Acta Chemica Scandinavica A 28 (1974) 185—193

Nonplanar Electron Transfer Complexes. I. The Chemistry of Five $Ni-N_2S_2^z$ Complexes derived from Nickel-bis-*N*,*N*-diethylphenylazothioformamide

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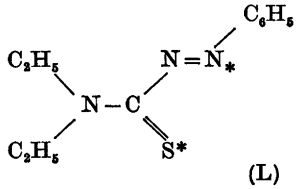
The existence of a series of five electron transfer complexes, of which the nonplanar nickel-bis-*N*,*N*-diethylphenylazothioformamide is the prototype, has been demonstrated by cyclic voltammetry and coulometric techniques. The nature of four members of the series has been elucidated by a combination of electrochemical, ESR, and electronic spectral studies and measurements of magnetic susceptibilities of solid samples. The properties of three members of the $Ni-N_2S_2^z$ 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 $M-N_2S_2^z$ (Refs. 1–6). Among the ligands used, arylazothioformamides are especially interesting in view of their ability to form planar electron transfer complexes with platinum,[5] as well as nonplanar complexes with nickel [6] and copper described in this and a following paper, respectively.

Additionally, *N*,*N*-diethylphenylazothioformamide (L) has been found to form a very unusual bis complex with zinc, $Zn(L)_2^0$, having a vanishingly small energy difference between a ^1B and a ^3B ground state.[6]



(L)

The pseudotetrahedral structure [6,7] of nickel-bis-*N*,*N*-diethylphenylazothioformamide (*3*) makes a detailed study of this compound attractive since, to our knowledge, it represents the first serious distortion from planarity ever reported for bis-chelate electron transfer complexes. 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 somewhat reduced in tetrahedral species [10] and thus do not contribute to the stability of tetrahedral $M-N_2S_2^z$ species.

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

In our first paper [6] we reported electrochemical results obtained in acetonitrile solutions which indicated that nickel-bis-*N*,*N*-diethylphenylazothioformamide [$Ni(L)_2^0$,(*3*)] was the neutral representative of a three-membered series of electron transfer complexes.

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

$$\underset{(1)}{Ni(L)_2^{2+}} \overset{e^-}{\rightleftharpoons} \underset{(2)}{Ni(L)_2^{+}} \overset{e^-}{\rightleftharpoons} \underset{(3)}{Ni(L)_2^{0}} \overset{e^-}{\rightleftharpoons} \underset{(4)}{Ni(L)_2^{-}} \overset{e^-}{\rightleftharpoons} \underset{(5)}{Ni(L)_2^{2-}}$$

RESULTS

Preparation. The preparation of (*3*) follows the general procedure for neutral $M(L)_2^0$ compounds, oxidation of the corresponding bisthiosemicarbazidates. It has been reported in detail elsewhere.[6] The most oxidized member (*1*) of the series was prepared by treatment of 1 mol of $Ni(ClO_4)_2.6H_2O$ dissolved in dry acetone with two mol of L (eqn. 1).

$$Ni^{2+} + 2L \rightarrow \underset{(1)}{Ni(L)_2^{2+}} \qquad (1)$$

This procedure, although simple-looking, deserves further comment. By cyclic voltammetry (see below) is has been shown that (*1*) is generated at a fairly positive potential ($E_{\frac{1}{2}} = +0.7$ V *vs.* SCE). This means that the solvent in which (*1*) is formed has to be stable towards oxidants of this strength. As shown below (*1*) 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.

$Ni(L)_2^{2+}$ (*1*) 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 (*1*) 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 (*1*) and (*3*) in dry CH_2Cl_2 (eqn. 2):

$$(1) + (3) \rightleftharpoons 2(2) \qquad (2)$$

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, unsuccesful.

