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Vacuum Electrochemical Studies of Nickel(I) Products and Intermediates Produced in the Reduction of Nickel Dithiolenes

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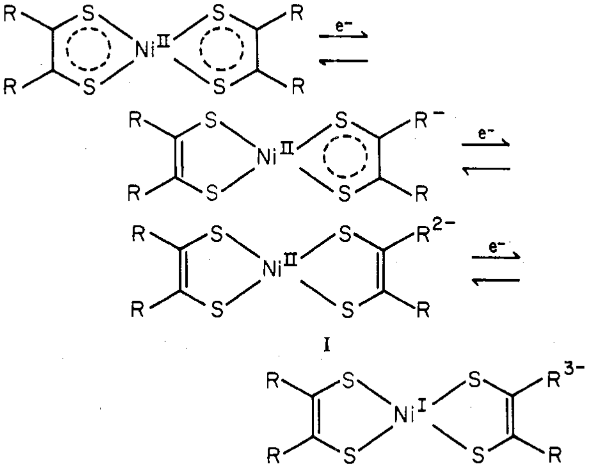
Redox properties of nickel 1,2-dithiolenes with strongly electron-withdrawing ligand substituents have been studied in nonaqueous solvents under rigorous vacuum-line conditions. Various electrochemical techniques, including voltammetry at the dropping mercury and rotating platinum electrodes, cyclic voltammetry, and controlled-potential coulometry, were employed. The reduction of nickel(II) dithiolene dianions proceeded reversibly to trianions containing Ni(I). $Ni[S_2C_2(CN)_2]_2^{3-}$ was stable in the absence of oxygen. However, $Ni[S_2C_2(CF)_2]_2^{3-}$ was subject to two parallel follow-up reactions in both acetonitrile and dimethoxyethane. The kinetics and mechanism of these reactions were investigated. Electrolytic preparation of $Ni[S_2C_2(CF_3)_2]_2$ and $\{Ni[S_2C_2(CN)_2]_2\}_n$ is reported. In both the CN- and CF_3-containing complexes only three of the four possible forms of the electron-transfer series (having 0 to 3− charge) are stable, with the more reduced forms being favored in the −CN complex and the more oxidized forms being favored in the $-CF_3$ complex.

Introduction

One of the most interesting areas of research in inorganic chemistry during the past decade has been concerned with the properties of metal 1,2-dithiolene complexes and their analogs. Of paramount interest have been the electron-transfer properties (e.g., eq 1) and metal–ligand delocalized ground states of the complexes, topics which have been exhaustively reviewed.[1-6] The first good indication that dithiolene ligands were capable of stabilizing metals in unusual oxidation states did not come until very recently, however, when it was discovered that a nickel bis(1,2-dithiolene) dianion could be reduced electrochemically to a trianion.[7] The special significance of this reduction was that, since the available π orbitals of the ligand were already filled in the dianion,[3] the extra electron was forced to go into a largely metal-based (d_{xy}) orbital, giving a rare[8-24] d^9, Ni(I), species. This conclusion was supported by the high g-value anisotropy in the ESR spectrum of the trianion.[7]



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In this paper we give the electrochemical details of the reduction of $Ni(mnt)_2^{2-}$ (I, R = CN)[25] and also report studies of the electroreduction of another nickel dithiolene, $Ni(tfd)_2^{2-}$ (I, R = CF_3),[25] which also involves formation of a Ni(I) product. These studies required development of certain vacuum electrolytic procedures which are reported herein. In addition, studies of the electrooxidation of the monoanions of $Ni(mnt)_2$ and $Ni(tfd)_2$ are reported.

Experimental Section

General Information. Na_2mnt, $Bu_4N[Ni(mnt)_2]$, $(Bu_4N)_2[Ni(mnt)_2]$, and $Bu_4N[Ni(tfd)_2]$ were prepared by the literature methods.[26] Acetonitrile (MCB Spectrograde) was stored under vacuum over calcium hydride and then vacuum distilled (bulb-to-bulb) immediately before use. 1,2-Dimethoxyethane (MCB) was stored similarly over lithium aluminum hydride. Dichloromethane (MCB Spectrograde) was refluxed over and then distilled from calcium hydride just before use. Bu_4NPF_6 (Ozark-Mahoning Co.) and Bu_4NClO_4 (G. F. Smith Co.) were recrystallized three times from ethanol and ethyl acetate, respectively, and dried under vacuum for 24 hr at 100°. Mercury was cleaned by repeated alternate washings in 10% solutions of nitric acid and potassium hydroxide separated by distilled water washings. Finally the mercury was distilled and stored in glass bottles. Uv-visible spectra were obtained on the Beckman DK-1A spectrophotometer, infrared spectra were recorded on the Beckman IR-10, and mass spectral analysis was achieved with the Consolidated Electrodynamics Corp. Type 21-104 mass spectrometer.

Electrochemical Procedures. All potentials are referred to the aqueous saturated calomel electrode (SCE). The potentiostat employed in these experiments was the Princeton Applied Research Model 173 (±100 V at 1 A). A conventional ramp input was used to provide a linear polarographic sweep, and a Hewlett-Packard Model 3300A/3302A function generator provided singular triangular wave forms for cyclic voltammetry. Voltammograms were recorded on either a Hewlett-Packard Model 7001A X-Y recorder (used for scan rates below ca. 0.8 V/sec) or a Tektronix Model 502A oscilloscope with camera attachment. Potentials were also monitored with a Simpson Model 2700 digital voltmeter. Coulometric measurements were performed by recording the current–time curve on a strip chart recorder and integrating the area under the curve. Voltammetry experiments at ambient pressure employed a conventional three-electrode configuration with a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode, separated from the solution by an agar bridge and a fine frit. The working electrode was either a dropping mercury electrode, a rotating platinum electrode (Sargent Synchronous rotator, 1800 rpm), or a Shain-type[27] hanging mercury drop electrode. When the platinum button electrode was used, the pretreatment consisted of refluxing the electrode in nitric acid, washing with water, and then soaking it in a saturated ferrous ammonium sulfate solution in 1 M sulfuric acid. After washing with water and drying with a Kimwipe, the electrode was inserted into the solution and poised first at −1.0 V and then at +0.1 V until, at each potential, a steady-state current was achieved. In a typical voltammetric experiment, the solvent was distilled under vacuum, then taken to a nitrogen-swept drybag, where the solution was made up and then transferred to the voltammetry cell. The solution was kept free of oxygen during the experiment by passing argon or nitrogen through a solvent saturation tower and then over the solution. Voltammetry experiments involving acetonitrile employed either 0.1 or 0.3 M Bu_4NPF_6 as supporting electrolyte, and in dimethoxyethane, 0.15 M Bu_4NPF_6 was used.

