Electron-Transfer Series of the $[M\text{-}O_2S_2]$ Type. Complexes Derived from o-Mercaptophenol, 1-Mercapto-2-naphthol, and 1-Hydroxy-2-pyridinethione

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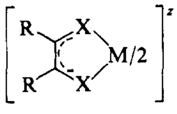
Abstract: The existence of an electron-transfer series of the $[M\text{–}O_2S_2]^z$ type has been investigated. The results are compared with those found for the $[M\text{–}O_4]^z$ and $[M\text{–}S_4]^z$ series. Dianionic complexes $M(mp)_2{}^{2-}$ (mp = *o*-mercaptolatophenolate) have been synthesized with Zn, Cu, Ni, Pd, and Co, and their electronic structures have been investigated. Polarographic studies show that each $M(mp)_2{}^{2-}$ except $Zn(mp)_2{}^{2-}$ can be oxidized to the corresponding $M(mp)_2{}^-$; $Ni(mp)_2{}^-$ and $Co(mp)_2{}^-$ have been isolated. A related complex $Ni(mn)_2{}^-$ (mn = 1-mercaptolato-2-naphtholate) has been prepared. Polarographic oxidation of $Ni(mp)_2{}^-$ and $Ni(mn)_2{}^-$ to the neutral complexes has been observed; $Ni(mn)_2{}^-$ also undergoes polarographic reduction to the dianion. These results indicate that the scope of the electron-transfer series for $[Ni\text{–}O_2S_2]^z$ is as extensive as in the $[Ni\text{–}S_4]^z$ case. The esr spectra of the spin doublet ions $Ni(mp)_2{}^-$ and $Ni(mn)_2{}^-$ reveal considerable *g*-tensor anisotropy (similar to that found for $[Ni\text{–}S_4]^-$). $Co(mp)_2{}^-$ is monomeric with a triplet ground state. Polarographic oxidation of $Co(mp)_2{}^-$ in dichloromethane solutions proceeds with the production of the dimers $Co_2(mp)_4{}^-$ and $Co_2(mp)_4$. Polarographic oxidation of $Cu(pt)_2$ and $Ni(pt)_2$ (which are isoelectronic with $Cu(mp)_2{}^{2-}$ and $Ni(mp)_2{}^{2-}$) has been observed (pt = anion derived from 1-hydroxy-2-pyridinethione).

It has been amply demonstrated that the dithiolene complexes **1** (X = S)[1] and **2** (X = Y = S)[2] of a wide variety of metals exist in several oxidation states which are related by one-electron transfer reactions. For example, the isolation of bis(toluene-3,4-dithiolene)nickel (**3**) $Ni(tdt)_2{}^z$, in three oxidation states ($z = -2, -1$, and 0) has been reported.[3,4] Polarographic measurements indicate that these members may be interconverted electrochemically.



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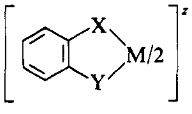

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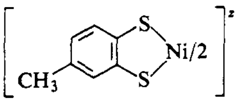

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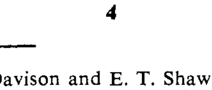
A number of recent studies have revealed that the unique properties of these complexes are not restricted to compounds involving sulfur donors. It has been shown that the scope of the electron-transfer series in the case of nickel is increased in the bis complexes **2** (X = Y = NH[5] and X = NH, Y = S[6]), in which nitrogen replaces sulfur in the coordination sphere. The electron-transfer behavior and physical properties of the complexes **1** (M = Ni, X = Se, R = CF_3) involving selenium donors are very similar to those of their sulfur-coordinated analogs.[7]

Studies of complexes derived from pyrocatechol and related ligands have shown that oxygen donors are less satisfactory for the stabilization of electron-transfer related series.[8] For example, with nickel a dianionic complex **2** (X = Y = O; M = Ni; $z = -2$) has been isolated, and polarographic oxidation of this complex is suggestive of the formation of a monoanion. However, this monoanion is apparently too unstable to isolate; moreover, it has not been detected by esr techniques. In contrast the monoanion in the $[Ni\text{–}S_4]^z$ series, **3** ($z = -1$), exhibits an easily detectable esr signal and is the most readily isolated member of the series.[2,3] Although other oxidized complexes whose stoichiometry is consistent with their formulation as members of an $[Ni\text{–}O_4]^z$ series have been isolated, these complexes cannot be reduced to the dianion **2** (X = Y = O; M = Ni) electrochemically or chemically.[8]

Herein are reported, in detail, results which establish the existence of an electron-transfer series of the type $[M\text{–}O_2S_2]^z$.[9] These studies involve the complexes **2** (X = S, Y = O), $M(mp)_2{}^z$, which are derived from *o*-mercaptophenol. The nickel complexes **4**, $Ni(mn)_2{}^z$, of



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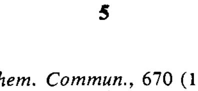

