

Non-Planar Electron-Transfer Complexes Derived from Thiosemicarbazides. New Cation-Stabilized Free Radicals

KAI ARNE JENSEN, KLAUS BECHGAARD and
CARL TH. PEDERSEN

*Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted
Institute, DK-2100 Copenhagen, Denmark*

The preparation and some of the properties of neutral, oxidized inner complexes of various thiosemicarbazides with Ni, Cu, Pt, and Zn (and Cd) are reported. The general preparative procedure was iodine oxidation of the corresponding inner complexes, but the nickel compounds were also obtained by the reaction between the oxidized ligands, or phenylazothioformamides, and Ni(0)-compounds. The Cu-complexes were obtained by quinone oxidation, as iodine oxidation yielded iodine-containing clusters. The neutral Ni-compounds were found to be weakly paramagnetic in solution and ^1H NMR-spectra showing hyperfine contact shifts are given. X-Ray analysis has shown that the N_2S_2 -coordination sphere is a distorted tetrahedron. ESR and susceptibility measurements have shown that the Zn-compounds possess a triplet ground state. The lack of measurable g -tensor anisotropy suggests that the Zn- (and Cd-)compounds may be formulated as containing Zn (or Cd) d^{10} and two radical-anion ligands. Zero-field splitting parameters, $D = 0.0113 \text{ cm}^{-1}$ and $E = \text{zero}$, were obtained from spectra in rigid media. Selected Ni-, Zn-, and Pt-complexes have been shown to undergo two one-electron reductions in acetonitrile and DMF. The preparation of the oxidized inner complexes of selenopivaloylhydrazine with Ni and Pt is also reported.

During the past decade extensive physical and chemical investigations have followed the demonstration¹ of the electron-transfer properties of bis-1,2-dithiolate transition metal complexes. The group of complexes which undergo one-electron transfer reactions has been extended considerably. An excellent review of the properties of the electron transfer complexes known up to 1968 has been given by McCleverty.²

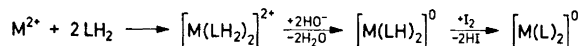
This paper reports results obtained by investigations of electron-transfer complexes derived from thiosemicarbazides (and selenopivaloylhydrazine).

When inner complexes of 1-methyl- and 1,4-dimethylthiosemicarbazide with nickel in ethanolic solution are shaken with air a deep blue colour develops. This fact and the report by Holm *et al.*³ indicating that $[\text{Ni}(\text{C}_6\text{H}_5\text{CSNNH}_2)_2]^0$,

first prepared by Jensen *et al.*,⁴ possesses electron-transfer properties made us believe that the inner complexes in question on oxidation form authentic electron-transfer compounds.

Unfortunately, the oxidized inner complexes derived from 1-methyl- and 1,4-dimethylthiosemicarbazide were too unstable for isolation. Various thiosemicarbazides were examined as ligands in order to obtain more stable compounds; very stable compounds were obtained with 1-aryl-4-alkyl- and 1-aryl-4,4-dialkylthiosemicarbazides (called LH₂).⁵

Preparation and electron-transfer properties. The compounds examined were prepared by two alternative methods:

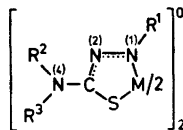


This procedure was used in preparing the Ni, Pt, and Zn (and Cd) complexes. A variety of oxidants could be used; usually iodine proved a good choice, except in the preparation of the Cu-complex where quinone was used (see below). Another procedure could be used when M(0)-compounds were available. The oxidized ligands, arylazothioformamides (called L), were treated with Ni(0)-compounds (both Ni(CO)₄ and [Ni(P(OC₂H₅)₃)₄] have been used):



The identity of the compounds prepared by the alternative procedures was confirmed by IR and ¹H NMR spectroscopy.

Table 1. Metal compounds of azothioformamides (L = R²R³N - CS - N = N - R¹).



