Polarographic Oxidation and Reduction of *O*-Ethyl Thioacetothioacetato Complexes of Zinc(II), Cadmium(II), and Mercury(II) in Acetone

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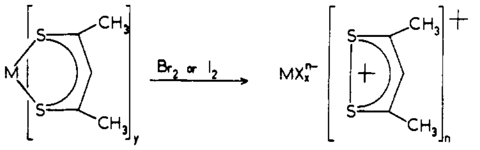
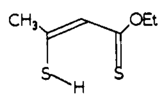
Abstract: Polarographic oxidation and reduction of complexes of *O*-ethyl thioacetothioacetate (OEt-SacSacH) with $n\mathrm{d}^{10}$ ions have been examined at the dme in acetone–0.1 *M* Et_4NClO_4. Coulometry has defined the oxidation of $Zn(OEt\text{-}SacSac)_2$ as a four-electron step which is believed to yield Zn(II) and the 3-methyl-5-ethoxy-1,2-dithiolium ion: $Zn(OEt\text{-}SacSac)_2 \rightarrow Zn(II) + 2[OEt\text{-}SacSac]^+ + 4e^-$. The oxidation has also been achieved chemically using iodine as an oxidant. $Cd(OEt\text{-}SacSac)_2$ exhibits similar behavior to $Zn(OEt\text{-}SacSac)_2$. With $Hg(OEt\text{-}SacSac)_2$, however, the oxidation is believed to occur *via* the electrode process $Hg(OEt\text{-}SacSac)_2 + Hg \rightarrow 2[Hg(OEt\text{-}SacSac)]^+ + 2e^-$. On reduction the zinc and cadmium complexes undergo consecutive one-electron reduction steps and mercury a single two-electron reduction with an associated prewave. The zinc complex is reduced reversibly to the $[Zn(OEt\text{-}SacSac)_2]^-$ and $[Zn(OEt\text{-}SacSac)_2]^{2-}$ species, although the reduced zinc complex exhibits only a short lifetime. Inverse voltammetry at a hanging drop mercury electrode for the Cd(II) and Zn(II) complexes reveals that the products of the reduction are not amalgams. Ac polarograms have been obtained and substantiate the dc findings on the reversibility or otherwise of the electrode processes.

Recent work on the electrochemical properties of transition metal complexes of dithioacetylacetone (SacSac) (I) has shown that these compounds (1,3-dithio chelates) in most instances undergo reversible one-electron reduction steps at the dropping mercury electrode (dme) in acetone.[1,2] The reduction steps for these complexes fall at potentials that are in accord with their known chemistry and spectroscopic properties. Although the known first-row transition metal complexes of dithioacetylacetone can be oxidized by the halogens (Br_2 and I_2) to yield stable 3,5-dimethyl-1,2-dithiolium halometalates,[3,4] no oxidation of the complexes, either by single-electron abstraction from the complex or a complete two-electron oxidation of a ligand to the dithiolium ion (II), has been achieved polarographically for the dithioacetylacetonato complexes.



I II

Dithioacetylacetonato complexes of Zn(II), Cd(II), and Hg(II) have proved elusive by the usual preparative method of Martin and Stewart (HCl, H_2S, acetylacetone, and the appropriate metal ion). However, the closely related 1,3-dithio complexes of these metals with *O*-ethyl thioacetothioacetate (OEt-SacSac⁻) as the ligand have recently been synthesized by metathetical reaction of OEt-SacSacH (III) with the zinc(II), cadmium(II), and mercury(II) acetates.[5] The three new complexes have been fully characterized by their spectral properties. The single-crystal X-ray diffraction study (Beckett and Hoskins[6]) of bis(*O*-ethyl thioacetothioacetato)zinc(II) $[Zn(OEt\text{-}SacSac)_2]$ shows the complex to be a monomeric tetrahedral species in the solid state. The spectral evidence suggests this geometry is retained in solution.[5]



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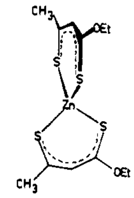

IV

In view of the interesting polarographic properties of the protonated ligand[7] (OEt-SacSacH) and the isolation of the new triad of unsaturated 1,3-dithio compounds, we have extended the study of the polarographic properties of these chelates in acetone to these recently prepared complexes with metal ions of the $n\mathrm{d}^{10}$ electronic configuration. Also described are ac polarography, coulometry at a mercury pool electrode, and stripping of zinc and cadmium from a hdme in the acetone–Et_4NClO_4 system.

Experimental Section

(a) Polarography. Conventional dc polarography was carried out in May and Baker Analytical Reagent acetone with tetraethylammonium perchlorate (0.1 *M*) as the supporting electrolyte. A three-electrode, iR compensated system as described in ref 1 was employed, the reference electrodes being Metrohm Ag|AgCl EA425 electrodes (0.1 *M* LiCl) in acetone. The glass capillary dropping mercury electrode had the following characteristics in acetone (0.1 *M* Et_4NClO_4) at open circuit and with a mercury column height of 40 cm: flow rate of Hg, m = 1.48 mg sec^{-1}; drop time, t = 4.70 sec; $m^{2/3}t^{1/6}$ = 1.68 mg$^{2/3}$ sec$^{-1/2}$. Short controlled drop times were achieved with a Metrohm Polarographie Stand E354

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

(2) A. M. Bond, G. A. Heath, and R. L. Martin, *Inorg. Chem.*, **10**, 2026 (1971).

(3) G. A. Heath, R. L. Martin, and I. M. Stewart, *Aust. J. Chem.*, **22**, 83 (1969).

(4) A. Furuhashi, K. Watanuki, and A. Ouchi, *Bull. Chem. Soc. Jap.*, **42**, 260 (1969).

(5) A. R. Hendrickson and R. L. Martin, *Aust. J. Chem.*, **25**, 257 (1972).

(6) R. Beckett and B. F. Hoskins, *Inorg. Nucl. Chem. Lett.*, **8**, 629 (1972).

(7) A. M. Bond, A. R. Hendrickson, and R. L. Martin, *J. Electrochem. Soc.*, **119**, 1325 (1972).

