$Cu(F_6acac)_2$ will be given in another paper.[31] Interpretation of the molecular orbital coefficients and bonding parameters calculated by the methods of Kivelson and Nieman[32] and Swalen and coworkers[33] will be presented there.

Registry No. Copper, 7440-50-8; $Zn(F_6acac)_2(py)_2$, 38402-93-6.

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Notes

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Electrochemical Generation and Spectral Characterization of the Bis(maleonitriledithiolato)nickel Trianion

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The oxidation-reduction behavior of metal-dithiolene complexes has attracted wide attention in the past decade and reports of complexes of the type $M(S_2C_2R_2)_2^{n-}$ (I), where $n = 0$, 1, or 2, have become commonplace.[1,2] It now appears certain that in most oxidation states of these complexes, molecular orbitals which are delocalized over the metal and ligands are responsible for their unusual electron-transfer properties. In the course of our electrochemical studies it has become apparent that the existence of more highly reduced complexes in this series, accessible at rather highly negative reduction potentials, has been overlooked. We report here the electrochemical generation and spectral characterization of the bis(maleonitriledithiolato)nickel trianion (I, M = Ni, R = CN, $n = 3$), $NiMNT^{3-}$, in which the unpaired electron appears to be largely localized on the metal.

Experimental Section

The maleonitriledithiolate ligand and the $NiMNT^{2-}$ complex were prepared by published methods.[3] Esr spectra were obtained on the Varian V-4502 spectrometer system employing 100-kHz field modulation and a 12-in. magnet. The Varian variable-temperature accessory was used to obtain spectra of frozen solutions, and diphenylpicrylhydrazyl (DPPH) served as a g-value reference. Optical spectra were obtained with the Beckman DK-1A spectrophotometer.

A Princeton Applied Research Model 173 potentiostat was employed in conjunction with a conventional ramp input and Hewlett-Packard Model 3300A function generator with Model 3302A trigger for polarographic and cyclic voltammetry experiments, respectively. Potentials are reported *vs.* the aqueous saturated calomel electrode (sce) and were monitored by a Simpson Model 2700 digital voltmeter. Data were read out with the Hewlett-Packard Model 7001A X-Y recorder or Tetronix Model 502A oscilloscope and camera. Cyclic voltammetry experiments were performed at the hanging mercury drop electrode. Other electrochemical techniques were conventional.

Spectrograde acetonitrile (Matheson Coleman and Bell) was dried over calcium hydride and kept under vacuum. Dimethoxyethane was dried with lithium aluminum hydride and distilled under vacuum onto either a potassium-anthracene mixture or lithium aluminum hydride. In a typical polarographic experiment, the solvent was distilled into a receiver flask and taken to a drybag where solutions were then prepared under a nitrogen atmosphere. Argon was used to purge residual oxygen from the solutions. The supporting electrolyte was tetrabutylammonium hexafluorophosphate, TBAHFP, obtained from Ozark Mahoning Co., recrystallized three times from 95% ethanol, and vacuum dried at 56°. Solutions were made 0.3 or 0.15 M in TBAHFP with acetonitrile and dimethoxyethane, respectively, and approximately 2×10^{-4} M in $NiMNT^{2-}$. Controlled-potential electrolyses with the PAR 173 potentiostat were performed under vacuum at a mercury pool in a cell which employed the platinum quasireference electrode in a compartment separated from the bulk of the solution by a fine frit. Details of the cell construction will be reported elsewhere. Electrolyzed solutions were withdrawn and sealed under vacuum into a sample holder having a quartz cell for optical spectroscopy and an esr sample tube.

Results and Discussion

We have studied the electrochemical reduction of $NiMNT^{2-}$ by polarography and cyclic voltammetry (CV) at a mercury electrode[4] in acetonitrile and 1,2-dimethoxyethane solutions, and the pertinent data are collected in Tables I and II. Plots of $-E$ *vs.* log $[i/(i_d - i)]$ from the polarographic data gave slopes close to that expected ($59/n$ mV) for a reversible one-electron change, and the I values compared well with those obtained for the known reversible one-electron reduction[5] of the monoanion, $NiMNT^-$. The polarographic waves were diffusion controlled.

The invariance of the cyclic voltammetry cathodic half-peak potentials and cathodic current functions ($i_{pc}/v^{1/2}$) with scan rate, as well as the unity ratio of anodic to cathodic peak currents, is diagnostic of reversible reductions uncomplicated by chemical reactions preceding or following the heterogeneous electron-transfer step.[6] Figure 1 shows a representative cyclic voltammogram.

