Structural study of four complexes of the M-N$_2$S$_2$ type derived from diethylphenylazothioformamide and the metals palladium, platinum, copper and nickel

Kim T. Nielsen,[a,b]* **Pernille Harris,**[b] **Klaus Bechgaard**[c] **and Frederik C. Krebs**[a]

[a]The Danish Polymer Centre, Risø National Laboratory, PO Box 49, DK-4000 Roskilde, Denmark, [b]Department of Chemistry, Technical University of Denmark, DTU-207, DK-2800 Kgs. Lyngby, Denmark, and [c]Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark

Correspondence e-mail:
kim.troensegaard.nielsen@risoe.dk

The four electron-transfer complexes *trans*-(di(N,N-diethyl-(2-phenyldiazenyl)thioformamide-$\kappa S,\kappa N^2$))nickel, *trans*-(di(N,N-diethyl-(2-phenyldiazenyl)-thioformamide-$\kappa S,\kappa N^2$))copper, *trans*-(di(N,N-diethyl-(2-phenyldiazenyl)thio-formamide-$\kappa S,\kappa N^2$))palladium and *trans*-(di(N,N-diethyl-(2-phenyldiaze-nyl)thioformamide-$\kappa S,\kappa N^2$))platinum have been crystallized, and their structures have been determined at low temperature. All the complexes are of the M-N$_2$S$_2$ type. The crystals of both the nickel and the copper complex belong to the tetragonal $P4_12_12$ system, in which the central metal ion lies on a twofold axis. The tetrahedral molecular symmetry around the central metal ion is unusual for the M-N$_2$S$_2$ electron-transfer complexes. The crystals of the palladium and platinum complexes on the other hand belong to the monoclinic $C2/c$ system in which the metal ion lies on an inversion centre. The molecular symmetry around these metal ions is square planar. It is demonstrated that the π electron density in the ligand planes has a high degree of delocalization. Furthermore, unusually large line broadening of the ^{1}H NMR spectra was observed and investigated as a function of temperature for the palladium complex.

1. Introduction

Thiosemicarbazides have been known for more than 100 years (Busch & Ridder, 1904); they can be transformed to azothioform-amides in a two-electron oxidation process (see Fig. 1; Pyl *et al.*, 1963).

During the 1960s and the early 1970s research concerning the azothioformamides progressed because of the discovery of antifungal activity (Pluijgers *et al.*, 1968), antibiotic activity (Kosower & Miya-dera, 1972) and their potential use as pesticides (Sasse & Hammann, 1971). These ligands also form electron-transfer complexes with many kinds of metals to give complexes analogous to metal dithio-lenes (Davidson *et al.*, 1963). In particular, Holm and Bechgaard have investigated the structural and electronic properties of series of electron-transfer complexes of the type M-N$_2$S$_2^z$ (see Fig. 2; Holm *et al.*, 1967; Forbes *et al.*, 1971; Jensen *et al.*, 1972; Bechgaard, 1973, 1974, 1977).

Recently, we have discovered that azothioformamides such as N,N-diethylphenylazothioformamide (L; see Fig. 3) and N,N-bis(tetra-ethyleneglycolmonomethylether)phenylazothioformamide have the ability to dissolve palladium and copper nanoparticles (Nielsen *et al.*, 2005, 2006). These nanoparticles are often produced through catalytic reactions, *e.g.* Sonogashira cross-coupling reactions (Sonogashira *et al.*, 1975). The azothioformamides dissolved the metals by forming
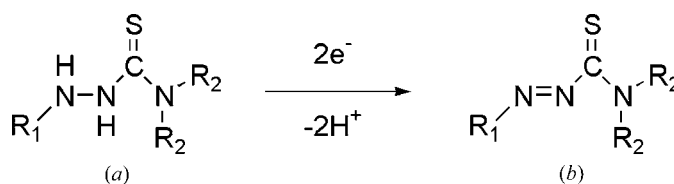
Figure 1
Oxidation of (*a*) thiosemicarbazide to (*b*) azothioformamide.

Table 1
Experimental details.