Table I. Oxidation Parameters of Compounds

	OEt-SacSacH[7]	$Zn(OEt\text{-}SacSac)_2$	$Cd(OEt\text{-}SacSac)_2$	$Hg(OEt\text{-}SacSac)_2$
$E_{1/2}$ (V) *vs.* Ag|AgCl	+0.26[a]	+0.244	+0.166	+0.145[b]
$(E_{1/4} - E_{3/4})$, mV	60	50[c]	47	50
Drop time, sec	1.78	1.80	1.85	6.00
Potential at which drop time was taken, V	+0.5	+0.4	+0.4	+0.2
Gradient of log $[(i_d - i)/i]$ *vs.* E_{de}, mV	63	53[c]	48[d]	

[a] Concentration dependent. [b] Nature of wave very drop-time dependent (*cf.* Table II). [c] See text. [d] Gradient at $E_{1/2}$.

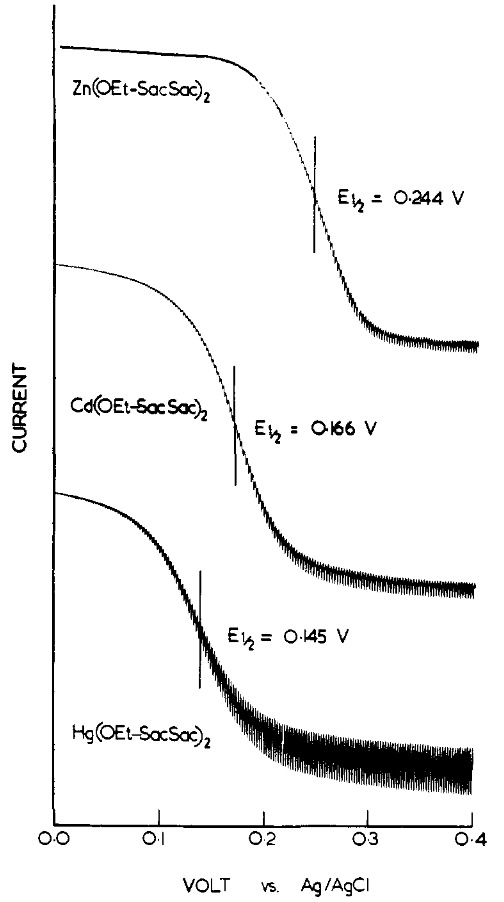

Figure 1. Oxidation waves exhibited at the dme by the three complexes.

Hanging mercury drops, produced by a Metrohm BM5-03 hanging drop mercury electrode (hdme), were 0.52 mm in diameter with a surface area of 1.38 ± 0.04 mm^2. The ac polarographic studies utilized a PAR Model 170 electrochemistry system (Princeton Applied Research Corp.) with a tungsten auxiliary electrode.

The test solutions, thermostated in a water-jacketed cell at 20°, were degassed with acetone saturated argon for 20 min before use, unless otherwise specified. A slow stream of argon was passed over the test solution while measurements were being taken. Both electrodes (reference and auxiliary) behaved identically, although they yielded an $E_{1/2}$ value for $Rh(SacSac)_3$ of −1.09 V to be compared with the published result of −1.05 V.[1] As reported,[1] the potential of the electrodes was stable (±2 mV) over a period of 3 months. The discrepancy of 40 mV for the $Rh(SacSac)_3$ reduction may be attributable to the use of acetone of a different origin from that employed in the previous work. In the present work, the use of May and Baker acetone has allowed the polarographically usable potential range to be extended to −2.2 V *vs.* Ag|AgCl. The addition of traces of water lowered this to −2.0 V *vs.* Ag|AgCl, the limit previously reported with BDH AnalaR acetone.[1] The decrease in the negative potential limit by addition of water to the acetone system has been commented on by Coetzee and Siao.[8]

(b) Coulometry. The number of electrons involved in the oxidation steps (*n*) has been determined by coulometry. Electrochemical oxidation of a 0.1 *M* Et_4NClO_4–acetone solution of the complex (~10^{-3} *M*) was achieved with 3.00 ml of solution on a mercury pool electrode having an area of approximately 2 cm^2. The mercury pool replaced the dme in the usual polarographic arrangement, with a Pt wire as the auxiliary electrode thereby reducing the bulk of the electrode system and enabling the employment of small volumes for electrolysis. The dme was also positioned in the solution enabling the concentration of unoxidized ligand and other electroactive species to be conveniently monitored.

The solution was thoroughly stirred by magnetic stirrer and concentrations of compounds determined at 5-min intervals. Current (~0.3 mA)–time curves were plotted by the recorder and manually integrated. After 30 min of electrolysis, *n* was calculated from plots of "charge consumed" *vs.* concentration of the relevant species. As the oxidation potential of the compounds are considerably more positive than the reduction potential of oxygen, degassing was not required. To minimize evaporation, the electrolysis vessel was surrounded by a moat of acetone and the apparatus sealed. Blank runs, where no electrolysis occurred, showed a slight *decrease* (<1%) in the concentration of the ligand over 1 hr, presumably due to acetone from the moat "distilling" into the 0.1 *M* Et_4NClO_4 solution.

(c) Materials. Tetraethylammonium perchlorate was prepared by neutralization of a 25% solution of Et_4NOH with 20% $HClO_4$. The precipitated product was recrystallized twice from EtOH (95%) and finally from MeOH (AR). Preparation of Et_4NClO_4 by this method obviates the need for many careful recrystallizations to remove the last traces of the electroactive halide ion, always present in samples of Et_4NClO_4 prepared by the metathesis of tetraethylammonium iodide[1] or bromide[8] with $NaClO_4$. Pure Et_4NClO_4 was dried and stored under vacuum over silica gel.

The complexes were prepared and purified as described previously.[5] May and Baker "Pronalys" acetone was used throughout.

Bis(3-methyl-5-ethoxy-1,2-dithiolium)tetraiodozincate(II) $[ZnI_4][OEt\text{-}SacSac]_2$. Iodine (0.61 g) in CCl_4 (50 ml) at 0° was added slowly with sitrring to $Zn(OEt\text{-}SacSac)_2$ (0.62 g) in CCl_4 (40 ml) also at 0°. The resulting pale yellow oil was separated from the mother liquors by decantation and solidified by stirring with diethyl ether (2 × 20 ml). The solid was collected and washed with benzene (4 × 20 ml) and diethyl ether. The pale cream complex (0.8 g) was finally dried under vacuum over $CaCl_2$ at room temperature, yield 75% based on iodine. *Anal.* Calcd for $C_{12}H_{18}I_4O_2S_4Zn$: C, 16.1; H, 2.0; I, 56.6; S, 14.4; Zn, 7.3. Found: C, 16.3; H, 2.0; I, 55.1; S, 14.6; Zn, 7.6.

