

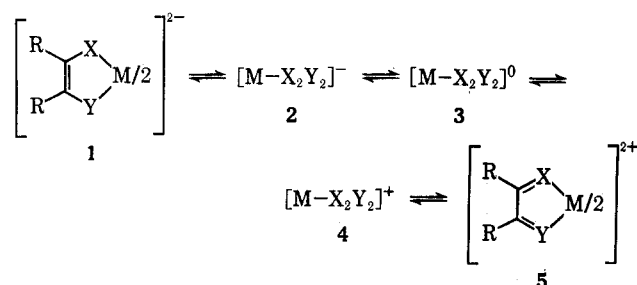
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139Complete Electron-Transfer Series of the Pt-N₂S₂ TypeBy C. E. FORBES,¹ A. GOLD, AND R. H. HOLM*

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Reaction of 1-phenyl-4-mono- or disubstituted thiosemicarbazides with platinum(II,IV) salts affords the diamagnetic intensely colored neutral complexes Pt(C₆H₅,R,R'-atf)₂ (8, R = R' = CH₃; R = H, R' = C₆H₅, *tert*-C₄H₉). The nature of these complexes has been elucidated by a combination of electrochemical, epr, and electronic spectral studies. They have been shown to be the central members of five-membered electron transfer series Pt(C₆H₅,R,R'-atf)₂^z whose component species ($z = 2-, 1-, 0, 1+, 2+$) are interrelated by one-electron-transfer reactions. Polarographic half-wave potentials in acetonitrile solution occur in the range of *ca.* -1.2 to +0.8 V *vs.* sce. Cyclic voltammetric studies of the Pt(C₆H₅,*tert*-C₄H₉-atf)₂^z series indicate reversible behavior for the processes $2- \rightleftharpoons 1-, 1- \rightleftharpoons 0$, and $0 \rightleftharpoons 1+$ at scan rates of 0.1-10 V/sec. Electronic spectra of all five members of this series are reported together with epr data for the spin-doublet $z = 1-, 1+$ members of all three series. This study provides a detailed demonstration of the validity of the electron-transfer series concept as applied to planar complexes containing unsaturated five-membered chelate rings.

Introduction

The concept of a complete electron-transfer series of bis-chelate complexes derived from unsaturated ligands has been introduced previously.²⁻⁵ For complexes with the generalized donor set X₂Y₂ the series may be represented by the species 1-5. The terminal reduced (1) and oxidized (5) members are formulated in terms of



M(II) and the reduced and oxidized forms of the ligand systems, respectively, which differ by two electrons. In a formal sense the series arises by combination of a stable valence state of the coordinated metal with the three oxidation levels of the ligand system. Using this simple description the ligand backbone structure may be varied from the ethylenic type with retention of electron-transfer potentiality. For example, the ethylenic unit may be replaced by one of the *o*-phenylene type or by ones in which C-R is replaced by an effectively isosteric group or atom such as nitrogen.

The largest single group of bis chelates which exhibit electron-transfer series are the dithiolenes. The properties of these complexes, which are of the [M-S₄]^z type, are described at length elsewhere.⁶ Electron-transfer series of varying numbers of components have been established for M-O₄^z,³ M-O₂S₂^z,⁷ and M-(NH₂)₂S₂^z⁵ complexes. These are usually of the M(C₆H₄XY)₂^z structure and like their dithiolene analogs, M(C₆H₄-S₂)₂^z and M(S₂C₂R₂)₂^z, form incomplete electron-trans-

fer series with members having $z = 2-, 1-, 0$. Persuasive evidence for the existence of the $z = 1+, 2+$ members, based upon identification of electrochemically generated species or synthesis and isolation, is lacking at the present time.

One of the most important uses of the electron-transfer series concept has been the identification and systematization of complexes possessing intermediate levels of oxidation, especially 3, which do not conform to an unambiguous assignment of metal and ligand formal oxidation states. The deep blue reaction products of bis(*o*-aminothiophenolato)nickel(II)⁸ and of nickel chloride and thiobenzoylhydrazine⁹ with oxygen in basic solution have been identified as Ni(C₆H₄(NH)-S)₂^{5,10} and Ni(C₆H₅CSNNH)₂⁵ respectively, and shown to be the neutral members of a three-membered series with $z = 2-, 1-, 0$.⁵ A similar reaction¹¹ of a nickel salt with *o*-phenylenediamine has been shown to yield Ni(C₆H₄(NH)₂)₂^{4,10b}. Epr and polarographic measurements and synthetic studies have revealed that this complex and its palladium and platinum analogs are the central members (3) of the only complete (five-membered) electron-transfer series thus far demonstrated.^{4,12} In this connection we became interested in the correct formulation of the uncharged complexes formed by platinum(IV) and 1-phenyl- and 1,4-diphenylthiosemicarbazide. These complexes have been isolated by Podchainova^{13,14} and, among simple platinum species, are noteworthy because of their intense green color in solution, which was observed prior to isolation¹⁵ and cited as a possible basis for colorimetric determination of the metal.¹⁶ The complexes were also

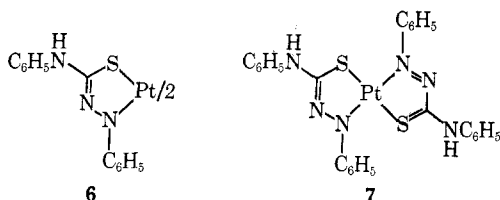
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reported¹⁴ to be diamagnetic and claimed to be tetrahedral! This structure and the platinum(IV) formulation 6 for the 1,4-diphenyl derivative presented by Podchainova, *et al.*,¹⁸ cannot be supported by any of the evidence cited by these authors. In particular, the empirical formula corresponding to 6 cannot be differentiated from that of the simple platinum(II)-thiosemicarbazide complex $\text{Pt}(\text{C}_6\text{H}_5\text{NHCSNHNC}_6\text{H}_5)_2$. Despite these uncertainties the complexes appeared to warrant further investigation for two reasons. First, the intense absorption band in the visible region (λ_{max} 750 m μ , ϵ 28,000 reported for the 1,4-diphenyl complex^{15b}) is suggestive of an unusual electronic structure potentially related to those of $\text{Pt-S}_2^{0,6}$ and $\text{Pt-(NH)}_4^{0,4}$ complexes which also show an intense absorption in this region. Second, the possibility that the reaction between platinum(IV) and the thiosemicarbazide is a redox process could not be discounted. In this event



the empirical formula of 6 could be correct and the complex reformulated in terms of a valence bond structure such as 7, containing platinum(II) and ligands with azothioformamido character. The formulation 7 is entirely equivalent to that generally accepted as the simplest feasible electronic description of the central member 3 of the electron-transfer series. This report describes our investigation of several platinum complexes derived from substituted thiosemicarbazides and provides evidence that these neutral species are in fact the central members of demonstrably complete electron-transfer series. In an apparently related study Jensen, *et al.*,¹⁷ have briefly reported some redox-active bis-(phenylazothioformamido)nickel complexes, but detailed results were not presented.