In situ monitoring of optical spectra of electrolysis solutions was accomplished with a three-electrode quartz cell which had a spectrophotometry cell serving as the working electrode compartment and which was placed directly in the spectrophotometer light path during the experiment.

Preparative-Scale Electrooxidations. A two-compartment electrolysis cell was employed with the anodic and cathodic half-cells separated by a 20-mm medium-porosity frit. A stopper inserted in

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the top of the anodic compartment held a platinum gauze cylinder, which served as the working electrode, and a fritted-glass tube (fine frit), into which an SCE with an agar salt bridge was inserted. A gas dispersion tube was also inserted if it was desired to purge the solution with an inert gas (this was found to be nonessential). A magnetic stirring bar was placed in the anodic compartment. Into the cathodic side was inserted a platinum spiral auxiliary electrode.

Preparation of Ni(tfd)$_2$. The electrolysis cell was filled (ca. 50 ml in the anodic side) with dried dichloromethane containing 0.1 *M* Bu_4NPF_6 and preelectrolysis treatment of the platinum gauze was carried out. The background current at +1.0 V was noted, and then 75 mg of $Bu_4N[Ni(tfd)_2]$ was added to the anodic compartment. The solution was not purged with inert gas. Electrolysis at +1.0 V vs. the SCE was initiated, and in the process of about 1 hr the originally brown solution had turned deep purple. Under our experimental conditions the current dropped typically to 4% of its initial value in 82 min. The solution from the anodic compartment was reduced to a few milliliters on a rotary evaporator. (If the solution was evaporated to dryness at this point, extensive decomposition to the monoanion occurred.) Addition of 50 ml of reagent grade isooctane precipitated most of the supporting electrolyte, and, after filtration, the purple solution was evaporated, then redissolved in pentane or isooctane, and refiltered. Finally, evaporation of this solution gave 41 mg of pure $Ni(tfd)_2$. The yield was 80% of theoretical based on the original quantity of monoanionic $Ni(tfd)_2$. This procedure may be scaled up to provide greater amounts of product, but longer electrolysis times may be required due to the high resistance of dichloromethane electrolysis solutions.

Preparation of Ni(mnt)$_2$. A 100-mg amount of $(Bu_4N)Ni(mnt)_2$ was added to the electrolyte in the anodic compartment of the cell previously described and electrolysis initiated at +1.2 V vs. SCE. As the electrolysis proceeded, a brown precipitate deposited on the cell walls and on the platinum gauze. The electrode had to be shaken periodically to allow completion of the electrolysis, which generally took 3–4 hr, the solution gradually becoming almost colorless during this time. The contents of the anodic side were filtered and the resulting solid washed with dry dichloromethane. After air-drying the yield was 40 mg. Coulometric measurements showed that approximately one electron per $Ni(mnt)_2^-$ molecule was consumed in the electrolysis. (This number ranged between 1.0 and 1.2 in four experiments.) Similar results were obtained using either Bu_4NClO_4 or Bu_4NPF_6 as supporting electrolyte, and it also appeared to be immaterial whether or not air was excluded by an argon purge.

The solid isolated from the electrolysis was insoluble in relatively nonpolar solvents, such as dichloromethane, chloroform, or hexane. If the solid was put into contact with more highly polar solvents, such as acetonitrile or acetone, the material gradually dissolved to give a brown solution, which could be shown by its absorption spectrum to correspond to quantitative conversion to $Ni(mnt)_2^-$. This behavior is reminiscent of the behavior of $Ni(tfd)_2$, which can be reduced to its monoanion by acetone or other polar, basic solvents. The absorption spectrum of the solid material in KBr showed bands at 900, 610 (sh), 500 (sh), 276 (the most intense band), and 220 nm. Although several of these bands fall at the same position in $Ni(mnt)_2^-$, the absence of the intense 313-nm band of $Ni(mnt)_2^-$ shows that the solid contained no significant fraction of the monoanion. The infrared spectrum of the air-dried solid in KBr showed features at 3350 (b, s), 2240 and 2210 (sp, s), 1610 (m), 1160 (m), 520 (m), and 500 cm^{-1} (m). After drying a sample for 24 hr at 100° under high vacuum, the water peaks at 3350 and 1610 cm^{-1} were no longer present. Anal. (dried sample). Calcd for $Ni[S_2C_2(CN)_2]_2$: C, 28.3; S, 37.8; N, 16.5; Ni, 17.3. Found: C, 29.7; S, 37.6; N, 16.5; Ni, 16.3.

Preparative-Scale Electroreductions. The vacuum electrolysis cell (Figure 1) was designed to meet the stringent requirements of dealing with air-sensitive electrolysis products while still allowing flexibility in the choice of electrochemical technique. The special features of this cell are (a) virtually grease-free operation, (b) no need for introduction of inert atmosphere after evacuation, and (c) freedom to do virtually any electrochemical experiment which could also be performed under normal, bench-top conditions. The rotating flask (V in Figure 1) used to fill the three electrode compartments ensured that the solvent would not contact grease, the sample-removal system and dropping mercury electrode (DME) were designed to operate at the solvent vapor pressure, and the movable cup (X) allowed flexibility in hanging mercury drops for cyclic voltammetry or in weighing drops (through transfer to the collecting flask) for evaluation of DME flow rate. Three electrode compartments comprised the main body of the cell. A small mercury pool in compartment B served as the auxiliary electrode and was separated from the working electrode compartment (C) by a 20-mm fine-porosity glass frit. Electrical contact to the pool was made with tungsten wire sealed through the cell wall. (For added strength, a small copper cap was cemented over the outside of all metal-to-glass seals.) Compartment A contained a platinum quasireference electrode. The wire was sealed through a 14/20 Pyrex glass stopper to facilitate cleaning of the cell and electrode. High-vacuum varnish (Varian Torr Seal) was used around the platinum-to-glass seal to ensure a vacuum-tight union. Solution contact between the reference and working electrode compartments was made through a 10-mm fine-porosity glass frit.

