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Electrochemical Study of the Reduction Pathways of Metal 1,3-Dithioketonate Complexes

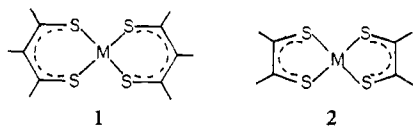
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Received June 8, 1977

Various voltammetric and physical methods have been employed in studying the reduction and oxidation pathways of nickel, palladium, and platinum 1,3-dithioketonate complexes. Studies at both mercury and platinum electrodes have been performed in several nonaqueous solvents, but mercury electrodes apparently interact with the complexes, so most of the work was carried out at platinum surfaces. The generalized complex MS_4 undergoes two successive reversible one-electron reductions in the range -0.8 to -1.8 V, leading to MS_4^- and MS_4^{2-} . The monoanion MS_4^- is generally not stable and undergoes a follow-up reaction which is higher order in the concentration of MS_4 . The product of this reaction is also electroactive, having a reduction wave near the potential of the MS_4^- to MS_4^{2-} couple and an oxidation wave near 0 V. Anodic oxidation of the product, for which a dimeric dianion structure is postulated, results in regeneration of the original MS_4 . An analysis of the reduction potentials of the eight complexes studied leads to the conclusion that the orbital involved in the reductions is mainly ligand based, in contrast to expectations based on previous theoretical treatments of the bonding in these molecules. Comparison is made of the redox behavior of these complexes with that of the analogous metal 1,2-dithiolates.

Introduction

Nickel-group metals form deeply colored square-planar 1,3-dithiolate complexes¹ of the type **1** reminiscent of the

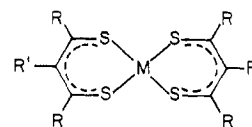


neutral metal 1,2-dithiolene complexes **2**.² The latter undergo a set of up to four electrochemical reductions²⁻⁹ which are generally reversible. The first two reductions involve a *predominantly ligand-based* orbital of B_{2g} symmetry,²⁻⁶ whereas subsequent reductions, leading to formation of rare d^9 and d^{10} complexes, involve a metal-based B_{1g} orbital.⁷⁻⁹ The facile reversible reductions of these complexes (called "dithiolene-type" behavior) attracted considerable interest as similar examples were sought in complexes with other ligands. Among the complexes which were proposed as being capable of "dithiolene-type" behavior were the metal(II) 1,3-dithioketonates, **1**.²

Schrauzer considered this problem from a theoretical point of view⁴ and concluded that "dithiolene-type" behavior would only be observed for complexes containing "even" ligands, that is, those containing an even number of ligand π centers. In this case, low-lying unfilled ligand orbitals, of proper symmetry to overlap metal orbitals, are available as a reduction site. It was argued that complexes containing ligands with an *odd* number of π centers, such as **1**, do not possess this important property and that "dithiolene-type" behavior is not expected for them. Later theoretical^{10,11} and experimental investigations¹¹⁻¹⁴ have tended to verify this "odd-even" hypothesis. Of central importance were the investigations of Holm and co-workers^{11,12} on metal dithiotropolonate complexes and the efforts of Martin et al.^{13,14} on the redox properties of 1,1-dithiolate complexes. These studies showed that reversible redox processes are only rarely observed in "odd" dithiolate complexes, and reversible reductions were ascribed to traditional changes of the metal oxidation state.^{13,14}

Understanding the electrochemical behavior of metal dithioacetylacetonate complexes (**1**) is crucial to an understanding of redox processes in "odd" dithiolate complexes. Bond, Heath, and Martin have shown¹⁵ that a number of these complexes undergo two or more reductions at a dropping mercury electrode. They also concluded that the reductions involved metal-based orbitals and postulated formation of

interesting and rare d^9 and d^{10} nickel-group (Ni, Pd, Pt) complexes. Because of our interest in metals in unusual oxidation states, we have investigated these and related complexes **3** by studying their redox processes at mercury and



M = Ni, Pd, Pt

- 3a**, R = CH₃, R' = H(sacsac)
b, R = H, R' = H(ptt)
c, R = H, R' = Br(Br(ptt))
d, R = NMe₂, R' = H(NMe₂,ptt)

platinum electrodes in a variety of nonaqueous solvents by polarography, cyclic voltammetry, and controlled-potential coulometry.

