and then this subsequently reacts in the presence of, at least, traces of water to give the dihalide $Cp^*Re(CO)_2X_2$. The function of the water has yet to be determined. In the case of the phosphine complex **1** some of the *cis*-dihalide complexes **2a–c** was always observed to be formed, also as a result of reaction of the hydride halide complexes **4a–c** with further aqueous HX. However, in the case of the phosphines this reaction is much slower, allowing the hydride halides to be isolated in good yield under conditions where they are not observed at all for the dicarbonyl.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada through an operating grant (to D.S.) and the award of an Undergraduate Summer Scholarship (to R.D.S.). The Universidad Católica de Valparaiso, Valparaiso, Chile, is thanked for providing a leave of absence (to A.H.K.-O.).

Registry No. **1**, 101835-36-3; *cis*-**2a**, 123002-21-1; *cis*-**2b**, 101915-09-7; *trans*-**2b**, 101835-39-6; *cis*-**2c**, 123002-22-2; *trans*-**3a**(HCl_2), 123002-24-4; *cis*-**3a**($SbCl_6$), 123050-32-8; *trans*-**3b**(Br_3), 123002-26-6; *cis*-**3b**(Br_3), 123050-34-0; *cis*-**3c**(I_3), 123002-28-8; **4a**, 123002-29-9; **4b**, 101835-40-9; **4c**, 123002-30-2; $Cp^*Re(CO)_2(PMe_3)$, 96791-01-4; $Cp^*Re(CO)_3$, 12130-88-0; $Cp^*Re(CO)_2N_2$, 92787-15-0; *trans*-$Cp^*Re(CO)_2(H)(Br)$, 123002-31-3; *cis*-$Cp^*Re(CO)_2Br_2$, 99341-48-7.

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Synthesis and Characterization of the Bis(1,3-bis(methylthio)-1,3-propanedithionate) Complexes $M[S_2C_3H(SCH_3)_2]_2$ ($M = Ni^{II}, Pd^{II}, Pt^{II}$)

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New dithionate (dtsacsac) complexes of the formula $M[S_2C_3H(SCH_3)_2]_2$ ($M = Ni^{II}, Pd^{II}, Pt^{II}$) have been synthesized by the reaction of reduced 3,5-bis(methylthio)-1,2-dithiolium triflate with nickel acetate, palladium acetate, and potassium tetrachloroplatinate(II), respectively. The new complexes show metal-dependent, reversible redox properties. $Ni(dtsacsac)_2$ is more planar and aromatic than the earlier reported nickel dithioacetylacetonato complex $[Ni(sacsac)_2]$ and forms uniform stacks. The $Ni(dtsacsac)_2$ complex is also unreactive toward electrophilic aromatic substitution. Oxidation of the new complexes with iodine affords 1,3-bis(methylthio)-1,2-dithiolium triiodide.

Introduction

Planar complexes of d^8 metals have long been considered as possible components of molecular metals.[1] Recently, two molecular superconductors[2,3] based on dithiolene complexes have been reported. While metal dithiolene complexes[4] (where the metal is part of a five-membered chelate ring) have been extensively studied, the corresponding dithioacetylacetonate complexes, where the metal would be part of a six-membered ring, have received less attention. We reasoned that planar propanedithionates with sulfur substituents at the 1 and 3 positions would have several features in common with dithiolene complexes and might lead to highly conducting complexes. Also, in connection with our work on the Y-aromatic sulfocarbons,[5] we wished to examine the reactivity of γ-C–H in these metal complexes. If this C–H bond could be replaced by a CS_2 moiety, then an entry into methanetris(dithiocarboxylate) derivatives could be developed.

We note that a wide range of complexes of the ligand dithioacetylacetone, sacsac (pentane-2,4-dithione), with both divalent and trivalent transition metals have been prepared.[6] The synthesis of these complexes have been carried out by using the method of Martin et al.[7] by the reaction of the metal ion, the oxo ligand, and HCl in ethanol with H_2S at 0 °C. Some complexes have also been prepared by the reduction of 1,2-dithiolium salts[8] to the corresponding dithioacetylacetonate anion.

