

responds to all of the trends characteristic of similar equatorial complexes (listed in Table I) that we submit $\text{Co}(\text{DTPA})\text{NO}_2^-$ is indeed an *equatorial* isomer.

Aquo Complex Intermediates.—In this work, the aquo complexes of the pentadentate aminocarboxylate ligands have been identified by pmr. The importance of these aquo species as synthetic intermediates has

not been adequately stressed in previous literature. A number of these interconversion reactions are shown in Scheme I. The details describing these interconversions are outlined in the Experimental Section.

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CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF MELBOURNE, PARKVILLE, 3052, VICTORIA, AUSTRALIA

Polarography of the Planar Dithioacetylacetonate Complexes of Cobalt(II), Nickel(II), Palladium(II), and Platinum(II) and Other Related Complexes of the Same Ligand in Acetone¹

By A. M. BOND, G. A. HEATH, AND R. L. MARTIN*

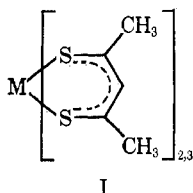
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The dc polarographic behavior of the planar dithioacetylacetonates $\text{M}(\text{SacSac})_2$ with $\text{M}(\text{II}) = \text{Co}, \text{Ni}, \text{Pd},$ and Pt , the octahedral complexes $\text{M}(\text{SacSac})_3$ with $\text{M}(\text{III}) = \text{Co}$ and Ir , and the ruthenium nitrosyl complex $\text{Ru}(\text{NO})(\text{SacSac})_2\text{Cl}$, using acetone as solvent and tetraethylammonium perchlorate as the supporting electrolyte, is described. It has been established that, in general, the transition metal dithioacetylacetonates have a well-defined capacity to accept one or more electrons in a reversible stepwise manner, the number varying systematically with the d-electron configuration and stereochemistry of the central metal ion. The magnitude of the reduction potentials and their reversible nature suggest that the isolation of metal dithioacetylacetonates in unusually low formal oxidation states should be possible.

Introduction

In a recent paper we described the polarographic behavior of the $\text{Fe}(\text{III}), \text{Ru}(\text{III}),$ and $\text{Os}(\text{III})$ low-spin octahedral d_e^5 complexes of dithioacetylacetonate in acetone.² The polarography of these systems was well-defined. Each of these complexes was found to undergo a ready reversible one-electron reduction which can be regarded as effectively completing the occupancy of the d_e subshell. In contrast, the low-spin d_e^6 complex $\text{Rh}(\text{SacSac})_3$ (where SacSac^- is the dithioacetylacetonate ligand $\text{S}_2\text{C}_5\text{H}_7^-$), in which the stabilized metal subshell is fully occupied, could only be reduced irreversibly at much more negative potentials.

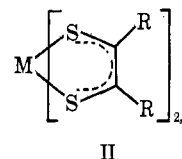
The polarographic behavior of these $\text{M}(\text{SacSac})_3$ complexes (I) is completely consistent with their known



chemical and spectroscopic properties and provides useful information on the chemistry of dithioacetylacetonate complexes. The results of this work suggested that further polarographic studies on other dithioacetylacetonate complexes should be fruitful.

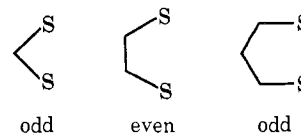
The recent discovery³ of ready stepwise reductions of

the neutral metal "dithienes" $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_x$ (II) and the



isolation of series of "dithiolene" complexes, $[\text{M}(\text{S}_2\text{C}_2\text{R}_2)_3]^{0,1-},^{2-},^{3-}$ and $[\text{M}(\text{S}_2\text{C}_2\text{R}_2)_2]^{0,1-},^{2-}$ provides a further incentive for extending our previous studies of the octahedral d^5 and d^6 complexes to the corresponding d^7 and d^8 planar complexes (I).

McCleverty has suggested that since the planar dithioacetylacetonates have resonance-stabilized delocalized ground states, they might show similar reversible redox properties³ to the dithiolenes which have nonclassical ground states. However, according to Schrauzer, there is a fundamental difference between the π -electronic structures of "even" and "odd" unsaturated organosulfur ligands⁴ and he predicted that the remarkable electron affinity of the dithiolenes should not be shared either by the dithioacetylacetonates or by complexes of 1,1-dithio ligands such as dithiocarboxylates and dithiocarbamates.



Extensive studies by Fackler⁵ and Gray and coworkers⁶ have confirmed that metal(II) bis(dithiocarba-

(4) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

(5) J. P. Fackler and D. Coucouvanis, *Chem. Commun.*, 556 (1965); *J. Amer. Chem. Soc.*, **88**, 3913 (1966).

(6) B. G. Werdén, E. Billig, and H. B. Gray, *Inorg. Chem.*, **5**, 78 (1966).

(1) This work is also described in a thesis presented by G. A. Heath to the University of Melbourne, in partial fulfillment of the requirements for the Ph.D. degree, Oct 1970.

(2) A. M. Bond, G. A. Heath, and R. L. Martin, *J. Electrochem. Soc.*, **117**, 1362 (1970).

(3) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

mates) and bis(dithiocarboxylates) do not tend to form anions by reduction and that, in general, complexes of 1,1-dithio ligands have no well-defined electron-transfer reactions.