M	R ¹	R ²	R ³	Symbol
Ni Zn Cu Pt	Ph	Et	Et	[M(L ¹) ₂] ⁰
Ni Zn Cu	Ph	-(CH ₂) ₄ -		[M(L ²) ₂] ⁰
Ni Pt	<i>p</i> -CH ₃ C ₆ H ₄	Bu ^t	H	[M(L ³) ₂] ⁰
Ni	Ph	Bu ^t	H	[Ni(L ⁴) ₂] ⁰
Ni	Bu ^t	Pr ⁱ	H	[Ni(L ⁵) ₂] ⁰

The compounds described below are named according to the second preparation, although it was only used in preparing the nickel compounds: thus, oxidized bis(1-phenyl-4,4-diethylthiosemicarbazidato)nickel(II) is called Ni-bis-*N,N*-diethylphenylazothioformamide and designated as $[\text{Ni}(\text{L}^1)_2]^0$. This and analogously derived symbols will be used in the following (see Table 1).

In addition to the thiosemicarbazides mentioned, 1-*tert*-butyl-4-isopropylthiosemicarbazide was found to form a reasonably stable oxidized inner complex.

The oxidized inner complexes are crystalline, high melting and strongly coloured substances.

The electron-transfer properties of three compounds, Ni-, Pt-, and $[\text{Zn}(\text{L}^1)_2]^0$, which were selected as representative, have been demonstrated by cyclic voltammetry. Each compound has been shown to undergo two one-electron reductions, although the electrode reactions were not strictly reversible ($\alpha = 0.8 - 0.9$). The peak potentials of the reduction waves are given in Table 2.

Table 2. Cyclic voltammetry data.

Complex	Couple z	Solvent	E_p Volts ^a
$[\text{Ni}(\text{L}^1)_2]^z b$	$0 \rightleftharpoons -1$	CH_3CN^d	-0.82
	$-1 \rightleftharpoons -2$	»	-1.15
$[\text{Ni}(\text{L}^1)_2]^z b$	$0 \rightleftharpoons -1$	DMF^e	-0.72
	$-1 \rightleftharpoons -2$	»	-1.15
$[\text{Ni}(\text{L}^1)_2]^z c$	$0 \rightleftharpoons -1$	»	-0.73
	$-1 \rightleftharpoons -2$	»	-1.12
$[\text{Pt}(\text{L}^1)_2]^z b$	$0 \rightleftharpoons -1$	CH_3CN^d	-0.91
	$-1 \rightleftharpoons -2$	»	-1.22
$[\text{Zn}(\text{L}^1)_2]^z b$	$0 \rightleftharpoons -1$	»	-0.70
	$-1 \rightleftharpoons -2$	»	-0.93

^a Versus SCE. ^b Platinum electrode. ^c Hanging mercury drop. ^d Supporting electrolyte 0.05 M Me_4NBF_4 . ^e 0.1 M Et_4NBr .

An attempt was made to synthesize the oxidized members, $[\text{M}(\text{L}^1)_2]^{2+}$, of the electron-transfer series established by cyclic voltammetry by treating the oxidized ligand *N,N*-diethylphenylazothioformamide (L^1) with metal salts in various solvents, but we have not yet been able to isolate the expected species. From ethanol $[\text{M}(\text{L}^1)_2]^0$ ($\text{M} = \text{Ni}$ and Pt) were isolated, indicating solvent oxidation, while in other solvents compounds of the type $[\text{M}(\text{L}^1)\text{X}_2]$ ($\text{M} = \text{Ni}$, Zn and Cd , $\text{X} = \text{Cl}^-$, Br^- , and NO_3^-) were formed. These compounds are reducible, forming paramagnetic species. The detailed results of an investigation of these compounds will be published in a forthcoming paper.⁶ $[\text{Cu}(\text{L}^1)_2]^0$ and $[\text{Ni}(\text{L}^5)_2]^0$ were also investigated by cyclic voltammetry but did not, under the conditions employed, undergo simple one-electron reductions.