The planar ML_2-type complexes of the Ni triad (Ni, Pd, Pt) were shown to undergo two successive one-electron reductions.[6e] The reduction potentials of complexes of dithioacetylacetonate and its derivatives were found to be shifted positive relative to the respective complexes with oxygen donor atoms.[6b,9] They were, however, only slightly dependent on the metal center.[6d] This, together with the observation that the potential differences between the successive reduction steps were remarkably constant for the Ni, Pd, and Pt complex of the same ligand, was taken as evidence for the ligand-based character of these processes.[6d] Interestingly, the reduced complexes were subject to a subsequent dimerization reaction the extent of which increased in the order Ni ≪ Pd < Pt.[6d,e] The dimerization was largely suppressed by substituting bulkier groups for the methyl groups in the sacsac ligand.[6d] In contrast, the cyclic voltammetrc oxidation remained chemically irreversible up to high scan rates,[6e] with the notable exception of $Pt(sacsac)_2$, where a reversible oxidation was found.[6e]

In this paper we report the synthesis of novel 1,3-bis(methylthio)-1,3-propanedithionate complexes via a "one-pot" procedure. We also describe briefly the X-ray structure of the Ni complex

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and, in more detail, the interesting electrochemical properties of these complexes and the precursor dithiolium salts. Of primary concern was the elucidation of the effect of methylthio groups and the metal atoms on the electrochemical and other properties of these complexes.

Experimental Section

General Procedures. Melting points were obtained with a Büchi 510 melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded in DMSO-d_6 (unless otherwise stated) on Varian EM360 and General Electric GN 500 spectrometers; chemical shifts are reported in ppm downfield from TMS. Infrared spectroscopy was performed on a Perkin-Elmer 1330 infrared spectrophotometer, and spectra are reported as wavenumbers in reciprocal centimeters. UV-visible spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer and are reported as λ values in nanometers. Mass spectral data were kindly collected by Dr. Hugh Webb at 70 eV and are reported as charge-to-mass ratios (*m/e*) with peak assignment and % abundance in parentheses. Combustion analyses were performed by Spang Microanalytical Laboratory.

Electrochemical Analyses. The complexes were barely soluble in acetonitrile, THF, methylene chloride, or 1,2-dichlorobenzene. Among these, Ni[$S_2C_3(SMe)_2H$]$_2$ was the most soluble. For comparison with literature data on the corresponding Ni($S_2C_3Me_2H$)$_2$[6d] one experiment was performed in CH_2Cl_2/0.5 M (TBA)BF_4 at +20 °C. To allow an internal comparison of the newly synthesized complexes, all other measurements were performed in 1,2-dichlorobenzene/0.05 M (TBA)PF_6 at +45 °C.

The electrochemical instrumentation used consisted of a BAS 100A electrochemical analyzer and a Houston PL-10 digital plotter. A three-electrode configuration was employed throughout. The working electrodes were platinum or glassy-carbon disks (diameter 1.9 or 3.5 mm, respectively), sealed in Kevlar. The working electrode for bulk electrolyses was a Pt foil (1.5 cm^2). A Pt foil was also used as the counter electrode. The reference electrode was a Ag wire, on which AgCl had been deposited. Relative to this reference electrode the formal potential of the ferrocene/ferrocenium couple was determined as +0.485 V. Positive feedback resistance compensation was employed. In the 1,2-dichlorobenzene electrolyte system the uncompensated resistance amounted to 2000 Ω (95% compensation). Under the experimental conditions the ohmic drop in potential never exceeded 5 mV.

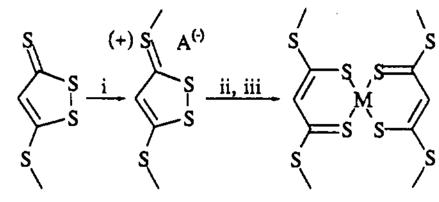
The experiments were performed in a vacuum-tight three-compartment cell that was attached to vacuum/inert-gas facilities by means of flexible tubing. All manipulations were carried out under an argon atmosphere.

Measurements on the dithiolium salts were carried out in acetonitrile/0.1 M (TBA)PF_6 by using a BAS C-1A cell assembly. The reference electrode used therein was Ag/AgCl, filled with a 3 M NaCl gel, that was separated from the working electrode compartment by means of a porous ceramic frit. Using this reference the ferrocene/ferrocenium couple gave a formal potential of +0.530 V. The supporting electrolytes used were obtained from Fluka (electrochemical grade) and dried in vacuo for 24 h prior to use. The solvent 1,2-dichlorobenzene was purified according to the literature[10] and finally passed onto activated basic alumina (Fluka). Acetonitrile was refluxed over CaH_2 and then distilled off. The acetonitrile/0.1 M (TBA)PF_6 solution was finally passed through activated basic alumina.