A choice from among three working electrodes was provided. A large mercury pool (F) located at the bottom of compartment C was used for controlled-potential electrolysis. In polarographic experiments, a dropping mercury electrode was used in place of the mercury pool. The former was equipped with a pressure equalization arm between the cell and the mercury column to avoid influence of a pressure differential on the column flow rate. The column height was changed by adjusting the pressure over the mercury reservoir (T) and opening the needle valve between the column and the cell. Given the relatively low vapor pressures of solvents commonly employed in electrochemical experiments, exposing the reservoir to atmospheric pressure through stopcock U will give a sufficiently high column. For experiments requiring a stationary mercury microelectrode, a hanging mercury drop electrode (HMDE), constructed as described elsewhere,[27] was provided through the ball–socket joint on the top of the cell, which also allowed for flexibility in positioning the electrode. A small glass cup (X), mounted on top of a glass-encased magnet and hung by a hook from the lip of the reference electrode compartment, was manipulated by an external horseshoe magnet and used to catch a drop of the DME and transfer it to the HMDE after the electrolyte solution has been added. After a few practice runs, this operation became trivial. The same cup was used to catch drops from the DME for transfer through funnel D into the collection flask, which could then be removed from the cell after closing stopcock K. Additional drops, perhaps taken at a different potential, could be removed after evacuation of a clean flask through stopcock J followed by reopening of stopcock K.

The vacuum-line manipulations required for operation of the cell (e.g., solvent transfer) were standard.[28] In a typical experiment, mercury for the counterelectrode and working electrode was placed in compartments B and C, supporting electrolyte in flask V and the electroactive species in cup X. After assembling the cell, the system, including the drop collection flask and sample receiving cell, was evacuated to 10^{-6} mm while heating the supporting electrolyte with a heat gun. The elevated temperature ensured removal of adsorbed air and moisture from the solid electrolyte. After evacuation, solvent was transferred into flask V via bulb-to-bulb distillation from a storage vessel on the vacuum line. The supporting electrolyte was dissolved in the melted solvent with aid of a magnetic stirring bar. After raising the DME, the electrolyte solution was poured into the three electrode compartments by proper rotation of flask V. The approximate volume of solution in the working electrode compartment was known from calibration marks on the side of the compartment. In our laboratory, the cell was operated at the vapor pressure of the solvent-supporting electrolyte system being used. If desired, however, the cell can be brought to atmospheric pressure with an inert gas.

A polarographic background scan was run on the solution before addition of electroactive species. The cup holding the electroactive species was then immersed in the working electrode compartment, after which it was returned to its original position, for use in further manipulations as described above. After a polarographic and/or cyclic voltammetric study of the preelectrolysis solution, controlled-potential coulometry at the large mercury pool was begun. At any time, the electrolysis could be interrupted and voltammograms of the electrolysis solution were obtained. At the completion of the electrolysis, the solution was withdrawn through valve L into cells appropriate for spectroscopic or ESR studies and sealed off with a torch. The authors will be happy to provide any other details about the construction and use of this cell to interested parties.

Results and Discussion

In a discussion of the electrochemical behavior of these compounds it is very important to distinguish between the