To serve adequately all the above purposes of this study, the polarographic behavior of the diamagnetic planar⁷⁻⁹ complexes $M(\text{SacSac})_2$ of $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Pd}(\text{II})$, and $\text{Pt}(\text{II})$ and of some additional low-spin octahedral¹⁰ complexes, $\text{Ir}(\text{SacSac})_3$ and $\text{Co}(\text{SacSac})_3$, and of the complex¹¹ $\text{Ru}(\text{SacSac})_2(\text{NO})\text{Cl}$ was studied and the results are reported below.

The electrochemical system employed acetone as the solvent with a completely nonaqueous $\text{Ag}-\text{AgCl}$ reference electrode, partly for convenience and partly because the compounds were known not to interact with acetone.²

Experimental Section

Polarographic studies were carried out in BDH Analar grade acetone with 0.1 *M* tetraethylammonium perchlorate as the supporting electrolyte.

A Metrohm Polarcord, E 261, was used in conjunction with a Metrohm IR Compensator, E 446, and a three-electrode system consisting of a dropping-mercury electrode and two identical acetone $\text{Ag}-\text{AgCl}$ (0.1 *M* LiCl) reference and auxiliary electrodes. Details of these, and other aspects of the polarography in acetone such as reproducibility, are described elsewhere.² In the rapid polarographic method, short controlled drop times of 0.16 sec were achieved with a Metrohm Polarographie Stand, E 354.

All potentials in this work are reported relative to the $\text{Ag}-\text{AgCl}$ reference electrode.

The dithioacetylacetonate complexes were prepared and purified as described in the literature.⁷⁻¹¹ The concentrations employed in the test solutions ranged from 10^{-3} to 10^{-5} *M*.

Test solutions were degassed with argon which was previously passed through two acetone-filled wash bottles and a spray trap. All solutions were thermostated at $20 \pm 0.1^\circ$.

Results and Discussion

(a) **The Planar Complexes.**—For all the planar dithioacetylacetonates, $M(\text{SacSac})_2$, two one-electron reductions are observed



Reduction to the zerovalent state at the dropping-mercury electrode, *dme*, implies that either the free metal (amalgam) or a zerovalent metal complex may be formed. The latter, even if chemically reactive and therefore short-lived, may still be a viable species in the electrode process and stable on the polarographic time scale (approximately 10^{-1} to 10 sec).

A conventional polarogram of $\text{Co}(\text{SacSac})_2$ is shown in Figure 1. Both wave heights are linearly dependent both on concentration and the square root of the mercury column height. Therefore, the electrode processes are diffusion controlled.

Plots of E_{dme} vs. $\log [(i_d - i)/i]$ are linear with slopes of 58 ± 2 and 59 ± 2 mV for the first (more positive) and second (more negative) waves, respectively, indicating that each wave involves a reversible one-electron reduction step.

With conventional polarography, as can be seen in Figure 1, the waves are not of equal height because the dependence of drop time with the applied potential is

(7) R. L. Martin and I. M. Stewart, *Nature (London)*, **210**, 522 (1966).

(8) R. Beckett and B. F. Hoskins, *Chem. Commun.*, 909 (1967).

(9) C. G. Barraclough, R. L. Martin, and I. M. Stewart, *Aust. J. Chem.*, **22**, 891 (1969).

(10) G. A. Heath and R. L. Martin, *Chem. Commun.*, 951 (1969).

(11) G. A. Heath and R. L. Martin, *Aust. J. Chem.*, **23**, 2297 (1970).

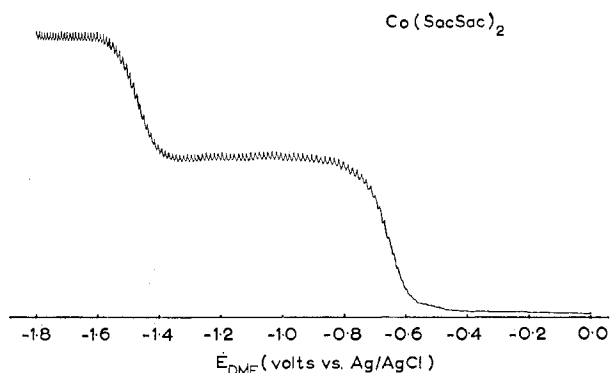


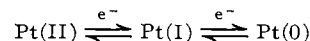
Figure 1.—Conventional dc polarogram of $\text{Co}(\text{SacSac})_2$ in acetone.

pronounced in acetone. However, under rapid polarographic conditions, with a short controlled drop time of 0.16 sec, the polarographic parameters remain unaltered and the waves are of equal height. Since the two rapid waves have equal diffusion currents, the same number of electrons must be involved in each electrode process. This demonstrates that in acetone rapid polarographic measurements are extremely useful for eliminating this problem and for assisting the interpretation of the polarographic data.

Thus, $\text{Co}(\text{SacSac})_2$ has two reversible one-electron reductions at -0.66 and -1.46 V vs. $\text{Ag}-\text{AgCl}$. If the initial reduced species is $\text{Co}(\text{SacSac})_2^-$, isoelectronic with neutral $\text{Ni}(\text{SacSac})_2$, then the first reduction step amounts to filling the highest half-occupied d orbital, $d^7 \rightarrow d^8$. This seems to be the most likely electrode process since an alternative process such as the loss of a bidentate dithioacetylacetonate ligand is unlikely to be rapid enough for the observation of a reversible electrode process, although the possibility cannot be ruled out. The second reversible one-electron reduction thus offers the interesting possibility that the product may be a zerovalent complex. The polarographic behavior of the $\text{Co}(\text{SacSac})_2$ complex may be contrasted with that of $\text{Co}(\text{ClO}_4)_2$ which undergoes an extremely irreversible two-electron reduction $\text{Co}(\text{II}) \rightarrow \text{Co}(0)$ in acetone at -0.85 V vs. $\text{Ag}-\text{AgCl}$ ($E_{1/4} - E_{3/4} = 190$ mV).