Ni-complexes. $[\text{Ni}(\text{L}^1)_2]^0$ has been investigated by Hazell⁷ by three-dimensional X-ray diffraction. The results presented here are believed to be

representative for neutral bis-aryl- and bis-alkylazothioformamides. It has been shown that the N_2S_2 -coordination sphere is a distorted tetrahedron. This fact is surprising, since the propensity to undergo one-electron transfers seemed for *tetra*-coordinated compounds to be combined with planarity, from which only very small deviations had been found.¹² Furthermore the C–N² bond (1.356 Å) has essentially single bond character. (The numbering refers to Table 1.) Planar but otherwise similar compounds have significantly shorter C–N bond lengths, as in bis-thiosemicarbazidatonickel (II), 1.25 Å,⁸ and bis-thioacetylhydrazidatonickel (II), 1.276 Å,⁹ and even compounds where the “double bond” character arises from delocalisation have shorter bonds of length 1.32–1.35 Å.^{10,11} The Ni–S and Ni–N distances are 2.215 Å and 1.869 Å. The interligand S–S distance is 3.82 Å. The very long C–N² distance found in this complex is an indication that delocalisation in the five-membered chelate ring is not so important in these compounds as in the metal bis-dithiolates¹ and the $[M-N_2S_2]^+$ electron-transfer series established by Holm *et al.*³ The formation of electron-transfer complexes in the alkyl- and arylazothioformamide series seems to be closely related to the stability of the radical anions formed (see below).

The nickel compounds described in Table 1 were all found to be weakly paramagnetic in the solid state as well as in solution. The nature of the hyperfine contact shifts found in the ¹H NMR-spectra (given in Table 3) seems to

Table 3. ¹H NMR contact shifts of Ni-bis-arylazothioformamides. Spectra recorded at 40°C in CDCl₃. The diamagnetic Pt-analogues were used as standards.

Complex	Substituents	Pos.	$\Delta\tau$ ppm
[Ni(L ¹) ₂] ⁰	R ¹ = Ph	<i>o</i>	$\sim -2.54^a$
		<i>m</i>	$\sim +0.48^a$
		<i>p</i>	$\sim -0.77^a$
	R ² = R ³ = Et	α	+0.97
		β	0.00
[Ni(L ³) ₂] ⁰	R ¹ = <i>p</i> -CH ₃ C ₆ H ₄	<i>o</i>	-2.54
		<i>m</i>	+0.32
		<i>p</i> -CH ₃	+1.55
	R ² = Bu ^t	α -CH ₃	0.00
	R ³ = H		...

^a Reference spectrum not resolved.

preclude their originating from paramagnetic impurities. The contact shifts are relatively unaffected by solvent and temperature. ESR-spectra of powdered samples of [Ni(L¹)₂]⁰ show the presence of triplet species ($\Delta m = 2$ transitions), but an ESR experiment in which the intensity of the absorption was determined

as a function of temperature (in the range 26–300 K) has shown that the behavior is due neither to antiferromagnetism nor to a triplet ground state.

A possible explanation of the presence of contact shifts in these compounds is that low-lying excited triplet and singlet states are in rapid equilibrium with a singlet ground state, but obviously the problem needs further investigation.

$[\text{Ni}(\text{L}^1)_2]^0$ and $[\text{Ni}(\text{L}^5)_2]^0$ were found to be volatile and their mass spectra were recorded. The fragmentation patterns are rather complicated; a characteristic feature is the loss of $\text{C}_6\text{H}_5\dot{\text{N}}=\text{N}$ or $\text{C}_4\text{H}_9\dot{\text{N}}=\text{N}$ from the molecular ions. Doubly-charged molecular ions were observed in both spectra.