Our results were unexpected, in that all of our data support the conclusion that the reductions of these 1,3-dithioketonate complexes are *ligand based*, and suggested that the simple "odd-even" theory must be used with caution in accounting for the redox behavior of "odd" dithiolate complexes.

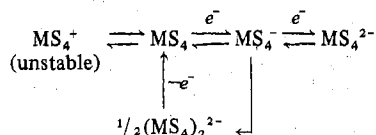
Experimental Section

The metal complexes Ni(sacsac)₂ and Pt(sacsac)₂ were prepared by a modification of the procedure of Barraclough et al.¹⁶ and were recrystallized from chloroform. Several attempts to prepare Pd(sacsac)₂ were unsuccessful. The complexes of propanedithiolate (ptt) and 2-bromopropanedithiolate (Br(ptt)) as well as Pd(NMe₂,ptt)₂ were obtained through the generosity of Dr. Ulrich Müller-Westerhoff of IBM at San Jose, Calif.

The purity of the M(sacsac)₂ complexes was a subject of concern since the synthesis of these materials involves intermediates in which oxygen takes the place of sulfur in the chelate structure, such as M(S₂C₃R₃)(SOC₃R₃), M(sacsac)(sacac). Indeed a mass spectrum of the crude reaction mixture of the Ni(sacsac)₂ preparation, run by Professor Peter Uden at the University of Massachusetts at Amherst, confirmed the presence of Ni(sacsac)(sacac) in the crude product (m/e 305). A careful vacuum fractional sublimation of the mixture yielded a fraction having a mass spectrum consistent with uncontaminated Ni(sacsac)₂. The electrochemical properties of this pure fraction were compared with those of the recrystallized samples used for most of our electrochemical work and were found to be identical with them.

Spectrograde solvents were purified before electrochemical use, except in the case of acetone, in which spectrograde solvent was used directly. Acetonitrile and dichloromethane were flash-distilled from calcium hydride and *N,N*-dimethylformamide (DMF) was fractionated through a 9-ft column from calcium hydride immediately before use.

Scheme 1



The variety of electrochemical solvents was used because of solubility problems with the complexes and in order to test the stability of the oxidized and reduced species in different media. Tetrabutylammonium hexafluorophosphate, Bu₄NPF₆, was employed as supporting electrolyte at approximately a 0.1 M concentration. It was prepared by metathesis of tetrabutylammonium iodide (Southwestern Analytical Chemicals) and ammonium hexafluorophosphate (Ozark-Mahoning) in acetone and precipitated by addition of water, purified by three recrystallizations from 95% ethanol, and vacuum-dried at 100 °C.

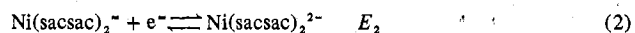
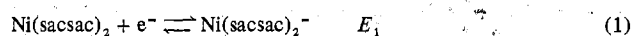
Commercially available mercury was pinholed several times through dilute nitric acid and distilled. Platinum electrodes were pretreated as given previously.⁸ All electrochemical experiments were conducted at ambient pressures in nitrogen-saturated solutions using conventional Metrohm cells for voltammetry or H-type cells for bulk electrolyses. Bulk electrolyses were taken to at least 95% completion for calculation of *n* values.

Electrochemical measurements were made with either a PAR 173 or 174 potentiostat and associated peripheral equipment.⁸ Electronic spectra were recorded on a Cary 14 spectrophotometer and attempts at recording ESR spectra of electrogenerated species employed a modified Geske-type cell¹⁷ and a Varian 4502 spectrometer with a 9-in. magnet.

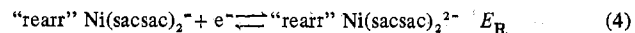
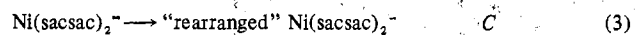
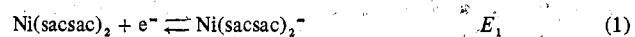
Results and Discussion

Effect of Electrode Material on Reduction Mechanism.

Previously published work on the reduction of the metal dithioacetylacetonate complexes involved voltammetry at the dropping mercury electrode.¹⁵ In that study, three waves were observed for the nickel and palladium complexes in the region -1.1 to -1.7 V (vs. SCE), and the heights of the last two waves were dependent on the polarographic drop time. On the basis of these measurements a reduction scheme was proposed which involved a stepwise two-electron reduction (the *E*₁*E*₂ mechanism shown in steps 1 and 2) from waves *A* and *B* in



competition with an *E*₁*C**E*_R mechanism involving waves *A* and *C* (steps 1, 3, and 4). Our initial polarographic studies were



consistent with the previous investigators' data. However, the relative heights of waves *A*, *B*, and *C* monitored during variable-sweep rate cyclic voltammetry at a mercury drop did not vary appreciably, as would be expected for a kinetically influenced process.

