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# Electrochemical Studies of Nickel(II) Complexes with Tri- and Bidentate Arsine Ligands. A Stereochemically and Electronically Accommodating Donor Set

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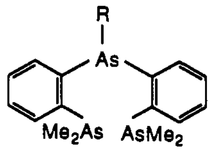
A cyclic voltammetric study in acetonitrile and dichloromethane of the five-coordinate nickel complexes $[\mathrm{Ni(mtas)_2}]^{2+}$ (mtas = bis(2-(dimethylarsino)phenyl)methylarsine), $[\mathrm{Ni(ptas)_2}]^{2+}$ (ptas = bis(2-(dimethylarsino)phenyl)phenylarsine), $[\mathrm{Ni(L_2)(mtas)}]^{2+}$ ($L_2$ = 1,2-bis(dimethylarsino)benzene (diars), 1,8-bis(dimethylarsino)naphthalene (dman), 1,2-bis(dimethylarsino)tetrafluorobenzene ($F_4$-diars)), and $[\mathrm{Ni(L_2)(ptas)}]^{2+}$ ($L_2$ = diars, dman) is reported. All nickel oxidation states from 0 to IV are formed within the accessible potential range and are stable with respect to disproportionation. Inspection of the electrochemical data identifies Ni–As bond formation and cleavage reactions accompanying electron transfer and reveals that Ni(I), Ni(II), and Ni(III) species are five-coordinate whereas Ni(0) and Ni(IV) species are four- and six-coordinate, respectively. The homoleptic Ni(IV) complexes have the $As_6$ donor set and are kinetically stable on the conventional cyclic voltammetric time scale. For the heteroleptic complexes, a molecule of solvent or an electrolyte anion coordinates to the Ni(IV) center and the kinetic stability is reduced. The thermodynamic and kinetic stabilities of the homoleptic complexes are compared to those of nickel complexes with $(\mathrm{diars})_2$ and $(F_4\text{-diars})_2$ coordination. The electrode kinetics of the Ni(III/II) couple of all complexes studied exhibit a marked dependence on solvent, electrolyte, and electrode material. This is attributed, in part, to ion-pairing phenomena.

## Introduction

Cyclic voltammetry is an electrochemical technique that readily affords information on the thermodynamic and kinetic stabilities of transition metal complexes. Detection of structural reorganization accompanying a change in oxidation state is also possible when the reorganization imposes kinetic limitations on the electron transfer resulting in electrochemical quasi-reversibility.[1] A dominant feature of transition metal chemistry is the wide range of oxidation states exhibited by the elements in a variety of complexes. It is generally the case that different coordination numbers and types of ligands are preferred as the metal oxidation state changes. As a consequence, it is rare to find mononuclear complexes for which more than three metal oxidation states are thermodynamically accessible and kinetically stable by conventional electrochemical techniques.

The redox chemistry of nickel complexes extends from Ni(0) to Ni(IV) with many well-characterized examples of each oxidation state.[2] Lower oxidation states are stabilized by soft donors capable of $\pi$ back-bonding; the majority of Ni(0) and Ni(I) complexes contain phosphine, arsine, or closely related ligands and have tetrahedral structures. Nickel(IV) strongly favors octahedral coordination, and Ni(III) is most commonly found in a tetragonally-distorted octahedral geometry. A large number of Ni(III) and Ni(IV) complexes have nitrogen and oxygen donor ligands which are capable of strong $\sigma$ donation to the hard acid metal center. Phosphines and arsines also exhibit strong $\sigma$-donor properties, and there are a significant number of well-characterized complexes with donor sets comprising both halides and phosphine or arsines.[2c]

The strong $\sigma$-donor and $\pi$-acceptor properties of arsines and phosphines (and the formation of both high and low oxidation states of nickel in complexes with coordination spheres incorporating these ligands) suggest the possibility of stabilizing all nickel oxidation states, 0 to IV, with a single donor set. In order to accommodate changing preferences for coordination numbers and geometries as the metal oxidation state changes, multidentate ligands with small steric requirements and some flexibility are expected to be important. The tridentate ($L_3$) ligands bis(2-(dimethylarsino)phenyl)methylarsine (mtas)[3] and bis(2-(dimethylarsino)phenyl)phenylarsine (ptas)[4] meet these requirements. Homoleptic, five-coordinate Ni(II) complexes of these ligands were recently fully characterized.[4] X-ray structural analyses show that $[\mathrm{Ni(mtas)_2}](\mathrm{ClO_4})_2$ and $[\mathrm{Ni(ptas)_2}](\mathrm{BF_4})_2$ adopt distorted square-pyramidal and trigonal-bipyramidal structures, respectively. In both complexes, only five sites are occupied by the two potentially tridentate ligands with a terminal $-\mathrm{AsMe_2}$ group uncoordinated. Variable-temperature $^1$H NMR studies indicate that, in both complexes, the dangling arsenic exchanges with some of the coordinated arsenic donors. A series of heteroleptic nickel complexes incorporating one tridentate arsine ligand and one bidentate ($L_2$) arsine ligand (1,2-bis(dimethylarsino)benzene(diars), 1,8-bis(dimethylarsino)naphthalene