Zn-complexes. (Results are set out in Table 4 and Fig. 1). The magnetic moment of $[\text{Zn}(\text{L}^1)_2]^0$ and $[\text{Zn}(\text{L}^2)_2]^0$ is in the range of 2.40 BM per zinc atom. This value fits rather well the expected value, 2.45 BM, for a true biradical. A characteristic feature of ESR spectra of biradicals is the presence of magnetic dipole-dipole interactions. ESR spectra of biradicals exhibiting these interactions have usually been found to fit a spin Hamiltonian of the form:

$$\mathcal{H} = g\beta\mathbf{H}\mathbf{S} + DS_x^2 + E(S_x^2 - S_y^2)$$

It has been shown¹³ that spectra of randomly oriented biradical species, when observable, are very useful in obtaining information about electronic and geometric structure. Detailed analyses of the line shapes of rigid media spectra have been given by Wassermann *et al.*,¹³ who has shown that the zero-field splitting parameters D and E can be obtained from the $\Delta m = 1$ region of the spectra. From the line shape in the spectrum of $[\text{Zn}(\text{L}^2)_2]^0$ in a toluene matrix at 153 K (Fig. 1) in the high-field region, we conclude that E is zero. D has been calculated to be 0.0113 cm^{-1} from the z -components of the spectrum.

Temperature variations seem to have very little effect on the magnitude of D and E although maximum resolution occurs at the temperature mentioned above. The zero value of E is surprising because it shows that the x and y axes are equivalent, thus indicating axial or tetrahedral symmetry. If it is assumed that the zinc compounds have the same distorted tetrahedral structure as is found for the nickel compounds (see above), strict symmetry considerations seem to preclude $E = 0$. A possible interpretation is that the orbitals containing the unpaired electrons are approximately perpendicular and relatively unaffected by the severe geometrical distortions. Within the resolution

Table 4. ESR and susceptibility results.

Complex	μ , BM	$\langle g \rangle$	$\langle A \rangle$, gauss	$g_1g_2g_3$	D , cm^{-1}	E , cm^{-1}
$[\text{Zn}(\text{L}^2)_2]^0$	2.40 ^a	2.0040 ^b	22.5 ^b	2.0024 ^c	0.0113 ^c	0 ^c
$[\text{Zn}(\text{L}^1)_2]^0$	2.42 ^a	2.0038 ^b	25.0 ^b

^a $\pm 0.5\%$, T : 70–300 K. ^b Toluene solution at room temp; line width at half height. ^c Toluene glass at 153 K.

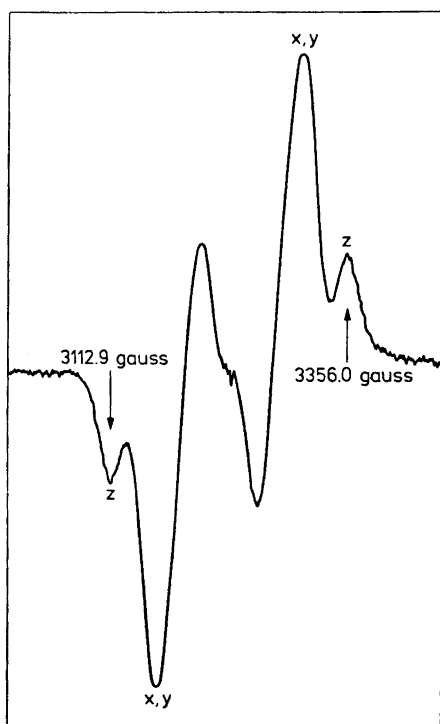


Fig. 1. ESR-Spectrum of $[\text{Zn}(\text{L}^2)_2]^0$ in frozen toluene at -153°C .

obtainable an isotropic g -tensor was found. The $\Delta m = 2$ region of the spectrum consists of rather broad lines of low intensity.

The characteristics of the susceptibility measurements and the ESR spectra suggest that the zinc compounds may be formulated as containing $\text{Zn}(\text{II}), d^{10}$, and two radical-anion ligands in a perpendicular arrangement. This means that the metal orbital character of the highest filled orbitals is vanishingly small, and that the "cation-stabilized free radical" formalism proposed by Holm *et al.*³ is valid for these compounds.

Attempts were made to synthesize the Cd-analogue of $[\text{Zn}(\text{L}^2)_2]^0$. A rather unstable product of the same colour and appearance was obtained. In frozen toluene the ESR-spectrum exhibits the same characteristics as the spectra mentioned above, although an accurate interpretation was prevented by the presence of paramagnetic impurities (probably monoradicals resulting from the breakdown of $[\text{Cd}(\text{L}^2)_2]^0$).