Synthesis. 3,5-Bis(methylthio)-1,2-dithiolium Iodide. Into a suspension of 5-(methylthio)-1,2-dithiole-3-thione[11] (47 mg, 0.26 mmol) in dichloromethane (10 mL) was syringed an excess of methyl iodide (2.5 mL). The reaction mixture was stirred overnight at room temperature to afford a yellow precipitate. Filtration, followed by vacuum drying, gave 60 mg of the salt in 80% yield, mp 164–65 °C dec. MS: 254 [I_2, 15), 195 (M^+- I, 16), 180 (M^+ - CH_3I, 45), 142 (CH_3I, 31), 101 (C_3HS_2, 100). ^{1}H NMR: 3.2 (s, SCH_3, 6 H), 8.5 (s, γ-CH, 1 H). IR: 1430, 1320, 1210, 1050. UV-vis (CH_3CN): 370, 245, 210. Anal. Calcd for $C_5H_7S_4I$: C, 18.63; H, 2.18; S, 39.79; I, 39.39. Found: C, 18.71; H, 2.16; S, 39.36; I, 39.51.

3,5-Bis(methylthio)-1,2-dithiolium Triflate. To a suspension of 5-(methylthio)-1,2-dithiolium-3-thione (0.18 g, 1 mmol) in dichloromethane (20 mL) was added methyl triflate (0.40 mL) and the reaction mixture stirred for 3 h. Evaporation of the solvent gave a brown salt in quantitative yield. ^{1}H NMR: 2.990 (s, 12 H), 7.860 (s, 2 H). ^{13}C NMR: 190.748 (s), 128.4 (s), 19.05 (s).

Scheme I



1 2 3, M = Ni
4, M = Pd
5, M = Pt

i, Me-A (A = I, CF_3SO_3); ii, $NaBH_4$/MeOH; iii, M(OAc)$_2$ or K_2PtCl_4

Nickel Bis(1,3-bis(methylthio)-1,3-propanedithionate) (Ni[(S_2C_3H-(SCH_3)$_2$]$_2$, 3). A solution of 5-(methylthio)-1,2-dithiole-3-thione (0.18 g/mmol) and methyl triflate (0.40 mL) in dichloromethane (10 mL) was stirred for 3 h in a 50-mL two-necked flask. After completion of the reaction (tlc), the volatiles were removed with a stream of nitrogen. Dry methanol (5 mL) was added, the solution was cooled to −50 °C, and $NaBH_4$ (100 mg) was added. Addition of more methanol (100 mg) to this heterogeneous mixture made it homogeneous. Stirring for an additional 1 h at room temperature, followed by filtration through Celite under N_2, gave a clear solution. To the filtrate was added Ni(OAc)$_2$·$4H_2O$ (0.1 g, 0.052 mmol) to give a deep red precipitate. The mixture was stirred overnight and filtered, the filtrate was dried under vacuum, and the solid was recrystallized from toluene to give dark violet needles in 35.% yield, mp 251.5–252 °C. Anal. Calcd for $C_{10}H_{14}S_8Ni$: C, 26.72; H, 3.13; S, 57.60. Found: C, 26.68; H, 3.48; S, 56.57. MS: 448 (M^+, 7), 195 (M^+ - $NiC_5H_7S_4$). UV-vis (CH_2Cl_2): 526, 335, 291, 260. IR (KBr): 1465, 1305, 1080.

Palladium Bis(1,3-bis(methylthio)-1,3-propanedithionate) (Pd[S_2C_3H-(SCH_3)$_2$]$_2$, 4). The palladium complex was prepared by the method described for the Ni complex to give a brownish red microcrystalline solid, which was recrystallized from toluene: yield 20%; mp 170 °C dec. Anal. Calcd for $C_{10}H_{14}S_8Pd$: C, 24.15; H, 2.83; S, 51.60. Found: C, 24.41; H, 2.88; S, 44.10. MS (CI): 498 (M^+, 6), 195 (M^+, - Pd($C_5H_7S_4$, 100). UV-vis (CH_2Cl_2): 472, 369, 266. IR (KBr): 1455, 1300, 1020, 955.

