Nonplanar Electron Transfer Complexes. I. The Chemistry of
Five Ni—N₂S₂⁺ Complexes derived from Nickel-bis-N,N-diethylphenylazothioformamide

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The existence of a series of five electron transfer complexes, of which the nonplanar nickel-bis-
N,N-diethylphenylazothioformamide is the pro-
prototype, has been demonstrated by cyclic vol-
ammetry and coulometric techniques. The
nature of four members of the series has been
elucidated by a combination of electrochemical,
ESR, and electronic spectral studies and meas-
urements of magnetic susceptibilities of solid
samples. The properties of three members of the
Ni—N₂S₂⁺ series (z = 1+, 0, and 1−) have been
rationalized in a simple bonding model for
nonplanar electron transfer complexes, in which
the highest occupied orbitals seem to be mainly
ligand-based.

In recent years several reports have appeared
concerning electron transfer complexes of the
general type M−N₂S₂⁺ (Refs. 1−6). Among the
ligands used, arylazothioformamides are espe-
cially interesting in view of their ability to form
planar electron transfer complexes with plati-
num, as well as nonplanar complexes with nickel
and copper described in this and a following paper, respectively.

Additionally, N,N-diethylphenylazothioform-
amide (L) has been found to form a very
unusual bis complex with zinc, Zn(L)₂⁺, having
a vanishingly small energy difference between
a 1B and a 2B ground state.

The pseudotetrahedral structure ⁶,⁷ of nickel-
bis-N,N-diethylphenylazothioformamide (3)
makes a detailed study of this compound attrac-
tive since, to our knowledge, it represents the
first serious distortion from planarity ever re-
ported for bis-chelate electron transfer com-
plexes. The stability of planar electron transfer
series is frequently ascribed to favorable out-of-
plane π type interactions which create MO’s
extensively delocalized over both metal and
ligands.⁸,⁹ These interactions tend to be some-
what reduced in tetrahedral species ¹⁰ and thus
do not contribute to the stability of tetrahedral
M−N₂S₂⁺ species.

It is the purpose of the present work to docu-
ment the existence of the series of electron
transfer complexes in question, to present re-
sults obtained for individual species, and to try
to rationalize some of these in a simple model
of the bonding.

In our first paper ⁴ we reported electro-
chemical results obtained in acetonitrile solu-
tions which indicated that nickel-bis-N,N-diethylphenylazothioformamide [Ni(L)₂⁺(3)]
was the neutral representative of a three-
membered series of electron transfer complexes.

The present work describes results mainly ob-
tained in the less coordinating solvent methylene
chloride, in which five discrete members have
been identified:

\[
\begin{align*}
\text{Ni(L)₂⁺} & \overset{\text{C.}}{\rightleftharpoons} \text{Ni(L)⁺} \overset{\text{C.}}{\rightleftharpoons} \text{Ni(L)} \overset{\text{C.}}{\rightleftharpoons} \text{Ni(L)} \overset{\text{C.}}{\rightleftharpoons} \text{Ni(L)⁺} \overset{\text{C.}}{\rightleftharpoons} \text{Ni(L)}₂⁺
\end{align*}
\]

(I) (2) (3) (4) (5)
RESULTS

Preparation. The preparation of (3) follows the general procedure for neutral \( M(L)_2 \) complexes, oxidation of the corresponding bis-thiosemicarbazides. It has been reported in detail elsewhere. The most oxidized member (I) of the series was prepared by treatment of 1 mol of Ni(ClO\(_4\))\(_2\).6H\(_2\)O dissolved in dry acetone with two mol of L (eqn. 1).

\[
\text{Ni}^{3+} + 2L \rightarrow \text{Ni}(L)_2^{2+} \quad (I)
\]

(1)

This procedure, although simple-looking, deserves further comment. By cyclic voltammetry (see below) it has been shown that (I) is generated at a fairly positive potential (\( E_1 = +0.7 \text{ V vs. SCE} \)). This means that the solvent in which (I) is formed has to be stable towards oxidants of this strength. As shown below (I) is also unstable towards acetonitrile, the reason being that this solvent is too good a ligand compared to L. This illustrates two important features, solvent oxidation and solvent coordination which have to be controlled in the preparation of individual members of electron transfer series.