Electrochemical evidence for the electron transfer series

CH_2Cl_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

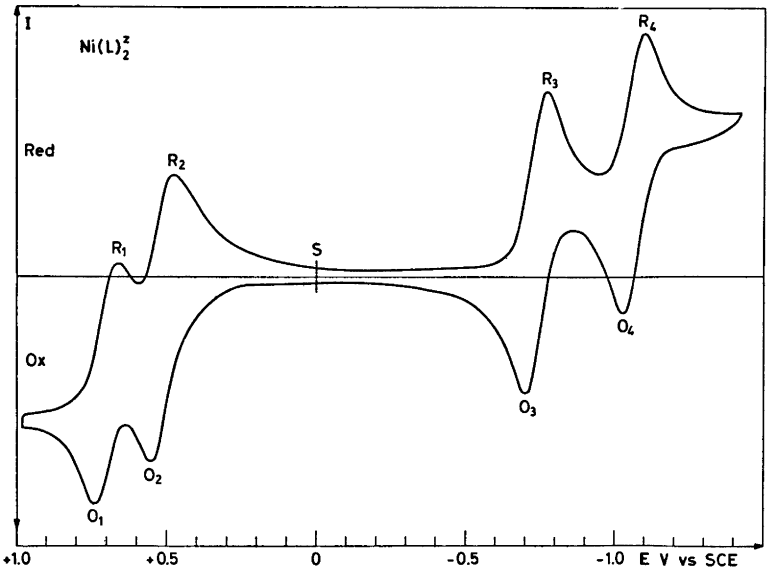


Fig. 1. Cyclic voltammogram of $Ni(L)_2^z$ in CH_2Cl_2.

process. Coulometric reduction [11] uses precisely 1 F/mol and (*4*) can be reoxidized to (*3*) in 95 – 100 % yield. The peak separation $R_3 - O_3$ 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.

CH_3CN. In CH_3CN the two reversible couples $R_3 - O_3$ and $R_4 - O_4$ are recognized from the investigation in CH_2Cl_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 $[Ni(CH_3CN)_6]^{2+}$ according to:

$$Ni(L)_2^0 + 6CH_3CN \xrightarrow{-2e^-} 2L + [Ni(CH_3CN)_6]^{2+} \quad (3)$$

(*3*)

The results obtained in CH_2Cl_2 clearly demonstrate the existence of an electron transfer series consisting of five discrete members (*1*) – (*5*). In CH_3CN 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.

ESR and magnetic susceptibilities. Results are set out in Tables 2 and 3 and Fig. 2. ESR spectra of (*2*) and (*4*) were recorded in frozen CH_2Cl_2 at liquid nitrogen temperature. Magnetic susceptibilities of powdered samples of $Ni(L)_2(ClO_4)_2.H_2O$ and $Ni(L)_2^0$ (*3*) were determined in the temperature range 80 – 278 K.

Electronic spectra of (*1*), (*2*), (*3*), and (*4*) were recorded in dry CH_2Cl_2. The solution spectra are shown in Fig. 3 and the results summarized in Table 4. The diffuse reflectance spectrum of $Ni(L)_2(ClO_4)_2.H_2O$ in $BaSO_4$ is shown in Fig. 4 together with the solution spectrum in CH_2Cl_2.

DISCUSSION

$Ni(L)_2^{2-}$ (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 $Ni(L)_2^z$ in CH_3CN and CH_2Cl_2.

Complex	Solvent	Peak Potentials [a] O_1	R_1	O_2	R_2	O_3	R_3	O_4	R_4
$Ni(L)_2^z$	CH_2Cl_2 [b]	0.74	0.67	0.55	0.48	−0.70	−0.76	−1.03	−1.09
$Ni(L)_2^z$	CH_3CN [b]		0.52 [c]			−0.76	−0.82	−1.09	−1.15

[a] Volts *vs.* SCE, scan rate 200 mV/s, $T = 298$ K. [b] Supporting electrolyte, n-Bu_4NBF_4 (0.2 M). [c] 2e Oxidation.

Table 2. ESR spectral data.

Complex	Medium	sol. [a] $\langle g \rangle$	frozen sol. [b] g_1	g_2	g_3
$Ni(L)_2^+$	CH_2Cl_2 [c]	2.000	–	2.000	–
$Ni(L)_2^-$	CH_2Cl_2 [d]	2.022	1.999	2.017	2.063

[a] $T = 298$ K. [b] Microcrystalline solid matrix at 77 K. [c] Gegenion ClO_4^-. [d] Containing n-Bu_4NBF_4 (0.2 M).