R = Me; mtas
= Ph; ptas

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[†] University of Canterbury.
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[●] Abstract published in *Advance ACS Abstracts,* November 15, 1993.
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(2) See the following recent reviews. (a) Ni(I)–Ni(IV): Lappin, A. G.; McAuley, A. *Adv. Inorg. Chem.* **1988,** *32,* 241. (b) Ni(0)–Ni(IV): Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds. *Comprehensive Coordination Chemistry*; Pergamon: London, 1987; Vol. 5. (c) Ni(III), Ni(IV) phosphines and arsines: Levason, W. *Comments Inorg. Chem.* **1990,** *9,* 331.
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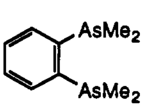
**Table I.** Electrochemical Data Recorded in Acetonitrile–$[Bu_4N]ClO_4$ and Dichloromethane–$[Bu_4N]PF_6$ at a Glassy Carbon Electrode[a]

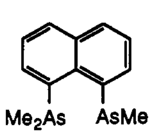
| complex | $E_{1/2}$(I/0) | $E_{1/2}$(II/I) | $E_{1/2}$(III/II) | $E_{1/2}$(IV/III) | solvent |
|---|---|---|---|---|---|
| $[Ni(mtas)_2]^{2+}$ | −1.16 (75) | −0.60 (60) | 0.89 (70) | 1.21 (60) | acetonitrile |
| $[Ni(ptas)_2]^{2+}$ | −1.10 (120) | −0.50 (70) | 0.89 (90) | 1.19 (70) | acetonitrile |
| $Ni(ptas)_2]^{2+}$ | −1.4[b] | −0.46 (90) | 1.02 (110) | 1.24[c] | dichloromethane |
| $[Ni(diars)(mtas)]^{2+}$ | −1.18 (120) | −0.66 (70) | 1.02 (100) | 1.38 (100)[d] | acetonitrile |
| $[Ni(diars)(mtas)]^{2+}$ | −1.4[b] | −0.54 (110) | 1.16 (130) | | dichloromethane |
| $[Ni(diars)(ptas)]^{2+}$ | −1.11 (240) | −0.54 (70) | 1.03 (200) | 1.33 (100)[d] | acetonitrile |
| $[Ni(diars)(ptas)]^{2+}$ | −1.4[b] | −0.51 (80) | 1.18 (240) | | dichloromethane |
| $[Ni(dman)(mtas)]^{2+}$ | −1.23 (190) | −0.61 (65) | 1.11 (130) | 1.45 (95)[d] | acetonitrile |
| $[Ni(dman)(mtas)]^{2+}$ | −1.6[b] | −0.54 (80) | 1.30 (130) | | dichloromethane |
| $[Ni(dman)(ptas)]^{2+}$ | −1.20 (260) | −0.56 (70) | 1.15 (170) | 1.41 (100)[d] | acetonitrile |
| $[Ni(dman)(ptas)]^{2+}$ | −1.5[b] | −0.50 (110) | 1.29 (120) | | dichloromethane |
| $[Ni(F_4\text{-}diars)(mtas)]^{2+}$ | −1.05 (370) | −0.51 (65) | 1.18 (80) | 1.44 (100)[d] | acetonitrile |
| $[Co(mtas)_2]^{3+}$ | −1.85 (60) | −0.61 (60) | 0.04 (60) | | acetonitrile |

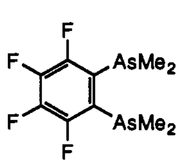
| ligand | $E_p^{ox}(1)$[b] | $E_p^{ox}(2)$[b] | solvent | ligand | $E_p^{ox}(1)$[b] | $E_p^{ox}(2)$[b] | solvent |
|---|---|---|---|---|---|---|---|
| mtas | 0.83 | 1.20 | acetonitrile | ptas | 0.91 | 1.24 | acetonitrile |

[a] $E_{1/2} = (E_p^a + E_p^c)/2$, in volts vs SCE. Values in parentheses indicate $\Delta E_p$ values in millivolts, from cyclic voltammograms recorded at 100 mV $s^{-1}$ (unless noted otherwise). [b] Peak potential for chemically irreversible process. [c] Response distorted by adsorption. [d] Scan rate = 500 mV $s^{-1}$.

(dman),[5] or 1,2-bis(dimethylarsino)tetrafluorobenzene ($F_4$-diars)[6])have also been prepared.[7,8] X-ray structural analyses of


diars


dman


$F_4$-diars

$[Ni(diars)(mtas)](ClO_4)_2$[4,7] and $[Ni(dman)(mtas)](ClO_4)_2$[8] reveal square-pyramidal structures for both complexes. All $-AsMe_2$ groups are coordinated, and only very limited fluxional behavior is observed in $^1H$ NMR experiments over the temperature range +25 to −50 °C.