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Table I. Analytical Data

Complex	Color	% C Calcd	% C Found	% H Calcd	% H Found	% S Calcd	% S Found	% miscellaneous Calcd	% miscellaneous Found	
$[(C_6H_5)_4As]_2[Zn(o\text{-}C_6H_4OS)_2]$	Yellow	66.70	66.70	4.48	4.32	5.94	5.59	6.05	6.08	(Zn)
$[(C_6H_5)_4As]_2[Cu(o\text{-}C_6H_4OS)_2]$	Green	66.80	67.10	4.49	4.55	5.95	5.78	5.89	5.63	(Cu)
$[(C_6H_5)_4As]_2[Ni(o\text{-}C_6H_4OS)_2]$	Red	67.12	66.85	4.51	4.72	5.97	6.08	5.47	5.49	(Ni)
$[(C_6H_5)_4As]_2[Pd(o\text{-}C_6H_4OS)_2]$	Brown	64.26	63.91	4.31	4.19	5.72	5.93			
$[(C_6H_5)_4As]_2[Co(o\text{-}C_6H_4OS)_2]$	Gray-green	67.10	66.80	4.50	4.36	5.97	5.89	5.49	5.56	(Co)
$[(C_4H_9)_4N][Ni(o\text{-}C_6H_4OS)_2]$	Green	61.20	61.28	8.07	8.10	11.67	11.55	2.55	2.37	(N)
$[(C_4H_9)_4N][Ni(o\text{-}C_{10}H_6OS)_2]$	Red	66.57	66.77	7.45	7.61			2.16	1.98	(N)
$[(C_4H_9)_4N][Co(o\text{-}C_6H_4OS)_2]$	Purple	61.18	60.95	8.07	7.95	11.66	10.82	10.72	10.72	(Co)
$[(C_4H_9)_4N][Ni_3(o\text{-}C_{10}H_6OS)_4]$	Green	60.26	60.70	5.42	5.56			1.26	1.32	(N)

1-mercapto-2-naphthol have also been investigated. The complexes **5**, $M(pt)_2$, which are derived from 1-hydroxy-2-pyridinethione, have been reported for nickel, copper, and zinc.[10] These uncharged complexes are isoelectronic with the $M(mp)_2{}^{2-}$ of the same metal. Consequently the complexes **5** have been examined to determine if they can undergo related electron-transfer reactions.

Experimental Section

Preparation of Compounds. *o*-Mercaptophenol[11] and 1-mercapto-2-naphthol[12] were prepared according to published methods. Complexes of 1-hydroxy-2-pyridinethione were prepared by the procedure of Robinson.[10]

$[(C_6H_5)_4As]_2[M(mp)_2]$ (M = Co, Ni, Pd, Cu, Zn). Because of the sensitivity of these complexes to oxygen, all synthetic operations were carried out using degassed solvents under an atmosphere of oxygen-free nitrogen. A solution containing 8.0 mmoles of the appropriate metal halide and 1.0 g of tetraphenylarsonium chloride in 50 ml of 50% aqueous ethanol was added slowly to a solution containing 2.0 g (16 mmoles) of *o*-mercaptophenol and 1.3 g (32 mmoles) of sodium hydroxide in 50 ml of 50% aqueous ethanol. The resulting solution was filtered and the filtrate was added slowly to a warm (50°) solution of 5.8 g (14 mmoles) of tetraphenylarsonium chloride in 150 ml of 50% aqueous ethanol. The crystalline complex which precipitated was collected by filtration, washed with three 25-ml portions of aqueous ethanol, and vacuum dried at 60°. The yield was nearly quantitative.

The zinc complex is exceptional; it is soluble in most polar organic solvents and is not readily oxidized by air. The complexes of the other metals are appreciably soluble only in N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine. The solutions are oxidized by air. Even as solids, the complexes are sensitive to air, especially when exposed to light.

$[(n\text{-}C_4H_9)_4N][Ni(mp)_2]$. A solution containing 2.3 g (8 mmoles) of nickel nitrate hexahydrate in 60 ml of 70% aqueous ethanol was added to a solution of 2.0 g (16 mmoles) of *o*-mercaptophenol and 1.3 g (32 mmoles) of sodium hydroxide in 60 ml of 70% aqueous ethanol. Tetrabutylammonium bromide (3 g, 9 mmoles) dissolved in 15 ml of ethanol was added to the red-brown solution. Oxidation was accomplished by passing air through the solution. The green precipitate was collected and dried. Four recrystallizations from acetone–toluene (1:3 v/v) produced a pure product as long green needles, mp 182–183°.

$[(n\text{-}C_4H_9)_4N][Co(mp)_2]$. A solution of 2.50 g (10.7 mmoles) of cobalt(II) chloride hexahydrate in 50 ml of 50% aqueous ethanol was added to a solution of 2.70 g (21.4 mmoles) of *o*-mercaptophenol and 1.70 g (43 mmoles) of sodium hydroxide in 50 ml of 50% aqueous ethanol. A solution of 4.0 g (12.4 mmoles) of tetrabutylammonium bromide in 80 ml of water was added to the green solution. A stream of air was passed through the solution. During this oxidation it is important to adjust the water content of the solution so that the violet complex precipitates as soon as it is formed. If the complex remains in solution it decomposes. The violet complex was collected, washed with water, and dried. Purification was effected by repeated recrystallization from acetone–toluene (1:7 v/v) or acetone–isobutyl alcohol, mp 172–174°.