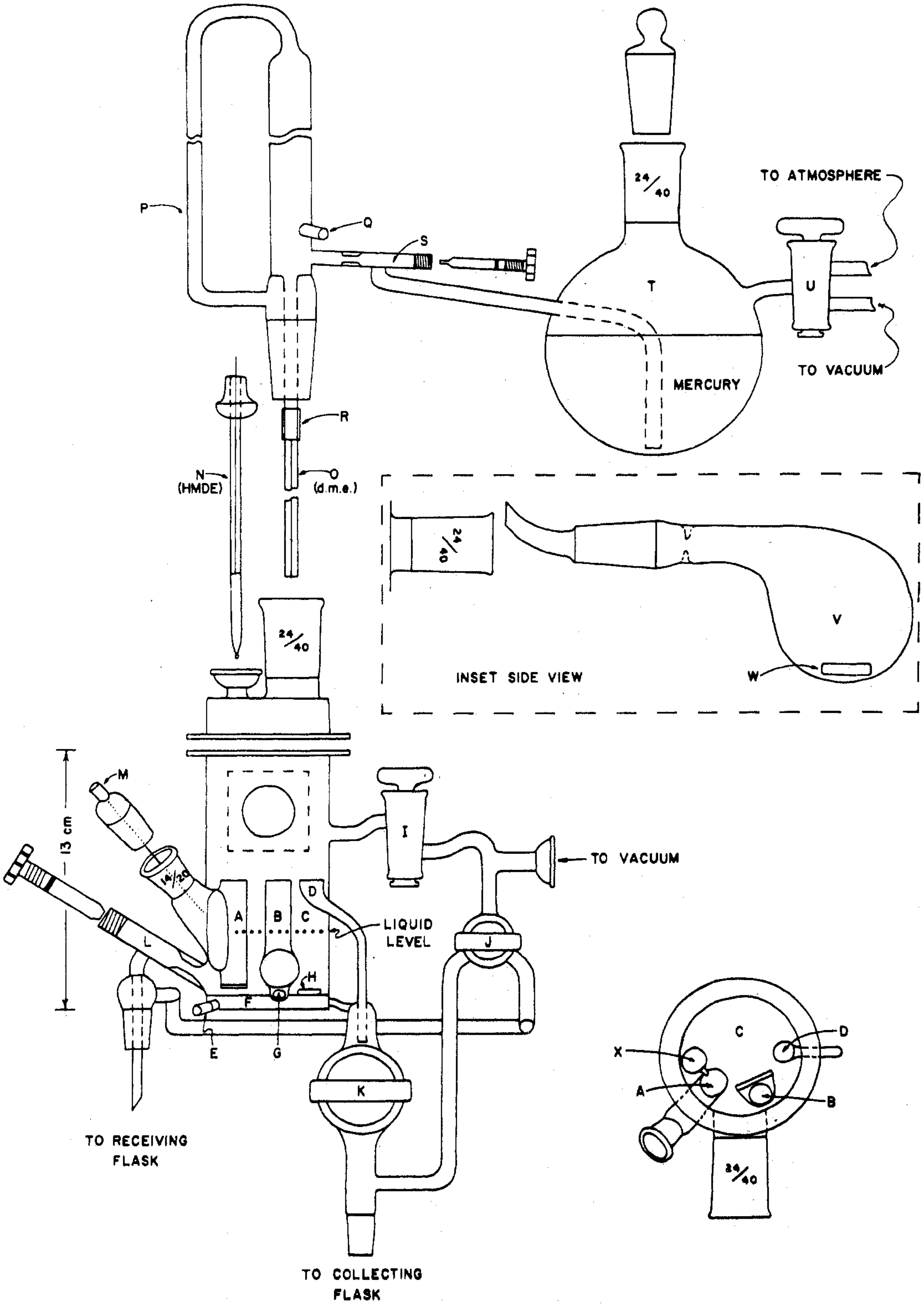


Figure 1. Side view and top view (lower right) of vacuum electrolysis cell: (A) reference electrode compartment, (B) auxiliary electrode compartment, (C) working electrode compartment, (D) funnel for transfer of mercury drops to collection flask, (E) electrode connection to working electrode mercury pool, (F) mercury pool, for use as working electrode, (G) electrode connection to auxiliary electrode mercury pool, (H) magnetic stirring bar, (I) 4 mm high vacuum stopcock, (J) 4 mm high three-way vacuum stopcock, (K) 6 mm high vacuum stopcock, (L) vacuum takeoff using a Fischer-Porter needle valve, (M) electrode connection to platinum wire quasireference electrode, (N) assembly for hanging mercury drop electrode, (O) capillary for dropping mercury electrode, (P) pressure-equalizing arm for DME, (Q) electrode connection for DME, (R) minimal length of neoprene tubing for joint of capillary tubing to DME column, (S) needle value to transfer mercury from (T) mercury reservoir, (U) three-way stopcock, (V) flask to hold supporting electrolyte and to collect solvent, (W) magnetic stirring bar, and (X) cup to hold sample and catch drops.

concepts of electrochemical reversibility and chemical reversibility. The reader who is unfamiliar with the distinction is referred to the electrochemical literature for detailed discussions,[29] but a few brief comments concerned with model electrode process, eq 2, will be made in order to facilitate the discussion below. *Electrochemical reversibility* refers strictly to the heterogeneous (electrode-to-electroactive species) electron-transfer step and is related in quantitative terms by

$$\mathrm{O} + n\mathrm{e}^- \underset{}{\overset{k_s}{\rightleftharpoons}} \mathrm{R} \xrightarrow{k_c} \mathrm{Z} \qquad (2)$$

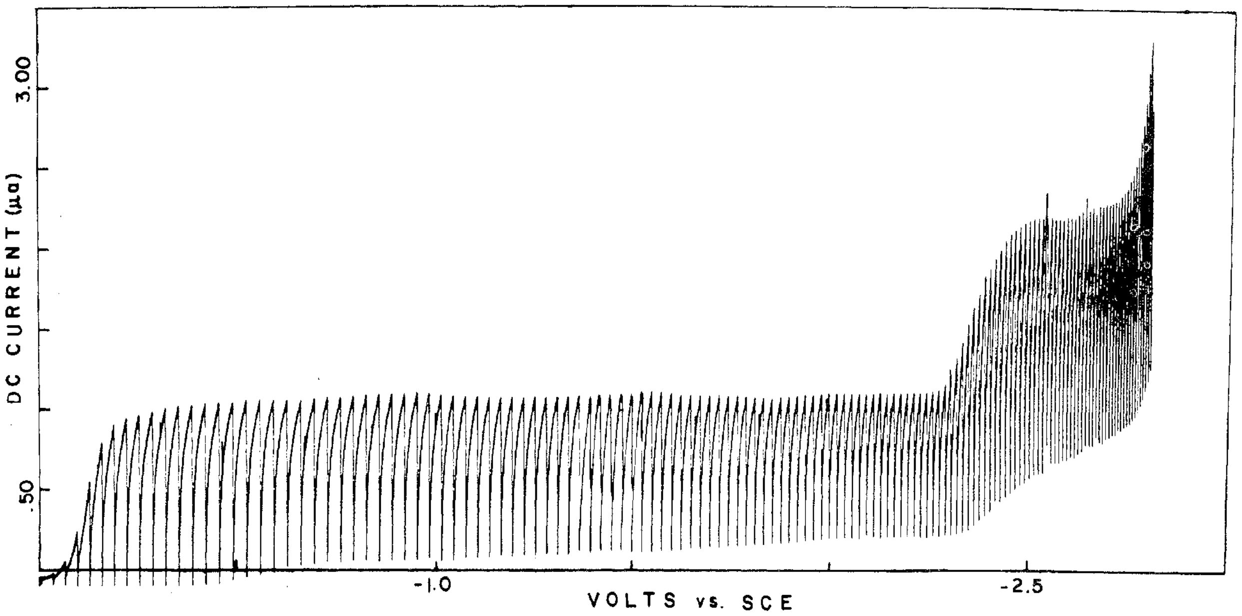


Figure 2. Polarogram of 2.0×10^{-4} *M* $[Bu_4N][Ni(tfd)_2]$ in CH_3CN–Bu_4NPF_6.