Further experiments, at platinum working electrodes, have shown that the "B" waves are present only when mercury is used for the reductions. We therefore have concluded that wave "B" is a spurious wave somehow associated with interaction of the complexes with the mercury electrode surface. Since this study was concerned primarily with the pure electron-transfer reactions of the complexes, all subsequent studies were conducted using platinum working electrodes (Pt buttons for cyclic voltammetry and Pt gauze for bulk electrolyses). Polarographic data were only employed for complexes in which the "B" wave was not observed.

General Redox Scheme. The overall redox behavior of the complexes is consistent with Scheme I, where MS₄ represents the neutral metal 1,3-dithioketonate.

Table I. Reduction and Oxidation Potentials (V) of Metal 1,3-Dithioketonate Complexes at Platinum Electrodes

Complex	Solvent ^a	E ₁ ^{b,c}	E ₂ ^d	E _d ^e	E _{ox} ^{a,f}
Ni(sacsac) ₂	CH ₃ CN	-1.10	-1.63		+1.15
Ni(ptt) ₂	DMF	-0.89	-1.40 ^g	-1.60 ^g	
Pd(sacsac) ₂	Acetone ^h	-1.20 ^h	-1.77 ^h		
Pd(ptt) ₂	CH ₃ CN	-0.87	-1.39	-1.45	+1.38
Pd(Me ₂ Nppt) ₂	CH ₂ Cl ₂	-1.87	<i>i</i>		+0.83
Pt(sacsac) ₂	CH ₃ CN	-1.21	-1.71	-1.8	+1.20
Pt(ptt) ₂	CH ₃ CN	-0.96		-1.57	+1.45
Pt(Br(ptt)) ₂	CH ₃ CN	-0.80		-1.68	

^a Solvent for reductions. In the case of M(sacsac)₂ complexes, CH₂Cl₂ was employed for oxidations. ^b Potential at 85% peak height in linear-scan voltammogram, corresponding to *E*_{1/2} for a reversible system. ^c Potential vs. saturated calomel electrode. ^d Potential of process ascribed to MS₄ → MS₄²⁻. ^e Potential of process ascribed to reduction of (MS₄)₂²⁻. ^f Potential of anodic peak current. All irreversible except for Pt(sacsac)₂. ^g Assignments as E₂ and E_d based on analogy to other complexes (see text). ^h From ref 15, with our assignment of authors' third wave as E₂. ⁱ Not observed because too negative for this solvent.

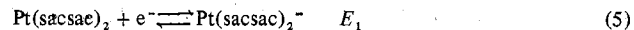
The neutral complexes MS₄ have an initial reduction wave at potentials ranging from -0.8 to -1.9 V vs. the saturated calomel electrode (Table I). The chemical reversibility of the reduction depends on the compound and the solvent employed, but the sacsac complexes generally show a greater degree of reversibility than do the ppt complexes. Cyclic voltammetric peak separations of 60–80 mV were observed for the reversible systems, confirming initial formation of the anion, MS₄⁻, via a one-electron change.

With the exception of the dimethylamino-substituted derivative 3d which has only one wave prior to solvent discharge, each complex also displays a second reduction, usually reversible, at a potential more negative than the first wave. In cases in which the monoanion MS₄⁻ is stable on the voltammetric time scale, this wave must be ascribed to the second one-electron reduction of the complex, E₂ (eq 2). However, if the anion is unstable and has reacted to form a product during the time of the electrochemical scan, the second wave is due to the reduction of that product. This wave is called E_d throughout the remainder of this paper.

The situation is made more complex by the fact that in the present case E₂ and E_d occur at very similar potentials. In certain instances we have been able to measure E₂ and E_d separately for a complex by varying the rate of the voltammetric scan. We have also gathered evidence that the product giving rise to E_d is a charged dimer of the original dithioketonate complex.

Reduction of Pt(sacsac)₂. The general cathodic behavior of these complexes can be illustrated by discussion of the reduction of Pt(sacsac)₂.