Cu-complexes. The nature of the compounds formed by copper with the arylazothioformamides is rather complicated. The tendency to form polynuclear clusters is strong. When the Cu inner complex of 1-phenyl-4,4-diethylthiosemicarbazide was oxidized by iodine an iodine-containing compound was formed. According to analyses and ^1H NMR- and IR spectra the formula is $[\text{Cu}(\text{L}^1)\text{I}]_n$.⁹ Molecular weight measurements in THF indicate that n equals 4.

Results obtained for $[\text{Cu}(\text{L}^1)_2]^0$ have shown that this compound is monomeric and has a doublet ground state.¹⁴

Pt-complexes. The platinum compounds were found to be diamagnetic. Podchainova *et al.*¹⁵ have studied a similar compound derived from PtCl_4 and 1,4-diphenylthiosemicarbazide and proposed a tetrahedral structure which seems to be correct in view of the results presented above.

$[\text{M}(\text{tert-C}_4\text{H}_9\text{CSeNNH})_2]^0$ ($\text{M} = \text{Ni}, \text{Pt}$). Due to the lack of material these compounds were not investigated by cyclic voltammetry. The electron-transfer properties are well established in the series of sulfur analogues,³ so we may expect the same properties to be found in the selenium compounds. The oxidized inner complexes of thiopivaloylhydrazine could be prepared by essentially the same procedure as the selenium compounds.

The arylazothioformamides represent an interesting ligand system due to their ability to form stable radical anions. The reason for the formation of non-planar structure with transition metals is undoubtedly steric hindrance of the planar configuration, which must be considered the most stable. Papers describing the direct reaction of arylazothioformamides with metals and metal amalgams are in preparation.¹⁶

EXPERIMENTAL

Metal bis-aryl- and alkylazothioformamides from thiosemicarbazides and Me^{2+} . The preparation of $[\text{Ni}(\text{L}^1)_2]^0$ is typical. 4 mmol of 1-phenyl-4,4-diethylthiosemicarbazide was dissolved under nitrogen in 30 ml of ethanol, and NiCl_2 (2 mmol) in ethanol was added. Following reflux for $\frac{1}{2}$ h the dark grey-brown solution was cooled in ice and methanol, and NaOH (4 mmol) was added with vigorous stirring. A grey powder precipitated. Approximately 1 g of $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ in 5 ml of water was added followed by 2 mmol of iodine in 10 ml of ethanol. The solution was left at room temperature; a dark, violet colour developed. After 1 h with stirring the precipitate was filtered off and dried *in vacuo* over conc. H_2SO_4 . Yield 1.00 g ($\sim 100\%$). The final product was obtained by Soxhlet extraction with 100 ml of dry diethyl ether, which yielded 0.70 g ($\sim 70\%$) of deep violet crystals, m.p. 163.5–164.0°C. Essentially the same procedure was used in preparing the zinc, platinum, and copper compounds, although it was necessary to add NaOH (or $(\text{C}_2\text{H}_5)_3\text{N}$) to the boiling solution in order to obtain the zinc inner complex. K_2PtCl_4 dissolved in water was used in the preparation of the platinum compounds, and quinone oxidation yielded the copper compounds. The physical data are summarized in Table 5.

Ni-Arylazothioformamides from Ni(0)-compounds and azothioformamides. *N-tert-Butylphenylazothioformamide* (L^4) (1.13 mmol) was dissolved in 30 ml of 2-propanol. Nickel-tetrakis(triethylphosphite)¹⁷ (0.58 mmol) was added slowly with stirring and the solution was kept for 1 h at 60°C. After cooling, the precipitate was filtered off and dried *in vacuo* over P_2O_5 . The final product was obtained by Soxhlet extraction with 80 ml of ether-pentane (1:4). Yield 0.200 g (70%), m.p. 173.5–174.0°C. (Found: C 52.66; H 6.10; N 16.54; S 12.64. Calc. for $\text{C}_{22}\text{H}_{30}\text{N}_6\text{S}_2\text{Ni}$: C 52.70; H 6.03; N 16.77; S 12.79.)