Experimental Section

Preparation of Compounds.—1-Phenyl-4,4-dimethylthiosemicarbazide was synthesized by a published procedure.¹⁸ 1,4-Diphenylthiosemicarbazide was prepared from phenylhydrazine and phenyl isothiocyanate using a method analogous to those reported for other 1,4-disubstituted thiosemicarbazides.^{18,19} The crude product was boiled as a suspension in water for 90 min and then recrystallized from ethanol to afford white needles, mp 178–179°. The compound was identified¹⁸ as the 1,4 rather than the 2,4 isomer by its failure to react with benzaldehyde or to give a color reaction with nickel chloride in neutral alcoholic solution and by adequate agreement of its melting point with that (177°) of a sample prepared by a different method.²⁰

1-Phenyl-4-*tert*-butylthiosemicarbazide.—*tert*-Butyl isothiocyanate (1.15 g, 10 mmol) was dissolved in 15 ml of diethyl ether and 1.08 g (10 mmol) of phenylhydrazine was added dropwise with stirring. The white precipitate which formed after 20 min was filtered and washed with pentane to yield 0.94 g (42%) of product, mp 178–180°. Recrystallization from ethanol gave white crystals, mp 178–180°. Ir (KCl-F mull): NH bands at 3290, 3210, 3170, 1595–1590 cm^{-1} . Pmr (acetone- d_6): –1.57 (9, CH_3), –6.8 to –7.2 (6, C_6H_5 multiplets and NH); the re-

maining NH signals could not be located with certainty. Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{N}_3\text{S}$: C, 59.16; H, 7.67; N, 18.81; S, 14.35. Found: C, 59.07; H, 7.76; N, 18.72; S, 14.41.

Phenylazo-*N-tert*-butylthioformamide.—This compound was prepared by quinone oxidation of the thiosemicarbazide.^{19,21} 1-Phenyl-4-*tert*-butylthiosemicarbazide (1.12 g, 5.0 mmol) was dissolved in 15 ml of boiling methanol and a solution of 0.54 g (5.0 mmol) of *p*-benzoquinone in methanol was added dropwise. The orange-red reaction solution was refluxed for 1 hr, and the solvent removed *in vacuo*. The residue was dissolved in chloroform and chromatographed on neutral alumina. Chloroform elution yielded the product as the first band (orange). The eluate was concentrated, and *n*-heptane added. The thioformamide was isolated as orange needles (0.53 g, 48%), mp 81–82°. Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{N}_3\text{S}$: C, 59.70; H, 6.83; N, 18.99; S, 14.49. Found: C, 59.98; H, 7.04; N, 18.04; S, 14.99.

Bis(phenylazo-*N-phenylthioformamido*)platinum (6, 7, $\text{Pt}((\text{C}_6\text{H}_5)_2\text{-atf})_2$).—1,4-Diphenylthiosemicarbazide (0.54 g, 2.2 mmol) was dissolved in 75 ml of 95% ethanol. This solution was added to a solution containing 0.44 g (1.1 mmol) of potassium tetrachloroplatinate(II) in 30 ml of 50% aqueous ethanol. After the addition of 6 ml of 1 *N* ammonium hydroxide the reaction mixture was stirred for 3 hr in the air. The crude product was obtained by filtration as a green powder (0.52 g) and was purified by recrystallization from chloroform–cyclohexane. The pure complex was obtained as dark green crystals which appeared red in reflected light; mp 287°. Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{N}_6\text{S}_2\text{Pt}$: C, 46.08; H, 3.27; N, 12.40; S, 9.46. Found: C, 46.18; H, 3.44; N, 12.35; S, 9.31. The compound is sparingly soluble in common organic solvents to give light green solutions. Infra-red data (KBr, Nujol mulls) are given for comparison with those reported elsewhere:¹⁴ 3350 (s), ~3050 (w), 1670 (w), 1590 (m), 1490 (s), 1480 (s), 1450 (s), 1350 (s), 1310 (w), 1295 (w), 1235 (s), 1190 (m), 1157 (s), 1152 (s), 1075 (m), 1025 (w), 1000 (w), 972 (w), 912 (w), 869 (w), 845 (w), 839 (w), 768 (m), 758 (m), 720 (m), 700 (m), 689 (m), 670 (w), 590 (w), 483 (m), 440 (w) cm^{-1} .

Bis(phenylazo-*N-tert*-butylthioformamido)platinum (8, $\text{R} = \text{H}$, $\text{R}' = \text{tert-C}_4\text{H}_9$, $\text{Pt}(\text{C}_6\text{H}_5, \text{tert-C}_4\text{H}_9\text{-atf})_2$).—This compound was prepared from 1-phenyl-4-*tert*-butylthiosemicarbazide and potassium tetrachloroplatinate(II) using the previous method. After stirring in air was completed, the reaction mixture was digested on the steam bath for 2 hr and then thoroughly extracted with chloroform. The residue obtained upon removal of the chloroform was recrystallized several times from *n*-heptane–dichloromethane to give the complex as very dark green crystals which appeared red in reflected light; mp 219–220°. The compound is soluble in common organic solvents to give green solutions. Pmr (CDCl_3): –1.36 (9, CH_3), –5.37 (~1, NH), –7.3 to –7.5 ppm (~5, C_6H_5 multiplets). Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{N}_6\text{S}_2\text{Pt}$: C, 41.93; H, 4.74; N, 13.18; S, 10.05. Found: C, 41.68; H, 4.88; N, 13.04; S, 10.17.

Bis(phenylazo-*N,N*-dimethylthioformamido)platinum.—(8, $\text{R} = \text{R}' = \text{CH}_3$, $\text{Pt}(\text{C}_6\text{H}_5, (\text{CH}_3)_2\text{-atf})_2$). 4,4-Dimethyl-1-phenylthiosemicarbazide (175 mg, 0.89 mmol) was added to a solution of 233 mg (0.44 mmol) of chloroplatinic acid in 50 ml of 95% ethanol. Sufficient 1 *N* ammonium hydroxide (~4 ml) was added to make basic the reaction solution, which was then stirred in the air for 2 hr. Initially a fine green precipitate formed which quickly dissolved to give a dark green solution. The solution was concentrated to ~15 ml and the deep red crystals which formed were collected by filtration. This material was recrystallized once from dichloromethane–*n*-heptane and dried at 80° *in vacuo* for 12 hr to afford 135 mg (53%) of the pure complex, mp 260–264° dec. Pmr (CDCl_3): –3.28 (6, CH_3), –7.3 to –7.5 ppm (~5, C_6H_5 multiplets). Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_6\text{S}_2\text{Pt}$: C, 37.17; H, 3.81; N, 14.45; S, 11.02. Found: C, 37.14; H, 3.79; N, 14.45; S, 10.92.