Conventional polarographic data for the planar d^8 platinum group complexes are collected in Table I. In each case, the first wave $M(\text{II}) + e^- \rightleftharpoons M(\text{I})$ represents a diffusion-controlled reversible one-electron reduction, according to the usual criteria. However, the detailed nature of the second electrode process $M(\text{I}) + e^- \rightarrow M(0)$ varies with the nature of the coordinated metal atom.

The platinum complex $\text{Pt}(\text{SacSac})_2$ has the simplest polarography, with two extremely well-defined waves. Under rapid polarographic conditions, the two waves are equal in height and both waves give linear $\log [(i_d - i)/i]$ plots consistent with two consecutive reversible one-electron reductions

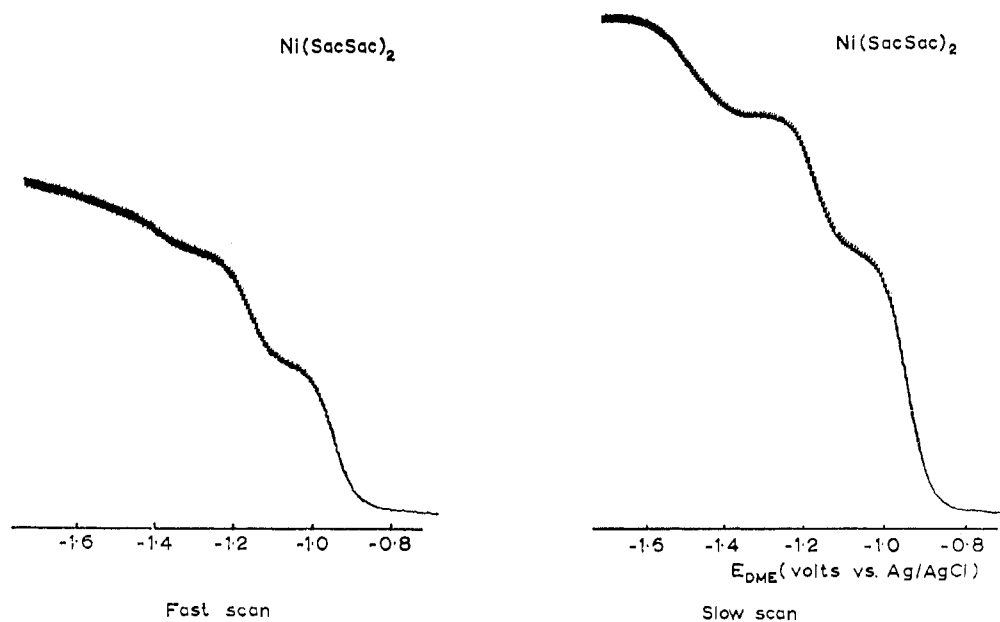


For $\text{Ni}(\text{SacSac})_2$ the first reduction step is reversible and well behaved. However, the polarography is less straightforward with respect to the $\text{Ni}(\text{I}) + e^- \rightarrow \text{Ni}(0)$ electrode process. Figure 2 shows the conventional and rapid dc polarograms. Analysis of plots of E_{dme} vs. $\log [(i_d - i)/i]$ indicates that the two prin-

TABLE I
 POLAROGRAPHIC PARAMETERS FOR THE PLANAR d^8 COMPLEXES $M(\text{SacSac})_2$

Drop time, ^a sec	$E_{1/2}$, ^b V	S_p , ^c mV	$E_{1/2}$, ^b V	S_p , ^c mV	$i_d(\text{B/A})$ ^d	$E_{1/2}$, ^b V	S_p , ^c mV	$i_d(\text{C/A})$ ^d
	Ni(II) $\xrightarrow{\text{A}}$ Ni(I)		Ni(I) $\xrightarrow{\text{B}}$ Ni(0)			Ni(I) $\xrightarrow{\text{C}}$ Ni(0)		
3.28	-0.944	54	-1.16	~70	0.43	-1.45	80	0.62
2.32	-0.944	56	-1.14	~70	0.48	-1.47	88	0.55
1.71	-0.940	54	-1.16	~62	0.50	-1.47	88	0.50
1.33	-0.940	58	-1.16	~60	0.54	-1.47	92	0.45
1.02	-0.940	54	-1.18	~70	0.60	-1.48	104	0.38
	Pd(II) $\xrightarrow{\text{A}}$ Pd(I)		Pd(I) $\xrightarrow{\text{B}}$ Pd(0)			Pd(I) $\xrightarrow{\text{C}}$ Pd(0)		
3.13	-0.952	60	-1.38	56	0.62	-1.52	68	0.35
2.00	-0.956	60	-1.38	50	0.69	-1.54	60	0.32
1.36	-0.960	60	-1.40	56	0.69	-1.55	56	0.27
1.11	-0.956	64	-1.40	64	0.65	-1.54	64	0.28
	Pt(II) $\xrightarrow{\text{A}}$ Pt(I)		Pt(I) $\xrightarrow{\text{B}}$ Pt(0)					
3.00	-0.992	50	-1.504	64	0.85			
2.00	-0.996	50	-1.504	70	0.83			
1.44	-1.000	52	-1.504	72	0.81			
1.11	-1.002	52	-1.502	72	0.81			
0.96	-1.000	56	-1.512	72	0.76			

^a Measured at E midway between $E_{1/2}$ (A) and $E_{1/2}$ (B); proportional changes occur throughout the potential range. ^b With reference to Ag-AgCl. ^c $S = E_{1/4} - E_{3/4}$. ^d Ratio of diffusion currents.