We describe here a cyclic voltammetric study of the complexes $[Ni(ptas)_2]^{2+}$, $[Ni(mtas)_2]^{2+}$, $[Ni(diars)(mtas)]^{2+}$, $[Ni(diars)(ptas)]^{2+}$, $[Ni(dman)(mtas)]^{2+}$, $[Ni(dman)(ptas)]^{2+}$, and $[Ni(F_4\text{-}diars)(mtas)]^{2+}$. It is demonstrated that, for the homoleptic complexes, all oxidation states from Ni(0) to Ni(IV) are accessible and kinetically stable on the conventional cyclic voltammetric time scale. Heteroleptic complexes exhibit a similar response; however, coordination of an electrolyte anion or solvent molecule is required to stabilize the Ni(IV) center. A preliminary account of some results has been reported.[9]

## Experimental Section

Cyclic voltammetric measurements were made using either a PAR Model 174A polarographic analyzer coupled to a PAR Model 175 universal programmer or a PAR Model 173 potentiostat/galvanostat coupled to a home-built waveform generator. Graphtec WX 1200 recorders were utilized with both systems. A conventional three-electrode cell was used with a glassy carbon (area = 0.07 $cm^2$) or Pt (area = 0.8 $mm^2$) disk working electrode, a Pt auxiliary electrode, and an $Ag/Ag^+$ (0.01 M in MeCN/0.1 M $[Bu_4N]BF_4$) reference electrode. Working electrodes were polished to a mirror finish using 1-μm diamond paste. Potentials are reported vs SCE after referencing to *in situ* ferrocene ($E^{\circ\prime}_{Fc^+/Fc}$ = 0.31 V vs SCE). Unless stated otherwise, solutions for analysis contained 1 mM complex, a scan rate of 100 mV $s^{-1}$ was used, and measurements were made at room temperature.

Acetonitrile was stirred over $CaH_2$ for 2 days, decanted, refluxed under $N_2$ with $P_2O_5$, distilled, and then refluxed under $N_2$ with $CaH_2$. Solvent was distilled from $CaH_2$ immediately prior to use. Dichloromethane was predried with $CaCl_2$, decanted, refluxed under $N_2$ with $P_2O_5$, distilled, and then stored over $P_2O_5$. Solvent was distilled under $N_2$ from $P_2O_5$ immediately prior to use. $[Bu_4N]ClO_4$ (Fluka) was recrystallized from ethyl acetate, and $[Bu_4N]PF_6$ (Aldrich) was recrystallized from ethanol; both electrolytes were dried under vacuum at 60 °C.

The complexes $[Ni(mtas)_2](ClO_4)_2$, $[Ni(ptas)_2](BF_4)_2$, $[Ni(diars)(mtas)](BF_4)_2$, and $[Co(mtas)_2](BF_4)_3$ were prepared as described elsewhere.[3,4,7,10] The new complexes $[Ni(diars)(ptas)](BF_4)_2$, $[Ni(dman)(mtas)](ClO_4)_2$, $[Ni(dman)(ptas)](BF_4)_2$, and $[Ni(F_4\text{-}diars)(mtas)](BF_4)_2$ were prepared by similar procedures.[8]

## Results and Discussion

**Cyclic Voltammetry in Acetonitrile–$[Bu_4N]ClO_4$ and Dichloromethane–$[Bu_4N]PF_6$ at Glassy Carbon.** Initial investigations of the electrochemistry of the complexes were made using a glassy carbon (GC) working electrode in two media: acetonitrile–0.1 M $[Bu_4N]ClO_4$ and dichloromethane–0.1 M $[Bu_4N]PF_6$. For some complexes, insolubility prevented measurements in dichloromethane. Results are presented in Table I.

Cyclic voltammetry in acetonitrile–$[Bu_4N]ClO_4$ of all nickel complexes shows two oxidation steps and two reductions. The peak currents and peak-to-peak separations ($\Delta E_p$ values) of ≥60 mV are consistent with the transfer of one electron at each step. All processes are chemically reversible at 100 mV $s^{-1}$ for $[Ni(mtas)_2]^{2+}$ and $[Ni(ptas)_2]^{2+}$ (see Figure 1a). For complexes of the type $[Ni(L_2)(L_3)]^{2+}$, the second oxidation process is chemically reversible only at scan rates greater than 500 mV $s^{-1}$ or temperatures below 0 °C. Figure 2a shows the response for $[Ni(diars)(mtas)]^{2+}$. The electrochemical response for each type of complex can be represented by eqs 1 and 2. As evidenced by $\Delta E_p$

$$[Ni(L_3)_2]^0 \xrightleftharpoons{e^-} [Ni(L_3)_2]^+ \xrightleftharpoons{e^-} [Ni(L_3)_2]^{2+} \xrightleftharpoons{e^-} [Ni(L_3)_2]^{3+} \xrightleftharpoons{e^-} [Ni(L_3)_2]^{4+} \qquad (1)$$

$$[Ni(L_2)(L_3)]^0 \xrightleftharpoons{e^-} [Ni(L_2)(L_3)]^+ \xrightleftharpoons{e^-} [Ni(L_2)(L_3)]^{2+} \xrightleftharpoons{e^-} [Ni(L_2)(L_3)]^{3+} \xrightarrow{-e^-} [Ni(L_2)(L_3)]^{4+} \qquad (2)$$

values measured at 100 mV $s^{-1}$, the rates of the second reduction and first oxidation processes are markedly slower than those of the other processes.