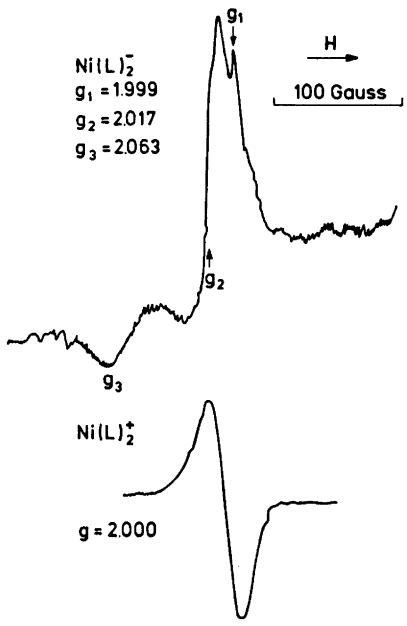


Fig. 2. X-band ESR spectra of (*4*) and (*2*) in frozen CH_2Cl_2 at 77 K.

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-

Table 3. Magnetic susceptibility results.

Complex	T, K	χ^a cgs/mol	μ_{eff} BM
	80	156.2×10^{-4}	3.16
$Ni(L)_2(ClO_4)_2$	150	866.4×10^{-5}	3.22
H_2O	278	482.1×10^{-5}	3.27
$Ni(L)_2^0$	...	...	dia.

[a] Dia. correction -200×10^{-6} cgs/mol.

Table 4. Electronic spectral data for $Ni(L)_2^z$ in CH_2Cl_2.

Complex	λ_{max} nm	ε [a]
$Ni(L)_2^{2+}$	375	24 520
	840	2 000
	570	5 570
$Ni(L)_2^+$	375 sh	15 000
	322	18 900
	290	20 000
	840	2 340
	572	11 700
$Ni(L)_2^0$	510 sh	7 950
	425	12 000
	320	27 000
	295 sh	22 100
	860	2 100
	580	2 200
$Ni(L)_2^-$	480 sh	2 400
	320	14 300

[a] Uncorrected for underlying absorptions.

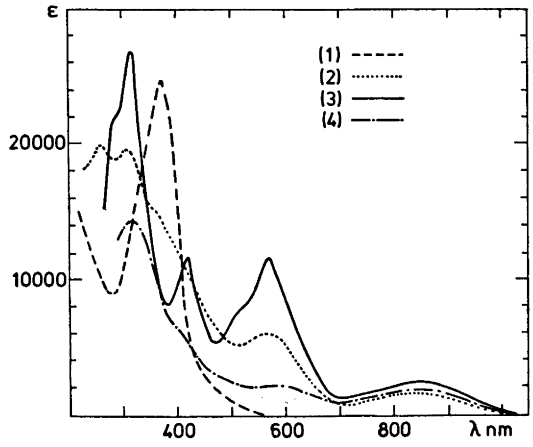


Fig. 3. Electronic spectra of $Ni(L)_2^z$ in CH_2Cl_2.

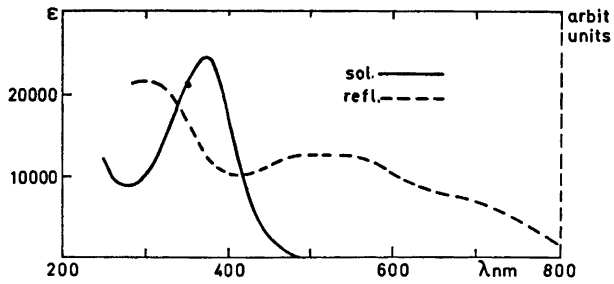


Fig. 4. Diffuse reflectance and solution spectra of $Ni(L)_2(ClO_4)_2H_2O$.

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

Species corresponding to (*5*) are in planar $M-S_4^{2-}$ and $M-N_2S_2^{2-}$ series normally described as Me^{2+} coordinated by two dianion ligands,[5,9] and it seems reasonable in view of the results discussed below to accept the same formalism when describing (*5*).