 Figure 2.—Conventional and rapid dc polarograms of $\text{Ni}(\text{SacSac})_2$ in acetone.

cipal waves, *i.e.*, the two most positive waves in Figure 2, represent reversible one-electron reductions. However, the presence of a third wave at more negative potentials, which is extremely drop time dependent, indicates that an alternative kinetically controlled pathway is also available for the second reduction $\text{Ni(I)} + e^- \rightarrow \text{Ni(0)}$. This alternative irreversible step is very much less apparent at the very short drop times and fast scan rates of potential of the rapid polarographic method (see Figure 2). As the drop time of rapid polarography is so much shorter than conventional dc polarography, the rapid method can be likened to a streaming mercury electrode. It is not surprising therefore to observe that the fast or reversible electrode process is considerably favored over the sluggish alternative for the reduction $\text{Ni(I)} + e^- \rightarrow \text{Ni(0)}$.

Table I shows clearly how the more reversible of the two $\text{Ni(I)} + e^- \rightarrow \text{Ni(0)}$ electrode processes also becomes favored at the shorter drop times even with conventional polarography and that the combined wave height for the two $\text{Ni(I)} + e^- \rightarrow \text{Ni(0)}$ waves is always almost equal to the height of the $\text{Ni(II)} + e^- \rightleftharpoons \text{Ni(I)}$ wave, as would be expected.

The palladium complex $\text{Pd}(\text{SacSac})_2$ exhibits intermediate behavior to $\text{Ni}(\text{SacSac})_2$ and $\text{Pt}(\text{SacSac})_2$. The third (most negative) wave is less apparent than for $\text{Ni}(\text{SacSac})_2$ with conventional polarography and disappears completely with the very short drop time of rapid polarography. The rapid polarogram is very similar to $\text{Pt}(\text{SacSac})_2$ and consists only of two reversible one-electron reduction steps. Conventional and rapid dc polarograms of $\text{Pd}(\text{SacSac})_2$ are shown in

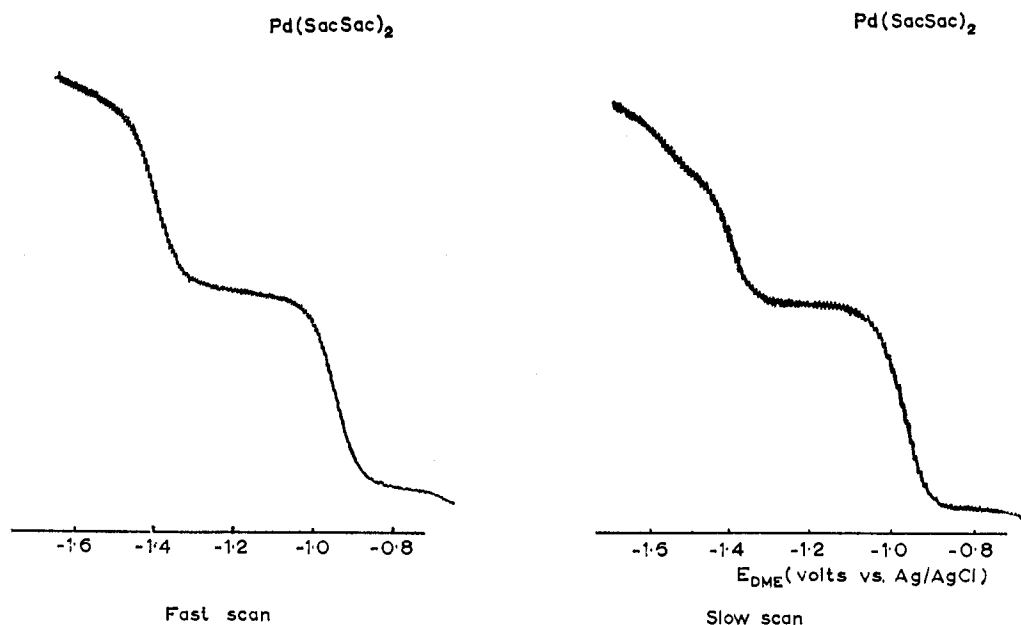
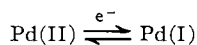


Figure 3.—Conventional and rapid dc polarograms of Pd(SacSac)₂ in acetone.

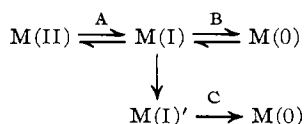
Figure 3. The combined heights of the two Pd(I) + e⁻ → Pd(0) waves are equivalent to the height of the



wave.