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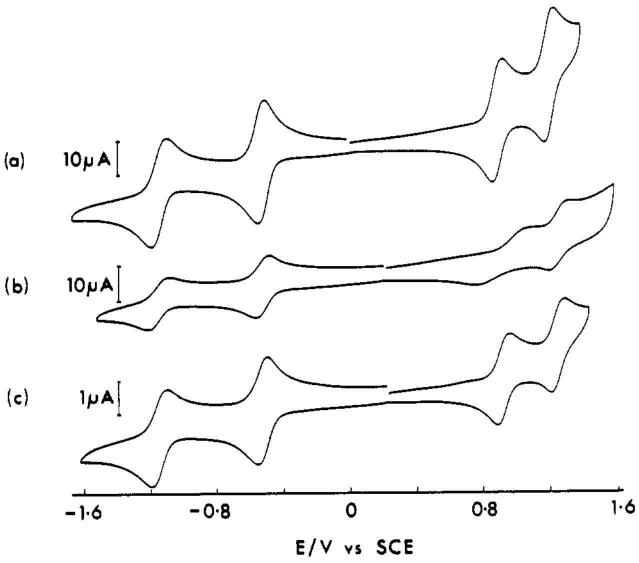

**Figure 1.** Cyclic voltammograms of $[Ni(ptas)_2]^{2+}$ recorded in acetonitrile (scan rate = 100 mV $s^{-1}$): (a) 1 mM complex, 0.1 M $[Bu_4N]ClO_4$ at GC; (b) 0.5 mM complex, 0.1 M $[Bu_4N]PF_6$ at GC; (c) 0.5 mM complex, 0.1 M $[Bu_4N]PF_6$ at Pt.

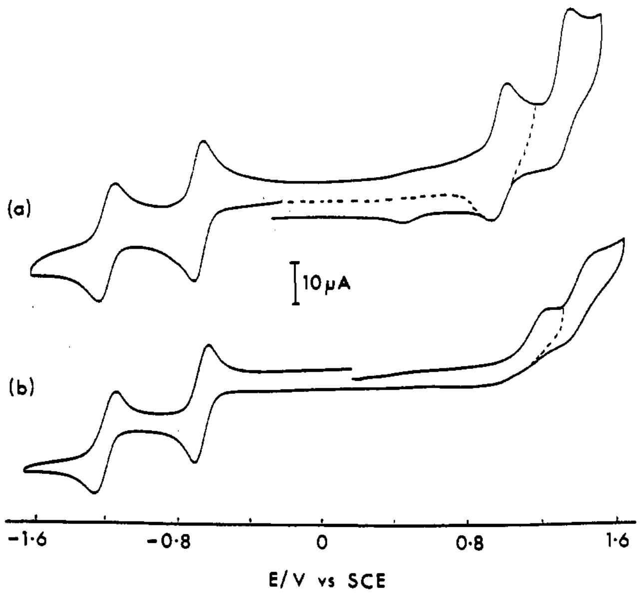

**Figure 2.** Cyclic voltammograms of $[Ni(diars)(mtas)]^{2+}$ recorded in acetonitrile at GC (scan rate = 100 mV $s^{-1}$): (a) 1 mM complex, 0.1 M $[Bu_4N]ClO_4$; (b) 1 mM complex, 0.1 M $[Bu_4N]PF_6$. Scan reversed after first oxidation.

In dichloromethane–$[Bu_4N]PF_6$, all complexes studied are reduced in a chemically reversible one-electron step followed by a chemically irreversible reduction. In this medium, $[Ni(ptas)_2]^{2+}$ exhibits a quasi-reversible one-electron oxidation followed by a chemically reversible oxidation which is complicated by adsorption of the doubly-oxidized species (see Figure 3a). All complexes of the type $[Ni(L_2)(L_3)]^{2+}$ show a quasi-reversible oxidation followed by a small peak of variable size and potential. The response for $[Ni(diars)(mtas)]^{2+}$, which is typical of these complexes, is shown in Figure 3b.

The cyclic voltammetry of $[Co(mtas)_2]^{3+}$ was examined for comparison. In acetonitrile–0.1 M $[Bu_4N]ClO_4$, the complex exhibits three chemically reversible one-electron reduction steps; no oxidation processes are observed within the solvent limit.

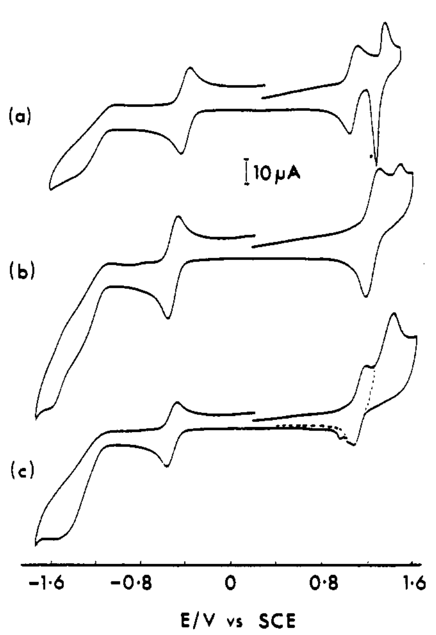

**Figure 3.** Cyclic voltammograms recorded in dichloromethane at GC (scan rate = 100 mV $s^{-1}$): (a) 1 mM $[Ni(ptas)_2]^{2+}$, 0.1 M $[Bu_4N]PF_6$; (b) 1.25 mM $[Ni(diars)(mtas)]^{2+}$, 0.1 M $[Bu_4N]PF_6$; (c) 0.8 mM $[Ni(diars)(mtas)]^{2+}$, 0.1 M $[Bu_4N]ClO_4$. Scan reversed after first oxidation.