Mass Spectra.—These spectra were obtained using an MS-9 or Hitachi Perkin-Elmer RMU-6D spectrometer operating at 70 eV. $\text{Pt}((\text{C}_6\text{H}_5)_2\text{-atf})_2$ proved insufficiently volatile for measurement. Spectra of the other two complexes were examined carefully in the parent ion region in order to establish molecular weights. Taking into account isotopic abundances of all constituent atoms the following results (mass number, observed relative peak intensity, calculated mass ratio) were obtained. $\text{Pt}(\text{C}_6\text{H}_5, \text{tert-C}_4\text{H}_9\text{-atf})_2$: 636, 1, 1; 637, 1.30, 1.31; 638, 1.18, 1.18; 639, 0.37, 0.35; 640, 0.34, 0.32. $\text{Pt}(\text{C}_6\text{H}_5, (\text{CH}_3)_2\text{-atf})_2$:

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580, 1, 1; 581, 1.27, 1.26; 582, 1.11, 1.12; 583, 0.32, 0.30; 584, 0.33, 0.30.

Voltammetry.—An ORNL Model 1988 polarograph equipped with a three-electrode configuration and modified for cyclic voltammetry or a Princeton Applied Research Model 170 Electrochemistry System was employed for electrochemical measurements. The usual polarographic measurements were carried out using a rotating platinum electrode as the working electrode. In order to promote linear diffusion the working electrode in cyclic voltammetry experiments consisted of a 0.10-in. diameter platinum wire sealed in a 5-mm o.d. glass tube. The flat surface of the wire served as the electrode and it was positioned 3 mm from the end of the tube, which was U-shaped and partially immersed in the solution so as to fill completely the small volume at the end. All potentials were determined at 25° vs. a saturated calomel reference electrode. Cyclic voltammetric current-potential curves obtained at scan rates of 0.001–0.2 V/sec were recorded on an X-Y recorder, and those obtained at faster scans up to 10 V/sec were displayed on a Tektronix storage oscilloscope. Acetonitrile used for voltammetric and the controlled-potential electrolysis experiments described below was purified by distillation from CaH₂, followed by fractional distillation from P₂O₅, and finally by fractional distillation from CaH₂. The distillation and storage of acetonitrile were done under a nitrogen atmosphere. Solutions were ~10⁻³ M in complex and 0.05 M in tetra-*n*-propylammonium perchlorate as the supporting electrolyte.

Magnetic Resonance.—Pmr spectra were obtained on a Varian T-60 spectrometer. A Varian Model V-4502 spectrometer was employed for the epr measurements. The magnetic field was monitored with a Harvey Wells proton gaussmeter. The microwave frequency was measured by means of a Hewlett-Packard Model 532 A/B frequency meter, the accuracy of which was checked using DPPH at various operating frequencies. Certain paramagnetic species were generated by controlled-potential electrolysis in a cell employing a three-electrode configuration. The working compartment consisted of a 10-cm length of 3-mm o.d. glass tubing which was positioned in the epr cavity. The working electrode was a piece of platinum wire extending from the top of the cell to the working compartment. This wire was protected from electrical contact with the counter electrode compartment by means of glass capillary tubing.

Infrared and Electronic Absorption Spectra.—Infrared spectra were recorded on a Perkin-Elmer Model 337 grating instrument. Electronic spectra were obtained at 25° using a Cary Model 14 spectrophotometer. Spectra of the species Pt(C₆H₅,*tert*-C₄H₉-atf)₂ $z = 2+$, $1+$, $1-$, were obtained by controlled-potential electrolysis of solutions of the $z = 0$ complex in an absorption cell similar in design to the one described by Fajer, *et al.*²² The design of the cell permitted optical measurements to be made *in situ*. The unit consisted of a quartz optical cell (0.5-cm path length) in conjunction with a three-electrode configuration. The working electrode was a platinum gauze basket suspended below the quartz cell. Two saturated calomel electrodes were used, one serving as the reference electrode and the other as a counter electrode. The counter electrode compartment was separated from the working electrode by a fritted disk of medium porosity. A soft glass-Pyrex cracked frit isolated the reference electrode compartment. In a typical run the cell was first dried at 120° for 12 hr and then positioned in the spectrophotometer. The cell was flushed with prepurified argon gas saturated with purified acetonitrile. An acetonitrile solution containing a known concentration of neutral complex (*ca.* 5 × 10⁻⁵ M) and 0.05 M in supporting electrolyte was placed in the cell with exclusion of air and moisture. Electrolysis was started at a controlled potential *ca.* 0.2 V greater than the half-wave potential of the species of interest (*cf.* Table I). The potential source was the ORNL Model 1988 polarograph, and the current was monitored by means of a recorder. Stirring was achieved by continual bubbling of presaturated argon gas through the working electrode compartment. Electrolysis was considered complete after the current had dropped to less than 1% of the original amount (*ca.* 30 min). Passage of argon was interrupted at this point and the spectrum recorded. The solution was then electrolyzed back to 0.0 V and its spectrum determined. Agreement between the number of coulombs passed in both steps and between the optical densities of the initial and final spectra of the neutral complex was within 10%. Electrochemical generation of the

TABLE I
POLAROGRAPHIC DATA FOR Pt-N₂S₂ COMPLEXES IN
ACETONITRILE SOLUTION AT 25°

Complex ^a	Process ($z - 1$) $\rightleftharpoons$ z	$E_{1/2}$, V	i_d/C , ^b $\mu A/mM$
Pt(C ₆ H ₅ , <i>tert</i> -C ₄ H ₉ -atf) ₂ ^z	1+ $\rightleftharpoons$ 2+	+0.84	-27
	0 $\rightleftharpoons$ 1+	+0.49	-23
	1- $\rightleftharpoons$ 0	-0.72	23
	2- $\rightleftharpoons$ 1-	-1.23	27
Pt(C ₆ H ₅ , (CH ₃) ₂ -atf) ₂ ^z	1+ $\rightleftharpoons$ 2+	+0.80	-20
	0 $\rightleftharpoons$ 1+	+0.44	-22
	1- $\rightleftharpoons$ 0	-0.76	21
	2- $\rightleftharpoons$ 1-	-1.19	20
Pt((C ₆ H ₅) ₂ -atf) ₂ ^z	1+ $\rightleftharpoons$ 2+	+0.85	-18
	0 $\rightleftharpoons$ 1+	+0.63	-20
	1- $\rightleftharpoons$ 0	-0.50	24
	2- $\rightleftharpoons$ 1-	-1.04	26

^a Data obtained from solution prepared from $z = 0$ species.