\( \text{Ni}(L)_2^{3+} \) (I) can be isolated as a perchlorate containing 1 mol of water. The water, which cannot be removed without destruction of the complex (ca. 180°C), seems to accompany the perchlorate ion, since an anhydrous tetrafluoroborate can be prepared, exhibiting the same properties as the perchlorate as solid as well as in solution. The perchlorate was used in the investigation of (I) because the tetrafluoroborate turned out to be unstable on storage.

Ni(L)\(_2\)^+ (2) can be prepared electrolytically by one-electron oxidation of (3) or by mol to mol mixing of (I) and (3) in dry CH\(_3\)Cl\(_2\) (eqn. 2):

\[
(I) + (3) \rightarrow 2(2)
\]

(2)

The identity of (2) generated by the different procedures was checked by means of its electronic spectrum.

Ni(L)\(_2\)^- (4) was generated electrolytically by one-electron reduction of (3) and was stable when protected from oxygen and moisture.

Attempts to prepare stable solutions of (5) by either electrolytic or Na-Hg reduction of (3) were, however, unsuccessful.

Electrochemical evidence for the electron transfer series

CH\(_3\)Cl\(_2\). The solution equilibria set up as a consequence of reduction or oxidation of (3) are illustrated by the cyclic voltammogram given in Fig. 1. In the cathodic scan starting at S (3) is reduced to (4) at \( R_3 \) in a reversible

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*Fig. 1. Cyclic voltammogram of Ni(L)\(_2\)^+ in CH\(_3\)Cl\(_2\).*

process. Coulometric reduction \(^{11}\) uses precisely 1 F/mol and (4) can be reoxidized to (3) in 95 - 100 % yield. The peak separation \(R_4 - O_4\) is 60 mV at 298 K, and the peak current ratio 1:1. Thus there is no doubt that (4) is formed by one-electron reduction of (3). At the more negative potential, \(R_4\), (4) is reduced to (5). Again the criteria for a reversible one-electron reduction are fulfilled, but (5) is not stable under the conditions employed, since the voltammograms taken after one-electron coulometric reduction of (4) change rapidly with time.

Starting at \(S\) and scanning anodically it has been shown, by the technique outlined above, that (3) undergoes two reversible one-electron oxidations to (2) and (1) at \(O_2\) and \(O_1\), respectively. (2) and (1) are both stable under the conditions employed.

\(\text{CH}_2\text{CN. In CH}_2\text{CN the two reversible couples R}_2 - O_2\) and \(R_4 - O_4\) are recognized from the investigation in \(\text{CH}_3\text{Cl}_2\). In the anodic scan, however, (3) is oxidized irreversibly at \(O_2\). Coulometric oxidation of (3) uses precisely 2F/mol. Electronic spectra show that the resulting solution consists of \(L\) and \([\text{Ni} (\text{CH}_2\text{CN})_4]^{2+}\) according to:

\[
\text{Ni} (\text{L})_2^{2+} + 6\text{CH}_2\text{CN}^{2-} \rightarrow 2L + [\text{Ni} (\text{CH}_2\text{CN})_4]^{2+}
\]

(3)

The results obtained in \(\text{CH}_2\text{Cl}_2\) clearly demonstrate the existence of an electron transfer series consisting of five discrete members (1) - (5). In \(\text{CH}_2\text{CN}\) only three members, (3) - (5), can be demonstrated owing to the higher affinity of the solvent for nickel which promotes destruction of the cationic complexes.

The voltammetric results are summarized in Table 1.

**DISCUSSION**

\(\text{Ni} (\text{L})_2^{2-}\) (5). This species is produced at potentials more negative than -1.0 V (vs. SCE). The one-electron relationship to (4) has been

### Table 1. Voltammetry of \(\text{Ni} (\text{L})_2^{2+}\) in \(\text{CH}_2\text{CN}\) and \(\text{CH}_2\text{Cl}_2\).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>O(_1)</th>
<th>R(_1)</th>
<th>O(_2)</th>
<th>R(_2)</th>
<th>O(_3)</th>
<th>R(_3)</th>
<th>O(_4)</th>
<th>R(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ni} (\text{L})_2^{2+})</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>0.74</td>
<td>0.67</td>
<td>0.55</td>
<td>0.48</td>
<td>-0.70</td>
<td>-0.76</td>
<td>-1.03</td>
<td>-1.09</td>
</tr>
<tr>
<td>(\text{Ni} (\text{L})_2^{2+})</td>
<td>(\text{CH}_2\text{CN})</td>
<td>0.52</td>
<td></td>
<td></td>
<td></td>
<td>-0.76</td>
<td>-0.82</td>
<td>-1.09</td>
<td>-1.15</td>
</tr>
</tbody>
</table>

\(a\) Volts vs. SCE, scan rate 200 mV/s, \(T = 298\) K. \(b\) Supporting electrolyte, n-Bu\(_4\)NBF\(_4\) (0.2 M). \(c\) 2e Oxidation.