The ligands ptas and mtas have qualitatively similar electrochemistry: two well-defined chemically irreversible oxidation peaks followed by a very broad wave with low current at more positive potentials. There are no reduction processes within the solvent limits. The number of electrons involved in each oxidation step is difficult to determine definitively. The ratio of the peak currents for the first and second steps is approximately 1.5:1, which is considerably lower than the 2.8:1 ratio predicted for a two-electron:one-electron step.[11] Repeat scans show that significant deactivation of the electrode occurs during each scan; hence a loss of electrode activity during the scan may lead to a decrease in current for the second step. Peak currents are higher than for equimolar solutions of the complexes, consistent with larger diffusion coefficients for the ligands. On the basis of the above observations, it is reasonable to assign the ligand electrochemistry to two one-electron oxidations, with the third oxidation process due to a decomposition product or impurities in the sample.

**Assignment of the Redox Processes.** The observation of the extended redox series represented by eqs 1 and 2 raises the question of ligand-based vs metal-based electron transfers. It is sometimes suggested that the higher and lower oxidation states of nickel, in particular Ni(0) and Ni(IV), have little physical reality owing to extensive delocalization of electron density over the metal and ligands.[12] Ligand-based redox chemistry giving rise to ligand radicals can, however, be meaningfully distinguished from redox chemistry based on orbitals which contain a significant metal contribution. Consistent with other workers, we use the term "metal-based" for such redox reactions which lead to changes in the formal oxidation state of nickel.

The electrochemistry of the nickel complexes described here is not consistent with ligand-centered processes. Considering the reduction processes, formation of Ni(I) and Ni(0) species is expected on the basis of the large number of well-characterized Ni(I) and Ni(0) phosphine and arsine complexes.[2a,b,13] Support for this assignment comes from the observations that the free ligands cannot be reduced and that the second reduction of the complexes is chemically irreversible in dichloromethane. Nickel(0) species are known to react with alkyl halides,[2c,14] and hence reaction with the solvent accounts for the irreversible electrochemistry.

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**Table II.** $\Delta E_p$ Values[a] at GC and Pt in Acetonitrile–$[Bu_4N]ClO_4$, Acetonitrile–$[Bu_4N]PF_6$, Dichloromethane–$[Bu_4N]ClO_4$, and Dichloromethane–$[Bu_4N]PF_6$

| | | | | $\Delta E_p$, mV | | | |
|---|---|---|---|---|---|---|---|
| complex | solvent | electrode | electrolyte anion | Ni(I/0) | Ni(II/I) | Ni(III/II) | Ni(IV/III) |
| $[Ni(ptas)_2]^{2+}$ | acetonitrile | GC | $ClO_4^-$ | 120 | 70 | 90 | 70 |
| | | | $PF_6^-$ | 110 | 70 | 300 | 100 |
| | | Pt | $ClO_4^-$ | 110 | 70 | 90 | 70 |
| | | | $PF_6^-$ | 100 | 70 | 85 | 80 |
| | dichloromethane | GC | $ClO_4^-$ | *b* | 100 | 110 | *c* |
| | | | $PF_6^-$ | *b* | 90 | 110 | *c* |
| | | Pt | $ClO_4^-$ | *b* | 80 | 100 | *c* |
| $[Ni(mtas)_2]^{2+}$ | acetonitrile | GC | $ClO_4^-$ | 75 | 60 | 70 | 60 |
| | | | $PF_6^-$ | 90 | 60 | 190 | 90 |
| | | Pt | $ClO_4^-$ | 120 | 70 | 60 | 55 |
| | | | $PF_6^-$ | 115 | 60 | 95 | 90 |
| $[Ni(diars)(mtas)]^{2+}$ | acetonitrile | GC | $ClO_4^-$ | 120 | 70 | 100 | *b* |
| | | | $PF_6^-$ | 120 | 70 | 300 | *b* |
| | | Pt | $ClO_4^-$ | 100 | 60 | 100 | *b* |
| | | | $PF_6^-$ | 120 | 60 | 120 | *b* |
| | dichloromethane | GC | $ClO_4^-$ | *b* | 100 | 120 | *b* |
| | | | $PF_6^-$ | *b* | 110 | 130 | |

[a] $\Delta E_p$ values from cyclic voltammograms recorded at 100 mV s$^{-1}$, with 0.1 M $[Bu_4N]ClO_4$ or $[Bu_4N]PF_6$. [b] Chemically irreversible process. [c] Response distorted by adsorption.