Table II. Conductivity and Magnetic Susceptibility Data

	μ_{eff}, BM[a]	Λ[b]
$[(C_6H_5)_4As]_2[Zn(mp)_2]$	Dia	149
$[(C_6H_5)_4As]_2[Cu(mp)_2]$	1.87	139
$[(C_6H_5)_4As]_2[Ni(mp)_2]$	Dia	...
$[(C_6H_5)_4As]_2[Pd(mp)_2]$	Dia	144
$[(C_6H_5)_4As]_2[Co(mp)_2]$	4.96	...
$[(n\text{-}C_4H_9)_4N][Ni(mp)_2]$	1.85	65
$[(n\text{-}C_4H_9)_4N][Ni(mn)_2]$	1.77	55
$[(n\text{-}C_4H_9)_4N][Co(mp)_2]$	3.20	67
$[Cu(pt)_2]$	1.68[c]	...
$[Ni(pt)_2]$	Dia[c]	...

[a] Data refer to solids at ~25°; diamagnetic susceptibilities not accurately measured. [b] $Cm^2\ mole^{-1}\ ohm^{-1}$ in $\sim 10^{-3}\ M$ nitromethane solution. [c] Data from ref 10.

$[(n\text{-}C_4H_9)_4N][Ni(mn)_2]$. A solution of 1.7 g (57 mmoles) of nickel nitrate hexahydrate in 40 ml of water was added to a solution of 2.10 g (12 mmoles) of 1-mercapto-2-naphthol and 1.34 g (24 mmoles) of potassium hydroxide in 50 ml of ethanol. Four grams (12 mmoles) of tetrabutylammonium bromide in 10 ml of ethanol was added. Enough acetone was added to the solution to dissolve the brown solid which had formed. Air was bubbled through the solution for 3 hr. The crystalline precipitate was collected, washed with water, and dried. Purification was achieved by recrystallization from methanol, mp 187–188°.

$[(n\text{-}C_4H_9)_4N][Ni_3(mn)_4]$. A solution of 3.15 g (18 mmoles) of 1-mercapto-2-naphthol and 1.50 g of sodium hydroxide in 60 ml of 50% aqueous ethanol was added to a solution of 2.6 g (9.0 mmoles) of nickel nitrate hexahydrate in 60 ml of aqueous ethanol. The solution was oxidized by a stream of air. Slow addition of tetrabutylammonium iodide (4 g, 10 mmoles) during the oxidation produced a green crystalline precipitate. The precipitate was collected and dried. Purification was achieved by soxhlet extraction into dichloromethane. The initial red extracts were discarded; the product which crystallized from the green extracts was collected. A second extraction yielded the pure complex as greenish black crystalline flakes, mp 148° dec.

Physical Measurements. Polarographic measurements in dimethyl sulfoxide solution were made using a rotating platinum electrode, a saturated calomel reference electrode, and a ORNL Model 1988 polarograph equipped with three-electrode geometry. Polarographic measurements in dichloromethane solution were obtained in the manner previously described.[13] Magnetic moments were measured using either a Faraday balance with $HgCo(CNS)_4$ as the magnetic standard or a Gouy balance with aqueous nickel chloride as calibrant. Electronic spectra were recorded on a Cary 14 spectrophotometer. Esr spectra were recorded on a Varian spectrometer employing a Varian V-FR 2503 field regulator. The microwave frequency was measured to ± 1 Mc by a frequency meter, and the magnetic field was calibrated by a Magnion nmr gaussmeter and frequency counter. Conductivities were measured with a Serfass conductivity bridge.

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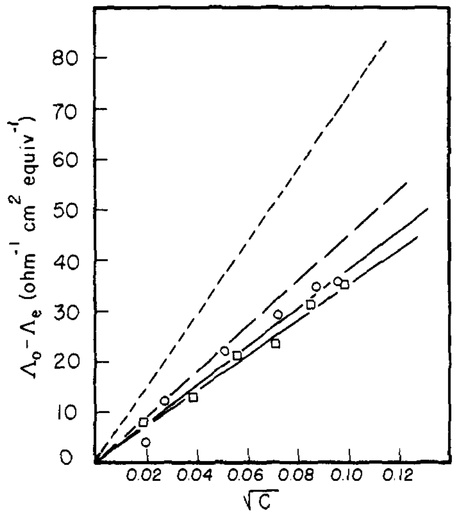

Figure 1. Conductivity of electrolytes in acetonitrile solution as a function of concentration: □, $(Bu_4N)[Ni(mp)_2]$; ○, $(Bu_4N)[Co(mp)_2]$; – – –, $(Bu_4N)[Co(tdt)_2]$; ----, $(Bu_4N)_2[NiS_4C_4(CN)_4]$.