### Table 2. ESR spectral data.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Medium</th>
<th>(g)</th>
<th>(g_1)</th>
<th>(g_2)</th>
<th>(g_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ni} (\text{L})_2^{2+})</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>2.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Ni} (\text{L})_2^{2-})</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>2.022</td>
<td>1.999</td>
<td>2.017</td>
<td>2.063</td>
</tr>
</tbody>
</table>

\(a\) \(T = 298\) K. \(b\) Microcrystalline solid matrix at 77 K. \(c\) Gegenion ClO\(_4\)\(^-\). \(d\) Containing n-Bu\(_4\)NBF\(_4\) (0.2 M).

Table 3. Magnetic susceptibility results.

<table>
<thead>
<tr>
<th>Complex</th>
<th>T, K</th>
<th>$\chi^a$ cgs/mol</th>
<th>$\mu_{eff}$ BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(L)$_2$(ClO$_4$)$_2$</td>
<td>80</td>
<td>$156.2 \times 10^{-4}$</td>
<td>3.16</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>278</td>
<td>$482.1 \times 10^{-5}$</td>
<td>3.27</td>
</tr>
<tr>
<td>Ni(L)$_2$</td>
<td></td>
<td>...</td>
<td>dia.</td>
</tr>
</tbody>
</table>

$^a$ Dia. correction $-200 \times 10^{-4}$ cgs/mol.

Table 4. Electronic spectral data for Ni(L)$_2$ in CH$_3$Cl$_2$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{max}$ nm</th>
<th>$\varepsilon^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(L)$_2$$^{2+}$</td>
<td>375</td>
<td>24 520</td>
</tr>
<tr>
<td></td>
<td>840</td>
<td>2 000</td>
</tr>
<tr>
<td></td>
<td>570</td>
<td>5 570</td>
</tr>
<tr>
<td>Ni(L)$_2$$^+$</td>
<td>375 sh</td>
<td>15 000</td>
</tr>
<tr>
<td></td>
<td>322</td>
<td>18 900</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>20 000</td>
</tr>
<tr>
<td></td>
<td>840</td>
<td>2 340</td>
</tr>
<tr>
<td></td>
<td>572</td>
<td>11 700</td>
</tr>
<tr>
<td>Ni(L)$_2$$^0$</td>
<td>510 sh</td>
<td>7 950</td>
</tr>
<tr>
<td></td>
<td>425</td>
<td>12 000</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>27 000</td>
</tr>
<tr>
<td></td>
<td>285 sh</td>
<td>22 100</td>
</tr>
<tr>
<td></td>
<td>880</td>
<td>2 100</td>
</tr>
<tr>
<td></td>
<td>580</td>
<td>2 200</td>
</tr>
<tr>
<td>Ni(L)$_2$$^-$$^-$</td>
<td>480 sh</td>
<td>2 400</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>14 300</td>
</tr>
</tbody>
</table>

$^a$ Uncorrected for underlying absorptions.

Fig. 2. X-band ESR spectra of (4) and (2) in frozen CH$_3$Cl$_2$ at 77 K.

demonstrated by coulometry. The instability of (5) has however, to date prevented further investigation. The cyclic voltammetry and coulometry results, which are the sole experimental evidence for the existence of (5) are uninformative with respect to structural changes on going from (4) to (5) since structural inter-

Fig. 3. Electronic spectra of Ni(L)$_2$$^-$ in CH$_3$Cl$_2$. 

Fig. 4. Diffuse reflectance and solution spectra of Ni(L)$_2$(ClO$_4$)$_2$H$_2$O.

Conversions (planar-tetrahedral) are not necessarily detected by the rather slow technique employed.

Species corresponding to (5) are in planar $M$-S$_4^{1-}$ and $M$-$N_4S_4^{1-}$ series normally described as Me$^{1+}$ coordinated by two dianion ligands, and it seems reasonable in view of the results discussed below to accept the same formalism when describing (5).