The Ni-compounds were prepared by this method in varying yields when the azothioformamides were obtainable. $[\text{Ni}(\text{L}^4)_2]^0$ was also obtained in very good yields (80–90%) from $\text{Ni}(\text{CO})_4$ and the corresponding azothioformamide by a similar procedure.

Preparation of ligands. The 1,4-dialkyl- and 1-aryl-4-alkylthiosemicarbazides were prepared by well-known procedures.¹⁸ 1-Aryl-4,4-dialkylthiosemicarbazides were prepared by essentially the procedure reported by Sasse.¹⁹ The arylazothioformamides were obtained by quinone oxidation of the corresponding thiosemicarbazides.^{20,21} The preparation of *N,N*-diethylphenylazothioformamide is typical: 4,4-diethyl-1-phenylthiosemicarbazide (4.7 mmol) was dissolved in 50 ml of refluxing 50% methanol, 4.7 mmol of quinone dissolved in 10 ml of water was added slowly and the solution was stirred at

Table 5. Metal-bis-azothioformamides.

M	R ¹	R ²	R ³	Symbol	Yield %	M.p., °C	Purific.	Formula	Analyses								
									C	H	N	S	M				
Ni	Ph	Et	Et	[Ni(L ¹) ₂] ⁰	70	163.5	c	C ₂₂ H ₃₀ N ₆ S ₂ Ni	Calc.: 52.70	6.03	16.77	12.79	Found: 52.60	6.06	16.75	13.02	
Ni	Ph	-(CH ₂) ₄ -	-	[Ni(L ²) ₂] ⁰	50	a	c	C ₂₂ H ₂₈ N ₆ S ₂ Ni	Calc.: 53.10	5.36	16.91	12.90	Found: 53.13	5.25	16.93	(13.50)	
Ni	<i>p</i> -Tolyl	H	Bu ^t	[Ni(L ³) ₂] ⁰	40	a	d	C ₂₄ H ₃₄ N ₆ S ₂ Ni	Calc.: 54.36	6.54	15.85	12.23	Found: 54.46	6.48	15.88	12.12	
Ni	Ph	H	Bu ^t	[Ni(L ⁴) ₂] ⁰	70	173	b	C ₂₂ H ₃₀ N ₆ S ₂ Ni	Calc.: 52.70	6.03	16.77	12.79	Found: 52.64	6.08	16.81	12.58	
Ni	Bu ^t	H	Pr ⁱ	[Ni(L ⁵) ₂] ⁰	25	a	c	C ₁₆ H ₃₄ N ₆ S ₂ Ni	Calc.: 44.35	7.91	19.39		Found: 44.14	7.95	19.44		
Zn	Ph	Et	Et	[Zn(L ¹) ₂] ⁰	25	a	c	C ₂₂ H ₃₀ N ₆ S ₂ Zn	Calc.: 52.01	5.95	16.54	12.62	Found: 51.80	5.93	16.54	12.92	12.65
Zn	Ph	-(CH ₂) ₄ -	-	[Zn(L ²) ₂] ⁰	50	a	b	C ₂₂ H ₂₈ N ₆ S ₂ Zn	Calc.: 52.45	5.20	16.68	12.73	Found: 52.62	5.21	16.72	12.81	
Pt	Ph	Et	Et	[Pt(L ¹) ₂] ⁰	73	a	f	C ₂₂ H ₃₀ N ₆ S ₂ Pt	Calc.: 41.45	4.75	13.17	10.05	Found: 41.68	4.88	13.02	9.96	
Pt	<i>p</i> -Tolyl	H	Bu ^t	[Pt(L ³) ₂] ⁰	80	a	c	C ₂₄ H ₃₄ N ₆ S ₂ Pt	Calc.: 43.29	5.15	12.63	9.63	Found: 44.09	5.47	12.13	9.56	28.55
Cu ^g	Ph	Et	Et	[Cu(L ¹) ₂] ⁰	60	a	b	C ₂₂ H ₃₀ N ₆ S ₂ Cu	Calc.: 52.20	5.97	16.60	12.65	Found: 52.00	5.98	16.57	12.64	
Cu ^g	Ph	-(CH ₂) ₄ -	-	[Cu(L ²) ₂] ⁰	20	a	b	C ₂₂ H ₂₈ N ₆ S ₂ Cu	Calc.: 52.60	5.21	16.73	12.76	Found: 52.45	5.30	16.54	12.77	