Results and Discussion

Oxidation. The three compounds exhibit an oxidation wave at the dme (Figure 1), being the first time six-membered ring dithio chelates have been observed to undergo polarographic oxidative activity. Except for $Hg(OEt\text{-}SacSac)_2$, the oxidation waves are well defined and show little drop-time dependence over a range of drop times from ~6 to 0.16 sec. The oxidation wave exhibited by solutions of $Hg(OEt\text{-}SacSac)_2$ is very drop-time dependent; the single wave observed at drop times of ~6 sec is "resolved" into two waves at drop times down to 0.16 sec.

Graphical plots of limiting currents (i_d) *vs.* the square root of the column height of mercury ($h^{1/2}$) are linear and pass through the origin. This is taken as evidence that the limiting currents are diffusion controlled.

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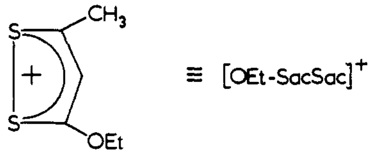
(8) J. R. Coetzee and W. S. Siao, *Inorg. Chem.*, 2, 14 (1963).

$Zn(OEt\text{-}SacSac)_2$ is the most difficult of the three complexes to oxidize with an $E_{1/2}$ value of 0.24 V (*cf.* Table I). In this instance the oxidation involves the transfer of four electrons from the complex, the value of n being arrived at by coulometric measurements at a mercury pool electrode. The mercury pool at open circuit does not appear to react with $Zn(OEt\text{-}SacSac)_2$. A controlled potential of +0.5 V *vs.* Ag|AgCl was employed for the electrolysis and the charge yielded by the electrode process was calculated by graphical integration of the current–time curves giving the number of electrons involved in the oxidation (n) as 4.0. This value is taken to indicate that both ligands are being oxidized to the 3-methyl-5-ethoxy-1,2-dithiolium ion (V) in accord with the equation

$$Zn(OEt\text{-}SacSac)_2 \longrightarrow Zn^{2+} + 2[OEt\text{-}SacSac]^+ + 4e^- \quad (1)$$



V

The chemical oxidation of alkyl substituted 1,3-dithio chelates[3,4] and the observation of the 1,2-dithiolium ion in the mass spectra of these compounds[9–11] are well documented. The characterization of these 1,2-dithiolium salts with simple anions (I^-, I_3^-, ClO_4^-, etc.) and halometalates[3,12–14] has illustrated the stability of these dithiolium ions. Although the dithiolium ion derived from OEt-SacSacH has not been isolated as a simple salt, its appearance in the mass spectra of its complexes[5] has indicated that it may be an accessible cation. Ouchi, *et al.*,[15] report that complexes of this dithiolium ion cannot be formed by the familiar acid-catalyzed reaction of H_2S[3] with the parent β-keto ester.

As $Zn(OEt\text{-}SacSac)_2$ is relatively stable, easily prepared, and readily oxidized at the dme, attempts were made in the present work to oxidize this complex with halogens in carbon tetrachloride after the general method of Heath, *et al.*[3] Iodine was observed to readily oxidize the compound and pure $[ZnI_4][OEt\text{-}SacSac]_2$ was isolated by using only three-quarters of the stoichiometric quantity of iodine. Equimolar or excess iodine reacts with the organic entity while some may coprecipitate as the triiodide salt. Bromine also oxidizes the complex under these conditions, although high bromine analyses and complexity of the ir spectrum of the product indicate this oxidant further reacts with the organic entity, presumably by substitution or addition. Although the iodide complex is analytically pure, due to the method of preparation, the possibility that the sample exists as an equimolar mixture of $[ZnI_3][OEt\text{-}SacSac]$ and $[OEt\text{-}SacSac]I$ cannot be dismissed.

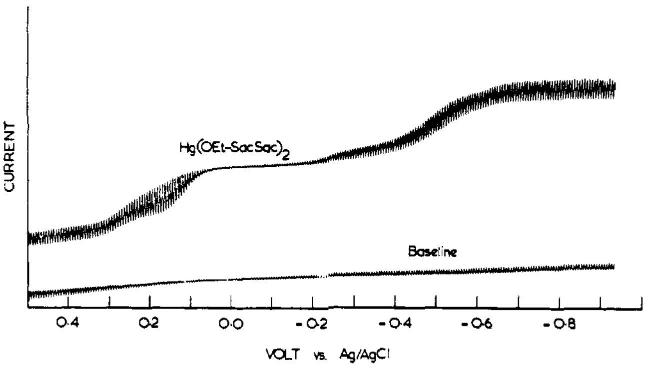


Figure 2. Total polarogram of $Hg(OEt\text{-}SacSac)_2$ at a controlled drop time of 0.32 sec. The vertically displaced baseline has been run at the same sensitivity as the polarogram of the complex.

The new off-white compound is insoluble in benzene, CH_2Cl_2, $CHCl_3$, CS_2, etc. Its ready solubility in water and alcohols supports the ionic formulation, although rapid decomposition of the compound precludes the solution-phase characterization of the dithiolium ion in these solvents (nmr and transmission spectra). Faust and Fabian[16] and Bouillon and Vialle[17] have prepared tetrafluoroborate salts of some ethoxy substituted 1,2-dithiolium ions by reaction of triethyloxonium tetrafluoroborate with the appropriate 1,2-dithiol-3-one. The former authors report that these compounds are very difficult to obtain pure, very sensitive to moisture, and revert to the 1,2-dithiol-3-one in the presence of alcohols. Neither of these reports contains the preparation of 3-methyl-5-ethoxy-1,2-dithiolium ion, but the behavior of the related compounds substantiates the conclusions drawn for the present compound. Although the chemical and electrochemical oxidation need not proceed to the same products, the collective evidence from both sources suggests the 1,2-dithiolium cation is formed on the oxidation of $Zn(OEt\text{-}SacSac)_2$.

The observations on the reduction of Zn(II) in acetone, $E_{1/2} \sim -0.95$ V for zinc chloride, substantiate the postulate that the zinc from the oxidized complex must exist as Zn(II) at the positive potential required to oxidize $Zn(OEt\text{-}SacSac)_2$ ($E_{1/2} = +0.24$ V).