^b Comparison data for one-electron oxidations of Cr(mnt)₃³⁻: -19, -24 $\mu A/mM$.

$z = 2-$ species did not lead to satisfactory spectra due to formation of contaminants at the rather negative potential (*ca.* -1.4 V) required. The spectrum of the dianion was obtained as follows. Degassed tetrahydrofuran was distilled from sodium-potassium alloy into a 1-cm vacuum cell containing a small amount of the neutral complex. The concentration of the resulting solution was determined spectrophotometrically. Reduction was carried out by addition of sodium amalgam and was considered complete upon disappearance of the 8400-cm⁻¹ band of the monoanion. The spectrum of this solution was recorded. Exposure to air regenerated the neutral complex, whose spectrum agreed to within 5% in optical density of that determined initially. The spectrum of the $z = 1-$ species was further checked by sodium amalgam reduction and found to be in good agreement with that obtained with electrolyzed solutions. The maximum estimated error in extinction coefficients of the generated anions and cations (*cf.* Table II and Figure 2) is $\pm 20\%$.

TABLE II
ELECTRONIC SPECTRAL DATA FOR Pt-N₂S₂^z
COMPLEXES IN SOLUTION

Complex	Solvent	$\lambda_{max}(\epsilon)^a$
Pt((C ₆ H ₅) ₂ -atf) ₂	95% C ₂ H ₅ OH	13,300 (32,500), 23,800 (5400), ~25,000 sh (5100), 29,700 (20,300), 36,900 (30,000), ~43,500 sh (24,000)
Pt(C ₆ H ₅ , (CH ₃) ₂ -atf) ₂	CH ₃ CN	14,000 (26,200), ~23,000 sh (3700), 25,400 (4900), 30,900 (20,200), 42,200 (23,400)
Pt(C ₆ H ₅ , <i>tert</i> -C ₄ H ₉ -atf) ₂	CH ₃ CN	14,400 (23,100), ~23,000 sh (3800), 25,300 (5400), 31,400 (19,100), 41,800 (21,000)
Pt(C ₆ H ₅ , <i>tert</i> -C ₄ H ₉ -atf) ₂ ^{-b}	CH ₃ CN	8400 (9900), ~23,000 sh (3500), ~26,000 sh (6200), 31,500 (16,500), 42,200 sh (20,100)
Pt(C ₆ H ₅ , <i>tert</i> -C ₄ H ₉ -atf) ₂ ^{-c}	THF	21,500 (750), ~28,000 sh (7100), 29,700 (8600)
Pt(C ₆ H ₅ , <i>tert</i> -C ₄ H ₉ -atf) ₂ ^{+b}	CH ₃ CN	6900 (4200), ~7400 sh (2800), 10,600 (5800), ~11,000 sh (3700), 17,700 (5000), ~22,000 sh (6300), 25,600 sh (9400), 28,400 (10,800), ~30,000 sh (10,100), 41,700 (21,300)
Pt(C ₆ H ₅ , <i>tert</i> -C ₄ H ₉ -atf) ₂ ^{+b}	CH ₃ CN	17,100 (5100), 23,500 (14,000), ~29,000 sh (8700), ~44,000 sh (25,100)

^a Cm⁻¹; apparent ϵ values, uncorrected for underlying absorption.

^b Generated by controlled-potential electrolysis. ^c Generated by Na-Hg reduction.

Results and Discussion

In the following discussion results are presented which demonstrate that the three neutral platinum complexes prepared in this work are in fact the central members 3 of five-membered electron-transfer series. Spectral, voltammetric, and epr data are set out in Tables I-III and Figures 1-3. In order to simplify

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TABLE III
EPR DATA FOR Pt-N₂S₂ COMPLEXES

Complex	Medium	Ox-Red ^d	Soln ^{a,b}		Glass ^{a,c}					
			$\langle g \rangle$	$\langle a \rangle$	g_1	g_2	g_3	a_1	a_2	a_3
Pt(C ₆ H ₅ , <i>tert</i> -C ₄ H ₉ -atf) ₂ ⁻	2-CH ₃ THF	Na-Hg	2.030	105	1.954	2.035	2.124	111	120	96
	CH ₃ CN ^e	Cpe	2.034	108	...	...	...	...	...	...
Pt(C ₆ H ₅ ,(CH ₃) ₂ -atf) ₂ ⁻	2-CH ₃ THF	Na-Hg	2.027	104	1.939	2.032	2.127	114	128	96
	CH ₃ CN ^e	Cpe	2.030	103	...	...	...	...	...	...
Pt((C ₆ H ₅) ₂ -atf) ₂ ⁻	2-CH ₃ THF	Na-Hg	2.030	109	1.942	2.033	2.130	115	132	96
	DMF ^e	Cpe	2.033	102	...	...	...	...	...	...
Pt(C ₆ H ₅ , <i>tert</i> -C ₄ H ₉ -atf) ₂ ⁺	CH ₃ CN ^{f,g}	Cpe	1.985	<i>h</i>	1.954	1.993	2.009	67	<i>h</i>	<i>h</i>
Pt(C ₆ H ₅ ,(CH ₃) ₂ -atf) ₂ ⁺	CHCl ₃ -DMF ^{f,i}	Br ₂	1.984	<i>h</i>	1.954	1.990	2.007	55	<i>h</i>	<i>h</i>
	2-CH ₃ THF ^e	Ni(tfd) ₂	1.984	<i>h</i>	...	...	...	...	...	...
Pt((C ₆ H ₅) ₂ -atf) ₂ ⁺	CH ₃ CN ^e	Cpe	1.983	<i>h</i>	...	...	...	...	...	...
	CH ₂ Cl ₂ ^e	Ni(tfd) ₂	1.984	<i>h</i>	...	...	...	...	...	...

^a Hyperfine splittings (gauss) refer to ¹⁹⁵Pt ($I = 1/2$, 33.7%). ^b Data at ~25°. ^c Data at ~-196° unless otherwise noted. ^d Method of generating $z = 1-$, $1+$ species from $z = 0$: cpe, controlled-potential electrolysis; Ni(tfd)₂, NiS₄C₄(CF₃)₄.⁰ ^e Fluid solution measurements only. ^f Fluid and frozen solution measurements. ^g Frozen solution measurement at ~-170°. ^h No hfs splitting observed. ⁱ 1:1 v/v.