For the planar d⁸ complexes it appears that the two principal electrode processes in each case represent reversible one-electron reductions and the polarographic behavior is similar to that for the d⁷ Co(SacSac)₂ complex. However, an alternative kinetically controlled pathway is also available for the second reduction step of the planar d⁸ complexes. It seems that this pathway becomes increasingly sluggish along the series Ni(SacSac)₂, Pd(SacSac)₂, Pt(SacSac)₂.

This behavior suggests that a relatively slow rearrangement of the first reduction product may occur so that there are two distinct univalent metal species available for further reduction as in the scheme



Polarographic data for the cobalt(II) and nickel(II) complexes have been reported independently by Ouchi and coworkers.¹² They employed acetonitrile and dimethylformamide as solvents in conjunction with an aqueous calomel reference electrode and aqueous KCl-agar salt bridges. In each case, extremely irreversible waves and complex polarograms were observed which were assumed to represent M(II) → M(0) reductions of intact and partly solvolyzed forms of the chelate. There seems to be no useful correlation which can be made with the present work.

(b) Ir(SacSac)₃.—Reduction of low-spin octahedral d⁶ complexes such as Ir(SacSac)₃ is expected to place electrons in molecular orbitals which are predominantly metal based and σ antibonding in character. Thus structural degradations such as suggested by the polar-

ography of Rh(SacSac)₃² could be anticipated and the polarography of Ir(SacSac)₃ might be expected to be similar. In fact, the detailed analysis below shows this not to be so.

Conventional polarograms of Ir(SacSac)₃ reveal a reduction wave with a slight inflection near the midpoint, suggesting some complexity in the electrode process. The overall wave has apparent (E_{1/4}* - E_{3/4}*) values of near 100 mV and E_{1/2}* of -1.17 V vs. Ag-AgCl.

The dependence of the total wave height i_d* on concentration is linear and plots of i_d* vs. square root of mercury column height are also linear, passing through the origin. The electrode process is therefore diffusion controlled. Inspection of Table II shows that E_{1/2}* and

TABLE II
POLAROGRAPHIC DATA FOR THE "OVERALL"
Ir(SacSac)₃ ELECTRODE PROCESS

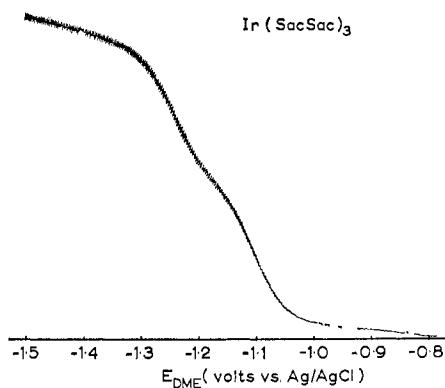
Drop time, sec	E _{1/2} * ^a , V	E _{1/4} * - E _{3/4} * ^a , mV	Drop time, sec	E _{1/2} * ^a , V	E _{1/4} * - E _{3/4} * ^a , mV
3.28	-1.172	108	1.33	-1.172	120
2.34	-1.164	112	1.16	-1.170	112
1.85	-1.172	112	1.05	-1.172	120
1.50	-1.165	112			

^a With reference to Ag-AgCl.

(E_{1/4}* - E_{3/4}*) values are independent of drop time so the electrode process is not the same as that for Rh(SacSac)₃.² It should be noted that the apparently large (E_{1/4}* - E_{3/4}*) values can indicate the presence of two separate but incompletely resolved, consecutive and reversible reduction steps. Fortunately the use of short controlled drop times of rapid polarography enabled the reduction of Ir(SacSac)₃ to be resolved (Figure 4) into two waves, of equal diffusion current, approximately 100 mV apart.

Analysis of the conventional dc wave is given in Figure 5. The plot of E_{dme} vs. log [(i_d* - i*)/i*] has an obvious inflection centered at -1.17 V vs. Ag-AgCl but approaching the Nernst slope (2.303RT/F = 58 mV) in the regions representing the "foot" and "top" of the total wave. Separate analysis of each section of the

(12) A. Furuhashi, S. Kawai, Y. Hayakawa, and A. Ouchi, *Bull. Chem. Soc. Jap.*, **43**, 553 (1970).

Figure 4.—Rapid dc polarogram of Ir(SacSac)₃ in acetone.

wave, using estimated diffusion currents, i_d ($\approx i_d^*/2$), results in two linear plots with Nernst slopes and with $E_{1/2}$ values separated by approximately 100 mV. The results are summarized in Table III. When two revers-

TABLE III
POLAROGRAPHIC DATA FROM THE SEPARATION OF WAVES
IN THE REDUCTION OF Ir(SacSac)₃

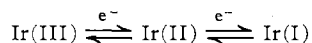
Mode	Drop time, sec	$E_{1/2}$, V ^a	Slope, mV	i_d , ^d μ A	Remarks
Fast scan	0.16	-1.172	108 ^b	2.36	Overall wave
		-1.108	52 ^b	1.17	Ir(III) \rightarrow Ir(II)
		-1.244	60 ^b	1.19	Ir(II) \rightarrow Ir(I)
Conventional	1.85	-1.130	58 ^c	3.3	Ir(III) \rightarrow Ir(II)
		-1.242	60 ^c	2.5	Ir(II) \rightarrow Ir(I)

^a With reference to Ag-AgCl. ^b Slope = $E_{3/4} - E_{5/4}$. ^c From the slope of the E_{dme} vs. $\log [i/(i_d - i)]$ plot. ^d [Ir(SacSac)₃] = 0.80×10^{-3} M.

ible consecutive one-electron reductions are scarcely separated, it is easily shown that the plot of the total wave E_{dme} vs. $\log [(i_d - i)/i]$ should approach the Nernst slope asymptotically at either extreme, though displaced by $\pm \log 2$ from the individual components.