Owing to gross decomposition of the complex on oxidation as postulated in eq 1 and the number of electrons involved in the oxidation step, the process is expected to be quite irreversible. Standard plots of log $[(i_d - i)/i]$, log $[(i_d - i)/i^2]$, and log $[(i_d - i)/i^3]$ *vs.* E_{de}, which are appropriate for possible reversible electrode processes, do not yield satisfactory straight lines over the potential range of the oxidation wave. The gradients of all the above plots, 53, 31, and 23 mV, respectively, are much larger than calculated for a reversible four-electron oxidation (14.5 mV at 20°). Gradients were evaluated at log $[f(i)] = 0$. This finding is in accord with the nonreversible process postulated.

The polarographic behavior of $Cd(OEt\text{-}SacSac)_2$ is quite similar to that of the zinc complex with the oxidation step involving a four-electron transfer

$$Cd(OEt\text{-}SacSac)_2 \longrightarrow Cd^{2+} + 2[OEt\text{-}SacSac]^+ + 4e^- \quad (2)$$

Once again the four-electron oxidation is quite irreversible as indicated by the $(E_{1/4} - E_{3/4})$ value of 48 mV,

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(9) R. L. Martin and I. M. Stewart, *Nature (London)*, **510**, 522 (1966).

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

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(15) A. Ouchi, Y. Takahashi, M. Nakatani, and A. Furuhashi, *Sci. Pap. Coll. Gen. Educ. Univ. Tokyo*, **19**, 53 (1969).

(16) J. Faust and J. Fabian, *Z. Naturforsch. B*, **24**, 577 (1969).

(17) C. Bouillon and J. Vialle, *Bull. Soc. Chim. Fr.*, 4560 (1968).

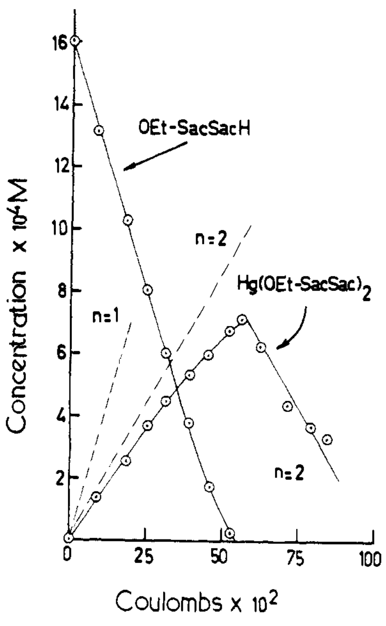


Figure 3. Complete electrolysis of OEt-SacSacH at a mercury pool electrode. Dashed lines, labeled $n = 1$ and $n = 2$, are calculated lines per mole of compound. Circles represent experimentally determined concentrations of OEt-SacSacH and Hg(OEt-SacSac)$_2$. Reproduced by permission of the Electrochemical Society.[7]

with the log $[(i_d - i)/i]$ *vs.* E_{de} plot and other related log plots again being nonlinear. Apparently this oxidation process is quite complex, involving slow charge transfer and coupled chemical reactions.

The polarographic behavior of Hg(OEt-SacSac)$_2$ is remarkably different from that of the other two complexes. At controlled drop times the total diffusion current for the oxidation steps is equal to that of the reduction steps (Figure 2). From coulometric measurements at +0.45 V *vs.* Ag|AgCl, n was determined as 2.02 and 1.91 (av 2.0) electrons for the oxidation process. Hence both the oxidation and reduction steps each involve two electrons.

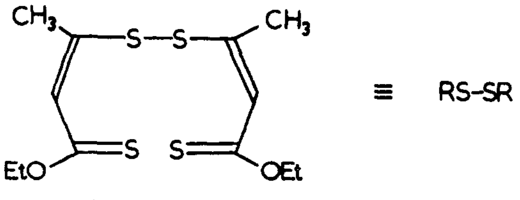
Four possibilities for the two-electron oxidation of Hg(OEt-SacSac)$_2$ solutions at the dme are

$$\mathrm{Hg(OEt\text{-}SacSac)_2 + Hg \longrightarrow 2Hg^+ + RSSR + 2e^-} \quad (3)$$

$$\mathrm{Hg(OEt\text{-}SacSac)_2 \longrightarrow Hg^{2+} + RSSR + 2e^-} \quad (4)$$

$$\mathrm{Hg(OEt\text{-}SacSac)_2 \longrightarrow [Hg(OEt\text{-}SacSac)]^+ + [OEt\text{-}SacSac]^+ + 2e^-} \quad (5)$$

$$\mathrm{Hg(OEt\text{-}SacSac)_2 + Hg \longrightarrow 2[Hg(OEt\text{-}SacSac)]^+ + 2e^-} \quad (6)$$



Coulometric studies on the free ligand (OEt-SacSacH) at a mercury pool electrode[7] have revealed that initially the oxidation process at the electrode is

$$\mathrm{OEt\text{-}SacSacH + Hg \longrightarrow [Hg(OEt\text{-}SacSac)]^+ + H^+ + 2e^-} \quad (7)$$

The cationic product subsequently reacts with the excess ligand to form Hg(OEt-SacSac)$_2$

$$\mathrm{OEt\text{-}SacSacH + [Hg(OEt\text{-}SacSac)]^+ \rightleftharpoons Hg(OEt\text{-}SacSac)_2 + H^+} \quad (8)$$

Apparently Hg(OEt-SacSac)$_2$ has sufficient stability to effect replacement of the ligand proton in the acetone–0.1 M Et_4NClO_4 medium although the reaction only exists as an equilibrium. The polarogram of a partially electrolyzed (oxidation) solution of OEt-SacSacH reveals the growth of the oxidation wave of Hg(OEt-SacSac)$_2$ at less positive potentials than that of OEt-SacSacH. This means that two electrode processes are now operative at the mercury surface: (i) the oxidation of the mercury in the presence of ligand as described by eq 7 and (ii) the two-electron (per mole of Hg(OEt-SacSac)$_2$) oxidation involving Hg(OEt-SacSac)$_2$ as described by one of the four equations (3–6).

Monitoring of the concentration of the free ligand and its mercury complex during the course of the coulometric experiment indicatest hat virtually all OEt-SacSacH is converted to Hg(OEt-SacSac)$_2$ (Figure 3). Hence it is concluded that no disulfide dimer is formed as an oxidation product, thereby eliminating reactions 3 and 4 and any related reactions leading to a disulfide compound.