$NiMNT^{3-}$ can be prepared from the dianion by controlled-potential electrolysis at a mercury pool, but the green solutions of the trianion are extremely air sensitive and revert to the orange color of the dianion upon exposure to even trace amounts of oxygen. We have not been successful in actual

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Table I. Polarographic Reduction Data for NiMNT^{2-}

Solvent	$E_{1/2}$,^{a} V	I^b	Slope,^{c} mV
Dimethoxyethane	−1.739	1.65	58.2
Acetonitrile	−1.676	2.60	60.1

^{a} *Vs.* sce. ^{b} Diffusion current constant; $I = 1.72$ in dimethoxyethane and 2.51 in acetonitrile for reduction of NiMNT monoanion to dianion. ^{c} Slope of plot of E *vs.* $-\log\,[i/(i_d - i)]$.

Table II. Cyclic Voltammetry Data for the Reduction of NiMNT^{2-}. Effect of Scan Rate

Solvent	i_a/i_c^{b}	$i_{pc}/v^{1/2}$ ^{c}	$e_{p/2}$,^{a,d} V	v,^{e} V/sec
Dimethoxyethane	1.00 ± 0.02	const ± 1%	−1.716 ± 0.004	0.06–20
Acetonitrile	1.00 ± 0.01	const ± 3%	−1.651 ± 0.006	0.05–45

^{a} *Vs.* sce. ^{b} Measured by Nicholson method: R. S. Nicholson, *Anal. Chem.*, **38**, 1406 (1966). ^{c} Current function measured at hanging mercury drop electrode. ^{d} Cathodic half-peak potential. ^{e} Scan rate.

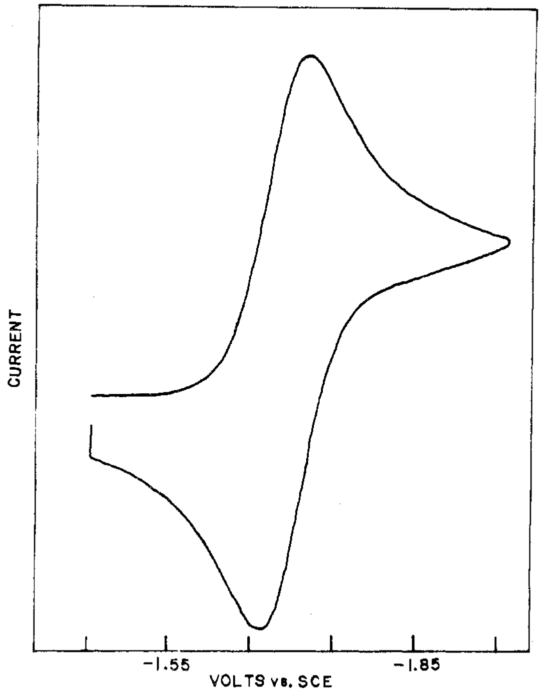

Figure 1. Cyclic voltammogram of the NiMNT^{2-} reduction in dimethoxyethane at a hanging mercury drop electrode, at 0.1 V/sec scan rate.

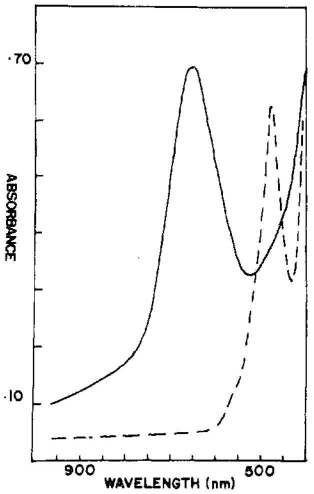

Figure 2. Absorption spectra of NiMNT^{2-} and NiMNT^{3-} obtained with *in situ* electrolysis cell having approximately 1.0-cm path length: dashed line, before electrolysis of NiMNT^{2-} solution and after exposing electrolyzed solution to the air (spectra were superimposable); solid line, spectrum after exhaustive electrolysis at −1.8 V under argon.