Considering oxidation processes, although the free ligands can be oxidized, it is apparent that when fully coordinated, the ligands cannot be oxidized. Octahedral $[Co(mtas)_2]^{3+}$ exhibits no oxidation processes, and oxidation of coordinated diars has not been observed in redox series such as $[Ni(diars)_2Cl_2]^{2+/+/0}$ [15] and $[Ru(diars)_2Cl_2]^{2+/+/0}$.[16] Thus for the complexes $[Ni(diars)(mtas)]^{2+}$ and $[Ni(dman)(mtas)]^{2+}$ (and presumably other complexes of the type $[Ni(L_2)(L_3)]^{2+}$), where all As donors have been shown to be coordinated, oxidations are not isolated on the ligands. In the case of $[Ni(mtas)_2]^{2+}$ and $[Ni(ptas)_2]^{2+}$, oxidation at the uncoordinated terminal $-AsMe_2$ group must be considered. However, for five-coordinate $[Pd(mtas)_2]^{2+}$, a single two-electron oxidation is observed, consistent with the formation of Pd(IV), and there is no evidence of ligand-based processes.[17] Further, the reversibility of the oxidations (in contrast to the irreversible oxidations of the free ligands) and the similarities of the electrochemistries of complexes of the types $[Ni(L_2)(L_3)]^{2+}$ and $[Ni(L_3)_2]^{2+}$ suggest similar processes, and hence we propose formation of Ni(III) and Ni(IV) species for all complexes.

Comparison of the cyclic voltammetric response in acetonitrile–$[Bu_4N]ClO_4$ and dichloromethane–$[Bu_4N]PF_6$ provides further confirmation of these assignments. In the very weakly coordinating dichloromethane medium, formation of Ni(IV) species is not observed for any complex of the type $[Ni(L_2)(L_3)]^{2+}$; this is consistent with the inability of these complexes to achieve octahedral coordination. In contrast, reversible formation of octahedral $[Ni(ptas)_2]^{4+}$ in the same electrolyte may occur via binding of the dangling $-AsMe_2$ group. In acetonitrile–$[Bu_4N]ClO_4$, formation of complexes based on $[Ni(L_2)(L_3)]^{4+}$ can occur via coordination of acetonitrile or perchlorate. Reversible formation of $[Ni(L_2)(L_3)]^{3+}$ species in dichloromethane–$[Bu_4N]PF_6$ suggests that this oxidation state is five-coordinate.

The relative electrode kinetics of the Ni(II/I) and Ni(I/0) couples (fast and slow, respectively) is opposite to that normally observed for square-planar nickel complexes.[18] For the latter species, a rate-limiting square-planar-to-tetrahedral structural change occurs at the Ni(II/I) step. In contrast, the five-coordinate Ni(II) complexes described here presumably generate five-coordinate Ni(I) complexes with a rate-limiting change to tetrahedral stereochemistry on formation of Ni(0). For all complexes where the $\Delta E_p$ values of the Ni(III/II) and Ni(IV/III) couples can be compared, larger values are found for the former couple, indicating slower electrode kinetics for the Ni(III/II) step (see Tables I and II). Hence we propose that a rate-limiting structural distortion occurs on formation of Ni(III) followed by relatively facile formation of octahedral Ni(IV). [For the Ni(I/0) couple, slow electron transfer is consistent with structural change accompanying a change in coordination number. However, structural change does not necessarily lead to slow charge transfer[1] and slow charge transfer need not arise from a change in coordination number.[18] Hence the results for the oxidation steps are not self-contradictory.] Equation 3 summarizes the results described above.

$$\underset{\text{4 coordinate}}{\mathrm{Ni(0)}} \overset{e^-}{\rightleftharpoons} \underset{\text{5 coordinate}}{\mathrm{Ni(I)}} \overset{e^-}{\rightleftharpoons} \underset{\text{5 coordinate}}{\mathrm{Ni(II)}} \overset{e^-}{\rightleftharpoons} \underset{\text{5 coordinate}}{\mathrm{Ni(III)}} \overset{e^-}{\rightleftharpoons} \underset{\text{6 coordinate}}{\mathrm{Ni(IV)}} \quad (3)$$

It is interesting to compare $\Delta E_p$ values for the Ni(I/0) and Ni(III/II) couples for $[Ni(mtas)_2]^{2+}$ with those for the complexes $[Ni(L_2)(mtas)]^{2+}$ and for $[Ni(ptas)_2]^{2+}$ with those for the complexes $[Ni(L_2)(ptas)]^{2+}$. $\Delta E_p$ values are in all cases larger for the heteroleptic complexes, indicating slower electrode kinetics for these complexes. This may be attributed to the greater flexibility of the tridentate ligands allowing faster structural reorganizations.

**Effects of Electrolyte, Solvent, and Electrode Material.** To further probe the role of solvent and electrolyte anions, cyclic voltammetry of $[Ni(mtas)_2]^{2+}$, $[Ni(ptas)_2]^{2+}$, and $[Ni(diars)(mtas)]^{2+}$ was performed in acetonitrile–0.1 M $[Bu_4N]PF_6$ and dichloromethane–0.1 M $[Bu_4N]ClO_4$ (latter complexes only), and the responses were compared at Pt and GC electrodes. Table II lists $\Delta E_p$ values for each couple, and representative cyclic voltammograms are shown in Figures 1b,c, 2b, and 3c. The behavior of $[Ni(mtas)_2]^{2+}$ and $[Ni(ptas)_2]^{2+}$ is qualitatively similar to that described earlier; for $[Ni(diars)(mtas)]^{2+}$ in dichloromethane, transient formation of a Ni(IV) species is observed in the presence of $[Bu_4N]ClO_4$ (Figure 3c).