Equations 5 and 6 imply that [Hg(OEt-SacSac)]$^+$ has a stability to further oxidation not exhibited by the Cd(II) and Zn(II) complexes. The existence of [Hg(OEt-SacSac)]$^+$ is substantiated by the data from the electrolysis of the free ligand at a mercury surface.[7] Attempts to isolate this cation from acetone have been thwarted by the lack of solubility of suitable starting materials in this medium, while in alcoholic solutions decomposition occurs and only compounds of inexact stoichiometry are obtained.

Despite the fact that Zn(OEt-SacSac)$_2$ and Cd(OEt-SacSac)$_2$ are suggested to be oxidized to the 1,2-dithiolium and M(II) ions (eq 1 and 2), eq 5 implies that Hg(OEt-SacSac)$_2$ is only oxidized to one dithiolium ion and [Hg(OEt-SacSac)]$^+$. Although the mechanism stipulated by this equation cannot be definitely disproved, its retention is in doubt in view of the course of the electrolytic oxidation of the mercury electrode in the presence of OEt-SacSacH as presented in Figure 3. If all the ligand present initially is converted to Hg(OEt-SacSac)$_2$, then the concentration of Hg(OEt-SacSac)$_2$ should reach 8.0×10^{-4} M at the end point. As the oxidation process involving OEt-SacSacH ($E_{1/2} \sim +0.23$ V) is more difficult to achieve than that with Hg(OEt-SacSac)$_2$ ($E_{1/2} = +0.15$ V), it is expected that with comparable rates any oxidation resulting in the conversion of Hg(OEt-SacSac)$_2$ to [OEt-SacSac]$^+$ should lead to a significant depletion of the concentration of Hg(OEt-SacSac)$_2$ at the end point. The fact that the concentration of this neutral product is slightly less than 8.0×10^{-4} M (*i.e.*, 7.2×10^{-4} M) is not expected to be due to loss of product caused by the formation of [OEt-SacSac]$^+$ but rather a slight acid dissociation of Hg(OEt-SacSac)$_2$ with eq 8 representing an equilibrium. The slight curve in the decaying concentration of OEt-SacSacH on the same plot substantiates this.

The only equation to completely satisfy all the data is eq 6, *i.e.*, $\mathrm{Hg(OEt\text{-}SacSac)_2 + Hg \rightarrow 2\,[Hg(OEt\text{-}SacSac]^+ + 2e^-}$. In the coulometric studies on OEt-SacSacH this reaction couples with eq 8 to give an overall reaction of

$$\mathrm{Hg + 2[OEt\text{-}SacSacH] \longrightarrow Hg(OEt\text{-}SacSac)_2 + 2H^+ + 2e^-} \quad (9)$$

The drop time dependence of the form of the oxidation and reduction waves involving $Hg(OEt\text{-}SacSac)_2$ are summarized in Table II. At long drop times the oxidation wave appears at +0.11 V but on shortening the drop time the wave "resolves" into two (Figure 2) with a wave at +0.29 V accounting for 40% of the total oxidation current at a drop time of 0.16 sec. This phenomenon suggests a kinetically controlled rearrangement process may be operative at the dme with a rate comparable to the polarographic time scale. As the compound exists as a monomer in solution,[5] the possibility that the complex is undergoing a depolymerization reaction at the dme prior to oxidation is eliminated. However, it is not unexpected that the electrode process described by eq 6 is drop-time dependent as the electron transfer step must be accompanied by the complicating reactions, rearrangements, adsorption, and ligand transfer required for the oxidative dissolution of the mercury electrode.

Table II. Drop-Time Dependence for the Reduction and Oxidation of $Hg(OEt\text{-}SacSac)_2$

Drop time, sec	i_d (0.1 V)/i_d (0.3 V)	$i_d(-0.4\ V)/i_d(-0.2\ V)$
0.16[a]	1.4	~6.0
0.24[a]	2.3	
0.32[a]	2.7	
2.50	7.1	4.5
6.0	>50	3.0

[a] Controlled drop time.

The absence of a drop-time dependence of the oxidation wave of the Zn(II) and Cd(II) complexes is entirely consistent with the different course of the oxidation of these two compounds.

Attempts at amperometric titration of OEt-SacSacH with Zn(II) and Hg(II) ions in the acetone-0.1 *M* Et_4NClO_4 medium to ascertain the relative stabilities of $[M(OEt\text{-}SacSac)]^+$ species have been thwarted by the reluctance of the solvent to accept the proton from the ligand. The perchlorate salt of Zn(II) does not react with OEt-SacSacH in this medium. With the nitrate salts of Zn(II) and Hg(II), the nitrate anion appears to accept the ligand proton with subsequent chelation of the ligand. However, the nitric acid formed leads to interfering decomposition products. Obviously careful considerations must be given to experiments conducted in this nonaqueous medium.

Table III. Reduction Parameters of Compounds

	OEt-SacSacH[7]	$Zn(OEt\text{-}SacSac)_2$		$Cd(OEt\text{-}SacSac)_2$		$Hg(OEt\text{-}SacSac)_2$	
$E_{1/2}$ (V) *vs.* Ag|AgCl	−1.428	−1.143	−1.45	−0.70	−1.22	−0.20[a]	−0.41
$(E_{1/4} - E_{3/4})$, mV	68	59	~63	130[b]	85[b]	~68	62
Drop time, sec	1.85	1.56	1.71	1.72	1.32	1.85	1.95
Potential at which drop time was taken, V	−1.6	−1.0	−1.4	−0.8	−1.3	−0.3	−0.6

[a] Prewave. [b] Evaluated from rapid controlled drop polarogram (0.16 sec) where interference from maxima is minimal.

Reduction. Under the conditions of conventional dc polarography the three complexes exhibit at least one reduction wave at negative potentials with respect to the Ag|AgCl electrode (Figures 2 and 4). These waves are well defined for $Zn(OEt\text{-}SacSac)_2$, although the reduction waves for $Cd(OEt\text{-}SacSac)_2$ are rather substantially distorted due to maxima. $Hg(OEt\text{-}SacSac)_2$ exhibits a major polarographic reduction wave and a smaller wave at a less negative potential. The latter wave is attributed to a reduction prewave.