In acetonitrile at slow cyclic voltammetry (CV) scan rates (ca. 100 mV/s), the first wave (*e*_{pc} = -1.23 V) is essentially irreversible (Figure 1) and the second peak (-1.83 V) is due to the product reduction, E_d (steps 5–7).



Hence the *ECE* mechanism predominates in this time frame. However, at faster scan rates, the first peak becomes reversible (at the same potential) and the second peak sharpens and moves to a more positive (peak) potential of -1.72 V. Such a shift is in an opposite direction to the negative shifts which would arise either from quasi-reversibility of the redox couple or from uncompensated IR drop and must be ascribed to formation of a different electroactive species. This wave is due to reduction of the monoanion, which is stable during this fast CV scan (Figure 2). The abnormally broad "second

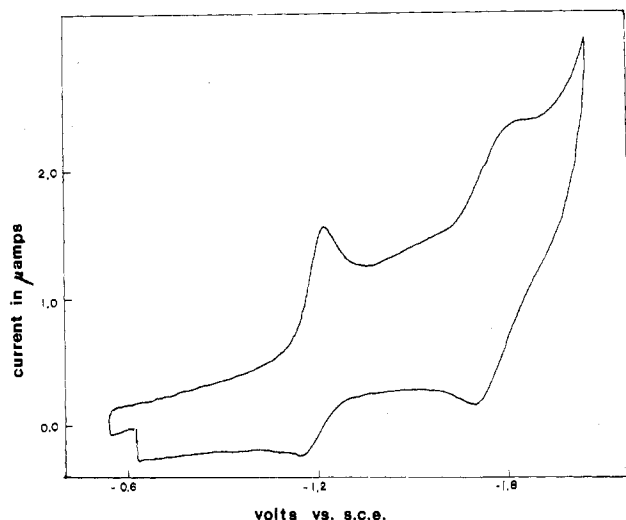


Figure 1. Slow cyclic voltammogram (ca. 100 mV/s) of cathodic waves of $\text{Pt}(\text{sacsac})_2$ in CH_3CN at a platinum-bead electrode. Note the broad peak in the vicinity of -1.7 V which actually contains contributions from two waves.

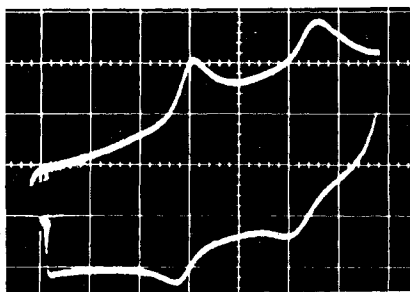
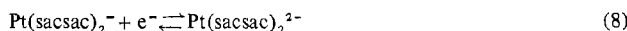


Figure 2. Fast cyclic voltammogram (ca. 5 V/s) of cathodic waves of $\text{Pt}(\text{sacsac})_2$ in CH_3CN at a platinum electrode. Same experiment as Figure 1.

wave" for $\text{Pt}(\text{sacsac})_2$ seen at slower CV scan rates (Figure 1) therefore arises from a mixture of E_2 (eq 8) and E_d (eq 7)



occurring on this time scale.

Bulk electrolysis studies at a platinum gauze in DMF (for greater solubility of the complex) support this scheme. Complete electrolysis at -1.4 V yields coulometry consistent with a one-electron change ($n = 0.97 e^-$). A fast CV scan of the solution after only *partial* electrolysis revealed two inflections in the "second wave" region, at -1.7 and -1.8 V, due to waves E_2 and E_d . Completion of the electrolysis resulted in a well-defined wave at -1.8 V due to the product of the follow-up reaction of the monoanion.

This product also showed an oxidation wave, at about 0 V, of about the same height as the original one-electron reduction wave. If the reduced solution was reoxidized at $+0.2$ V, the original neutral monomer $\text{Pt}(\text{sacsac})_2$ was regenerated. This can be shown either by CV scans from $+0.2$ to -1.4 V, in which the reduction peak for $\text{Pt}(\text{sacsac})_2$ reappears, or in partial bulk reelectrolysis, which we did not take to completion due to filming of the Pt gauze.