The electrolyte, solvent, and electrode material have a strong influence on $\Delta E_p$ values for Ni(III/II) couples. In acetonitrile, using a GC electrode, $\Delta E_p$ values are dramatically larger when $[Bu_4N]PF_6$ replaces $[Bu_4N]ClO_4$ as the electrolyte. For example,

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in the case of $[Ni(mtas)_2]^{3+/2+}$, $\Delta E_p$ increases from 70 to 190 mV, representing a decrease by a factor of approximately 20 in the standard heterogeneous rate constants.[19] Changing from a GC to a Pt electrode in the presence of $[Bu_4N]ClO_4$ does not significantly alter $\Delta E_p$ but $\Delta E_p$ in the presence of $[Bu_4N]PF_6$ is reduced. For $[Ni(mtas)_2]^{3+/2+}$, $\Delta E_p$ decreases from 190 mV (GC) to 95 mV (Pt) corresponding to an increase by a factor of approximately 5 in the standard heterogeneous rate constants.[20] In contrast, measurements in dichloromethane reveal no systematic dependence of $\Delta E_p$ on electrode material or electrolyte anion. Using GC and $[Bu_4N]PF_6$ as electrolyte, $\Delta E_p$ for the Ni(III/II) couple decreases on changing the solvent from acetonitrile to dichloromethane. In the case of $[Ni(ptas)_2]^{2+}$ for example, $\Delta E_p$ decreases from 300 to 110 mV, representing a 10-fold increase in the rate of the electrode kinetics in dichloromethane.[20]

The influence of medium and electrode material on electrode potentials was also examined. In most cases, the Ni(II/I) couples are electrochemically reversible, and hence $E_{1/2}$ values are a good approximation to $E^{\circ\prime}$ values. For these couples, there is no dependence of $E^{\circ\prime}$ on experimental conditions. The quasi-reversibility of the other couples prevents determination of thermodynamically significant data, and hence $E^{\circ\prime}$ values cannot be compared under different experimental conditions.

The kinetic effects described above may originate either in ion-pairing phenomena or in changes in the coordination sphere of Ni(III) via coordination of solvent and/or anions. Considering the possibility of coordination effects, to account for the differences in rate of the Ni(III/II) couples in different media at GC, it must be proposed that when present, perchlorate coordinates leading to relatively fast electrode kinetics and in the absence of perchlorate, acetonitrile coordinates, resulting in significantly slower electron transfer. Further, in the absence of both perchlorate and acetonitrile (i.e. in dichloromethane–$[Bu_4N]PF_6$), Ni(III) remains five-coordinate and the electrode kinetics are fast relative to those in acetonitrile–$[Bu_4N]PF_6$. While this scheme cannot be completely discounted, we are unable to suggest any physical basis for the dependence of the electrode kinetics on the coordination sphere. Ion-pairing effects on the other hand provide a simple explanation if it is assumed that the rate of electron transfer increases as the strength of ion pairing between the nickel complex and anion of the supporting electrolyte increases. Stronger ion pairs form in dichloromethane than in the more polar acetonitrile, and perchlorate is expected to ion-pair more strongly than hexafluorophosphate, consistent with the known ion-pairing ability of perchlorate in nonaqueous solvents.[21] The kinetics of the Ni(III/II) couple in dichloromethane do not, however, show a dependence on electrolyte anion, and this indicates that both anions form strong ion pairs in dichloromethane (a solvent leveling effect). In contrast, there is discrimination between the anions in acetonitrile, resulting in stronger ion pairs and faster kinetics in the presence of perchlorate. Ion-pair formation is expected to be stronger for the more highly charged Ni(IV) complexes, but the dependence of the rate of electron transfer on anion is considerably less marked for the Ni(IV/III) couples. This may be attributed to an inherently higher rate of electron transfer for this couple. Although association of perchlorate with Ni(II) arsine complexes in dichloromethane and acetone solutions has previously been reported,[22] the insensitivity of the kinetics of the Ni(II/I) couples to electrolyte anion indicates that this interaction is not significant for the complexes described here.

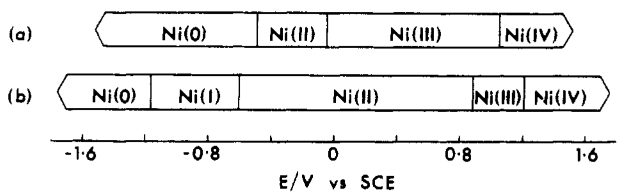

**Figure 4.** Approximate stability ranges (assuming $E^{\circ\prime} \simeq E_{1/2}$) of oxidation states of (a) $[Ni(diars)_2]^{2+}$ and (b) $[Ni(mtas)_2]^{2+}$ in acetonitrile. For $[Ni(diars)_2]^{2+}$, $E_{1/2}$ values are from ref 17 and have been converted from vs $Ag/Ag^+$ to vs SCE by adding 0.22 V.

Electrolyte effects on the rates of electrochemical reactions are well-known; the reduction of cyclooctatetraene (COT) is a good example. COT is reduced in two one-electron steps; the rate of the first step is slower than that of the second under all experimental conditions. In DMF and DMSO, the rate of electron transfer for the first reduction step increases as the cation size of the supporting electrolyte decreases, whereas the rate of the second reduction is unchanged.[23,24] It has been demonstrated that the extent of ion-pair formation depends on cation size, with the strongest ion pair occurring with the smallest cation. Hence the rate of the electrode reaction may also be assumed to depend on the strength of ion pairing.