Table I. Voltammetric Data for Nickel Dithiolenes

		$E_{1/2}$[a]				I_d[e]	
Compd	Solvent	$0 \rightleftharpoons 1-$[b,c]	$1- \rightleftharpoons 2-$	$2- \rightleftharpoons 3-$	Slope[d] of $2- \rightleftharpoons 3-$	$1- \rightleftharpoons 2-$	$2- \rightleftharpoons 3-$
$Ni(mnt)_2^z$	Glyme[i]	*f*	+0.23	−1.74	57 (3)[g]	1.8 (1)	1.7 (1)
$Ni(mnt)_2^z$	CH_3CN	+1.02[h]	+0.23	−1.68	60 (2)	2.5 (1)	2.6 (1)
$Ni(tfd)_2^z$	Glyme	*f*	−0.13	−2.30	55 (2)	2.4 (1)	2.3 (1)
$Ni(tfd)_2^z$	CH_3CN	+0.92[h]	−0.12	−2.44	87 (14)	2.8 (2)	4.6 (2)

[a] Volts vs. SCE. [b] Value of z (charge). [c] Data for $0 \rightleftharpoons 1-$ couple obtained with rotating platinum electrode. Others obtained with dropping mercury electrode. [d] Slope from plot of $-E$ vs. log $[i/(i_d - i)]$ in millivolts. [e] Diffusion current constant ($= i_d/m^{2/3}t^{1/6}c$). The values given are for each individual wave, rather than for a composite total of both waves. [f] Not measured. [g] Numbers in parentheses give uncertainty in last figure (standard deviation). [h] Data from A. Davison et al., *Inorg. Chem.*, **2**, 1227 (1963). [i] 1,2-Dimethoxyethane.

k_s, the standard heterogeneous rate constant. A rapid (i.e., reversible) electron-transfer step (Nernstian behavior) implies that no gross structural changes occur between the oxidized form (O) and reduced form (R) of the redox couple,[30,31] but the k_s value gives no information on the chemical stability of R. In studies primarily concerned with the generation, reaction pathways, and ultimate fate of the electrode product R, the factor of paramount importance is the *chemical reversibility* of the redox couple, referring to chemical stability of R (related to follow-up reaction k_c).[32] In the present study a variety of techniques was used to show that (a) the *reduction* of $Ni(mnt)_2^{2-}$ is both chemically and electrochemically reversible, (b) both aspects of the reversibility of the $Ni(tfd)_2^{2-}$ reduction are solvent dependent, and (c) the *oxidation* of $Ni(mnt)_2^-$ is chemically irreversible.

The Reduction $Ni^{II}L_2^{2-} \rightleftharpoons Ni^{I}L_2^{3-}$. Both $Ni(mnt)_2^{2-}$ and $Ni(tfd)_2^{2-}$ were reduced in aprotic solvents. (Figure 2 shows the two successive reductions of $Ni(tfd)_2^-$ in acetonitrile.) Although both of these complexes had been previously subjected to electrochemical studies,[35,36] reduction of the dianion had not been reported by other groups. Use of a mercury working electrode extended the cathodic window to approximately −2.8 V vs. SCE, using various aprotic solvents and tetraalkylammonium supporting electrolytes, and allowed observation of the dianion reductions. Since the 1,2-dithiolate complexes are not labile,[37] reaction between the mercury electrode and the sulfur-containing ligands was not expected. Indeed, no evidence for kinetic control or preelectrode reaction coupled to the electron-transfer step was found. Furthermore, in the case of $Ni(mnt)_2^{2-}$, the reduction to the Ni(I) species occurred at a positive enough potential so that the reduction could also be monitored at a platinum electrode showing that the observed reduction was characteristic of the nickel complex alone and was not due to reaction with the electrode material.

The $Ni(mnt)_2^{2-}$ Reduction. The reduction of $Ni^{II}(mnt)_2^{2-}$ to $Ni^{I}(mnt)_2^{3-}$ was electrochemically and chemically reversible in both acetonitrile and dimethoxyethane. A number of criteria were employed in establishing this reversibility. (The process was shown to be diffusion controlled by plots of polarographic limiting currents vs. square root of the corrected mercury column height,[38] which were linear and passed through the origin in both solvents.) Linear plots of polarographic dc potential vs. −log $[i/(i_d - i)]$ were obtained (Table I) with slopes within experimental error of that expected for a Nernstian one-electron process (59 mV). The reduction was confirmed as a one-electron process by comparison of the diffusion current constants, I_d (Table I), with those of the known[36] one-electron oxidation of $Ni(mnt)_2^{2-}$ in each solvent. For reasons discussed above, the stability of the one-electron reduction product had to be established by other methods, and this was first established by cyclic voltammetry experiments. As Nicholson and Shain have pointed out,[34] a completely reversible electrode process is characterized by a unity value of the anodic-to-cathodic current ratio (i_a/i_c), cathodic–anodic peak separations of about 61 mV,[39] and values of the half-peak potential ($e_{p/2}$) and peak current function ($i_{p_c}/v^{1/2}$, where v is the scan rate) which are independent of scan rate. CV experiments at the HMDE over the scan rate range of 0.03–50 V/sec confirmed that these criteria held for the $Ni(mnt)_2^{2-}$ reduction in CH_3CN. Similar data were obtained in glyme, but at higher scan rates (≥3 V/sec), peak current separations exceeded the reversible value due to the high uncompensated resistance of this poorly conducting electrolyte.

Dilute solutions of $Ni^{I}(mnt)_2^{3-}$ were prepared in either

Table II. Selected Cyclic Voltammetry Data for the Reduction of 3×10^{-4} *M* $Ni(tfd)_2{}^{2-}$ at a Hanging Mercury Drop Electrode[a]

ν[b]	i_a/i_c[c]	$i_{p_c}/\nu^{1/2}$[d]	$e_{p_a} - e_{p_c}$[e]	$e_{p/2}$[f]
In Glyme–Bu_4NPF_6				
0.05	0.92	6.7	68	−2.260
0.07	0.94	6.6	66	−2.260
0.09	0.97	6.5	66	−2.260
0.11	0.98	6.5	66	−2.260
0.13	0.98	6.4	66	−2.262
0.16	0.98	6.3	68	−2.262
0.45	0.99	6.4	68	−2.262
0.81	1.00	6.2	64	−2.264
0.99	1.00	6.2	68	−2.260
In Acetonitrile–Bu_4NPF_6				
0.10		8.2	*g*	−2.325
0.14		7.0	*g*	−2.341
0.19		6.6	*g*	−2.323
0.24		6.5	250	−2.327
0.47		6.1	264	−2.337
0.95		5.8	300	−2.349
4.74		5.6	377	−2.382
11.1		5.6	462	−2.391
23.7		5.6	508	−2.429

[a] The data quoted are for the second reduction process of a solution containing the monoanion $Ni(tfd)_2{}^-$. [b] Scan rate in volts per second. [c] Anodic to cathodic current ratio. [d] Current function given in arbitrary units. No correspondence between the current functions in the two different solvents is intended, because the data were taken on electrodes of different size. [e] Peak potential separation in millivolts. [f] Potential in volts at half-peak height vs. SCE. [g] Not measured because of broad anodic peak.