Table III. Polarographic Data for $[M\text{–}O_2S_2]$ Complexes

Complex	Solvent	Process	$E_{1/2}$, V	id/C, μA/mM
$Cu(mp)_2{}^z$	DMSO	$-2 \rightleftarrows -1$	−0.19	4.5
$Cu(pt)_2$	DMSO	$0 \rightleftarrows +2$	+1.03	12
$Ni(mp)_2{}^z$	DMSO	$-2 \rightleftarrows -1$	−0.43	6.9
		$-1 \rightleftarrows 0$	+0.38	7.5
	CH_2Cl_2	$-2 \rightleftarrows -1$	−0.32	24
		$-1 \rightleftarrows 0$	+0.53[a]	...
$Ni(mn)_2{}^z$	DMSO	$-2 \rightleftarrows -1$	−0.49	6.5
		$-1 \rightleftarrows 0$	+0.22	6.8
		$0 \rightleftarrows +2$ (?)	+0.61	11.2
	CH_2Cl_2	$-2 \rightleftarrows -1$	−0.37	20
		$-1 \rightleftarrows 0$	+0.37	20
$Ni(pt)_2$	DMSO	$0 \rightleftarrows +1$	+0.78	7.5
$Pd(mp)_2{}^z$	DMSO	$-2 \rightleftarrows -1$	−0.13	6.2
$Co(mp)_2{}^z$	DMSO	$-2 \rightleftarrows -1$	−0.62	6.5
		$-1 \rightleftarrows 0$	+0.29	6.8
	CH_2Cl_2	$-2 \rightleftarrows -1$	−0.60	19
		$-2 \rightleftarrows (-1)^b$	+0.46	10
		$(-1)^b \rightleftarrows (0)^b$	+0.62	11

[a] Wave shape indicates film forming on the electrode. [b] Dimeric species with the charge per dimeric unit indicated.

Results

Synthetic Studies. Treatment of the appropriate metal ion with the dianion derived from *o*-mercaptophenol yields $M(mp)_2{}^{2-}$ (M = Zn, Cu, Ni, Pd, or Co) which may be isolated as the tetraphenylarsonium salt. Because of the oxygen sensitivity of the free ligand and of the metal complexes, these preparations have been performed in an oxygen-free environment. The analytical data for these complexes are set out in Table I. The conductivity data (Table II) indicate that the Zn, Cu, and Pd complexes are typical 2:1 electrolytes in nitromethane.

Polarographic data (*vide infra*) indicate that these dianions, with the exception of the zinc dianion, should be easily oxidized to monoanions. Aerial oxidation in the case of nickel or cobalt is capable of producing the expected monoanions $M(mp)_2{}^-$, which have been isolated as the tetrabutylammonium salts. The conductivity of these salts as a function of concentration[14] (Figure 1) in acetonitrile solution reveals that they are both 1:1 electrolytes. Attempts to isolate the palladium and copper monoanions have been unsuccessful. Oxidation of $Pd(mp)_2{}^{2-}$ with air, iodine, or the powerful one-electron oxidizing agent $[NiS_4C_4(CF_3)_4]$[1a] did not produce any paramagnetic species with the esr spectrum that would be expected for $Pd(mp)_2{}^-$. However, controlled-potential electrolysis of $Pd(mp)_2{}^{2-}$ in DMSO solution has produced a paramagnetic species which has been identified as $Pd(mp)_2{}^-$ from its esr spectrum. Attempts to oxidize $Cu(mp)_2{}^{2-}$ to $Cu(mp)_2{}^-$ with air or iodine have failed to yield the desired species.

It has been possible to isolate red $[(n\text{-}C_4H_9)_4N][Ni(mn)_2]$ (4, $z = -1$) and green $[(n\text{-}C_4H_9)_4N][Ni_3(mn)_4]$ from the reaction of nickel ion with the dianion of 1-mercapto-2-naphthol. These products presumably arise from the aerial oxidation of the $Ni(mn)_2{}^{2-}$ which must be formed initially. Paramagnetic $Ni_3(mn)_4{}^-$ is stable only in the solid and in dichloromethane solution; in other solvents it decomposes to yield $Ni(mn)_2{}^-$ as the major product.

Polarographic Studies. The polarographic data are presented in Table III. Each of the $M(mp)_2{}^{2-}$ complexes with the exception of $Zn(mp)_2{}^{2-}$ exhibits a well-defined oxidative wave. On the basis of the diffusion current this wave involves one electron and results from oxidation of $M(mp)_2{}^{2-}$ to $M(mp)_2{}^-$. In the cases (M = Ni, Co) where $M(mp)_2{}^-$ has been isolated, the polarography of the monoanion reveals a one-electron cathodic wave at the same potential as found for the oxidation of the corresponding dianion. In addition oxidation of $Ni(mp)_2{}^-$ to the neutral complex $Ni(mp)_2$ has been detected. $Ni(mn)_2{}^-$ undergoes both reduction and oxidation polarographically to produce $Ni(mn)_2{}^{2-}$ and $Ni(mn)_2$, respectively. A further oxidation, possibly leading to the formation of $Ni(mn)_2{}^{2+}$, has been observed in DMSO solution, but this wave is not observed in other solvents.