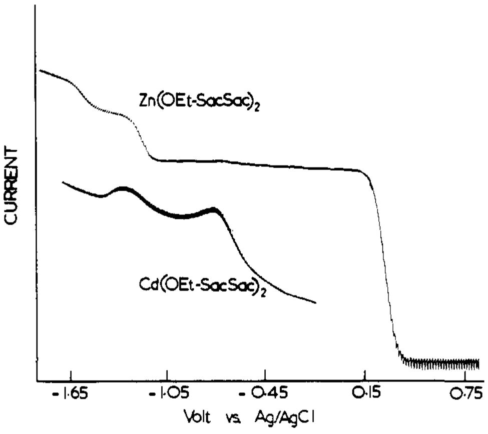


Figure 4. Total polarogram of $Zn(OEt\text{-}SacSac)_2$ and the reduction waves of $Cd(OEt\text{-}SacSac)_2$, drop time 1.60 sec.

The two reduction steps of $Zn(OEt\text{-}SacSac)_2$ occur at −1.14 and −1.45 V *vs.* Ag|AgCl (*cf.* Table III). Both waves are drop-time dependent, the −1.45-V wave severely so. At the most rapid drop time available (0.16 sec) the system exhibits fewest complications. At this drop time the limiting current for the two reduction steps are almost equal, and each is one-quarter the value of the diffusion current for the oxidation step. As *n* has been determined coulometrically to be 4 for the oxidation step, it follows from these current ratios and the Ilkovic equation that each reduction step involves one electron.

Detailed studies on the less negative reduction wave reveal that the electron transfer for this step is extremely rapid. The electrode process behaves reversibly at the short drop time of 0.16 sec. At this drop time the log $[(i_d - i)/i]$ *vs.* E_{de} plot is linear with a slope of 59 mV at 25°.

Ac results also support this postulate. A plot of peak current (I_p) *vs.* the square root of the ac frequency ($\omega^{1/2}$) at an ac perturbing potential of 5mV is a straight line passing through the origin, up to the frequency limit available (1100 Hz, drop time = 1.25 sec). This evidence together with a peak width at half-height of 100 ± 5 mV, also up to 1100 Hz, confirms that the electron transfer is extremely rapid and reversible for the first reduction step (*cf.* Table IV).

At longer drop times, the dc logarithmic plot becomes quite curved at the more negative potentials on the wave. The ac peak width at half-height also broadens slightly. In view of the very rapid electron transfer it becomes obvious that the product of reduc-

Table IV. Some Ac Polarographic Data on the Zn(II), Cd(II), and Hg(II) Chelates of [OEt-SacSac]$^-$

	$Zn(OEt\text{-}SacSac)_2$			$Cd(OEt\text{-}SacSac)_2$			$Hg(OEt\text{-}SacSac)_2$		
E_p (V) *vs.* Ag|AgCl	+0.22	−1.14	−1.47	+0.23[b]	−0.57 −0.30	−1.37 −1.48	+0.28	+0.11	−0.54
Ac half-width	175	100	130	~160	130	?	210	?	155
Ac frequency, Hz	100	900	900	250	400	250	300	300	300
Drop time, sec	0.91[a]	1.25	1.25	0.32	0.32	0.32	0.16	0.16	0.16
No. of electrons in overall reaction	4[c]	1	1	4	1	1	2[c]		2

[a] Natural drop times, calculated at −0.6 V. [b] Very irregular peak. [c] Coulometric determination.

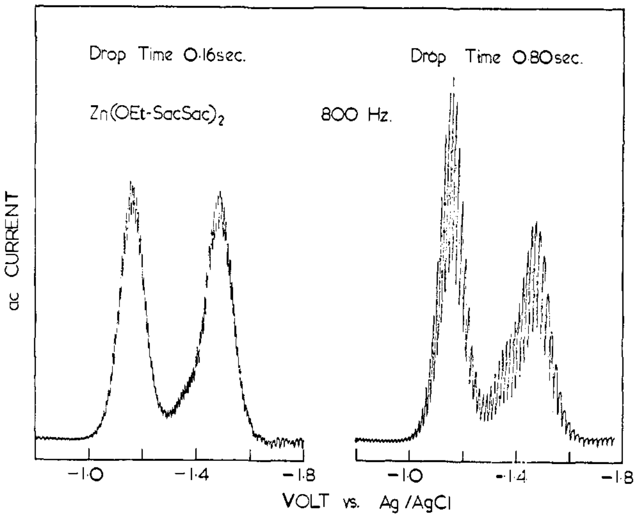


Figure 5. Drop-time dependence of ac reduction of $Zn(OEt\text{-}SacSac)_2$.

tion undergoes a kinetically controlled "rearrangement" on the same time scale as the polarographic experiments.

An examination of the second reduction wave sheds more light on this process. The limiting current of this wave falls away sharply from ~90% of the value for the first wave at a drop time of 0.16 sec to 45% at 5.15 sec (*cf.* Table V). The same decay of the second peak current with increasing drop time is also evident in the ac studies (Table V). At a drop time of 1.25 sec the I_p *vs.* $\omega^{1/2}$ plot of this peak is linear to 1100 Hz with a gradient of only 40% of that of the first peak. This plot does not extrapolate exactly through the origin. At a rapid controlled drop time (0.16 sec) the first and second ac peaks are almost identical at 800 Hz with regard to peak height (Figure 5). The second peak is slightly broader than the first. It has been established from the measurements, however, that the second electron transfer is also quite rapid. The postulated electrode processes are summarized below.