The initially purple $\text{Pt}(\text{sacsac})_2$ solution became deep red during the reduction and a spectrum of the electrolyzed solution had absorption maxima at 565 and 337 nm. These are close to the bands at 550 and 357 nm reported for $\text{Pt}(\text{sacsac})_2$ ¹⁸ and suggest that the electronic structure of $\text{Pt}(\text{sacsac})_2$ and the reduction product may be similar. Repeated attempts at measuring ESR spectra of the reduced solutions failed, implying that the reduced product is diamagnetic. These and

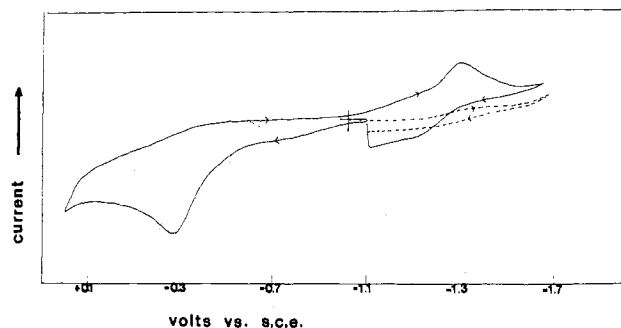


Figure 3. Cyclic voltammograms (ca. 100 mV/s) at Pt bead taken after bulk reduction at -1.3 V of $\text{Ni}(\text{sacsac})_2$ in DMF. Dotted line shows absence of wave for $\text{Ni}(\text{sacsac})_2$ when potential is scanned negative from -1 V. But if oxidation wave is first scanned (solid line), $\text{Ni}(\text{sacsac})_2$ peak appears from regeneration during oxidation of bulk product.

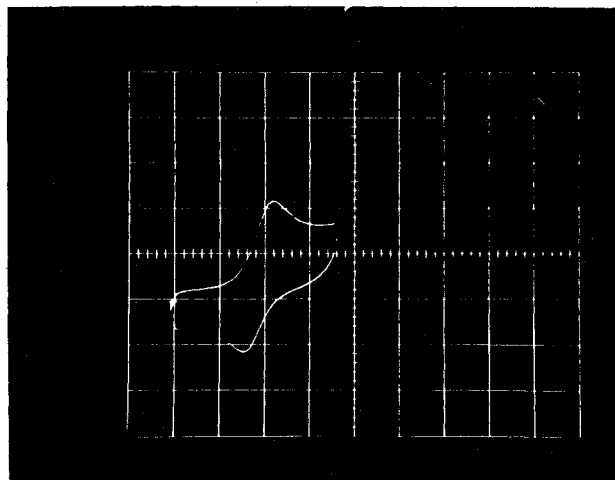


Figure 4. Fast cyclic voltammogram (ca. 5 V/s) of first reduction of $\text{Ni}(\text{ptt})_2$ in DMF at Pt bead.

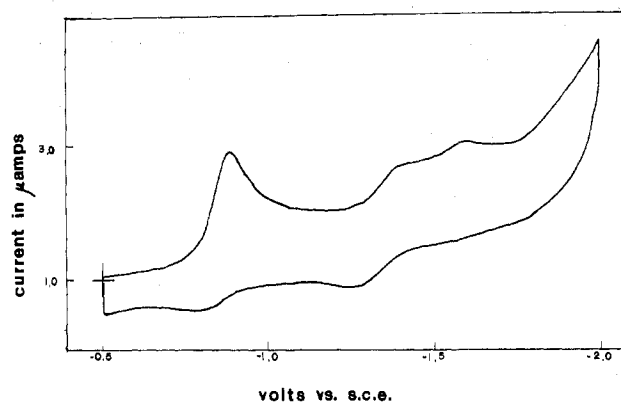


Figure 5. Slow cyclic voltammogram (ca. 50 mV/s) of $\text{Ni}(\text{ptt})_2$ in DMF showing two waves due to E_2 and E_d (see text) in vicinity of -1.5 V.

other data are used below to argue for a dimeric structure of the reduction product.

Reduction of $\text{Ni}(\text{sacsac})_2$. $\text{Ni}(\text{sacsac})_2$ was quite extensively studied, the reduction being investigated in DMF, CH_3CN , acetone, and methylene chloride. The monoanion is reasonably stable, with CV experiments yielding ratios of the anodic to cathodic currents (i_a/i_c)¹⁹ close to 1.0 at moderate scan rates. An increased rate of the follow-up reaction of $\text{Ni}(\text{sacsac})_2^-$, as measured by a decrease of i_a/i_c , was measured for higher concentrations of the complex. For instance, in methylene chloride solution at a 200 mV/s scan rate the i_a/i_c values and

concentrations observed were 0.99 (4.5×10^{-4} M), 0.94 (6.5×10^{-4} M), and 0.86 (9.3×10^{-4} M). This provides evidence that the follow-up reaction of Ni(sacsac)₂ is higher order in the complex. A dependence of i_a/i_c on concentration was qualitatively noted for the first reduction of Pt(sacsac)₂, but we do not report quantitative data due to measurement problems arising from the poor solubility of Pt(sacsac)₂ and the higher reactivity of its monoanion.