The influence of the electrode material on the response of the Ni(III/II) couple indicates the participation of interfacial phenomena in the overall rate of electron transfer. Given the sensitivity of the electron transfer to the electrolyte, differences in the electrical double layer at Pt and GC may account for rate differences. Alternatively, stabilization of Ni(III) species via interactions between the arsine ligands and Pt may be important. A dependence of the rate of electrode reactions on electrode material is not uncommon; however, in most instances the origin of the dependence has not been elucidated.[25]

It is important to stress that although the rate of electron transfer for each couple depends to a variable extent on solvent, electrolyte, or electrode material, the first oxidation and second reduction steps always exhibit the slowest kinetics. This is consistent with rate-limiting structural changes concurrent with these electron transfers.

**Stabilities of the Oxidation States.** The ability of the ligands mtas and ptas to stabilize nickel oxidation states 0 to IV with respect to oxidation and/or reduction may be assessed from the electrochemical data, assuming $E^{\circ\prime} \approx E_{1/2}$. Figure 4 shows the stability range for each oxidation state of $[Ni(mtas)_2]^{2+}$ in acetonitrile–$[Bu_4N]ClO_4$. Also shown in the figure are the same data for $[Ni(diars)_2]^{2+}$ in acetonitrile.[15] This complex is reduced in a single two-electron step to $[Ni(diars)]^0$ and in the presence of chloride is oxidized to $[Ni(diars)_2Cl_2]^+$ and $[Ni(diars)_2Cl_2]^{2+}$. The patterns of stabilities for the complexes are dramatically different. Notably, $[Ni(mtas)_2]^+$ is stable over a potential range of 0.56 V whereas $[Ni(diars)_2]^+$ is unstable with respect to disproportionation. The stability range for $[Ni(mtas)_2]^{2+}$ is 1.49 V compared to 0.64 V for $[Ni(diars)_2]^{2+}$ whereas $[Ni(mtas)_2]^{3+}$ is stable over only 0.32 V compared to 1.10 V for $[Ni(diars)_2Cl_2]^+$.

The origin of these effects must lie in the different steric strains, ligand-field stabilization energies, and coordination numbers and geometries of each complex, and the relative contribution of each factor is difficult to determine. However, it appears that formation of Ni(II) species with the $As_5$ donor set is of major importance. Since the Ni(II) complexes adopt five-coordinate rather than four-coordinate geometries, additional stability must result from coordination of the fifth As donor. This may be the principal factor determining the stability of the Ni(II) species to oxidation

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(and the instability of Ni(III) complexes to reduction). The stability of the five-coordinate Ni(I) complexes is not unexpected, as Ni(I) complexes incorporating tetradentate tripodal np$_3$ ligands and halides have been isolated and characterized.[26] On the other hand, Dubois and co-workers[18] have demonstrated that, for four-coordinate nickel complexes of bidentate phosphines, minimum stability of the Ni(I) complexes occurs for undistorted square-planar geometry in the Ni(II) species. The rigidity and relatively small bite size of diars leads to a square-planar structure for $[Ni(diars)_2]^{2+}$ and hence to the lack of stability of the Ni(I) oxidation state.

The stabilities of the higher oxidation states to ligand dissociation can also be compared for each type of complex on the basis of the chemical reversibility of the redox couples. Clearly, Ni(IV) complexes derived from $[Ni(L_2)(L_3)]^{2+}$ are not entirely stable on the cyclic voltammetric time scale whereas the complexes $[Ni(L_3)_2]^{4+}$ are stable under these conditions. However, we have been unable to isolate any Ni(III) or Ni(IV) complex by bulk electrolysis and observe rapid decomposition of the electrogenerated species in solution. In contrast, the complexes $[Ni(diars)_2Cl_2]^{n+}$ and $[Ni(F_4\text{-}diars)_2Cl_2]^{n+}$ ($n = 1, 2$) and the bromo analogues have been isolated and characterized.[27-29] The lower stabilities of the complexes $[Ni(L_3)_2]^{n+}$ ($n = 3, 4$) are understandable on the basis of steric crowding of the As$_6$ and As$_5$ donor sets and greater flexibility of ptas and mtas, which facilitates ligand dissociation. Further, Ni–As bonding is expected to be weaker in the complexes $[Ni(L_3)_2]^{n+}$ ($n = 3, 4$) than in complexes incorporating halides. Halides reduce the effective charge on the metal center, reducing its hardness and hence promoting binding of the soft As donors.

## Conclusion

Formation of all nickel oxidation states 0 to IV for the complexes $[Ni(mtas)_2]^{2+}$ and $[Ni(ptas)_2]^{2+}$ can be attributed to the electronically and stereochemically accommodating donor sets. The strong $\sigma$-donor and $\pi$-acceptor properties of arsine ligands make them well suited to stabilization of a range of oxidation states. Tridenticity of the ligands allows the requisite Ni–As bond formation and cleavage reactions to occur without loss of complex integrity. Oxidation states I–III are five-coordinate, and the moderate flexibility of ptas and mtas permits conversion to tetrahedral Ni(0). Formation of Ni(IV) involves coordination of a dangling $-AsMe_2$ group; however, the moderate flexibility of the ligands contributes to the relatively low kinetic stabilities of the Ni(III) and Ni(IV) complexes.

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