Polarographic oxidation of $Co(mp)_2{}^-$ in dichloromethane solution reveals two waves with diffusion currents of about one-half the value of the diffusion current of the cathodic wave which produces $Co(mp)_2{}^{2-}$. The anodic waves can be accounted for if the dimeric species $[Co_2(mp)_4]^-$ and $[Co_2(mp)_4]$ are formed upon oxidation. Although the most closely analogous $[Co\text{–}S_4]^-$ species, $Co(tdt)_2{}^-$, does not undergo polarographic oxidation, other $[Co\text{–}S_4]^-$ species can be oxidized to dimeric species.[13] The difference in polarographic behavior of $Co(mp)_2{}^-$ in DMSO solution, that is, the failure to observe two oxidative waves leading to dimer formation, is not unexpected. Basic solvents are known to interfere with the polarography of $Co\text{–}S_4$ species by either cleaving or reducing the dimeric species.[13]

The limited data available for $M(pt)_2$ complexes suggest that an $M(pt)_2$ electron-transfer series analogous to the $M(mp)_2{}^z$ series exist. On the basis of diffusion current data $Ni(pt)_2$ undergoes a one-electron oxidation. $Cu(pt)_2$ can also be oxidized polarographically, but the diffusion current for this wave is indicative of a two-electron process. $Zn(pt)_2$ like $Zn(mp)_2{}^{2-}$ and $[ZnS_4C_4(CN)_4]^{2-}$ [12] cannot be cleanly oxidized polarographically. No attempts at chemical oxidation of the $M(pt)_2$ species have been made.

Magnetic, Esr, and Electronic Spectral Studies. The

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(14) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

Table IV. Esr Data

Complex	Solution[a] $\langle g \rangle$	Solution[a] $\langle a \rangle$, G	Glass[a] g_1	Glass[a] g_2	Glass[a] g_3
$Ni(mp)_2^-$	2.083		2.016	2.036	2.191
$Ni(mn)_2^-$	2.062		2.003	2.031	2.142
$Ni(tdt)_2^-$	2.082[b]		2.016	2.048	2.183
$Pd(mp)_2^-$	2.028[c]	14 Pd^{105}			
$Pd(tdt)_2^-$	2.022[b,d]				
$Cu(mp)_2^{2-}$	2.082	82 $Cu^{63,65}$	$g_\perp = 2.041$		$g_\parallel = 2.161$[e]
$Cu(pt)_2$	2.079	86 $Cu^{63,65}$	$g_\perp = 2.046$		$g_\parallel = 2.143$[f]

[a] Unless otherwise stated, all measurements made in 1:1 v/v $CHCl_3$–DMF; glass measurements performed at ~100°K. [b] Data from ref 3. [c] DMSO solution. [d] DMF solution. [e] $A_\parallel = 183$ G. [f] $A_\parallel = 190$ G.

magnetic moments for the complexes are set out in Table II. Table IV contains the pertinent esr data, and Table V the electronic spectral data.

The zinc complexes $Zn(mp)_2^{2-}$ and $Zn(pt)_2$ are conventional diamagnetic d^{10} complexes. The diamagnetism of $Ni(mp)_2^{2-}$ and $Ni(pt)_2$ is indicative of monomeric, square-planar geometry. Diamagnetic $Pd(mp)_2^{2-}$ is also undoubtedly planar.

As would be expected from their isoelectronic relationship, $Cu(mp)_2^{2-}$ and $Cu(pt)_2$ exhibit considerable similarity. The magnetic and esr data for these complexes are indicative of the conventional doublet ground state which has been found for most complexes of Cu(II) including complexes of the $[Cu\text{-}O_4]^{2-}$ and $[Cu\text{-}S_4]^{2-}$ types. In DMF solution $Cu(mp)_2^-$ reveals two ligand field absorptions at 11,000 cm^{-1} (ε 25) and 16,900 cm^{-1} (ε 210); for $Cu(pt)_2$ similar transitions occur at slightly higher energies, 12,500 cm^{-1} (ε 15) and 17,700 cm^{-1} (ε 126).

In contrast to the other $M(mp)_2^{2-}$ complexes the data available for $Co(mp)_2^{2-}$ indicate that this complex is polymerized in the solid with approximate octahedral coordination about cobalt. The magnetic moment of 4.96 BM is within the range (4.3–5.2 BM) typical for six-coordinate Co(II) but is slightly above the range (4.2–4.8 BM) generally found for tetrahedral Co(II).[15] The electronic spectrum of crystalline $(Ph_4As)_2$ $Co(mp)_2$ is reproduced in Figure 2. This spectrum exhibits strong similarities to the spectra[16] of known six-coordinate Co(II) complexes such as bis(acetylacetonato) cobalt (II)[17] and bis(acetylacetonato)cobalt(II) dihydrate.[18] The spectrum of $Co(mp)_2^{2-}$ is even more similar to the spectrum of bis(tetrachloropyrocatacholato)cobalt(II) dianion which also is believed to involve a polymeric structure with six-coordinate cobalt.[8]

The magnetic properties of the nickel monoanions, $Ni(mp)_2^-$ and $Ni(mn)_2^-$, are consistent with spin doublet ground states for both ions. The esr spectra of these ions in frozen glasses reveal the marked g-tensor anisotropy which is now recognized as characteristic of species of this type.[19] It is especially interesting to note that the g tensors of the $[Ni\text{-}O_2S_2]^-$ and $[Ni\text{-}S_4]^-$ species, $Ni(mp)_2^-$ and $Ni(tdt)_2^-$, are nearly identical. $Ni(mp)_2^-$ and $Ni(mn)_2^-$ also exhibit two electronic spectral features which are typical of other analogous oxidized species. These features are the extremely intense absorption (ε ~14,000) in the near-infrared region and an insensitivity of the spectrum to solvent effects.[2,3] The spectra of these species show essentially no difference in solvents ranging in coordinating ability from dichloromethane to pyridine.