Under controlled drop time conditions it can be assumed that the i_d values of both waves are identical and analysis of the waves are likely to be more exact. Estimates of $E_{1/4} - E_{3/4}$ from rapid polarograms are given in Table III.

The electrode process for Ir(SacSac)₃ therefore involves two consecutive reversible one-electron reductions. It may be represented formally as



The observed reversibility of the electrode reactions is consistent with the complex remaining structurally intact or, alternatively, undergoing a rapid dissociative equilibrium upon reduction. For example, the iridium(II) or iridium(I) species could be degraded to a bis complex. Insertion of electrons in the σ -antibonding orbitals should labilize the metal-ligand bonds and increase the possibility of rapid reversible loss of a bidentate ligand.

It seems that for Rh(SacSac)₃ and Ir(SacSac)₃ the completely filled d^6 level is associated with two properties: highly negative $E_{1/2}$ values and the absence of low-energy ligand-to-metal charge-transfer bands.^{2,13} In comparison, one-electron reduction of d^6 systems occurs relatively easily (around 0 V vs. Ag-AgCl) to fill the d_e level.^{2,13} Not surprisingly, by analogy with

(13) G. A. Heath and R. L. Martin, *Aust. J. Chem.*, **23**, 1721 (1970).

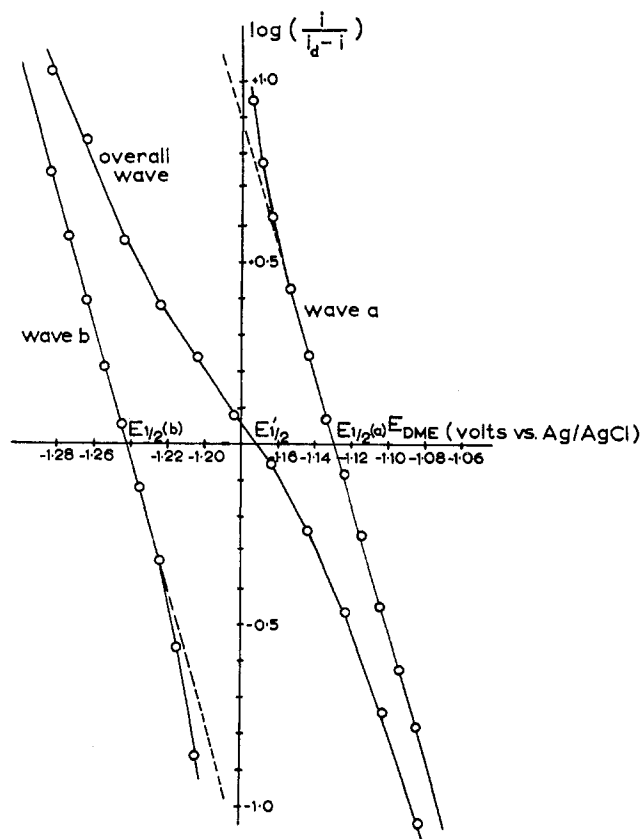
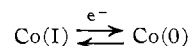


Figure 5.—Mathematical analysis of the Ir(SacSac)₃ electrode process in acetone. Plots of E_{dme} vs. $\log [i^*/(i_d^* - i^*)]$ are given for the overall wave and E_{dme} vs. $\log [i/(i_d - i)]$ assuming $i_d = i_d^*/2$ for Ir(III) + $e^- \rightleftharpoons$ Ir(II) (wave a) and Ir(II) + $e^- \rightarrow$ Ir(I) (wave b).

d^6 Ir(III) and Rh(III) complexes, no further reduction is observed.

(c) **Co(SacSac)₃**.—The polarography of the other d^6 complex Co(SacSac)₃ is not included with the above discussion because of the uncertainty of the results. Polarograms of Co(SacSac)₃ are superficially similar in appearance to those of Co(SacSac)₂ and it seems that the latter is generated at the electrode by electrochemical reduction or chemical decomposition in acetone. The available polarographic data are in accord with Co(SacSac)₃ undergoing a two-electron reduction, coincident with the first one-electron reduction of Co(SacSac)₂, at ~ -0.7 V vs. Ag-AgCl (*vide infra*), and then a subsequent reversible one-electron reduction completely coincident and identical with the Co(I) \rightarrow Co(0) wave described previously for Co(SacSac)₂. That is, the first wave is believed to be similar to reduction of Rh(SacSac)₃ and is an irreversible two-electron step $\text{Co(SacSac)}_3 + 2e^- \rightarrow \text{Co(SacSac)}_2^- + \text{SacSac}^-$ and the second wave is then



and therefore identical with the second wave for reduction of Co(SacSac)₂.

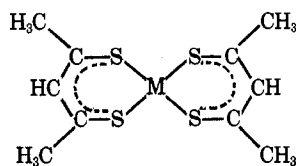
However, the polarography was observed to change with time, even under stringent degassing procedures, and the system is not properly characterized.