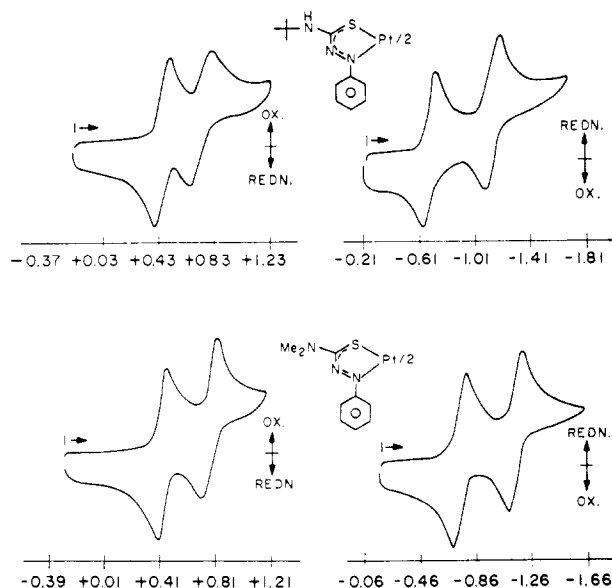


Figure 1.—Cyclic voltammograms of Pt(C₆H₅,*tert*-C₄H₉-atf)₂^z (upper) and Pt(C₆H₅,(CH₃)₂-atf)₂^z (lower) redox series in acetonitrile at 25°. The traces were recorded oscillographically at a scan rate of 0.145 V/sec.

nomenclature the complexes are designated as derivatives of substituted azothioformamides, which are the terminal oxidation products of thiosemicarbazides. Thus the species **8** are denoted generally as Pt(C₆H₅, R,R'-atf)₂^z, with R or R' = H not stated. The notation is not necessarily intended to convey oxidation levels of coordinated ligands.

Synthesis and Characterization of Neutral Complexes.—Pt((C₆H₅)₂-atf)₂ and Pt(C₆H₅,*tert*-C₄H₉-atf)₂ were readily prepared by reaction of the appropriate thiosemicarbazide with tetrachloroplatinate(II) in ammoniacal aqueous-ethanol medium in the presence of air. The reactions are considered to take the following course, in which the initially formed cationic complex **9** is deprotonated to a classical inner complex **10** which rapidly undergoes deprotonation to the dianion **11** and oxidation to **8** ($z = 0$). Although complexes **9** and **10** were not isolated, the proposed reaction sequence is supported by prior preparation of platinum(II) complexes of these types derived from thiosemicarbazide^{23,24} as well as similar complexes of nickel(II) and pal-

(23) K. A. Jensen and E. Rancke-Madsen, *Z. Anorg. Allg. Chem.*, **219**, 243 (1934); K. A. Jensen, *ibid.*, **221**, 6 (1934).

(24) R. A. Haines and K. K. W. Sun, *Can. J. Chem.*, **46**, 3241 (1968).

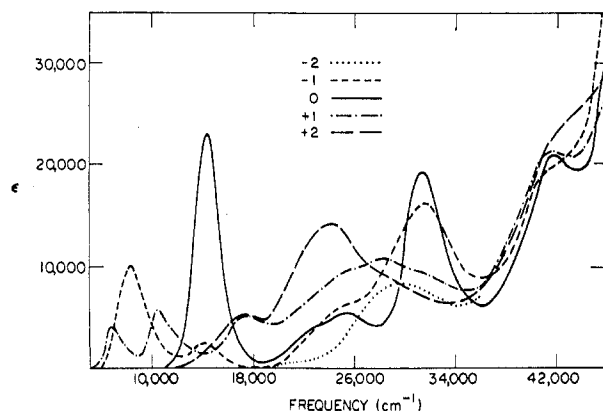


Figure 2.—Electronic absorption spectra of Pt(C₆H₅,*tert*-C₄H₉-atf)₂^z species. The $z = 1-$, $1+$, $2+$ ions were generated by controlled-potential electrolysis of acetonitrile solutions of $z = 0$, and the $z = 2-$ ion was produced by sodium amalgam reduction of $z = 0$ in THF. The band at 14,400 cm⁻¹ in the spectrum of the monoanion arises from incomplete reduction of the neutral complex.

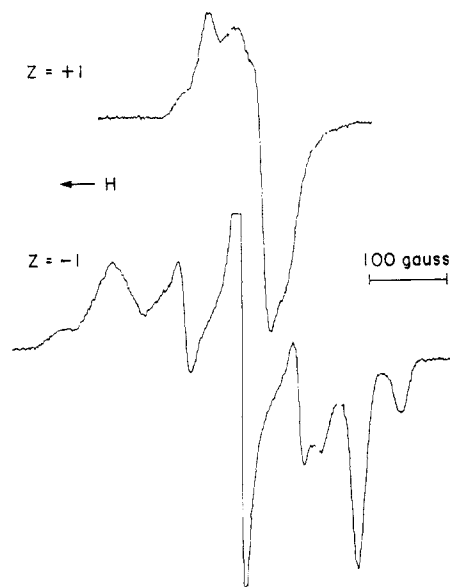
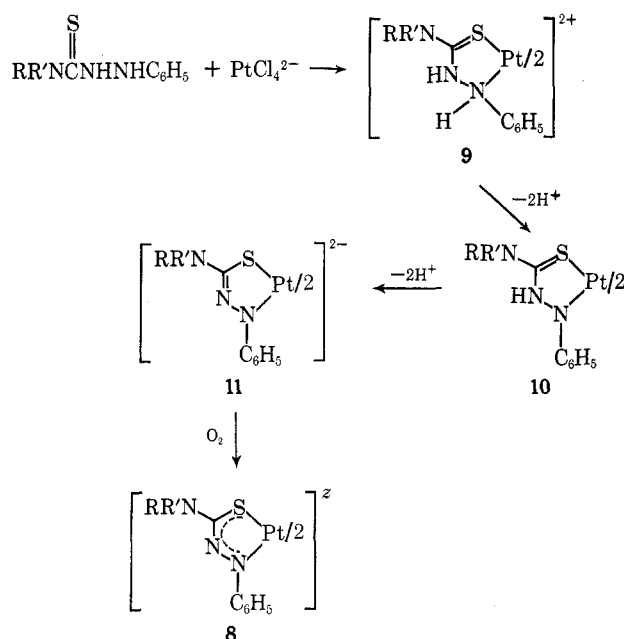


Figure 3.—Epr spectra of Pt(C₆H₅,(CH₃)₂-atf)₂^z species in glasses at ~-196°: upper, $z = 1+$ produced by oxidation of $z = 0$ with bromine in CHCl₃-DMF; lower, $z = 1-$ generated by reduction of $z = 0$ with sodium amalgam in 2-CH₃THF.

adium(II).²⁵ Additionally, the complexes obtained under similar conditions from thiobenzoylhydrazine,

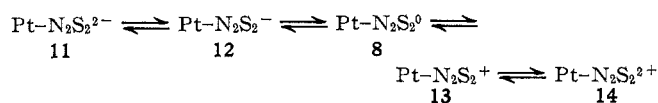
(25) For a brief review of thiosemicarbazide complexes, cf. R. H. Holm and M. J. O'Connor, *Progr. Inorg. Chem.*, **14**, 241 (1971).