Table V. Electronic Spectra of Monoanions in Dichloromethane Solution[a]

$[Ni(mp)_2]^-$	5020 (570); 5350 (430 sh); 6500 (590 sh); 9840 (14,600); 12,700 (1800); 15,600 (1600); 22,700 (1100)
$[Ni(mn)_2]^-$	6200 (4000 sh); 7300 (9400 sh); 8300 (12,300 sh); 9000 (13,700); 14,000 (693); 17,100 (1030); 19,000 (981); 22,000 (1770)
$[Co(mp)_2]^-$	5300 (23); 11,900 (1500 sh); 14,700 (5360); 17,800 (5620)

[a] Position given in cm^{-1}; molar extinction coefficients are in parentheses; sh = shoulder.

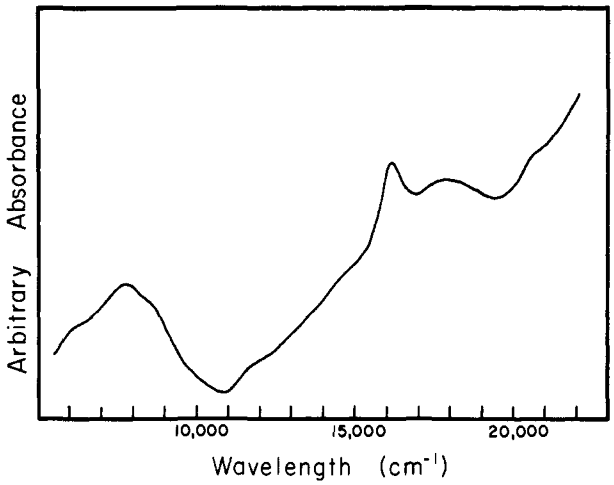

Figure 2. Electronic spectrum of $(Ph_4As)_2[Co(mp)_2]$ in a Nujol mull.

In order to further establish the existence of $Pd(mp)_2^-$, this ion was generated electrochemically by oxidation of $Pd(mp)_2^{2-}$ in DMSO solution. Examination of the resulting solution by esr revealed the presence of a paramagnetic species whose esr spectrum consisted of six hyperfine components superimposed on a broad absorption centered around $g = 2.028$. The similarity of this g value and the g value of 2.022 reported[3] for $Pd(tdt)_2^-$ along with the fact that a six-line hyperfine spectrum is expected from the 22.2% of naturally occurring Pd^{105} ($I = {}^5/_2$) leads to the conclusion that the observed radical was $Pd(mp)_2^-$.

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(16) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964).
(17) F. A. Cotton and R. C. Elder, *ibid.*, **4**, 1145 (1965).
(18) G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).
(19) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

On the basis of its conductivity behavior $Co(mp)_2^-$ is formulated as a monomer. Its magnetic moment indicates that it has a triplet ground state. The only other four-coordinate cobalt complexes with triplet ground states are the related monomers of the type $[Co–S_4]^-$. X-Ray crystallographic examination[20] of a representative member of this group, $Co(tdt)_2^-$, has shown that the anion has square-planar coordination around cobalt. Because of the similarities between $Co(mp)_2^-$ and $Co(tdt)_2^-$, we place $Co(mp)_2^-$ in this class of high-spin, planar complexes. The spectrum of $Co(mp)_2^-$ is unchanged in going from inert solvents like dichloromethane to solvents of moderate coordinating ability such as DMSO and DMF. However, addition of triphenylphosphine to dichloromethane solutions of $Co(mp)_2^-$ causes a color change from violet to red; in pyridine solution $Co(mp)_2^-$ is green. This behavior suggests the formation of adducts of these Lewis bases with $Co(mp)_2^-$. Similar behavior and the isolation of some adducts of the types $[base–Co–S_4]^-$ and $[base_2–Co–S_4]^-$ have been reported for a number of $[Co–S_4]^-$ species.[21] Further, more quantitative studies of the presumed adducts of $Co(mp)_2^-$ have been thwarted by the rapid, irreversible decomposition of these materials.