Table V. Drop-Time Dependence of Reduction (ac and dc) of $Zn(OEt\text{-}SacSac)_2$

Dc polarography		Ac polarography	
Drop time,[a] sec	i_{d2}/i_{d1}[b]	Drop time,[a] sec	I_{p2}/I_{p1}[b]
0.16	0.89	0.16	0.98
0.20	0.93	0.24	0.92
0.24	0.89	0.32	0.86
0.28	0.81	0.52	0.66
0.32	0.82	0.80	0.56
0.50	0.67	1.25	0.40
1.00	0.57		
1.33	0.54		
1.60	0.54		
2.00	0.50		
2.57	0.47		
3.52	0.47		
5.15	0.45		

[a] 0.16–0.50 rapid, mechanically controlled drop times; 1.00–5.15 natural drop times, obtained by altering the height of the mercury column. [b] Ratio of limiting currents (dc, i_d) and peak currents (ac, I_p) for the second and first reduction waves.

$$\begin{tikzcd}
Zn(OEt\text{-}SacSac)_2 \arrow[r, shift left, "e"] & {[Zn(OEt\text{-}SacSac)_2]^-} \arrow[l, shift left] \arrow[d, "\text{kinetically controlled}" right, "\text{``rearrangement''}" left] \arrow[r, shift left, "e"] & {[Zn(OEt\text{-}SacSac)_2]^{2-}} \arrow[l, shift left] \\
 & \text{``}[Zn(OEt\text{-}SacSac)_2]^-\text{''} &
\end{tikzcd} \qquad (10)$$

No definition of the oxidation state of the zinc ion is implied by these formulas. The product of the "rearrangement" step is electroinactive to the negative potential limit available (−2.2 V). It is interesting to note, however, that the d^{10} zinc complex can exhibit behavior similar to that found for related transition metal complexes[1,2] and that one electron stepwise reversible charge transfer, not usually associated with such systems, is found.

The $E_{1/2}$ and E_p values reflect the kinetic phenomena also. For the first reduction $E_{1/2}$ and E_p (800 Hz) change from −1.17 V at 0.16 sec through to −1.19 V at ~1 sec drop times. Over the same drop-time range, E_p for the second wave changes from −1.49 to −1.47 V.

It is worth noting that the dithioacetylacetonato complexes of Ni, Pd, and Pt exhibit similar kinetically controlled "rearrangement" of the product of a one electron reduction.[2] Unlike the present example, the "rearranged" reduction products of these compounds are electroactive.

The drop-time dependence of $E_{1/2}$ and the nature of the ac and dc electrode processes indicate coupled chemical reactions or complete decomposition of the zinc complex occurs after the reduction steps.

One mode of decomposition and one possible end product of the reduction process involve the formation of zero-valent zinc (Zn(0)) after the addition of two electrons to the complex, with any free metal formed at the electrode amalgamating with the drops. Alternatively, Zn(0) can result if Zn^{2+} is released in a side reaction at any stage. If a single hanging mercury drop electrode is utilized for the reduction of Zn(II) in aqueous medium at more negative potentials than the half-wave potential for reduction, the concentration of Zn(0) in the amalgam quickly becomes quite appreciable, even from very dilute solutions of Zn(II). The presence of Zn(0) in the amalgam is readily detected by scanning to more positive potentials where the zinc "strips out" of the amalgam with the simultaneous registration of a very large oxidation current[18]

$$\text{Zn/Hg (amalgam)} \longrightarrow \text{Hg} + \text{Zn(II)} + 2\text{e} \qquad (11)$$

The process also works well for cadmium, although (obviously) the oxidation of the mercury electrode itself precludes the detection of Hg by "stripping" at a hdme.

The behavior of anhydrous zinc(II) and cadmium(II) chlorides in acetone–0.1 *M* Et_4NClO_4 has been examined to establish the viability of the stripping process in this medium.

At the dme, cadmium(II) chloride reduces at $E_{1/2}$ = −0.148 V *vs.* Ag|AgCl with $(E_{1/4} - E_{3/4})$ = 60 mV. Zinc(II) chloride shows a more complex two-step reduction wave with an overall $E_{1/2} \sim -0.95$ V. At the hdme, Zn(II) yields a well defined voltammogram with E_p = −0.876 V at a scan rate of 0.033 V sec^{-1} while Cd(II) exhibits a complex peak with $E_p \sim -0.15$ V at the same scan rate. Both elements strip back into solution with well defined peaks at −0.280 (Zn) and −0.048 V (Cd) at the same scan rate, indicating that the technique may be validly applied to the acetone–Et_4NClO_4 medium for these elements (see Figure 6).

Current–voltage curves at the hdme in unstirred solutions of $Zn(OEt\text{-}SacSac)_2$ are readily correlated with the conventional dc polarogram for the first scan on a freshly prepared drop, with two reduction processes being observed. However, repeated scans using the same drop produce diminished currents. Holding a fresh drop at potentials slightly more negative than the reduction potential in unstirred solutions resulted in the current decaying to <1% of its initial value within a few minutes. With vigorously stirred solutions, significant currents pass and no decay with time was evident. These observations are consistent with adsorption of a product inhibiting reduction of $Zn(OEt\text{-}SacSac)_2$. Stirred solutions of $Zn(OEt\text{-}SacSac)_2$ electrolyzed with the hdme at −1.25 and −1.75 V *vs.* Ag|AgCl, *i.e.*, more negative potentials than the first and second reduction steps, respectively, showed no evidence of Zn(0) in the mercury drop on scanning in the positive direction even at unusually high instrument sensitivities of 1×10^{-9} A/mm. Addition of $ZnCl_2$ to a solution of the complex showed normal stripping behavior at the correct potential, indicating that on reduction of $Zn(OEt\text{-}SacSac)_2$ free Zn(0) is not formed at or near the electrode surface of the hdme. It is not possible to predict further the nature or behavior of the reduced species from this work, although the electrode process is obviously complex and adsorption and probably other phenomena appear to be coupled with the charge transfer.

The fact that the reduction potential of the second wave is identical with the reduction potential of the protonated ligand[7] is coincidental and not due to the loss of a ligand from the $[Zn(OEt\text{-}SacSac)_2]^-$ species. A lost ligand in the nonprotonating solvent would be negatively charged, and, as has been shown by work on the free ligand, the deprotonated form is electroinactive up to −2.0 V.

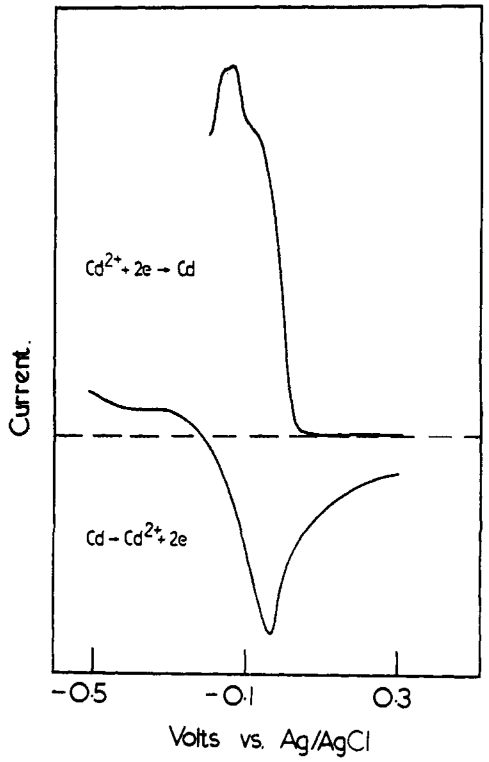


Figure 6. Normal and inverse voltammograms of cadmium(II) chloride at a hdme in acetone–0.1 *M* Et_4NClO_4, scan rate 0.033 V sec^{-1}.