CH_3CN or glyme by electrolysis of approximately millimolar solutions of the Ni(II) precursor at a large mercury pool in the vacuum electrolysis cell at −1.8 V. The color changed from orange to green as the electrolysis progressed and the number of electrons transferred (*n*) was measured by coulometry at 1.00 ± 0.01. Polarograms of the reduced solution gave the oxidation wave (at a half-wave potential equal to that of the original reduction wave) of the Ni(I) species; comparison of the plateau height with that of the original Ni(II) reduction wave indicated that a quantitative conversion to Ni(I) had been achieved. The Ni(I) species was extraordinarily air sensitive, and our many attempts to transfer electrolyzed solutions quantitatively from the cell into evacuated (10^{-6} mm) sample tubes met with failure due to partial regeneration of the Ni(II) complex in the takeoff process. (In situ techniques were employed to obtain uncontaminated spectra of the Ni(I) complex.[7]) Therefore, no attempt at isolation of the Ni(I) salt was made. Resetting the electrode potential positive of −1.6 V resulted in complete regeneration of the original Ni(II) complex.

The $Ni(tfd)_2{}^{2-}$ Reduction. In this case, the polarographic slope and I_d value in glyme were consistent with a one-electron electrochemically reversible process, and CV measurements of peak separations (Table II) confirmed this. At CV scan rates above ~0.1 V/sec, the ratio i_a/i_c indicated a stable Ni(I) trianion, but this value fell significantly below unity at slower scan rates (Table II). Concomitant with the decrease in i_a/i_c was a slight increase in the cathodic current function which was barely outside of experimental error. These deviations from *chemically* reversible behavior, diagnostic of follow-up reaction(s) coupled to the electron-transfer step, were manifested near the lower scan rate limit for reliable CV data,[40] so the reactions were more appropriately studied by long-term, large-scale electrolytic procedures. Inspection of the current–time curve for this electrolysis compared to that obtained in the $Ni(mnt)_2{}^{2-}$ electrolysis (Figure 3) showed that whereas the reduction of $Ni(mnt)_2{}^{2-}$ was 90% complete in less than 0.1 hr, a decrease of 60% in electrolysis current required approximately 2.0 hr for $Ni(tfd)_2{}^{2-}$. Electrolysis conditions were nominally identical. Our coulometric measurements indicated that in this 2-hr period, the equivalent of approximately 6 electrons/molecule was consumed. Polarograms obtained periodically throughout the electrolysis showed no waves except those due to the starting material (never was there an indication of an anodic current from the presence of $Ni(tfd)_2{}^{3-}$), and the plateau currents for those waves decreased as the electrolysis proceeded. This indicated that the steady-state concentration of the Ni(I) product was zero[41] and that the effect of the follow-up reaction(s) was to exhaust the original Ni(II) compound while providing no electroactive product(s). The electrolysis was monitored spectrally in the uv–vis range with the in situ electrolysis cell. In several experiments, including one which proceeded until virtual exhaustion of the original Ni(II) compound, only spectral features characteristic of the Ni(II) starting material were observed. The color of solutions exhaustively electrolyzed was a light brown. Serious attempts to characterize the ultimate electrolysis products were not made, but their lack of electroactivity and measurable electronic spectra suggest a gross structural change from that of the original dithiolene, probably involving disruption of the metal–ligand complex.

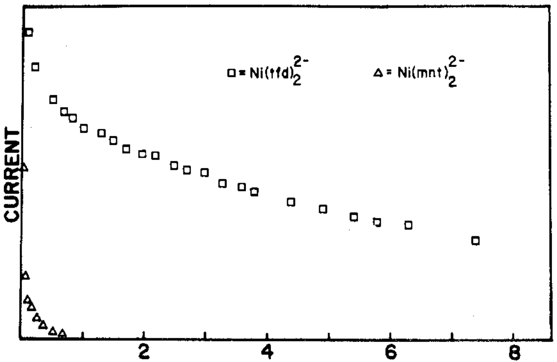
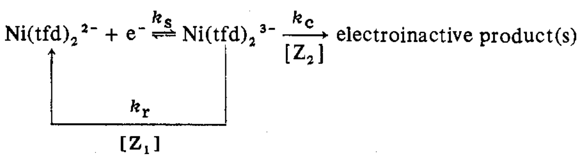


Figure 3. Normalized current–time curves from controlled-potential coulometry of the reduction of (Δ) $Ni(mnt)_2{}^{2-}$ and (□) $Ni(tfd)_2{}^{2-}$ in dimethoxyethane–Bu_4NPF_6.