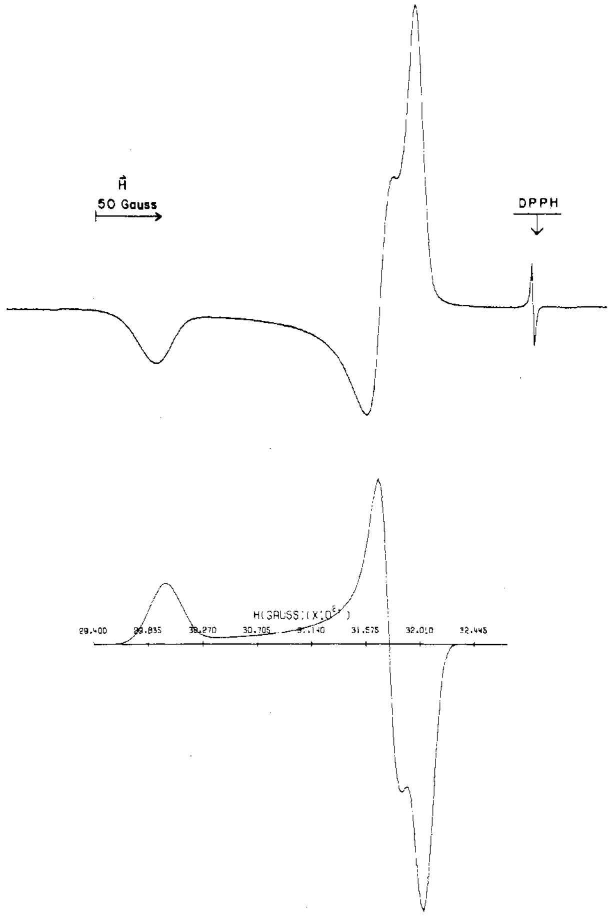

Figure 3. Top: esr spectrum of a frozen solution (−100°) of NiMNT^{3-} in dimethoxyethane. The data were taken at a microwave frequency of 9.25 × 10^9 Hz. Bottom: computer-simulated spectrum[7] using the g values reported in the text and lorentzian line widths of 25 G for the low-field feature (g_1) and 14 G for the g_2 and g_3 components. Note that the calculated and observed spectra are plotted in opposite phases.

isolation of NiMNT^{3-} but have succeeded in preparing it by two different *in situ* methods. The optical spectrum of NiMNT^{3-} was first obtained with the aid of an electrolysis cell, sealed under argon, which was placed in the sample port of the DK-1A spectrophotometer and which allowed *in situ* monitoring of the electrolysis solution. Figure 2 shows the spectra obtained in dimethoxyethane before and during electrolysis and after exposure of the electrolyzed solution to the air. The results clearly indicate that the strong absorption band centered at 650 nm is due to the NiMNT trianion. A similar spectrum was obtained in acetonitrile. It proved to be more convenient to prepare the trianion under vacuum and then withdraw samples for optical and esr spectroscopy without exposure to air. The esr spectrum of an electrolyzed solution of NiMNT^{3-} in dimethoxyethane showed a single line with $g = 2.116$. The corresponding monoanion is a spin $^1/_2$ system and has $g = 2.063$.[7] The esr spectrum of a frozen dimethoxyethane solution (−100°) of NiMNT^{3-} is shown in Figure 3 and is clearly indicative of

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[7] M. J. Hove, B. M. Hoffman, and R. J. Loyd, *J. Phys. Chem.*, **76**, 1849 (1972).

a spin $^1/_2$ system with three unique g values, $g_1 = 2.2055$, $g_2 = 2.081$, and $g_3 = 2.062$. A computer-simulated spectrum[7] calculated using these parameters is also presented in Figure 3.

The electronic structure of NiMNT^{3-} is a matter of considerable interest. Most workers are now agreed that the *dianion* approximates a Ni(II) in which the ligands each carry a charge of 2−. In an extension of this treatment,[2] the trianion would be expected to have an unpaired electron in an orbital of B_{1g} symmetry, composed of a metal in-plane d_{xy} orbital and sulfur in-plane p orbitals. This is the configuration favored in the esr studies of Maki, *et al.*,[8] for the formally isoelectronic CuMNT^{2-}, in which a high degree of metal-ligand delocalization is found. It is interesting to note, however, that the observed g-value anisotropy for NiMNT^{3-} is much greater than that of the copper complex,[9] even though the spin-orbit coupling parameter is smaller for nickel. In fact, the spin-Hamilton parameters obtained from our esr spectra are reminiscent of those observed in genuine d^9 complexes[10] and argue strongly that the orbital containing the unpaired electron is largely metal in character. The observed g-value anisotropy cannot be accounted for if a large amount of spin density is located on the ligands.[11] Thus our data favor a d^9, or Ni(I), formulation for the metal in the bis(maleonitriledithiolato)nickel trianion. This is clearly consistent with the previous description of the corresponding dianion as containing Ni(II), provided that in the formation of the trianion a primarily metal-based orbital is involved.