$Cd(OEt\text{-}SacSac)_2$ shows two irreversible single-electron reduction steps although a maximum on each wave (Figure 4) makes accurate analysis of the polarogram impossible. The $E_{1/2}$ values of the two reduction waves, −0.70 and −1.22 V, show that the complex is easier to reduce than $Zn(OEt\text{-}SacSac)_2$. Other data are collected in Table III. The behavior of $Cd(OEt\text{-}SacSac)_2$ at the hdme is similar to that of $Zn(OEt\text{-}SacSac)_2$ and shows that Cd(0) does not amalgamate into the mercury drop, although the complex undergoes two one-electron reduction steps.

As $Hg(OEt\text{-}SacSac)_2$ is not completely stable in solution, the polarograms were run immediately on solutions prepared by addition of the complex to a thoroughly degassed solution of 0.1 *M* Et_4NClO_4 in acetone. An extra reduction wave at the rather negative potential of −0.7 V appears some time after dissolution of the complex. On standing for 1 week the polarogram becomes almost featureless except for a reduction wave at about −0.5 V. Fresh solutions exhibit a single reduction wave at $E_{1/2}$ = −0.41 V. A comparison of the diffusion current of this wave with that of the oxidation wave indicates that the reduction step involves two electrons. The rather small wave at ~ -0.2 V is probably a prewave of the reduction step. This wave does show a small drop-time dependence (Table II). For the two-electron step the $(E_{1/4} - E_{3/4})$ value of ~67 (expected for a reversible two-electron addition 28 mV) indicates the reduction of $Hg(OEt\text{-}SacSac)_2$ at the dme is irreversible. As $Hg(OEt\text{-}SacSac)_2$ is easier to reduce at the dme than either the Zn(II) or Cd(II) analogs, the order of ease of reduction of the complexes, Hg > Cd > Zn, parallels the earlier reported stabilities of the compounds.[5]

Ac Polarography. This technique is particularly amenable to the study of electrode reactions involving

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[18] E. Barendrecht, "Electroanalytical Chemistry," Vol. II, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1967, p 53.

fast charge transfer with coupled chemical reactions.[19,20] The ac findings complement the dc findings with respect to the "reversibility" of the electron transfer steps and have been particularly informative in studying the reversible reduction steps for $Zn(OEt\text{-}SacSac)_2$. The very large wave widths at half peak height (Table IV) together with the asymmetric nature of the peaks confirm that all electrode processes apart from those due to the reduction of the zinc complex are quite irreversible and are undoubtedly complicated by complex chemical reactions and adsorption phenomena in many instances.

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Solute Structuring in Aqueous Copper(II) Chloride Solutions[1]

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Abstract: The predominant solute species in aqueous $CuCl_2$ solutions of 3.18 and 4.35 *M* are similar as measured by X-ray diffraction. In each case the average Cu(II) has six nearest neighbors, and extensive sharing of chlorides by adjacent Cu(II) species is observed. The extent of chloride *vs.* oxygen occupation of the nearest neighbor sites as well as the extent of solute association depends upon the solution composition. The mean species are *ca.* $Cu_3Cl_6(H_2O)_8$ and *ca.* $Cu_5Cl_{10}(H_2O)_{12}$ in the 3.18 and the 4.35 *M* solutions. For each species the average Cu–O and Cu–Cl bond distances are measured to be 1.93 (±0.03) and 2.43 (±0.01) Å. The former is indicative of Cu–O contacts for oxygens occupying equatorial coordination sites, and the latter is indicative of chlorides occupying both axial and equatorial sites about Cu(II).

Of the crystalline metal halide complexes, none have been investigated more thoroughly than the chloro complexes of copper(II). Particular interest in these complexes has been related to examination of the Jahn–Teller effect and also toward the extent of "direct" Cu(II)–Cu(II) bonding.[2]

In chloro and chloroaquo complexes of Cu(II), the tendency for Cu(II) to fit into interstitial "octahedral" holes has been well established. Furthermore, the chain formation either by dichloro bridges between adjacent Cu(II) ions,[3–8] by mono halo bridges between adjacent cations,[9] by dihydroxy bridges between adjacent cations,[10] or by chloro–aquo bridges[11,12] have been found. In each of these cases the coordination geometry about Cu(II) is distorted octahedral with the bridging ligands occupying equatorial coordination sites. Discrete units of $[CuCl_4(H_2O)_2]^{2-}$ are found in $K_2CuCl_4 \cdot 2H_2O$.[13] The existence of $Cu_2Cl_6{}^{2-}$ dimers, where Cu(II) has four equatorial chloride and two axial chloride neighbors, has also been well documented.[14–16]

On the other hand, in Cs_2CuCl_4 crystals, Cu(II) has a distorted tetrahedral coordination environment.[17] Distorted $CuCl_4{}^{2-}$ tetrahedra also exist in crystals when the cations are complex ammonium species,[18,19] large organic species,[20] or a substituted phosphonium oxide.[21]

"Square-planar" complexes of copper(II) chloride with dimethyl sulfoxide have been reported.[22] In this complex the axial coordination sites about Cu(II) are apparently unoccupied.

X-Ray studies[23] of an aqueous $CuCl_2$ solution of composition $CuCl_2 \cdot 25H_2O$ suggest that Cu(II) has four oxygen (water) nearest neighbors and two chloride nearest neighbors at this concentration range. The X-ray studies have been interpreted to indicate that Cu(II) has an anisotropic electron density distribution, *i.e.*, the Jahn–Teller distortion.

Extensive magnetic,[2b] electrometric,[24–26] spectral,[27–30]

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[1] The research support of the Research Corporation, the Society of the Sigma Xi, the University of Southern Mississippi Computer Center, and the Board of Trustees of the Institutions of Higher Learning of the State of Mississippi are gratefully acknowledged.

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