Electrochemical data on the $Ni(tfd)_2{}^{2-}$ reduction were consistent with eq 3 in which the Ni(I) product is subject to



$$Ni(tfd)_2{}^{2-} + e^- \underset{}{\overset{k_s}{\rightleftharpoons}} Ni(tfd)_2{}^{3-} \xrightarrow[{[Z_2]}]{k_c} \text{electroinactive product(s)} \qquad (3)$$
$$Ni(tfd)_2{}^{3-} \xrightarrow[{[Z_1]}]{k_r} Ni(tfd)_2{}^{2-}$$

two competing follow-up reactions, R and C. Reaction R (rate constant k_r), resulting in regeneration of the Ni(II) complex, occurs through reaction of the Ni(I) species with some component of the electrolyte solution—most likely the solvent itself, although undetected solvent impurities cannot be ruled out. It is likely that the oxidant Z_1 is in manyfold excess of the nickel complex and that in the absence of reaction C (rate constant k_c) a high steady-state electrolysis current would be obtained. However, the parallel reaction C effectively used up the Ni(II) starting material and caused the slow decrease in electrolysis current. The current–time curve obtained in the controlled-potential coulometry experiments can be used to help to measure the rate of the follow-up reactions. The basic theory for the case of parallel catalytic regeneration and irreversible follow-up reactions was treated by Geske and Bard.[42] Their treatment assumed a pseudo-first-order rate constant for k_r but a second-order rate constant for k_c. A simple modification of their treatment, assuming a pseudo-first-order rate constant for k_c also, allows an analytical solution of the equation relating the bulk concentration of electroactive species, [O], to the electrolysis time, t. Equation 4 presents this solution in terms of the rate constants k_r and

$$\ln\,[\mathrm{O}] - \ln\,[\mathrm{O}]_0 = p_0\left(\frac{k_r}{k_r + k_c} - 1\right)t \qquad (4)$$

k_c and the experimental hydrodynamic parameter, p_0, which is dependent on cell geometry, diffusion coefficient, and stirring rate. In this expression, $[\mathrm{O}]_0$ is the original concentration of $\mathrm{Ni(tfd)_2}^{2-}$. p_0 was evaluated in the traditional manner[43] by plotting ln i vs. t for the one-electron $\mathrm{Ni(tfd)_2}^- \rightarrow \mathrm{Ni(tfd)_2}^{2-}$ electrolysis used to prepare our $\mathrm{Ni(tfd)_2}^{2-}$ starting solution. This procedure ensured that p_0 would be obtained for electrolysis conditions identical with those employed in the $\mathrm{Ni(tfd)_2}^{2-}$ reduction. A plot of ln $[\mathrm{Ni(tfd)_2}^{2-}]$ (measured by the polarograms taken during the electrolysis) vs. t yielded a straight line and a value for $k_r/(k_r + k_c)$ of 0.17. A value for the rate constant k_c was obtained directly from CV measurements of the i_a/i_c ratio at slow scan rates, using the method of Nicholson and Shain.[44] A value of 0.018 sec^{-1} was obtained, and when this was inserted into the value of $k_r/(k_r + k_c)$ obtained by controlled-potential coulometry, a value of 0.0037 sec^{-1} was obtained for k_r, the rate of the regeneration reaction.

Effect of Solvent on the $\mathrm{Ni(tfd)_2}^{2-}$ Reduction. When the solvent was changed from glyme to acetonitrile, several changes in the reduction characteristics of $\mathrm{Ni(tfd)_2}^{2-}$ were noted: (1) the reduction potential shifted negatively by ca. 150 mV (Tables I and II), (2) the polarographic wave height increased (Table I), and (3) the redox couple showed a considerable degree of *electrochemical* irreversibility. (In CV, large anodic–cathodic peak separations were observed—see Table II.) Thus, both the electron-transfer step and the follow-up reactions were affected by the solvent change. From a measurement of the CV peak separations as a function of scan rate,[39] a k_s value of 1.0×10^{-3} cm sec^{-1} was obtained. This represented a 200-fold decrease from the value of 0.2 measured by the same method for the $\mathrm{Ni(mnt)_2}^{2-}$ reduction in the same solvent. Both $\mathrm{Ni(mnt)_2}^{2-}$ and $\mathrm{Ni(tfd)_2}^{2-}$ gave rapid, reversible electron transfers in glyme, in which the k_s measurement was limited by electrolyte resistance, with $k_s > 0.05$ cm sec^{-1}. The Marcus theory[30] of electron-transfer rates suggests that slow electron transfers such as that observed for $\mathrm{Ni(tfd)_2}^{2-}$ in acetonitrile are due to either reorganization of the solvent dielectric around the electroactive species or actual structural changes in the molecule which occur in the transition state of the electron-transfer process. Since the k_s values in glyme for both $\mathrm{Ni(mnt)_2}^{2-}$ and $\mathrm{Ni(tfd)_2}^{2-}$ are high, it is probable that the $\mathrm{NiS_4}$ moiety is not subject to a stereochemical rearrangement, e.g., from square planar to tetrahedral, upon reduction from Ni(II) to Ni(I). However, the solvent dependence of the $\mathrm{Ni(tfd)_2}^{2-}$ k_s value suggests that a change in solvent coordination occurs in acetonitrile when $\mathrm{Ni^{II}(tfd)_2}^{2-}$ is reduced to $\mathrm{Ni^{I}(tfd)_2}^{3-}$.

Electrochemical experiments on the preparative-scale (controlled-potential coulometry, in situ electrolysis in optical cell, etc.) gave results qualitatively the same as those observed in glyme, so it was assumed that parallel catalytic and irreversible follow-up reactions were also present in this solvent. Under this assumption, the enhancement of the I_d value for the $\mathrm{Ni(tfd)_2}^{2-}$–$\mathrm{Ni(tfd)_2}^{3-}$ reduction over that of $\mathrm{Ni(tfd)_2}^{-}$–$\mathrm{Ni(tfd)_2}^{2-}$, a factor of 1.6 (Table I), would reflect the extent of the catalytic regeneration reaction. Using the method of Delahay and Stiehl,[45] a value of 1.7 sec^{-1} was calculated for k_r in acetonitrile. An independent measurement of this rate constant was obtained from consideration of the CV cathodic current function. Values of $i_{p_c}/v^{1/2}$ were higher at slower sweep rates (Table II), again reflecting the effect of the regeneration step at longer experiment lifetimes. Nicholson and Shain have shown how to use these enhanced currents to measure the rate of a regeneration reaction.[34] One employs a working curve of $(k_r/a)^{1/2}$, where a is a parameter proportional to the scan rate, vs. the ratio of the observed cathodic peak current to the diffusion-controlled peak current (the latter obtained from the fast CV current function). A value for k_r of 2.5 sec^{-1} was obtained using this procedure, in reasonably good agreement with the value of 1.7 sec^{-1} obtained polarographically. We were not able to measure a rate constant for k_c due to the drawn-out nature of the anodic portion of the cyclic voltammogram, and coupled polarographic–coulometric experiments, such as those used to measure $k_r/(k_r + k_c)$ in glyme, were not pursued. A summary of the heterogeneous and homogeneous rate constants found in this study is given in Table III.