$Ni(L)_2^{2-}$ (4). This species is readily produced by electrochemical reduction of (3) and is stable when protected from oxygen and moisture. The electronic spectrum of (4) in CH$_2$Cl$_2$ is shown in Fig. 3. It is characteristic that the shifts to longer wavelengths always found on going from neutral (3) to monoanionic nickel group members of planar electron transfer series are lacking. In fact, the electronic spectrum of (4) exhibits nearly the same transitions as the spectrum of (3), although the extinction coefficients are smaller. This strongly indicates that the electronic and geometric (tetrahedral) structures are similar, and the additional electron on going from (3) to (4) is placed in a nonbonding orbital (probably an orbital of predominantly ligand $\pi^*$ character).

The ESR spectrum of (4) in frozen CH$_2$Cl$_2$ (Fig. 2) supports this conclusion. A predominant feature is a rather small $g$-tensor anisotropy, which is significantly smaller than the rhombic anisotropy normally found in planar Ni-$N_4S_4^{2-}$ species.

Provided the odd electron is located in an orbital of predominant ligand $\pi^*$ character, a slight or unresolvable $g$-tensor anisotropy is to be expected. If, on the other hand the odd electron resides in an orbital or primarily $3d$ character fairly large $g$-tensor anisotropies are expected in tetrahedral system both of high and of low symmetry.

The experimental spectrum of Ni(L)$_2^{2-}$ favours the first description ($A_g = 0.06$), although it must be stated that the use of $g$-tensor anisotropies as criteria of metal orbital involvement in the odd-electron orbital can be misleading.

$Ni(L)_4^+$ (3). All previously investigated bis complexes showing electron transfer properties have either been found or are assumed to be planar, exhibiting only small tetragonal distortions. However, the structure of Ni(L)$_4^+$, as described in detail elsewhere, is pseudo-tetrahedral, with a dihedral angle of $70^0$ between the average planes of the chelate rings. Another important feature is that the chelate rings and the phenyl groups are not strictly coplanar (the dihedral angle is $30^0$).

The nonplanarity of Ni(L)$_4^+$ is indeed surprising since L would be expected to exhibit the same coordinative properties as the ligands giving rise to planar electron transfer species. Furthermore L can form planar electron transfer complexes with platinum and palladium.

The phenyl group, which singles L from other ligands evidently introduces both steric and electronic chances.

Steric effects are not easily elucidated. Ni-bis-dithizionate (6), which has a coordination sphere similar to that of Ni(L)$_4^+$, has been shown to be planar. In (6) the chelate ring and the phenyl group attached to it are perpendicular.

Furthermore a group of Ni and Co-$N_4S_4$ complexes in which the metal is part of a six-membered ring have been shown to vary be-
tween planar and tetrahedral depending on the bulk of the ring substituents. Phenyl groups have a moderate effect, and typical energy differences are as low as 0–3 kcal/mol in CDCl₃ at 40°C.¹⁸

Likewise the electronic effects are not easily explained. The nonplanarity of Ni(L)₄⁺ allows the ligand to be nearly planar and it is probably not a bad approximation to take in account interactions between the π orbitals of the chelate ring and the phenyl group attached to it. The intense long wavelength transitions found in the electronic spectrum of Ni(L)₄⁺ are probably M→L, L→L, or L→M transitions rather than ligand field transitions since their positions and relative intensities are very dependent of the substituent pattern of L. It might be mentioned that an analogue of Ni(L)₄⁺ derived from N-isopropyl-tert-butylazothioformamide exhibits the first detectable electronic transitions at 570 nm (εₚ = 1500) and 479 nm (εₚ = 16 600) in accordance with the hypsochromic shifts expected on going from phenyl to tert-butyl substituents.

It seems reasonable to conclude from the data mentioned above that the major effect of the phenyl (and tert-butyl) groups is steric hindrance of the planar geometry, but it has further been demonstrated that other azothioformamides carrying less bulky substituents form planar nickel complexes which are unstable.⁶

The electronic structure of diamagnetic Ni(L)₄⁺ is interesting. Characteristic are the very small, but significant, temperature independent contact shifts found in the ¹H NMR spectra of Ni(L)₄⁺ and analogous compounds.⁷ The paramagnetism found is not arising from second order Zeeman terms, since direct unpaired spin densities are observed in the ¹H NMR spectra, but probably arises from thermal population of low lying exited states.⁸ The electronic spectrum of Ni(L)₄⁺ given in Fig. 3 is complicated and has not been interpreted.