Registry No. Bis(maleonitriledithiolato)nickel trianion, 38117-63-4; bis(maleonitriledithiolato)nickel dianion, 38123-73-8.

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(11) Part of the increased anisotropy could be due to the presence of low-lying excited states. The energies of such states are not easily determined in these systems (see ref 8), and unequivocal assignment of the exact electronic structure of the trianion cannot be accomplished without measurement of metal or ligand hyperfine splittings.

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Pentadentate Ligands. VI. Cobalt(II) Complexes of *N,N'*-Bis(salicylidene)-2,2'-bis(aminoethyl) Sulfide

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It is well known that cobalt(II) shows a more pronounced tendency for the formation of tetrahedral complexes than does either nickel(II) or copper(II).[2] This has been illustrated with bis-bidentate complexes[3] and metal complexes containing tetradentate ligands derived from salicylaldehyde[4,5] and pyrrole-2-carboxaldehyde[6] with various polymethylene diamines. For example the well-known oxygen-active complex *N,N'*-bis(salicylidene)ethylenediaminocobalt(II) exhibits an essentially low-spin square-planar structure.[7,8] An oxygen-inactive form has been shown to have square-pyramidal coordination about cobalt which is achieved by bridging an oxygen atom from a second Co(SALEN) molecule.[9] The analogous trimethylene derivative contains high-spin four-coordinate cobalt(II) in which a strongly distorted tetrahedral geometry has been suggested.[10] The corresponding cobalt(II) complexes with four to ten carbon atoms in the central chelate ring exhibit a regular tetrahedral geometry.[4,11]

Incorporation of a donor atom into the polymethylene bridge thereby forming a linear pentadentate ligand may produce interesting results concerning structure and reactivity at the metal site. Such factors as the ligand strength of the inserted donor, the length of the carbon bridge, and the metal ion involved should prove important. This report deals with the interaction of cobalt(II) with the linear potentially pentadentate ligands derived from substituted salicylaldehydes and 2,2'-bis(aminoethyl) sulfide, hereafter referred to as SALDAES, and the physical and chemical properties of the resulting complexes.

Experimental Section

Materials. 5-Bromosalicylaldehyde (5-BrSAL) was prepared by a method described previously.[12] 5-Methylsalicylaldehyde (5-CH_3SAL) was prepared by a modification of the Reimer-Tieman reaction.[12] 3-Isopropylsalicylaldehyde (3-$(CH_3)_2$CHSAL) was prepared according to the general procedure of the Duff[13] reaction starting with *o*-isopropylphenol. All other chemicals were of reagent grade or equivalent.

Preparation of the Cobalt(II) Complexes. The cobalt(II) complexes were prepared by several independent methods under nitrogen in order to ensure each sample's integrity. The general method of preparation was as follows. To a refluxing anhydrous ethanol or methanol solution (50 ml) of 0.01 mol of pentadentate Schiff base ligand[12] to which had previously been added 0.01 mol of triethyl orthoformate and 0.2 mol of triethylamine was added 0.01 mol of either Co$(C_2H_3O_2)_2 \cdot 4H_2O$ or $CoCl_2 \cdot 6H_2O$ dissolved in anhydrous methanol or ethanol (100 ml) which contained 0.025 mol of triethyl orthoformate. The reaction mixture was refluxed 1.5 hr and then allowed to come to room temperature. Red-brown to orange crystals appeared upon cooling, which were filtered under nitrogen, washed with a minimum amount of anhydrous ethanol, and dried *in vacuo* for 12 hr. The complexes could also be prepared by a coordinated ligand reaction by allowing a refluxing ethanol suspension of the appropriate bis(salicylaldehydo)cobalt(II) to react with DAES for 1 hr. Isolation and drying were as described above. The resulting complexes were normally analytically pure. Recrystallization, if desired, could be accomplished from hot *N,N*-dimethylformamide (DMF). Analytical data are presented in Table I.

Results and Discussion

Complexes of general formula [Co(XSALDAES)]·nH_2O

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