Table III. Rate Constants Involved in the Electrochemical Reduction of Nickel Dithiolene Dianions

Compd	Solvent	10^3k_s, cm sec^{-1}	k_r, sec^{-1}	k_c, sec^{-1}
$\mathrm{Ni(mnt)_2}^{2-}$	Glyme	$>50^a$	Trianion stable	
$\mathrm{Ni(mnt)_2}^{2-}$	$\mathrm{CH_3CN}$	200	Trianion stable	
$\mathrm{Ni(tfd)_2}^{2-}$	Glyme	$>50^a$	3.7×10^{-3}	1.8×10^{-2}
$\mathrm{Ni(tfd)_2}^{2-}$	$\mathrm{CH_3CN}$	1	2.1	b

[a] Lower limit given. Measurement limited by uncompensated resistance. [b] Not measured.

The Oxidation $\mathrm{NiL_2}^- \rightleftharpoons \mathrm{NiL_2}^0$. Since stable neutral nickel dithiolenes are known with a variety of substituents,[46] a brief word of explanation is in order explaining our interest in this oxidation process. First, we were interested in designing a synthetic route to $\mathrm{Ni(tfd)_2}^0$ which circumvented the use of highly toxic nickel carbonyl. It was felt that a safer route to the complex would lead to greater utility of $\mathrm{Ni(tfd)_2}^0$ as a one-electron oxidant, for it has been shown to have definite advantages in studies of donor–acceptor complexes[47-49] and ion–radical salts.[48,50] Since Davison et al.[51] had already shown that the monoanion $\mathrm{Ni(tfd)_2}^-$ could be synthesized starting with nickel(II) salts, it was only necessary to develop conditions for the macroscale oxidation of the monoanion to the neutral compound. As detailed in the Experimental Section, a high yield of $\mathrm{Ni(tfd)_2}^0$ was obtained from the electrolytic oxidation of $\mathrm{Ni(tfd)_2}^-$ at a platinum electrode in carefully dried $\mathrm{CH_2Cl_2}$ solution containing $\mathrm{Bu_4NPF_6}$ as supporting electrolyte.

It was decided also to attempt preparation of neutral $\mathrm{Ni(mnt)_2}^0$, which had not been previously isolated and which promised to be an even stronger oxidant because of its higher reduction potential (Table I). The neutral dithiolenes are stabilized by relatively nonbasic solvents such as dichloromethane, and the oxidation of $\mathrm{Ni(mnt)_2}^-$ in the more basic solvent dimethyl sulfoxide was reported to be a multielectron irreversible process,[51] but the oxidation was widely assumed to be reversible in dichloromethane.[52-54] However, brief inspection of this redox couple by cyclic voltammetry on a platinum microelectrode in $\mathrm{CH_2Cl_2}$–$\mathrm{Bu_4NPF_6}$ showed that the oxidation of $\mathrm{Ni(mnt)_2}^-$ did not simply involve formation of $\mathrm{Ni(mnt)_2}$. Indeed, there was no evidence on this time scale (several seconds) for the existence of neutral $\mathrm{Ni(mnt)_2}$. If the scan was extended to potentials far more positive of the peak (e.g., another 0.5 V) before switching the scan direction, a more reversible-looking voltammogram was obtained. This behavior is sometimes found in electrode reactions where film formation occurs at the electrode surface. When the oxidation of this anion was performed on a macroscale at a large platinum gauze, a brown precipitate formed as the product. This solid material could not be obtained in high purity; it was invariably contaminated with trace amounts of $\mathrm{(Bu_4N)Ni(mnt)_2}$ and more appreciable amounts of water which were apparently picked up in the work-up procedure. Analysis of a dried sample was in good agreement with that expected for the empirical formula $NiS_4C_8N_4$. Recrystallization was impossible because the only solvents in which the material was soluble reduced it immediately to $Ni(mnt)_2^-$. If the solid material was put into contact with a fairly basic solvent, such as acetone or acetonitrile, it dissolved to give virtually quantitative conversion to the monoanion. This same tendency toward reduction in basic solvents has been observed for $Ni(tfd)_2^0$ and is in fact the basis of a popular preparation of $Ni(tfd)_2^-$.[26] The intractable nature of the solid material we have isolated from the electrooxidation of $Ni(mnt)_2^-$ makes certain assignment of its structure difficult, but the available evidence is at least consistent with an oligomeric (possibly dimeric) $[Ni(mnt)_2]_n$ neutral species. Mass spectral analysis using a direct heated probe was consistent with this interpretation. Above 150°, peaks were found at m/e ratios of 676, assigned as M_2,[55] 618 (M_2 − Ni), 548 (M_2 − Ni − $^1/_2$mnt), 536 (M_2 − mnt), 396 (M_2 − 2 mnt), 280 (2mnt), 248 (2mnt − S), 216 (2mnt − 2S), 172 (mnt + S), 140 (mnt), 128 (S_4), 96 (S_3), 70 ($^1/_2$mnt), 64 (S_2). Where resolution was sufficient, these assignments were confirmed by isotope peak ratios. Higher m/e peaks were observed at approximately 770 and 860, indicating that even higher molecular weight units were also present.

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Registry No. $Ni(tfd)_2$, 55401-06-4; $[Ni(mnt)_2]_n$, 55401-09-7; $Bu_4N[Ni(tfd)_2]$, 55401-11-1; $Bu_4N[Ni(mnt)_2]$, 55401-12-2; $Ni(tfd)_2^{2-}$, 50762-68-0; $Ni(mnt)_2^{2-}$, 38123-73-8; $Ni(tfd)_2^{3-}$, 55401-13-3; $Ni(mnt)_2^{3-}$, 38117-63-4.

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