Discussion

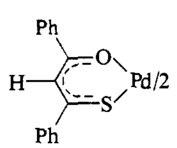
The properties of the $[M–O_2S_2]^z$ species are, as might be expected, intermediate between those of the $[M–O_4]^z$ and $[M–S_4]^z$ types. The $[M–O_2S_2]^z$ complexes are more robust and more easily handled than their $[M–O_4]^z$ counterparts but are less stable than their $[M–S_4]^z$ analogs. For example, it has been possible to isolate $Co(mp)_2^-$ and $Ni(mp)_2^-$ whereas the analogous $[M–O_4]^-$ species have only been detected polarographically and have defied isolation. Our inability to isolate $Cu(mp)_2^-$ and $Pd(mp)_2^-$ must be traced to their chemical instability, since the relevant electrochemical potentials indicate that these species should be easily obtained by mild oxidation of the respective $M(mp)_2^{2-}$. Oxidation by iodine, which is very useful in preparing complexes of the $[M–S_4]^z$ series, is not feasible in the $[M–O_2S_2]^z$ series because of the occurrence of side reactions which probably involve ring halogenation. The rapid decomposition of what appear to be Lewis base adducts of $Co(mp)_2^-$ is further evidence of the reduced chemical stability of the $[M–O_2S_2]^z$ species in comparison with the $[M–S_4]^z$ complexes.

Like their $[M–S_4]^z$ counterparts most of the $[M–O_2S_2]^z$ species appear to involve square-planar coordination; however, the tendency for polymerization and increased coordination is somewhat greater in the $[M–O_2S_2]^z$ series. Although the possibility of *cis–trans* isomerization exists with planar $[M–O_2S_2]^z$ complexes, no evidence (except possibly in the case of the copper complexes $Cu(mp)_2^{2-}$ and $Cu(pt)_2$) of the formation of a second isomer of these complexes has been found. These complexes may exist as a rapidly equilibrating mixture of *cis* and *trans* isomers, or it is possible that only one isomer has been synthesized. Very little information exists which would allow us to guess which geometry would be preferred for planar O_2S_2 coordination. The relevent data concerns bis(1,3-diphenyl-3-thioloprop-2-en-1-one)palladium(II) (**6**) and its isomorphous platinum analog, which have been shown[22] by X-ray crystallography to exist as the *cis* isomers in the solid, and bis(methylthiohydroxamoto)nickel(II) (**7**). Both the *cis* and the *trans* isomers of **7** have been isolated and identified.[23,24]

Table VI. Comparison of Half-Wave Potentials for the $[M–X_2Y_2]^{2-} \rightleftarrows [M–X_2Y_2]^- + e^-$ Couples

Donor set	Co	$E_{1/2}$, V[a] Ni	Cu
N_4	−1.83[b]	−1.59[b]	...
S_2N_2	...	−1.04[b]	...
S_4	−0.84	−0.51[b]	−0.59
S_2O_2	−0.62	−0.43	−0.19

[a] All data obtained in DMSO solution with 0.05 *M* $(n\text{-Pr})_4NClO_4$ as supporting electrolyte and a saturated calomel reference electrode. [b] Data from ref 5.



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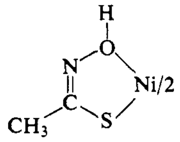
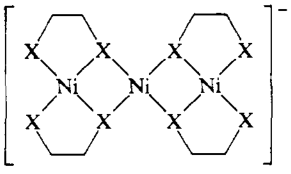


7



8, X = O or S

In the course of preparing $Ni(mn)_2^-$ an unusual polynuclear species $Ni_3(mn)_4^-$ has been isolated. Although our characterization of $Ni_3(mn)_4^-$ is as yet incomplete, we tentatively propose a laterally bridged structure **8** for it. Similar complexes involving both sulfur[25] and oxygen[26] donors as bridging units have been reported. The only dithiolene complexes which might have related lateral bridging are $[(C_4H_9)_3PPd(4\text{-}ClC_6H_3S_2)]_2$[27] and $[(C_6H_5)_3PPdS_2C_2(C_6H_5)_2]_2$.[28]

The ability of an O_2S_2 coordination sphere to support an electron-transfer series is clearly demonstrated by the synthetic and polarographic data at hand. In the case of nickel the scope of the electron-transfer series as revealed by polarographic measurements is as extensive in the $[M–O_2S_2]^z$ case as in the related $[M–S_4]^z$ case. For both $Ni(mp)_2^z$ and $Ni(tdt)_2^z$ a three-membered series embracing

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(20) R. Eisenberg, Z. Dori, H. B. Gray, and J. A. Ibers, *Inorg. Chem.*, 7, 741 (1968).

(21) A. L. Balch, *ibid.*, 6, 2158 (1967); N. G. Connelly, J. A. McCleverty, and C. J. Winscom, *Nature*, **216**, 999 (1967); C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 2958 (1964).

(22) E. A. Shygam, L. M. Shkol'nikov, and S. E. Livingstone, *Zh. Strukt. Khim.*, **8**, 550 (1967).

(23) T. Sato, K. Nagata, M. Shiro, and H. Koyama, *Chem. Commun.*, 192 (1966); T. Sato, K. Nagata, Y. Tsukuda, M. Shiro, and H. Koyama, *ibid.*, 215 (1967).

(24) The doubly deprotonated form of this complex should in principle be the terminal reduced member of an electron-transfer series analogous to the series observed for $Ni(mp)_2^z$ and $Ni(pt)_2^z$.