Ni(L)₄⁺ (2). An important property of this monocation is found in the ESR spectrum given in Fig. 2. The spectrum of (2) in frozen CH₂Cl₂ is centered around g = 2.000 and exhibits a complete lack of g-tensor anisotropy. If the arguments given above are valid, this means that the odd electron resides in an orbital of primarily ligand character.

The electronic spectrum of (2) is remarkable, since it, except for the 290 nm transition, appears to be a superposition of the spectra of (1) and (3). This raises the question whether (2) has a real existence or the solution is an equilibrium mixture consisting mainly of (1) and (3) (note also that (2) was generated by mol to mol mixing of (1) and (3), as well as electrochemically).

Against this the well-defined ESR spectrum may be emphasized, and also the cyclic voltammetry results. Analysis of these, in terms of the Nernst equation (differences in peak-potentials are taken to be representative of differences in redox potentials), tells us that a solution of (2) in CH₂Cl₂ will disproportionate after eqn. 4:

\[ 2(2) \rightarrow (1) + (3) \]  

in such a way that less than 1% is found as (1) + (3). The influence of these in the spectrum of (2) may thus be regarded as vanishingly small.

Obviously the spectral similarities between (3) and (2) means the removal of an electron on going from (3) to (2) are unimportant for the relative ordering of the orbitals in the two species. This strongly indicates that the highest filled orbital of Ni(L)₄⁺ is essentially a non-bonding ligand based orbital, since spectral similarities of this type are frequently found when comparing spectra of organic cation radicals (n electrons) with the spectra of the corresponding dications (n−1 electrons), where only the intensities of the long wave length bands [as in comparing (3) and (2)] are different.

Ni(L)₄⁺⁺ (I). The results obtained for this species are somewhat confusing. It is thus important to note the difference between solid state and solution properties.

The solid state magnetic moment is 3.27 BM

per nickel atom at 278 K (falling to 3.12 BM at 77 K). These values were determined for the hydrated perchlorate, Ni(L)\textsubscript{3}ClO\textsubscript{4}\textsubscript{3}H\textsubscript{2}O. These values are uninformative with regard to structure\textsuperscript{31} due to the low symmetry (C\textsubscript{1}) of (I) in a possible tetrahedral geometry.

As demonstrated by Fig. 4, the diffuse reflectance spectrum of Ni(ClO\textsubscript{4})\textsubscript{3}H\textsubscript{2}O is very different from the solution spectrum. This strongly indicates that (I) has a different structure in the solid state than in solution.

The electronic spectral similarities of (I) and (2) in solution, as well as the nature of the \textsuperscript{1}H NMR spectrum of (I) in (CD\textsubscript{3})\textsubscript{2}CO indicate however that (I) is tetrahedral in solution. An X-ray structure determination of Ni(L)\textsubscript{3}ClO\textsubscript{4}\textsubscript{3}H\textsubscript{2}O is in progress, but has not yet been completed. Only a few tetrahedral cationic nickel complexes have been described previously; characteristic of these is bulky groups in the ligands\textsuperscript{29,30} as in (I).

**Simplified bonding model for tetrahedral Ni–N\textsubscript{2}S\textsubscript{4} complexes**

A very important feature of the Ni(L)\textsubscript{3} series is the electronic spectra similarities of (2), (3) and (4). This strongly indicates that addition of one or two electrons to (2) has only a minor effect, and thus that the orbitals in question are essentially nonbonding.

We can utilize this in treating at least (2), (3), and (4) in the same simple model of the bonding. Examination of the X-ray data\textsuperscript{9} of Ni(L)\textsubscript{3} suggests that it is not a bad approximation to treat the chelate as a butadiene-like system carrying \(\sigma\) binding lone pairs directed towards the metal. From arguments given above it seems also to be a reasonable approximation to treat the phenyl group of the ligand as having an inductive effect on the \(\pi\) system of the chelate, rather than influencing the \(\sigma\) type bonding to the metal.

Tetrahedral Ni(L)\textsubscript{3} possesses a structure (7) of C\textsubscript{1} symmetry. The important orbitals in the ground state description are assumed to be the d metal orbitals transforming as \(a; (d_{xy}, d_{xz}, d_{yz},\) and \(d_{xy})\) and \(b; (d_{xx} and d_{yy})\) together with the ligand \(\pi^*\) orbitals (see Fig. 8). The eigenvector properties of the ligand orbitals were determined from a simple Hückel (or a CNDO/2) calculation. These calculations suggest that the energy of the third \(\pi\) orbital of the N–N–C–S chelate is of the same order as the d orbitals of nickel. Addition of one electron to the neutral chelate corresponds to formation of the radical anion of the ligand and half fills the \(\pi\) orbital in question, this \(\pi\) orbital is therefore in the following denoted as a \(\pi^*\) orbital.