Platinum Bis(1,3-bis(methylthio)-1,3-propanedithionate) (Pt[S_2C_3H-(SCH_3)$_2$]$_2$, 5). Sodium tetrahydroborate (0.1 g) was added cautiously to a sodium hydroxide solution (0.2 g/5 mL) cooled in an ice bath. On dissolution of the $NaBH_4$, methanol was added dropwise and the resulting solution added to freshly prepared 3,5-bis(methylthio)-1,2-dithiolium triflate [from 5-(methylthio)-1,2-dithiole-3-thione (0.180 g) and methyl triflate (0.4 mL)] in methanol (10 mL). This solution was added to a solution of potassium tetrachloroplatinate(II) (0.208 g) in water (5 mL). After the solution was stirred for 15 min, toluene (15 mL) was added and the new solution stirred for 30 min. A thick red precipitate separated at the interface. The precipitate was filtered out and dried. The organic layer was also worked up to give a dark red complex. The combined solids were recrystallized from boiling carbon disulfide, the solvent was evaporated, and the residue was digested with ether to give a violet, microcrystalline solid in 45% yield, mp 220 °C dec. Anal. Calcd for $C_{10}H_{14}S_8Pt$: C, 20.50; H, 2.40; S, 43.78. Found: C, 20.46; H, 2.40; S, 34.30. MS (CI): 586 (M^+, 47), 539 (M^+ - SCH_3, 35), 195 (M^+ - Pt, 100). UV-vis (CH_2Cl_2): 528, 375, 324, 291, 250. IR (KBr): 1450, 1290, 1050.

3,5-Bis(methylthio)-1,2-dithiolium Triiodide. Single crystals of the triiodide were obtained by the slow diffusion method in a standard H-cell. The cell compartments were connected at the top. The nitrogen-flushed compartments were charged with Ni[$S_2C_3H(SCH_3)_2$]$_2$ (17 mg) and iodine (17.3 mg) separately, followed by chloroform injection (30 mL). Slow diffusion was carried out on a vibration-free table for 2 weeks. After 15 days, the brown needles were harvested, washed with chloroform, and dried in vacuum: yield 45%; mp 156–58 °C. Anal. Calcd for $C_5H_7S_4I_3$: C, 10.42; H, 1.22; S, 22.26. Found: C, 10.43; H, 1.19; S, 22.05. MS: 254 (I_2, 90), 180 (M^+ - CH_3I_3, 80), 142 (CH_3I, 50), 127 (I, 80), 101 (C_3HS_2, 100). NMR [$(CD_3)_2CO$]: 3.2 (s, S-CH_3, 6 H), 8.3 (s, γ-C-H, 1 H). UV-vis (CH_3CN): 370, 290, 245, 210. IR (KBr): 1430, 1200, 1070, 935.

Results

Synthesis and Chemical Properties of 3. Facile methylation of 1[9] with methyl iodide or methyl triflate provided the corresponding 1,2-dithiolium salt (2), precursor to the transition-metal complexes (Scheme I). The Ni and Pd complexes were prepared by the reaction of the in-situ-generated dithionate with the acetate

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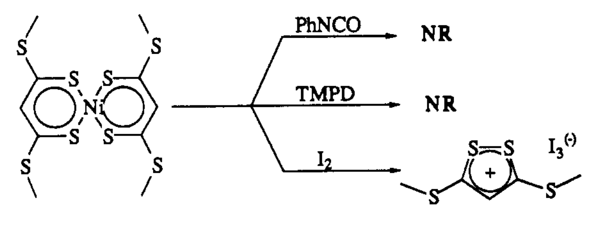
Scheme II



salts of the metals in methanol. The platinum analogue was synthesized by a slightly modified procedure in which potassium tetrachloroplatinate(II) was used as a source of Pt^{II}. Physical measurements and structure determination (vide infra) confirm that dithio-β-diketones function as bidentate ligands, forming complexes with substantial electron delocalization within the chelate ring.

The strongly colored complexes are monomeric (MS, X-ray) and stable in air and moisture but decompose on heating to ~200 °C. These complexes have been characterized by elemental analysis, mass spectrometry, and IR and UV–vis spectroscopy. It is noted that the very strong band in the near-IR region for neutral dithiolenes of Ni, Pd, Pt, and their monoanions[12] is absent in the spectra of these dithionates. In the dithiolenes, this long-wavelength absorption can be attributed to resonance contribution of an α-dithione, a functionality absent in the dithionates.