^a Not well-defined. ^b Ether. ^c Pentane. ^d Ether—pentane (1:1). ^e Ether—pentane (2:1). ^f Ether—pentane (2:1). ^g Obtained by quinone oxidation.

75°C for 1 h. After cooling the solution was kept at -20°C for two days. The brick-red precipitate was filtered off, vacuum-dried, and recrystallized twice from pentane. Yield 0.6 g (60%), m.p. 57.0–58.0°C.

The physical data for this compound and two other new azothioformamides are given in Table 6.

Table 6. Arylazothioformamides.

R ² R ³ N-CS-N=N-C ₆ H ₅									
R ²	R ³	M.p., °C	Yield %	Recryst.	Analyses				
					C	H	N	S	
H	Bu ^t	80–81.5	46	methanol – – water 1:1	Calc.:	59.65	6.84	19.02	14.51
					Found:	59.74	6.92	18.88	14.37
Et	Et	56–57	60	pentane	Calc.:	59.65	6.84	19.02	14.47
					Found:	59.94	6.88	19.24	14.63
–(CH ₂) ₄ –		132.5	40 ^a	ethanol – – water 1:1	Calc.:	60.35	5.98	19.18	14.63
					Found:	60.60	6.09	19.48	14.80

^a Prepared in abs. ethanol.

(Cu(L)I)_n. 4,4-Diethyl-1-phenylthiosemicarbazide (2 mmol) was dissolved in 30 ml of boiling ethanol and CuCl₂ (1 mmol) was added under stirring. The solution was cooled in ice; 2 mmol NaOH was added and a deep red colour developed. KOAc (0.6 g) was added, followed by iodine (1 mmol) dissolved in ethanol, whereupon the solution turned deep green. After ½ h 20 ml of water was added and the precipitated material was filtered off, vacuum-dried, and purified by Soxhlet extraction with 80 ml of dry ether. Yield 0.20 g of black crystals. (Found: C 32.44; H 3.70; N 10.22; S 7.83; I 31.06; Cu 15.43. Calc. for (C₁₁H₁₅N₃SCuI)_n: C 32.08; H 3.67; N 10.20; S 7.79; I 30.80; Cu 15.43.)

Ni- and Pt(tert-C₄H₉CSeNNH)₂. Selenopivaloylhydrazine²² (0.17 mmol) was dissolved in 10 ml of ethanol and the solution cooled to -15°C. K₂PtCl₄ (0.085 mmol) in 10 ml of water was added. After 1 h NaOH (0.17 mmol) was added. After 1 h quinone (0.085 mmol) was added and the solution kept at -20°C for 2 h. The product was precipitated with water, filtered off and dried *in vacuo*. The material was dissolved in 5 ml of ether and filtered and 10 ml of pentane was added. After 2 days at -20°C black needles precipitated, which were filtered off and air-dried. Yield 14.7 mg. The nickel compound was prepared analogously. (Found: C 21.93; H 3.67. Calc. for C₁₀H₂₀N₄Se₂Pt: C 21.86; H 3.67. Found: C 29.32; H 4.81. Calc. for C₁₀H₂₀N₄Se₂Ni: C 29.09; H 4.88.)