The \(\pi^*\) orbitals of the two ligands in the complex are mixed during the C\textsubscript{4} operation to form a degenerate set of \(a\) and \(b\) symmetry, respectively.

**Fig. 6.**

To a first approximation let us assume a complete removal of degeneracy of the d-orbitals in the distorted low symmetry structure, as well as the ordering of d-orbitals given in Fig. 7. It is important that the \(d_{xy}\) orbital is expected to rise continuously in energy as the tetrahedron flattens. The relative ordering of d-orbitals in systems of low symmetry is uncertain, but the suggestion made has some support from MO calculations and single crystal spectra.\textsuperscript{34}

We may then consider the effect of a set of \(\pi^*\) ligand orbitals energetically situated slightly higher than the d-orbitals. Inspection of the \(\pi^*\) eigenvectors show that \(\pi^*\) (b) and \(d_{xy}\) (b) are

**Fig. 7. Schematic d-orbital splitting in T\textsubscript{d} and C\textsubscript{s} symmetry.**

Fig. 8. Qualitative molecular orbital diagram for tetrahedral Ni–N₂S₄⁺⁻.

expected to mix more heavily than π* (b) and dₓᵧ (b).

This may, if other effects are neglected, lead to the restricted, qualitative MO diagram of Fig. 8, which has strong support in the experimental results summarized below.

The neutral complex contains 10 electrons in these orbitals (Fig. 8), and the highest occupied orbital is predicted to be the ligand π* (a) orbital.

The present model predicts the first two transitions of Ni(L)₁⁺ to be L→L and L→M in accordance with the large intensities found.

One-electron oxidation of Ni(L)₁⁺ would give Ni(L)₂⁺, a ^A ground state. The model predicts that the odd electron will be in a π* (a) “ligand” orbital, in accordance with the lack of g-tensor anisotropy found in the ESR spectrum.

One-electron reduction half fills the π* (b) orbital. The model predicts this orbital to have some dₓᵧ character, in accordance with the slight, but resolvable, rhombic g-tensor anisotropy of Ni(L)₁⁻.

The bonding model outlined above seems useless in interpreting the results obtained for Ni(L)₂⁺. However, there might be unaccounted structural changes on going from (2) to (1).

The possibility of a reversal of the ordering of the two π* orbitals and dₓᵧ is recognized. However, this description has no support in the experimental results, since greater changes in electronic spectra on going from (3) to (2) or (4) would then be expected, as well as some g-tensor anisotropy of (2).

EXPERIMENTAL

N,N Diethylphenylazothioformamide and Ni(L)₁⁺ were prepared as described in Ref. 6.

Ni(L)₂(CIO₄)₂·H₂O, Ni(CIO₄)₂·6H₂O (2 mmol) dissolved in 10 ml of dry acetone was mixed with L (4 mmol) in 5 ml of dry acetone. After standing for 30 min 40 ml of dry diethyl ether was added, and the precipitate was filtered off. Sxshit extraction with 80 ml of CH₂Cl₂-diethyl ether (1:3) yielded 0.7 g (50 %) of shining black-brown crystals, m.p. 183°C (d). (Found: C 36.75; H 4.50; N 11.64. Calc. for C₃₅H₃₃Cl₂N₅NiO₇S₂: C 36.80; H 4.46; N 11.70).

Analytical grade CH₂CN and CH₂Cl₂ were purified by passage through basic alumina (Woelm W 200), deoxygenated by purging with argon and stored in sealed siphon bottles until use. Equipment and techniques used for voltammetry and coulometry have been described elsewhere. The reference electrode was a saturated aqueous calomel electrode. The working electrode for voltammetry was a Beckman platinum button and for coulometry a platinum gauge.

ESR spectra were recorded on a JES-ME-IX spectrometer, and g-values standardized by use of DPPH and Mn⁺⁺ in MgO. Susceptibilities were obtained by the Faraday method using Hg(Co(NCS))₂ as a calibrant.

Electronic (and ESR) spectra of (2) and (4) were recorded in sealed cuvettes filled directly from the electrolysis chamber, which was placed in an argon-filled glove box.

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