Ni(C₆H₅CSNHNH₂)₂²⁺, Ni(C₆H₅CSNHNH)₂, and Ni(C₆H₅CSNNH)₂, which correspond to 9, 10, and 8, respectively, have been characterized.^{5,9} Pt(C₆H₅,-(CH₃)₂-atf)₂ was obtained in the same medium from reaction of hexachloroplatinate(IV) and the semi-carbazide. In this case base-assisted deprotonation affords directly a neutral complex which, if the canonical form analogous to 7 is accepted, may be visualized to arise by an internal redox process resulting in reduction of platinum(IV) and oxidation of ligand dianions. Pt(C₆H₅,R,R'-atf)₂ complexes were isolated as intensely colored diamagnetic solids which produce deep green solutions in organic solvents. Evidence that these compounds conform to the composition of 8 and hence are not the analytically similar bis-thiosemicarbazidato complexes 10 has been obtained from mass spectra. Mass numbers and relative peak intensities in the parent ion regions of Pt(C₆H₅,*tert*-C₄H₉-atf)₂ and Pt(C₆H₅,-(CH₃)₂-atf)₂, given in the Experimental Section, are in good agreement with the formulation 8 and definitely exclude 10. These complexes also do not show any pmr signals or infrared bands clearly ascribable to the chelate ring NH unit of 10. Because of its low solubility and volatility, similar spectral measurements could not be performed on Pt((C₆H₅)₂-atf)₂. However, the close resemblance of its properties (*vide infra*) to those of the other two complexes leaves no doubt that it has a corresponding composition and electronic structure. At this point it is to be noted that all three complexes display an intense absorption band in the 13,300–14,400-cm⁻¹ range (*cf.* Table II), implying equivalent electronic structures presumably analogous to other neutral redox-active bis chelates of the nickel group.^{4–6} In the subsequent sections electrochemical, epr, and spectral results are examined. Qualitative comparisons of these results are made with similar data for M-X₂Y₂^z complexes, especially for M = Pt species, whose redox and electronic properties are well established.



Electrochemical Evidence for Electron-Transfer Series.—The polarographic data in Table I and the cyclic voltammograms in Figure 1 demonstrate that the three

neutral Pt(C₆H₅,R,R'-atf)₂ complexes undergo two one-electron reductions and oxidations in acetonitrile solution. No other waves were observed at more negative or positive potentials up to the limits imposed by breakdown of the medium. These results indicate the existence of the five-membered electron-transfer series below. The central members 8 are thus similar to Pt(C₆H₄(NH)₂)₂, which exhibits the same redox pat-



tern,⁴ and are clearly related to several Pt-S₄⁰ species, which undergo two one-electron reductions.⁶ The observed similarities of half-wave potentials for a given step are not unexpected because the complexes differ only in the R, R' substituents. The relatively negative potentials associated with formation of the z = 1-, 2- species indicate that they are readily oxidized, as required for the facile conversion 11 → 8 proposed above, and no attempt to isolate these ions was made. Cationic species are produced at potentials exceeding +0.4 V and also were not isolated. The half-wave potentials given in Table I and elsewhere^{4,6} indicate that the order of oxidative stability of redox-active platinum species is Pt-S₄^z > Pt-N₂S₂^z > Pt-N₄^z, which is consistent with the trend established previously for Ni-X₂Y₂^z complexes.^{4,7} In these cases redox potentials are evidently more strongly dependent upon the donor atom set than upon the exact nature of the remaining chelate ring structure.

Reversibility of the four redox steps in the Pt(C₆H₅,*tert*-C₄H₉-atf)₂^z electron-transfer series was investigated by cyclic voltammetry. The two reductions and the first oxidation were found to be well behaved within the interval of potential scans V = 0.01–10 V/sec and to satisfy criteria for reversible charge transfer.²⁶ Peak potentials and ratios of anodic and cathodic peak currents were independent of sweep rate, and plots of *i*_p/V^{1/2} vs. V were linear with zero slope.²⁷ The second oxidation (1+ ⇌ 2+) was examined in the scan range of 0.01–1.0 V/sec. An anodic shift of E_p by 44 mV and a decrease of *i*_p/V^{1/2} from 20.6 to 16.9 μA sec^{1/2} V^{-1/2} indicated possible kinetic complications, although *i*_{p,a}/*i*_{p,c} showed no systematic change (average value 0.97 (0.04)). The electrochemical details of this process were not investigated further.

Epr and Spectral Studies.—In order to provide additional evidence for the existence and nature of members of the electron-transfer series, electronic absorption and epr spectra have been determined under conditions appropriate for generation of the ionic species 11–14 from the isolated neutral complexes 8.

(26) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, Chapter 5.

(27) The following average values of E_p (V), *i*_{p,c}/*i*_{p,a} (or the inverse), and *i*_p/V^{1/2} (μA sec^{1/2} V^{-1/2}) were obtained for the indicated processes from initial cyclic voltammograms recorded at 10 scan rates in the interval 0.01–10 V/sec. 0 ⇌ 1-: -0.740 (0.006), 1.01 (0.01), 24.5 (0.4); 1- ⇌ 2-: -1.248 (0.007), 1.01 (0.01), 23.2 (0.5); 0 ⇌ 1+: +0.511 (0.002), 1.03 (0.04), 23.6 (0.4). Mean deviations are given in parentheses. At scan rates up to 50 V/sec the 0 ⇌ 1- and 0 ⇌ 1+ processes continued to exhibit reversible behavior. Within the stated scan rate interval E_p for the 1- ⇌ 2- process showed a slight but discernible dependence on V which became more pronounced at faster scan rates, reaching -1.319 V at 50 V/sec. This process evidently departs from strict reversibility when V ≳ 10 V/sec.

These species were produced by controlled-potential electrolysis of acetonitrile solutions and/or by chemical redox reactions. The selection of potentials and redox reagents follows from the half-wave potentials in Table I. Spectral and epr data are given in Tables II and III, respectively.