(d) **Ru(SacSac)₂(NO)Cl**.¹¹—Two reduction waves occur in the polarography of Ru(SacSac)₂(NO)Cl at -0.27 and -1.43 V vs. Ag-AgCl. Plots of E_{dme} vs.

TABLE IV^a

HALF-WAVE POTENTIALS FOR POLAROGRAPHIC REDUCTION OF METAL DITHIOACETYLACETONATES									
d ⁶		d ⁶	d ⁷		d ⁸		d ⁹		d ¹⁰
FeL ₃	↔ -0.21	Fe(II)							
RuL ₃	↔ +0.04	Ru(II)							
OsL ₃	↔ -0.05	Os(II)							
		CoL ₃	↔ ?	CoL ₂	↔ -0.65	Co(I)	↔ -1.45	Co(0)	
		RhL ₃	↔ -1.11		↔ -1.05	Rh(I)			
		IrL ₃	↔ -1.11	Ir(II)	↔ -1.24	Ir(I)			
						NiL ₂	↔ -0.94	Ni(I)	↔ -1.18
						PdL ₂	↔ -0.96	Pd(I)	↔ -1.39
						PtL ₂	↔ -1.01	Pt(I)	↔ -1.48
									Pt(0)

^a Most half-wave potentials are reported from rapid polarographic measurements with controlled drop time of 0.16 sec. The Rh(III) → Rh(I) process alone is completely irreversible at the dme (see text). The nature of the products is specified only by the oxidation state of the metal. Conditions: solvent, acetone-0.1 M (C₂H₅)₄NClO₄; reference electrode, Ag-AgCl (0.1 M LiCl); potential range, +0.8 to -1.8 V. The structure of ML₂ is



og $[(i_d - i)/i]$ are linear with slopes of 58 ± 2 and 60 ± 2 mV for the first (more positive) and second (more negative) waves, respectively, confirming that each is a reversible one-electron step. The two waves are equal in height when rapid controlled drop rates are employed.

The first reduction wave of Ru(SacSac)₂(NO)Cl falls between those of Ru(SacSac)₃ and Rh(SacSac)₃, the relevant $E_{1/2}$ values being -0.27, +0.04, and -1.05 V vs. Ag-AgCl, respectively. If one accepts the spectroscopic evidence that the central ion is effectively Ru(II), d₆, in the chloronitrosyl derivative,¹¹ then it is likely that the first reduction is localized to some extent on the nitric oxide ligand. A similar effect has been noted in the reversible one-electron reduction of Fe(CN)₅NO²⁻.¹⁴

Little can be said of the second reduction since the fate of the first reduced species (e.g., whether it releases a monodentate ligand) is not known.

(e) **General Considerations.**—Inspection of Table IV makes clear the widespread capacity of the metal dithioacetylacetonates to accept electrons in a reversible stepwise fashion.

It is emphasized that the present studies characterize the various reductions only in terms of the number of electrons involved, their polarographic reversibility or otherwise, and the $E_{1/2}$ values (most of which have thermodynamic significance).

Detailed characterization of the course of an electrode reaction calls for sophisticated investigations of the kind outlined by Vlček.¹⁵ The unavailability of the free ligand is a hindrance in this instance, since examination of the polarographic dependence on complexing agent concentration would help to define dissociative equilibria involving the electroactive species.

Nonetheless, the present results have important im-

plications for the synthesis of dithioacetylacetonates with hitherto inaccessible electronic configurations. The utility of synthetic studies based on systematic voltammetric data has been amply demonstrated in connection with the metal dithiolenes.³ Whether or not chemical reducing agents can be successfully employed, the application of controlled electrochemical reduction is straightforward. If necessary, important properties such as optical and esr spectra may be surveyed without isolating the reduced species from solution.

To take just one example, Cu(SacSac)₂ has long been sought because it represents the d⁹ "one-hole" configuration with the attendant theoretical advantages for interpretation of spectroscopic and magnetic properties. However the compound has not been prepared, owing to the ability of Cu(II) to oxidize the ligand. Conversion of Pt(SacSac)₂ to Pt(SacSac)₂⁻ (?) by reduction at a controlled potential in the well-defined plateau region is a possible route to this interesting electronic configuration.

Certain general conclusions can be drawn in relation to the observations in Table IV.

Firstly, the polarographic behavior varies systematically according to the formal electronic configuration of the central ion. It seems evident that the additional electrons do not enter a nonbonding ligand orbital. The number and position of polarographic steps are unlikely to be affected to such an extent merely by the different effective charge on the metal in the various complexes.

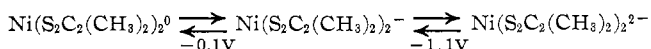
It is equally true that the reversible one-electron steps encountered are not typical of the simple (solvated) metal cations or indeed of many of their coordination compounds.¹⁵ Clearly, the appropriate valence orbitals are delocalized over the entire molecule, though for the present purposes the processes in Table IV have been usefully interpreted as changes in the oxidation state of the central ion.

(14) A. Vlček, *Rev. Chim. Miner.*, **5**, 299 (1968).

(15) A. Vlček, *Progr. Inorg. Chem.*, **5**, 211 (1963).

The occurrence of uncommon lower oxidation states (*e.g.*, Ir(II), Co(I), Ni(I), . . .) which are stable, on the polarographic time scale at least, no doubt reflects the ability of the dithioacetylacetonate ligand to delocalize electronic charge otherwise accumulated on the metal.