Bulk electrolysis on the first wave, at -1.3 V, in DMF gave a one-electron reduction ($n = 0.95 e^-$). The product gave the characteristic waves at -1.6 V (reduction) and +0.1 V (oxidation). A CV scan of the electrolysis solution going negative from -0.7 V (curve A in Figure 3) showed that no unreduced Ni(sacsac)₂ remained in solution, but if the potential was first scanned to include the oxidation wave, the Ni(sacsac)₂ peak reappeared (curve B, Figure 3), indicating regeneration of the starting material from oxidation of the reduction product. This reduced solution was also apparently diamagnetic, eliminating the possibility that the reduced product is simply a structurally rearranged¹⁵ (e.g., tetrahedral) Ni^I(sacsac)₂⁻.

Metal Propanedithiolate Complexes. All of the ptt complexes have very unstable anions and fall in the E_1CE_d class (steps 5-7), in which the anions undergo rapid reaction to give a product with a wave in the region of -1.4 to -1.6 V. Fast CV measurements of Ni(ptt)₂ (Figure 4) and Pd(ptt)₂ establish that the first wave involves initial formation of the monoanion, and slower scans on Ni(ptt)₂ clearly show the two separate waves for E_2 ($NiS_4^- \rightleftharpoons NiS_4^{2-}$) and E_d (Figure 5). At higher scan rates, the peaks merge into a very broad feature and we were not able to definitively assign the separate peaks to E_2 and E_d , so the assignment (Table I) was made by analogy to Pd(ptt)₂ and Pt(sacsac)₂, in which E_d was more negative.

One interesting feature of the ptt complexes is that when the voltage is scanned out to potentials negative of E_d , as in Figure 5, the anodic oxidation of M(ptt)₂⁻ is not observed; that is, the first reduction appears completely irreversible. This effect is observed for all M(ptt)₂ complexes, and we cannot account for this behavior, except to note the obvious implication that the product of the E_d reduction product reacts with M(ptt)₂⁻ in the electrochemical reaction layer.

The complexes Pd(ptt)₂, Pt(ptt)₂, and Pt(Br(ptt))₂ all gave highly reactive anions, and CV scan rates of at least 20 V/s were necessary to see evidence for reversibility of the initial reduction. Each complex also gave an E_d wave from reaction of the anion, and bulk electrolysis on the first wave of Pt(ptt)₂ gave $n = 1.05 e^-$.

Pd(Me₂Nppt)₂, in which the 1,3 hydrogens of the ptt ligand have been replaced by the NMe₂ group, gave a reversible reduction in CH₂Cl₂, the only solvent in which we were able to dissolve the complex to an appropriate extent.

Oxidation of the Neutral Complexes. The oxidation of the MS₄ complexes was briefly investigated, and anodic waves were observed for several of the complexes. The oxidation of Pt(sacsac)₂ was reversible, indicating the formation of Pt(sacsac)₂⁺, but all other oxidations were irreversible, even at fast CV scan rates. The mechanism of the irreversible oxidation of metal 1,3-dithioketonates has been investigated by Martin and co-workers and the reader is referred to their paper for further details.²⁰

Fate of the MS₄ Monoanions. As noted above, bulk electrolyses of representative complexes like Pt(sacsac)₂, Pt(ptt)₂, and Ni(sacsac)₂ at the potential of their first reduction wave gave a one-electron change resulting in highly colored (blue to red) air-sensitive solutions which decompose in air to give yellow-brown solutions. However, if these colored solutions were anodically reoxidized, at a platinum anode, the original neutral complex was regenerated in good yield. This general route appears to be unaltered by solvent composition, except for minor kinetic effects. The reduced solutions were

Table II. Differences in Potential between the First Two One-Electron Reductions of Nickel-Group Dithiolate and Related Complexes