(25) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872, 878 (1962); R. L. Girling and E. L. Amma, *ibid.*, **6**, 2009 (1967).

(26) S. J. Gruber, C. M. Harris, and E. Simm, *ibid.*, **7**, 268 (1968).

(27) J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1949 (1938).

(28) V. P. Mayweg and G. N. Schrauzer, *Chem. Commun.*, 640 (1966).

a dianion, a monoanion, and a neutral complex has been established.

Detailed comments concerning the effects of donor atoms on the electron-transfer behavior of nickel complexes of the type **2** have been presented previously.[5,8] The data in Table VI allow this comparison to be extended to cobalt and copper complexes. Where comparisons can be made among the three metals, the order of oxidative stability remains the same, *viz.*, $[M\text{–}N_4]^{2-} < [M\text{–}N_2S_2]^{2-} < [M\text{–}S_4]^{2-} < [M\text{–}S_2O_2]^{2-}$. However, it is noteworthy that the metals are not equally sensitive to a change in donor atoms. From the data on the $[M\text{–}S_4]^{2-}$ and $[M\text{–}O_2S_2]^{2-}$ species the order of sensitivity increases: Ni < Co < Cu. That copper is the most sensitive appears reasonable. Oxidation of $[Cu\text{–}X_2Y_2]^{2-}$ probably involves removal of an electron from the σ^* orbital composed largely of a copper d_{xy}[29] contribution. Esr studies show that this orbital is particularly sensitive to the donor atom set. The mixing coefficient α^2 for the MO containing the unpaired electron, $\psi(\sigma^*) = \alpha d_{xy} - \alpha'\sigma_L$, may be estimated from the esr data for $Cu(mp)_2{}^{2-}$ and $Cu(pt)_2$ by use of the relation $\alpha^2 = -(A_{\parallel}/P) + (g_{\parallel} - 2.0023) + {}^3/_7(g_{\perp} - 2.0023) + 0.04$.[30] Taking P as 0.036 cm^{-1}, the data give α^2 as 0.73 for both $Cu(mp)_2{}^{2-}$ and $Cu(pt)_2$. In comparison, α^2 for bis(pyrocatecholato)copper(II) dianion has been estimated at 0.86,[8] while for certain $[Cu\text{–}S_4]^{2-}$ species α^2 has been placed at about 0.6.[31] Clearly, the degree of covalency in this σ^* orbital is sensitive to the donor set, and it increases as more sulfur atoms are placed in the coordination sphere. In the case of the nickel complexes $[Ni\text{–}X_2Y_2]^-$ esr studies appear to indicate that the nature of the half-filled orbital (which presumably is filled in the reduction of $[Ni\text{–}X_2Y_2]^-$ to $[Ni\text{–}X_2Y_2]^{2-}$) is much less sensitive to the donor atom set, and consequently the potential relating the nickel complexes is effected to a lesser extent by the nature of the donor atoms.

Oxidation of the $Ni(mn)_2{}^z$ species is slightly easier than oxidation of the corresponding $Ni(mp)_2{}^z$ complex. Considering the arguments of Vlcek[32] and those of our previous work,[5,8] the potentials for the $[Ni\text{–}O_2S_2]^z$ oxidations should respond to changes in the related ligand potentials (*e.g.*, $C_6H_4OS^{2-} \rightarrow C_6H_4OS^-$, $C_6H_4OS^- \rightarrow C_6H_4OS$). The necessary ligand potentials are unavailable since oxidation of mercaptophenols produces disulfides rather than semithioquinones and thioquinones. However, it is reasonable to expect that changes in extent of the π system will produce similar effects on the ease of oxidation of the free OO and OS ligands to their respective semiquinones or hypothetical semithioquinones.[33] Oxidation of *o*-pyrocatecholate to the semiquinone is 0.12 V more difficult than the corresponding oxidation of 1,2-naphthalenediolate.[33] Consequently, it is expected that the oxidation of mp^{2-} and $Ni(mp)_2{}^z$ will be more difficult than the oxidation of mn^{2-} and $Ni(mn)_2{}^z$. It is apparent that $Ni(pt)_2$ is much more difficult to oxidize than either of the other $[Ni\text{–}O_2S_2]^z$ species. The origin of this difference is unclear. It may be due to a simple charge effect or it may result from more subtle electronic effects.

Acknowledgment. The advice and encouragement of Professor R. H. Holm is gratefully acknowledged.

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[29] A planar geometry is assumed with *z* axis perpendicular to the molecular plane and the *x* axis bisecting the chelate rings.

[30] D. Kivelson and R. Neiman, *J. Chem. Phys.*, 35, 149 (1961).

[31] H. A. Kuska, M. T. Rogers, and R. E. Drullinger, *J. Phys. Chem.*, **71**, 109 (1967). Although the rigorous application of the equation used to obtain α^2 may be questioned, the trend of increasing covalency with increasing numbers of sulfur donors is certainly valid.

[32] A. A. Vlcek, *Progr. Inorg. Chem.*, **5**, 211 (1963).

[33] M. E. Peover, *J. Chem. Soc.*, 4540 (1962).