Comparisons with the electron-transfer properties of the dithiolenes³ must be drawn carefully. The most reduced (dithiolato) forms of these, MS_4^{2-} and MS_6^{3-} , formally contain dinegative ligands and place the metals in the ordinary oxidation states, M(II) and M(III), respectively. The dithiolato complexes are susceptible to stepwise oxidations which remove electrons from molecular orbitals of predominantly ligand character. For example, in dimethylformamide³ *vs.* Ag- $AgCl$



It is emphasized that $Ni(SacSac)_2$ is properly compared with the dianionic "dithiolate" rather than the neutral "dithiene." Stepwise oxidations of the dithioacetylacetonates are obviously relatively inaccessible, the present polarographic range extends only to +0.8 V with reference to $Ag-AgCl$, though their possible occurrence could be further investigated.

Comparison of this work with other polarographic or voltammetric studies carried out in other solvents on the same or other similar compounds is unwise because of possible solvolysis effects. It is believed that acetone is noncoordinating toward the dithioacetylacetonate complexes and this may explain for instance why the relatively simple polarographic behavior is observed in this work for planar complexes compared with that of Ouchi, *et al.*,¹² in acetonitrile or dimethylformamide, where solvolysis problems were encountered.

CONTRIBUTION FROM THE BROWN CHEMICAL LABORATORY,
UNIVERSITY OF DELAWARE, NEWARK, DELAWARE 19711

Solvent-Induced Linkage Isomerizations

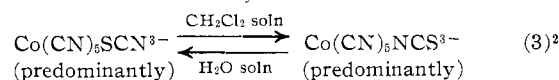
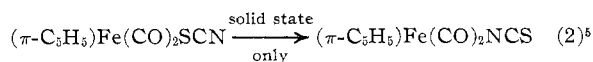
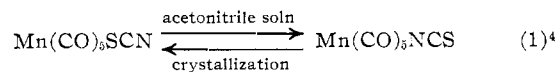
By JOHN L. BURMEISTER,* ROBERT L. HASSEL, AND ROBERT J. PHELAN

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A systematic study of the behavior of complexes of the types ML_2X_2 ($M = Pd(II), Pt(II)$; $L =$ a variety of neutral ligands; $X^- = -SCN^-, -NCS^-, -SeCN^-, -NCO^-$), $Rh(P(C_6H_5)_3)_2(CO)NCS$ ($X = O, S, Se$), and $Ir(P(C_6H_5)_3)_2(CO)NCS$ in solvents of varying polarity has resulted in the discovery that, in most cases, the bonding mode adopted by the thiocyanate and selenocyanate groups in solution is determined by the nature of the solvent, whereas the bonding mode of the cyanate group is insensitive to solvent effects. The results of infrared and electronic spectral studies of the solutions indicate that, with the exception of the $Rh(I)$ and $Ir(I)$ complexes, all of the thiocyanate and selenocyanate complexes adopt only the S- or Se-bonded mode in solvents which are generally characterized by their relatively high dielectric constants, *e.g.*, DMF and DMSO. In solvents which, in general, have relatively low dielectric constants, *e.g.*, benzene and chloroform, the thiocyanate and selenocyanate complexes (with the exception of $Pd(phen)(SCN)_2$) exhibit either a mixture of X- and N-bonding modes or N-bonding alone ($M-SCN-M$ bridging is also observed when $L =$ triphenylarsine or -stibine). Except for the methanol and ethanol solutions, where the equilibria involved are attained more slowly, the solutions exhibit spectra which do not change with time following their initial preparation. A possible explanation of the solvent effect, in terms of Klopman's treatise on charge-controlled *vs.* frontier orbital-controlled reactions, is presented.

Introduction

The bonding modes of various ambidentate ligands have been shown to be subject to a variety of directive influences,^{1,2} among them being the nature of the coordinated metal atom, the electronic or steric requirements of other ligands in the coordination sphere, the physical state of the complex, the mechanism of the reaction used to synthesize the complex, and the nature of the counterion used to isolate ionic complexes. The occurrence of a specific solvent effect has been noted in only a few cases. The solid nitrito complexes $[Ni(N,N'-diethylethylenediamine)_2(ONO)_2]$ and $[Ni(N,N'-dimethylethylenediamine)_2(ONO)_2]$ have been found³ to exist in a nitrito-nitro equilibrium in chloroform solution and three rather disparate examples involving the thiocyanate ion have been reported, *i.e.*



No rationale was offered for the behavior exhibited in reaction 1; that shown in reaction 2 was attributed to a process which requires an ordered and close arrangement of the molecules, two possible bridged activated complexes being suggested. Reaction 3 will be discussed in the context of the present work. In an effort to ascertain the nature of the role played by the solvent in linkage isomeric systems, we have systematically studied the effects of dissolution of a number of thiocyanate, cyanate, and selenocyanate complexes in a series of solvents of differing polarity. We now wish to present the results of these studies

(1) See J. L. Burmeister and J. C. Lim, *Chem. Commun.*, 1346 (1968), for examples and references.

(2) D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 3105 (1969).

(3) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **5**, 1303 (1966).

(4) M. F. Farona and A. Wojcicki, *ibid.*, **4**, 857 (1965).

(5) T. E. Sloan and A. Wojcicki, *ibid.*, **7**, 1268 (1968).