The mass spectra of the complexes are characterized by the presence of the parent ion along with that of the 3,5-bis(methylthio)-1-2-dithiolium cation and its fragmentation products.

Substitution reactions at γ-C-H of the transition-metal β-diketonates have been widely studied to show quasi-aromaticity of the coordinated ligand.[13] Patel et al.[14] have commented that, due to possible bonding between the metal and sulfur, quasi-aromaticity is expected to be more pronounced in the metal thio-β-diketonates than in the corresponding β-diketonate. Replacement of oxygen by S in β-diketonate complexes causes downfield NMR shifts for both the vinyl and the methyl position signals. This has been taken as indicative of greater aromatic character of dithioacetylacetonate complexes. Reaction of nickel dithioacetylacetonate with phenyl isocyanate has been reported to give electrophilic substitution derivatives.[14] However, treatment of our Ni complex with phenyl isocyanate gave no indication of any reaction, the starting material being recovered unchanged (Scheme II).

To further evaluate the quasi-aromaticity of the complex, Friedel–Crafts acylation was attempted under different conditions. In no case was the electrophilic substitution observed. This unusual unreactivity may be ascribed to a combination of steric and electronic factors. The latter are probably a result of the fact that the electronegativity of sulfur is higher than that of carbon[15] and sulfur is a relatively poor electron donor by resonance.[16]

Attempts to reduce the complex for the generation of the monoanion of the Ni complex chemically and electrochemically did not afford an insoluble, crystalline product. The chemical reduction was attempted by treating with tetramethyl-*p*-phenylenediamine; only unreacted starting material was recovered. The bulk cathodic reduction was attempted by using $LiClO_4$ as supporting electrolyte and applying up to 6 V of potential across the electrodes for several days, but no deposition on the cathode was observed. However, the oxidation reaction with I_2 led to the formation of the starting dithiolium salt.[17] As the experiment was performed in the presence of excess I_2, the triiodide salt was obtained. This mode of reaction is in accord with a very short transannular S–S distance in the chelate rings (vide infra). The structure of the salt was confirmed by comparison of IR and MS data with those of authentic samples of 3,5-bis(methylthio)-1,2-dithiolium triiodide synthesized by the reaction of the iodide salt with I_2. It is interesting to note that electrochemical oxidation of sacsac complexes have also been reported to give the dithiolium salt.[18]

Table I. Electrochemical Data[a]

no.	compd	$E^\circ_{0/1}$, mV	$E^\circ_{1-/-}$, mV	$E_{p,ox}$, mV[b]
3	Ni	−940 ± 5	−1300 ± 50	+1170
4	Pd	−1025 ± 5	−1285 ± 50	+1080
5	Pt	−1065 ± 5	−1435 ± 50	+1200

[a] Cyclic voltammetry at platinum electrode in 1,2-dichlorobenzene/0.05 M $(TBA)PF_6$ at +45 °C; potentials vs Ag/AgCl. [b] Kinetically controlled oxidation peak potential at 0.1 V/s.

Discussion

Structure. The crystal structure of the nickel complex **3** was recently determined, and full details are being published elsewhere.[19] Crystal data are as follows: $NiS_8C_{10}H_{14}$; $M_r = 449.43$; triclinic, $P\bar{1}$; $a = 4.0633$ (5), $b = 9.091$ (1), $c = 11.532$ (1) Å; $\alpha = 80.632$ (4), $\beta = 95.917$ (3), $\gamma = 93.701$ (4)°; $V = 417.6$ Å^3; $Z = 1$; $D_m = 1.76$, $D_c = 1.79$ g/cm^3; λ(Mo Kα) = 0.71069 Å; μ(Mo Kα) = 21.12 cm^{-1}; $F(000) = 230$; $T = 296$ K; $R = 0.041$ for 1582 observed reflections.