$Ni(L)_2^-$ (*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_2Cl_2 is shown in Fig. 3. It is characteristic that the shifts to longer wavelengths always found [12] 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 π^* character).

The ESR spectrum of (*4*) in frozen CH_2Cl_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 $Ni\text{-}N_2S_2^-$ species.[1,*]

Provided the odd electron is located in an orbital of predominant ligand π^* character, a slight or unresolvable g-tensor anisotropy is to be expected.[1] If, on the other hand the odd electron resides in an orbital or primarily 3*d* character fairly large g-tensor anisotropies are expected in tetrahedral system both of high and of low symmetry.[13,14]

The experimental spectrum of $Ni(L)_2^-$ favours the first description ($\Delta g = 0.06$), 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.[1,2]

$Ni(L)_2^0$ (*3*). All previously investigated bis complexes showing electron transfer properties have either been found [15] or are assumed to be planar,[12] exhibiting only small tetragonal distortions. However, the structure of $Ni(L)_2^0$, as described in detail elsewhere,[6,7] is pseudo-tetrahedral, with a dihedral angle of 70° 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°).

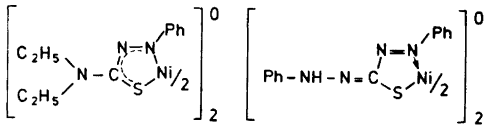
The nonplanarity of $Ni(L)_2^0$ is indeed surprising since L would be expected to exhibit the same coordinative properties as the ligands giving rise to planar electron transfer species. Furthermore L can form planar electron transfer complexes with platinum [5] and palladium.[16]

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

Steric effects are not easily elucidated. Ni-bis-dithizonate (*6*), which has a coordination sphere similar to that of $Ni(L)_2^0$, has been shown to be planar.[17,18] In (*6*) the chelate ring and the phenyl group attached to it are perpendicular.

Furthermore a group of Ni and $Co-N_2S_2$ complexes in which the metal is part of a six-membered ring have been shown to vary be-

* $[Ni(o\text{-}C_6H_4(NH)S)_2]^-$ has $g_1 = 2.005$, $g_2 = 2.028$, and $g_3 = 2.128$, and $[Ni(C_6H_5CSNNH)_2]^-$ has $g_1 = 2.006$, $g_2 = 2.028$, and $g_3 = 2.126$.[1]



(3) (6)

Fig. 5.

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 $CDCl_3$ at 40°C.[19]

Likewise the electronic effects are not easily explained. The nonplanarity of $Ni(L)_2^0$ 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 $Ni(L)_2^0$ 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 $Ni(L)_2^0$ derived from *N*-isopropyl-*tert*-butylazothioformamide [6] exhibits the first detectable electronic transitions at 570 nm ($\varepsilon_{app} = 1500$) and 479 nm ($\varepsilon_{app} =$ 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 sterical 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 $Ni(L)_2^0$ is interesting. Characteristic are the very small, but significant, temperature independent contact shifts found in the ^1H NMR spectra of $Ni(L)_2^0$ and analogous compounds.[6] 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.[20] The electronic spectrum of $Ni(L)_2^0$ given in Fig. 3 is complicated and has not been interpreted.

$Ni(L)_2^+$ (*2*). An important property of this monocation is found in the ESR spectrum given in Fig. 2. The spectrum of (*2*) in frozen CH_2Cl_2 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 CH_2Cl_2 will disproportionate after eqn. 4:

$$2(2) \rightleftharpoons (1) + (3) \qquad (4)$$

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 $Ni(L)_2^0$ is essentially a nonbonding 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.

$Ni(L)_2^{2+}$ (*1*). 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, $Ni(L)_2(ClO_4)_2.H_2O$. These values are uninformative with regard to structure [21] due to the low symmetry (C_2) of (*1*) in a possible tetrahedral geometry.

As demonstrated by Fig. 4, the diffuse reflectance spectrum of $Ni(ClO_4)_2.H_2O$ is very different from the solution spectrum. This strongly indicates that (*1*) has a different structure in the solid state than in solution.