Pt-N₂S₂²⁻ Complexes.—These species are produced at potentials more negative than *ca.* -1.0 V. Their two-electron relationship to the neutral complexes and the lack of detection of a higher stage of reduction indicate that they are the terminal reduced members of the series. The formulation 11 implies a straightforward platinum(II)-ligand dianion formal electronic structure and is consistent with the absorption spectrum of Pt(C₆H₅,*tert*-C₄H₉-atf)₂²⁻ given in Figure 2. This ion was obtained by sodium amalgam reduction in THF. Its spectrum lacks the intense near-infrared band encountered with *z* = 1⁻, 0 species and is therefore in accord with the spectra of the well-characterized bis-dithiolato dianions of the nickel group.⁶ A band was observed at 21,500 cm⁻¹ (ϵ 750) and is assigned as a d-d transition. Similar assignments have been made for relatively weak bands of Pt-S₄²⁻ complexes in the 14,000–21,000-cm⁻¹ region.^{6a}

Pt-N₂S₂⁻ Complexes.—Monoanions were readily generated by controlled-potential electrolysis or by sodium amalgam reduction in 2-CH₃THF. They are characterized by epr and spectral properties quite similar to those of all other M-X₂Y₂⁻ species 2 of the nickel group.⁴⁻⁷ Epr spectra in fluid solution exhibit a strong signal at *g* ~ 2.03 and hyperfine splittings of about 100 G due to ¹⁹⁵Pt (33.7%, *I* = 1/2). Glass spectra reveal three principal *g* values²⁸ and anisotropic hyperfine interactions; a representative spectrum is shown in Figure 3. In no case was ¹⁴N superhyperfine splitting observable in fluid or glassy media. Rhombic *g* tensors are also found for all other M-X₂Y₂⁻ monoanions of the nickel triad, although anisotropies of their *g* tensors are somewhat larger.³⁰ Three principal components of the *a*(¹⁹⁵Pt) tensor have been previously observed only in Pt(C₆H₄(NH)₂)₂⁻⁴ and PtS₄-C₄(CF₃)₄⁻³¹ and follow the order *a*₂ > *a*₁ > *a*₃, consistent with the data in Table III for Pt-N₂S₂⁻. Values of *a* for the latter ions are intermediate between those for Pt-S₄⁻ (~80 G^{6a}) and Pt(C₆H₄(NH)₂)₂⁻ (~140 G⁴). The same order of principal *a* values provides quite reasonable evidence that the species Pt-N₂S₂⁻ and Pt-N₄⁻ possess equivalent ground states in their respective symmetries, since in the absence of large magnetic anisotropy these quantities depend more heavily on ground-state rather than excited-state

properties.³² For just this reason principal *g* values are less reliable for establishing ground-state congeneracy because of varying admixtures of excited states by spin-orbit coupling. However, the general similarities in *g* anisotropies and certain spectral features (*vide infra*) among a large body of M-X₂Y₂⁻ species^{4-7,32-34} (in which chelate rings are not connected by conjugated bridges⁵) suggest that they have ground states analogous to ²B_{3g} for Ni-S₄⁻ complexes. This ground state³⁵ has been established by single-crystal epr studies³² and is consistent with semiempirical MO calculations.³⁶ In Ni(mnt)₂⁻ the odd-electron MO has *ca.* 50% ligand character.^{32b} Analogous electron configurations, in which the odd-electron MO contains an admixture of an out-of-plane d π metal orbital, certainly apply to several cis and trans planar Ni-N₂S₂⁻ complexes^{5,34} and that appropriate to a trans structure is considered probable for the monoanions 12. More certain definition of the ground state would require single-crystal epr measurements of these ions in order to establish directions of principal *g* and *a* values in a molecular axis system. Suitable diamagnetic host compounds for such an experiment are not presently available.

Further evidence that the species 12 possess ground states analogous to those of M-S₄⁻ complexes is afforded by the spectrum of electrolytically generated Pt(C₆H₅,*tert*-C₄H₉-atf)₂⁻ (*cf.* Figure 2). Essentially the same spectrum can be obtained during the course of reduction of the neutral complex to the dianion by sodium amalgam in THF. The most significant feature is the intense band at 8400 cm⁻¹. Similar intense absorptions in the near-infrared region have been found in the spectra of Ni-O₂S₂⁻⁷ and all nickel group dithiolene monoanions.⁶

Pt-N₂S₂⁰ Complexes.—These are obtained by the synthetic methods described earlier. As their half-wave potentials imply,^{6a} they are stable to aerial oxidation and to reduction by water and basic solvents. The spectrum of Pt(C₆H₅,*tert*-C₄H₉-atf)₂ is shown in Figure 2 and is quite similar to those of the other two *z* = 0 complexes, for which data are given in Table II. The aforementioned intense bands in the 13,300–14,400-cm⁻¹ interval find analogy with absorptions of comparable intensity in the near-infrared region of all redox-active M-S₄^{0 6} and M-N₄^{0 4} complexes of the nickel group. Similar bands are observed in the spectra of the reducible⁵ Ni-N₂S₂⁰ complexes Ni(C₆H₅-CSNNH)₂ and Ni(C₆H₄(NH)S)₂.³⁷ In the neutral dithiolenes these features have been reasonably assigned as π - π^* transitions^{6,36} in which the vacant π^* MO is of b_{3g} symmetry. Upon reduction to the monoanion this orbital becomes half-filled and the π - π^* absorption persists but without exception is

(28) Small discrepancies exceeding experimental error have been found between observed solution *g* and *a* values and *g*_{av} and *a*_{av} as calculated from the glass spectra. For example, the following results were obtained for Pt(C₆H₅,*tert*-C₄H₉-atf)₂⁻: *g* = 2.027, *g*_{av} = 2.033; *a* = 104 G, *a*_{av} = 113 G. In order to check measurements of glass spectra computer simulation of these spectra was carried out using a local modification of a program developed by Venable.²⁹ The following best-fit parameters were obtained by visual comparison of calculated and experimental spectra: *g*₁ = 1.938, *g*₂ = 2.033, *g*₃ = 2.129, *a*₁ = 110, *a*₂ = 136, *a*₃ = 98 G. These values are in satisfactory agreement with the observed values in Table III. Slight variation between observed and calculated *g* and *a* values are apparently real and may arise from differences in temperature and other environmental effects in solutions and glasses.

(29) J. H. Venable, Ph.D. Thesis, Yale University, 1965.

(30) Values of *g*₃ - *g*₁ are ~0.40 for Pt-S₄⁻ ^{6a} and 0.46 for Pt(C₆H₄(NH)₂)₂⁻⁴.

(31) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

(32) (a) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964); (b) R. D. Schmitt and A. H. Maki, *ibid.*, **90**, 2288 (1968).

(33) C. G. Pierpont, B. J. Corden, and R. Eisenberg, *Chem. Commun.*, 401 (1969); A. Davison and E. T. Shaw, *Inorg. Chem.*, **9**, 1820 (1970).