The complex is planar with bond distances and angles in agreement with those found for the sacsac analogue.[20] However, there are some important differences. The coordination around Ni(II) is distorted square-planar with a 98.47 (3)° angle formed by the coordinated sulfurs. This value is slightly higher than the one found in $Ni(sacsac)_2$, which is also in agreement with the higher planarity of **3**. Another consequence of the larger S–Ni–S angle is that the intramolecular S–S distance is shorter by 0.012 Å in **3** relative to $Ni(sacsac)_2$. Since this value is 0.76 Å shorter than the sum of the van der Waals radii for sulfur, one can assume existence of some interaction between those two atoms. This observation is reflected in the chemical properties of **3**: (a) treatment with iodine gives clean transannular S–S bond formation, resulting in dithiolium triiodide and NiI_2 (see above) and (b) the predominant MS fragmentation affords the same ions. The Ni–S bond distance is slightly longer than previously reported values for square-planar-coordinated Ni(II) complexes containing Ni–S bonds[21] but it is still much shorter than values recorded for octahedral Ni(II) complexes.[22] The ring C–C and C–S distances (1.377–1.382 and 1.682–1.686 Å, respectively) reflect the aromatic character of the six-membered rings. The crystal packing, which is rather unusual for this type of complex, consists of stacks where the Ni atoms are separated by a lattice repeat of only 4.0633 (5) Å, the shortest reported Ni–Ni contact for this kind of compound. A similar way of "stacking" of the planar molecules but with much longer lattice repeat of 8.04 Å was found in $[(CH_3)_4N]_2[Ni(mnt)_2]$.[23] The structure does not have any remarkably short intermolecular contacts.

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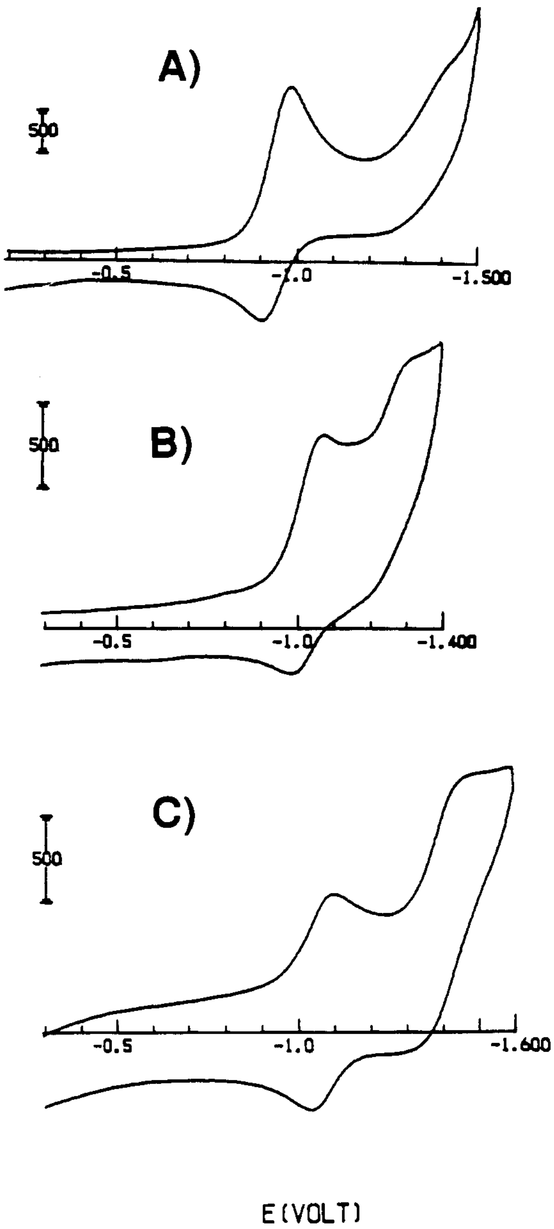

Figure 1. Cyclic voltammograms for the reduction of sacsac complexes at platinum in 1,2-dichlorobenzene with 0.05 M (TBA)PF$_6$ at 45 °C (scan rate 0.3 V/s): (A) **3**, 2.7 × 10^{-4} M; (B) **4**, 1.8 × 10^{-4} M; (C) **5**, 2.0 × 10^{-4} M. The scale mark for the current is in nanoamperes.