The electronic spectral similarities of (*1*) and (*2*) in solution, as well as the nature of the ^1H NMR spectrum of (*1*) in $(CD_3)_2CO$, indicate however that (*1*) is tetrahedral in solution. An X-ray structure determination of $Ni(L)_2(ClO_4)_2.H_2O$ is in progress, but has not yet been completed. Only a few tetrahedral cationic nickel complexes have been described previously; characteristic of these are bulky groups in the ligands [22,23] as in (*1*).

Simplified bonding model for tetrahedral $Ni-N_2S_2^x$ complexes

A very important feature of the $Ni(L)_2^x$ 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 [6] of $Ni(L)_2^0$ suggests that it is not a bad approximation to treat the chelate as a butadiene-like system carrying σ 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 π system of the chelate, rather than influencing the σ type bonding to the metal.

Tetrahedral $Ni(L)_2^x$ posses a structure (*7*) of C_2 symmetry. The important orbitals in the ground state description are assumed to be the *d* metal orbitals transforming as *a*; (d_{z^2}, $d_{x^2-y^2}$, and d_{xy}) and *b*; (d_{xz} and d_{yz}) together with the ligand π^* 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 π 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 π orbital in question, this π orbital is therefore in the following denoted as a π^* orbital.

The π^* orbitals of the two ligands in the complex are mixed during the C_2 operation to form a degenerate set of *a* and *b* symmetry, respectively.

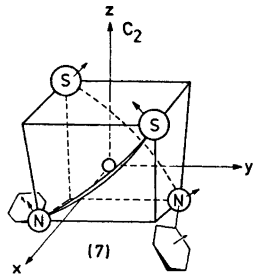


Fig. 6.

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.[24]

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

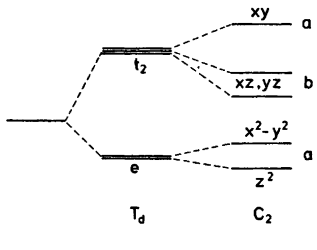


Fig. 7. Schematic *d*-orbital splitting in T_d and C_2 symmetry.

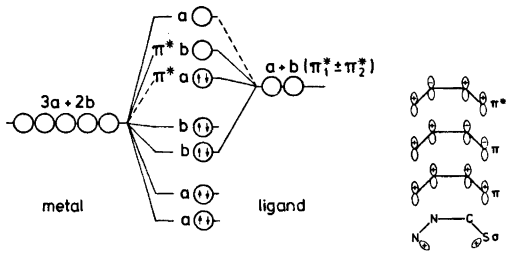


Fig. 8. Qualitative molecular orbital diagram for tetrahedral $Ni-N_2S_2^0$.

expected to mix more heavily than π^* (*b*) and d_{yz} (*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 $Ni(L)_2^0$ to be L→L and L→M in accordance with the large intensities found.

One-electron oxidation of $Ni(L)_2^0$ would give $Ni(L)_2^+$, a ^2A 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 d_{xz} character, in accordance with the slight, but resolvable, rhombic *g*-tensor anisotropy of $Ni(L)_2^-$.

The bonding model outlined above seems useless in interpreting the results obtained for $Ni(L)_2^{2+}$. 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 d_{xy} 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 $Ni(L)_2^0$ were prepared as described in Ref. 6.

$Ni(L)_2(ClO_4)_2.H_2O$. $Ni(ClO_4)_2.6H_2O$ (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. Soxhlet extraction with 80 ml of CH_2Cl_2-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 $C_{22}H_{32}Cl_2N_6NiO_9S_2$: C 36.80; H 4.46; N 11.70).

Analytical grade CH_3CN and CH_2Cl_2 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.[11,25] The reference electrode was a saturated aqueous calomel electrode. The working electrode for voltammetry was a Beckman platinum button and for coulometry a platinum gauze.

ESR spectra were recorded on a JES-ME-IX spectrometer, and *g*-values standardized by use of DPPH and Mn^{2+} in MgO. Susceptibilities were obtained by the Faraday method using $Hg[Co(NCS)_4]$ 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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Received October 1, 1973.