88825-95-0; Ni(cyclops)$ClO_4$, 75400-07-6; Ni(cyclops)NCS, 88825-86-9; Ni(cyclops)I, 78452-89-8; [Ni(cyclops)($C_5H_5N$)]$ClO_4$, 88825-88-1; [Ni(cyclops)(*N*-BzIm)]$PF_6$, 88825-90-5; [$Ni_2$(cyclops)$_2$I]$ClO_4$, 88825-92-7; [$Ni_2$(cyclops)$_2N_3$]$ClO_4$, 88825-94-9.

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[19] Peng, S.-M.; Ibers, J. A.; Miller, M.; Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 8037.

[20] Peng, S.-M.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 8500.

[21] Stephens, F. S.; Vagg, R. S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 3159.

[22] The reduction potentials approach limiting values of −926 and −1320 mV vs. 0.01 M Ag/Ag$ClO_4$ in 0.1 M $NEt_4ClO_4$ in $CH_3CN$. These values are used for $E_0$.