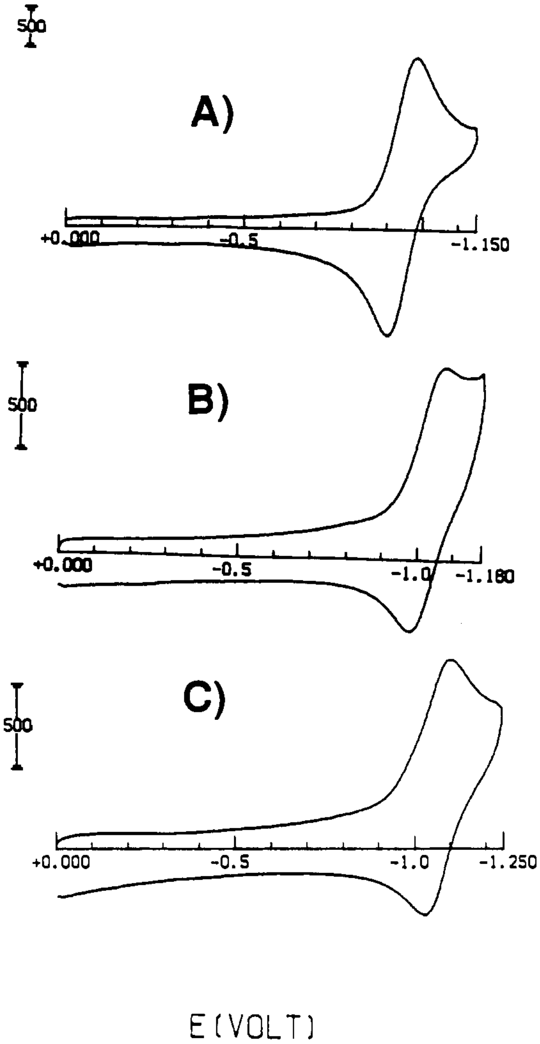

Figure 2. Extended range cyclic voltammograms for the reduction of sacsac complexes (**3**–**5**) under the same conditions as described for Figure 1. The scale mark for the current is in nanoamperes.

Electrochemistry. Cyclic voltammograms for the first reduction steps of the three $M[S_2C_3(SMe)_2H]_2$ complexes (M = Ni (**3**), Pd (**4**), Pt (**5**)) are shown in Figure 1. A chemically and electrochemically reversible reduction process can be inferred for **3**, while the lower peak current ratio values i_{pa}/i_{pc} for the Pd and Pt analogues **4** and **5** point to slow follow-up reactions of the reduced complexes. At lower scan rates peak current ratios of less than 1 are also observed for **3**. However, the scan rate dependencies of the peak current ratios are in all cases less pronounced than what would be expected for irreversible follow-up reactions (of first or second order).[24,25]

In Table I electrochemical data are given for both reduction steps and the oxidation step. Since the second reduction wave was less reversible and in some cases merged into waves of the solvent/electrolyte system (Figure 2), the formal potential could be determined only approximately. The data clearly reveal a metal dependence of the first reduction potential of the $M[S_2C_3(SMe)_2H]_2$ complexes. The ease of reduction decreases in the order Ni > Pd > Pt. The potential differences between the two reduction steps for the Ni and Pt complex are fairly constant, while the data indicate a lower potential separation in the Pd complex **4** (see also Figure 2). This trend does not correlate with the Pauling electronegativity of the transition metals (Ni, 1.8; Pd, 2.2; Pt, 2.2).

It should be noted here that ligand-based reduction processes are discussed for the corresponding sacsac and similar bis(dithioacetylacetonate) complexes.[6c,d] This was shown by electrochemical studies, where only a small metal dependence of the reduction potential was found,[6d] and by ESR studies.[6c] The deviations from this behavior that we observe might indicate a shift from ligand- to metal-based reductions.

A further point of interest was the effect of the increased number of methylthio groups on the reduction potential as compared to the corresending sacsac complexes. **3**, being the most soluble among the compounds studied, was therefore subjected to cyclic voltammetry under the same conditions as in ref 6d for Ni(sacsac)$_2$ (CH_2Cl_2/0.5 M (TBA)BF$_4$). It turned out that **3** is reduced 150 mV easier than Ni(sacsac)$_2$. Coulometric electrolyses at potentials 60 mV beyond the formal potentials were carried out to provide further insight into the electrode processes. Strong deviations from the exponential decay of the current expected for simple electron-transfer processes[26] were found. However, cyclic voltammograms recorded after the transfer of