(34) F. Lalor, M. F. Hawthorne, A. H. Maki, K. Darlington, A. Davison, H. B. Gray, Z. Dori, and E. I. Stiefel, *J. Amer. Chem. Soc.*, **89**, 2278 (1967); Z. Dori, R. Eisenberg, E. I. Stiefel, and H. B. Gray, *ibid.*, **92**, 1506 (1970).

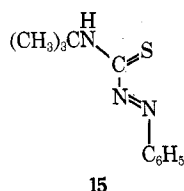
(35) The ground-state designation refers to the ion lying in the *xy* plane with the $\pm z$ axes bisecting the chelate rings. The odd-electron MO thus has y_z symmetry.

(36) G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 3585 (1965).

(37) Spectral data ($\lambda_{\max}$, ϵ) in chloroform solution: Ni(C₆H₅CSNNH)₂, 13,400 cm⁻¹, 18,100; Ni(C₆H₄(NH)S)₂, 12,100 cm⁻¹, 34,100.

shifted to lower energies. Conversion to the diamagnetic dianion fills this orbital as the added electron in effect reduces the ligand to the dithiolate level; the $\pi-\pi^*$ band is thus no longer present. This spectral behavior is observed for the $z = 2-, 1-, 0$ series of complexes in Figure 2, emphasizing the electronic similarities between these species and dithiolenes of the same overall charge.

Pt-N₂S₂⁺ Complexes.—Monocations were generated electrolytically in acetonitrile or by chemical oxidation in other solvents using bromine or the strong one-electron oxidant NiS₄C₄(CF₃)₄.³⁸ When Pt(C₆H₅-(CH₃)₂-atf)₂ was oxidized by these methods, good agreement among the observed g values was obtained. Hyperfine splitting from ¹⁹⁵Pt was not observed in solution but was found on the g_1 signal of two of the radicals (*cf.* Figure 3), further confirming their identity. The electronic spectrum of Pt(C₆H₅,*tert*-C₄H₉-atf)₂⁺ differs from those of other members of its series in the near-infrared region due to the presence of two fairly intense bands at 6900 and 10,600 cm⁻¹. These spectral and epr features serve to detect the monocations but are uninformative with respect to a detailed ground-state description. However, evidence in addition to the hyperfine splitting in the glass was obtained which indicates that a limiting platinum(II)-stabilized free-radical formulation is not strictly appropriate. Reduction of phenylazo-*N-tert*-butylthioformamide (15)



with 1 equiv of sodium naphthalenide in THF afforded a species with $\langle g \rangle = 2.005$. The species was identified as the anion radical by its hyperfine splitting pattern arising from three inequivalent nitrogens ($\langle a_1 \rangle = 11.4 \pm 0.5$ G, $\langle a_2 \rangle = 3.0 \pm 0.2$ G, $\langle a_3 \rangle \lesssim 1$ G). In frozen solutions (-195°) the signal was found at $g = 2.006$ with no observable anisotropy. The lower g values and the g anisotropies in the monocations must derive from metal orbital admixture in the odd-electron MO. The only other monocations corresponding to the members 4 of electron-transfer series which have been identified³⁹ are $M(C_6H_4(NH)_2)_2^+$ ($M = Co, Ni, Pd, Pt$).⁴ The platinum species has magnetic properties quite similar to those of Pt(C₆H₅-,*tert*-C₄H₉-atf)₂⁺.

Pt-N₂S₂²⁺ Complexes.—The terminal oxidation steps in the three-electron-transfer series have half-wave potentials of *ca.* +0.8 V. The absence of more anodic waves and, as with the dianions, the two-electron relationship to the neutral complexes leads to the con-

clusion that the species formed at this potential are the fully oxidized members 14 of the series. The most anodic redox cycle of Pt(C₆H₅,*tert*-C₄H₉-atf)₂⁺ does not correspond to a simple reversible charge transfer by electrochemical criteria. However, a two-electron oxidation product could be electrolytically generated from the neutral compound, whose electronic spectrum was recovered with about 90% of the original absorbance of the intense 14,400-cm⁻¹ band by back-electrolysis. In this sense the redox cycle is effectively reversible and the spectrum shown in Figure 2 is concluded to be that of the dication.⁴⁰ The structure of the dications is proposed to be the equivalent of 5, in which Pt(II) is coordinated to two neutral oxidized ligands such as 15.

Summary

The synthetic, electrochemical, epr, and spectral results described herein provide the most detailed demonstration to date of the validity of the electron-transfer series concept as applied to planar bis chelates containing unsaturated five-membered rings. As recognized earlier,²⁻⁶ the existence of five oxidation levels of the complexes is critically dependent upon the ability of the ligands to assume, at least formally, three oxidation states (dianion, anion radical, neutral form). The mere presence of conjugated five-membered chelate rings is not a sufficient criterion for the existence of electron-transfer series. This point is well illustrated by the behavior of bis(dithiotropolonato)nickel(II),⁴¹ whose electrochemical properties and detailed structure⁴² are consistent with a classical Ni(II)-ligand monoanion formulation. The present work also serves to augment the available information on M-N₂S₂²⁻ electron-transfer series, which have been previously confined mainly to nickel bis chelates⁵ and bridge-saturated and unsaturated complexes^{5,34,43} and involve the $z = 0, 1-, 2-$ species only. The detection of only these three oxidation levels for Ni(C₆H₅CSNNH)₂²⁻ compared to the complete series observed for Pt(C₆H₅-,*R,R'*-atf)₂²⁻ of related ligand structure is striking. The comparison suggests that the kinetic stability associated with planar platinum complexes might be advantageous in extending existing or developing new M-X₂Y₂²⁻ electron-transfer series.

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(40) The azothioformamide 15 is a possible oxidation product although it could not have been formed in large amount. The 2+ spectrum shown in this figure does not resemble the spectrum of 15 in acetonitrile (λ_{max} , ϵ): 24,400 (sh), 1500; 28,600 (sh), 2700; 35,600, 11,200; 39,500, 13,000; 46,100, 10,200.

(41) C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 2297 (1970).

(42) G. P. Khare, A. J. Shultz, and R. Eisenberg, *ibid.*, **93**, 3597 (1971).

(43) N. A. Bailey, S. E. Hull, C. J. Jones, and J. A. McCleverty, *Chem. Commun.*, 124 (1970); C. J. Jones and J. A. McCleverty, *J. Chem. Soc., A*, 2829 (1970).

(38) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 1227 (1964).

(39) Certain neutral metal dithiolenes are oxidized to presumed cationic complexes whose solvolysis products have been identified: G. N. Schrauzer and H. N. Rabinowitz, *J. Amer. Chem. Soc.*, **92**, 5769 (1970).