Ligand	Metal	ΔE , V	Ref
1,2-S ₂ C ₂ (CN) ₂	Ni	0.86	9
	Pd	0.72	9
	Pt	0.85	9
1,2-S ₂ C ₂ (CF ₃) ₂	Ni	0.97	2
	Pd	0.88	2
	Pt	1.05	2
1,2-S ₂ C ₂ (CH ₃) ₂	Ni	1.05	2
	Pd	0.81	2
	Pt	0.94	2
1,2-S ₂ C ₂ H ₂	Ni	1.09	2
	Pd	0.89	2
1,2-(NH) ₂ C ₂ (CN) ₂	Ni	0.77	9
	Pd	0.60	9
	Pt	0.76	9
1,3-S ₂ C ₃ (CH ₃) ₂ H	Ni	0.53	This work
	Pd	0.57	15
	Pt	0.50	This work
1,3-S ₂ C ₃ H ₃	Ni	0.51	This work
	Pd	0.52	This work

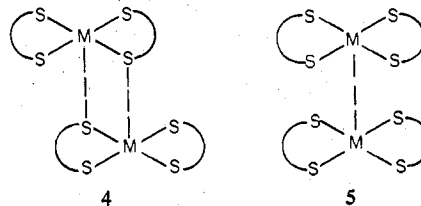
apparently diamagnetic, as shown by the absence of an ESR signal, and CV data for the sacsac complexes indicate that the rate of decomposition of MS₄⁻ is higher order in the concentration of the complex.

All of these data are consistent with formation of a dimeric dianion as the product of the follow-up reaction of MS₄⁻. This process (9) could occur either by reaction of MS₄ and MS₄⁻

$$MS_4 + e^- \rightleftharpoons MS_4^- \longrightarrow \frac{1}{2}(MS_4)_2^{2-} \quad (9)$$

to form (MS₄)₂²⁻, followed by the immediate one-electron reduction of the dimer monoanion, or by direct reaction of two MS₄ monoanions. Oxidation of the dimer (at about +0.1 V) results in cracking of the dimer and formation of the initial, monomeric, starting material MS₄.

Dimerization of planar dithiolate complexes is not uncommon. Dimers of cobalt and iron 1,2-dithiolate complexes are well-known,²¹⁻²³ Pd(S₄C₄H₄)₂ as well as its Pt analogue has been shown to be dimeric in the crystal,²⁴ and weaker interactions between monomeric metal dithiolene anions are also known.²⁵⁻²⁷ The majority of these dimers involve formation of a bond between the metal of one unit and a sulfur atom of another unit, as in **4**, but direct metal-metal bonded species like **5** are also known.²⁴



Site of the MS₄ Reduction. The molecular orbital calculations of Fresco and co-workers¹⁸ predicted that the reductions of the MS₄ complexes reported here would involve metal-based orbitals, due to the lack of low-lying empty ligand orbitals. However, our electrochemical data are not consistent with this hypothesis.

Let us consider in some detail the effects of changes in the metal and in the ligand substituents on the potentials of E_1 and E_2 . We note the following: (1) The potential of the first reduction is highly dependent on the identity of the ligand substituent [a 1-V change from Pd(ptt)₂ to Pd(NMe₂ptt)₂]. Since we have a maximum of three substituent groups for an individual metal, we do include quantitative correlations of

$E_{1/2}$ potentials with substituent constants, but a correlation of the half-wave potentials of the three palladium complexes (with $R = H, CH_3, Me_2N$) with Hammett σ functions was found. (2) The first reduction potential is virtually independent of the metal. For a particular ligand (i.e., ptt or sacsac) the potential of the MS_4 reduction varies by 100 mV or less as the metal is changed from Ni to Pd to Pt. (3) The difference in potential between the two reductions E_1 and E_2 , ΔE , is virtually constant (see Table II) as the metal is changed.

The last point deserves elaboration. Table II gives ΔE values available from previous literature on 1,2-dithiolato (MS_4) and 1,2-diamino (MN_4) reductions. These reductions are known to involve a highly delocalized but largely ligand-based orbital^{4,28,30} and are responsible for the "dithiolene-type" redox behavior of these MS_4 complexes with "even" dithiolate ligands.⁴ In each case, ΔE is fairly constant in going from Ni to Pd to Pt, indicative of the small amount of metal involvement in the redox orbital. In our sacsac complexes, about 70 mV separates ΔE in the Ni, Pd, and Pt cases, and the ΔE 's for the Ni- and Pd-ptt complexes are virtually identical [E_2 for Pt(ptt)₂ could not be measured due to the rapid decomposition of Pt(ptt)₂⁻].