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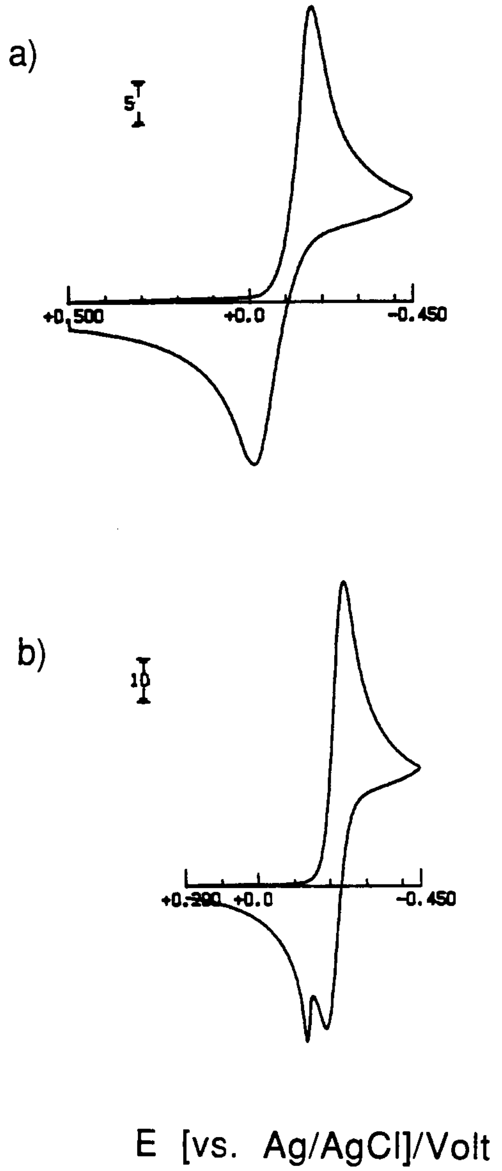

Figure 3. Cyclic voltammograms for the reduction of 3,5-bis(methylthio)-1,2-dithiolium hexafluoroarsenate (6×10^{-4} M) and 3,4,5-tris(methylthio)-1,2-dithiolium hexafluoroarsenate (10^{-4} M) at glassy carbon in acetonitrile with 0.1 M (TBA)PF_6 at 20 °C (scan rate 0.1 V/s). The scale mark for the current is in nanoamperes.

1 electron/molecule indicated only a minor decomposition of the reduced complexes.

This, together with the observation of a low-scan-rate dependence of the peak current ratios, might be taken as evidence for a reversible follow-up reaction (possibly a dimerization[6d,e]). However, the limited solubility of the complexes prevented us from carrying out detailed studies. In particular, waves attributable to the further reduction of possible dimers could not be clearly discerned.

Table II. Electrochemical Data[a] for Dithiolium Ions

compd	$E_{1+/0}$, mV
$S_2C_3(SMe)_2H^+$	-100
$S_2C_3(SMe)_3^+$	-215

[a] In acetonitrile/0.1 M (TBA)PF_6; formal potentials taken as the medium of the reduction and oxidation peak potentials in the quasi-reversible cyclic voltammograms.

The oxidation of complexes **3**–**5** (Table I) gave rise to irreversible waves in cyclic voltammetry (up to scan rates of 100 V/s). The oxidation peak currents were 2–2.5-fold larger than the peak currents for the respective reversible reduction processes, which is indicative of multielectron oxidation processes for all complexes under study. The oxidation of these complexes probably leads to the formation of the corresponding dithiolium ions[27] (vide supra).

Cyclic voltammograms for the reduction of dithiolium cations on glassy carbon are shown in Figure 3. The spike in Figure 3b at -0.1 V, which increases in subsequent cyclic voltammograms, is attributable to absorption. The peak potential separations observed were larger than expected for a Nernstian one-electron transfer. In particular, the values for platinum were generally larger than for glassy carbon, indicating slower electron transfer at platinum compared with glassy carbon. From the cyclic voltammmograms, formal potentials for the dithiolium ions could be inferred (Table II).

Interestingly, $S_2C_3(SMe)_2H^+$ is more easily reduced than the tris(methylthio) analogue[28] $S_2C_3(SMe)_3^+$. The neutral dithiolium radicals probably give rise to dimers.[29] No additional redox processes attributable to the dithiolium system were observed between +2.0 and -1.9 V.

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