Physical measurements. Voltammetric data were obtained using a signal generator (JUUL Electronic) combined with a three-electrode system as described by Schwarz and Shain.²³ The cell, which was described earlier,²⁴ was thermostated at 25°C. Acetonitrile and DMF were purified according to Moe.²⁵ Tetraethylammonium bromide (Fluka, *purum*) was recrystallized several times from ethanol/benzene and tetraethylammonium fluoborate was prepared by essentially the same procedure as that described by Moe.²⁶ Deoxygenation of the solutions was accomplished by purging with prepurified nitrogen. A platinum electrode or a hanging mercury drop served as working electrode, the mercury pool as the counterelectrode, and an aqueous calomel electrode as the reference electrode. Sweep 0.2 V/sec.

ESR measurements were made using a Varian 4500-X spectrometer equipped with a frequency counter and a Varian F-8 nuclear fluxmeter, or a JES-ME-1X spectrometer. Susceptibilities were obtained by the Faraday method using Hg[Co(NCS)₄] as calibrant.

¹H NMR spectra were recorded on a Varian A-60A spectrometer using tetramethylsilane as internal reference, and mass spectra were recorded on an AEI MS-902 double focusing mass spectrometer using the direct inlet probe. Elemental analyses were carried out in the microanalytical department of this laboratory by Mr. Preben Hansen and his staff.

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REFERENCES

1. Davidson, A., Edelstein, N., Holm, R. H. and Maki, A. H. *J. Am. Chem. Soc.* **85** (1963) 2029.
2. McCleverty, J. A. *Progr. Inorg. Chem.* **10** (1968) 49.
3. Holm, R. H., Balch, A. L., Davidson, A., Maki, A. H. and Berry, T. E. *J. Am. Chem. Soc.* **89** (1967) 2866.
4. Jensen, K. A. and Miquel, J. F. *Acta Chem. Scand.* **6** (1952) 189.
5. Jensen, K. A., Bechgaard, K. and Pedersen, C. Th. *Acta Chem. Scand.* **22** (1968) 3341.
6. Bechgaard, K. *Acta Chem. Scand. To be published.*
7. Hazell, R. G. *Acta Chem. Scand. To be published.*
8. Calcava, L., Nardelli, M. and Fava, G. *Acta Cryst.* **15** (1962) 1139.
9. Olsen, B. and Watson, K. J. *Private communication.*
10. Grønbaek, R. and Rasmussen, S. E. *Acta Chem. Scand.* **16** (1962) 1139.
11. Hazell, R. G. *Acta Chem. Scand.* **22** (1968) 2171.
12. Eisenberg, E. *Progr. Inorg. Chem.* **12** (1970) 295.
13. Wasserman, E., Snyder, L. C. and Yager, W. A. *J. Chem. Phys.* **41** (1964) 1763.
14. Bechgaard, K. *To be published.*
15. Podchainova, V. N., Chechneva, A. N. and Krylov, E. I. *Russ. J. Inorg. Chem.* **10** (1965) 288.
16. Bechgaard, K. *To be published.*
17. Vinal, R. S. and Reynolds, L. T. *Inorg. Chem.* **3** (1964) 1062.
18. Jensen, K. A., Anthomi, U., Kägi, B., Larsen, C. and Pedersen, C. Th. *Acta Chem. Scand.* **22** (1968) 1-50.
19. Sasse, K. *Ann.* **735** (1970) 158.
20. Pluijgers, C. W., Berg, J., Sijpesteijn, A. K., Tempel, A. and Verloop, A. *Rec. Trav. Chim.* **87** (1968) 833.
21. Pyl, Th., Scheel, K. H. and Beyer, H. *J. prakt. Chem.* [4] **20** (1963) 255.
22. Jensen, K. A., Mygind, H. and Nielsen, P. H. *Acta Chem. Scand. To be published.*
23. Schwarz, W. M. and Shain, I. *Anal. Chem.* **35** (1963) 1770.
24. Moe, N. S. In Hills, G. J., Ed., *Polarography 1964* MacMillan, London 1966, p. 1077.
25. Moe, N. S. *Acta Chem. Scand.* **21** (1967) 1389.
26. Moe, N. S. *Acta Chem. Scand.* **19** (1965) 1023.

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