We believe that all of these data are consistent with the MS_4 reduction site being largely *ligand based* in the metal 1,3-dithioketonates. If stepwise reduction from M(II) to M(I) and M(0) complexes were being observed, we would expect ΔE to vary to a much greater degree as the metal is changed. Several examples of apparent $d^8 \rightarrow d^{10}$ stepwise reductions involving congeneric first-, second-, and third-row transition-metal complexes of the same ligand support this statement.^{9,30-32}

In principle, we can also obtain information on the nature of the oxidation site (metal vs. ligand) by the potential difference between the first reduction and first oxidation wave. If both orbitals are ligand based, this value should remain fairly constant as either the metal or ligand is changed. Such an analysis has been successfully employed by Davis et al. in an extensive study of metalloporphyrin complexes. They found that the ligand-based reductions and oxidations of a series of metal octaethylporphyrin complexes were separated by 2.25 ± 0.15 V. In the present case, we have been able to obtain a value for five metal 1,3-dithioketonate complexes and found that 2.47 ± 0.23 V includes all the complexes studied. However, the oxidation potentials are irreversible (giving nonthermodynamic potentials) and the number of complexes measured is small. So although these data would support a claim that the *oxidations* are also ligand based, we believe it would be dangerous to base such a conclusion on our data alone.

Conclusions

The nickel-group 1,3-dithioketonate complexes undergo two successive one-electron reductions in aprotic solvents involving an orbital that is apparently mostly ligand in character. In this respect, the redox behavior of these "odd" dithiolate complexes is similar to that of the "even" 1,2-dithiolate complexes.

Important differences do exist, however, in the odd and even cases. The odd dithiolate complexes have a lower electron affinity than the even dithiolate complex with the same ligand substituent (e.g., H or Me) by about 1 V. Also, the MS_4 anions derived from the odd chelate are much less stable than those derived from the even ligand and undergo fairly rapid reaction to form what is apparently a dimeric dianion, $(MS_4)_2^{2-}$, from which the starting complex can be regenerated.

Thus it can be stated that although the simple "odd-even"

theory of Schrauzer is a generally useful concept, it should not be used blindly to predict redox behavior (especially, the reversibility) of complexes derived from "odd" chelates.

Clearly, a more quantitative knowledge of the composition of the half-filled orbital in the monoanions of the complexes we have studied is desirable, and efforts to obtain ESR data on anions generated by reduction under stabilizing conditions (e.g., low temperatures) would be worthwhile.

Acknowledgment. The authors are grateful to the National Science Foundation for support of this work and to the Matthey Bishop Co. for a generous loan of platinum and palladium salts. We are also indebted to Dr. Ulrich Müller-Westerhoff for samples of the ptt complexes and to Dr. Alan Bond for extensive discussions concerning his work on metal dithiolate electrochemistry.

Registry No. Ni(sacsac)₂, 10170-79-3; Ni(sacsac)₂⁻, 64705-81-3; Ni(sacsac)₂²⁻, 64705-82-4; Ni(ptt)₂, 64705-83-5; Ni(ptt)₂⁻, 64705-84-6; Ni(ptt)₂²⁻, 64705-85-7; (Ni(ptt)₂)₂²⁻, 64705-86-8; Pd(ptt)₂, 64705-87-9; Pd(ptt)₂⁻, 64705-77-7; Pd(ptt)₂²⁻, 64705-78-8; (Pd(ptt)₂)₂²⁻, 64705-79-9; Pd(Me₂Nptt)₂, 64705-80-2; Pd(Me₂Nptt)₂⁻, 64705-68-6; Pt(sacsac)₂, 10210-73-8; Pt(sacsac)₂⁻, 64705-69-7; Pt(sacsac)₂²⁻, 64705-70-0; (Pt(sacsac)₂)₂²⁻, 64728-19-4; Pt(sacsac)₂⁺, 64705-71-1; Pt(ptt)₂, 64705-72-2; Pt(ptt)₂⁻, 64705-73-3; (Pt(ptt)₂)₂²⁻, 64705-74-4; Pt(Br(ptt))₂, 64705-75-5; Pt(Br(ptt))₂⁻, 64705-76-6; (Pt(Br(ptt))₂)₂²⁻, 64728-20-7.

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