	NiL_2^0	CuL_2^0	PdL_2^0	PtL_2^0
Crystal data				
Chemical formula	$C_{22}H_{30}N_6NiS_2$	$C_{22}H_{30}CuN_6S_2$	$C_{22}H_{30}N_6PdS_2$	$C_{22}H_{30}N_6PtS_2$
M_r	501.35	506.18	549.04	637.73
Cell setting, space group	Tetragonal, $P4_12_12$	Tetragonal, $P4_12_12$	Monoclinic, $C2/c$	Monoclinic, $C2/c$
Temperature (K)	118 (2)	118 (2)	118 (2)	118 (2)
a, b, c (Å)	10.2852 (3), 10.2852 (3), 22.286 (1)	10.2643 (4), 10.2643 (4), 22.352 (1)	16.0360 (16), 12.456 (1), 12.331 (1)	15.9317 (7), 12.5300 (5), 12.3798 (5)
β (°)	90.00	90.00	100.952 (2)	100.755 (1)
V (Å^3)	2357.6 (2)	2354.9 (2)	2418.3 (4)	2427.9 (2)
Z	4	4	4	4
D_x (Mg m^{-3})	1.413	1.428	1.508	1.745
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.02	1.13	0.96	5.97
Crystal form, colour	Quadratic bi-pyramidal shaped, brown	Quadratic bi-pyramidal shaped, black	Plate, green	Plate, dark green
Crystal size (mm)	$0.50 \times 0.30 \times 0.05$	$0.40 \times 0.35 \times 0.15$	$0.30 \times 0.25 \times 0.01$	$0.25 \times 0.20 \times 0.15$
Data collection				
Diffractometer	CCD area detector	CCD area detector	CCD area detector	CCD area detector
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	Empirical (using intensity measurements)	Empirical (using intensity measurements)	Empirical (using intensity measurements)	Empirical (using intensity measurements)
T_{min}	0.74	0.661	0.761	0.255
T_{max}	0.96	0.849	0.990	0.408
No. of measured, independent and observed reflections	31 608, 3630, 3436	16 807, 2832, 2788	8430, 2847, 2431	14 253, 2937, 2632
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.043	0.027	0.043	0.120
θ_{max} (°)	31.0	28.0	28.0	28.0
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.080, 1.17	0.024, 0.070, 1.10	0.049, 0.107, 1.16	0.037, 0.098, 1.09
No. of reflections	3630	2832	2847	2937
No. of parameters	141	141	142	144
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.3442P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0000P)^2 + 0.1079P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 13.3379P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	<0.0001	<0.0001	<0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.61, −0.26	0.36, −0.17	1.48, −2.28	3.08, −4.14

the intensely coloured electron-transfer complexes PdL_2^0 and CuL_2^0 (see Fig. 3), which belongs to the series shown in Fig. 2.
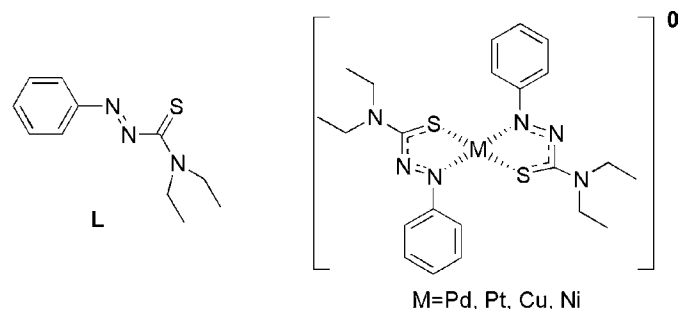
We have demonstrated that this finding can be utilized to quantitatively analyze and remove remnants of catalyst from organic samples (Nielsen et al., 2005, 2006). Remnants of metal catalysts in organic compounds present a huge problem in the pharmaceutical industry (Garrett & Prasad, 2004). It is therefore promising that the azothioformamides may offer an inexpensive and easy way to solve this problem. We therefore believe that the trend of decreased interest in the azothioformamides during the 1980s and 1990s will be reversed.

In the context of the ML_2^0 compounds as electron-transfer complexes, we present here a structural study of the PdL_2^0, PtL_2^0, NiL_2^0 and CuL_2^0 complexes. Before Hazell's (1976) finding of the tetrahedral structure of the NiL_2^0 complex, it was assumed that all bis-chelate electron-transfer complexes in the series showed a planar coordination around the central metal ion (Bechgaard, 1974; Eisenberg, 1970). A powder diffraction study later led to the conclusion that the CuL_2^0 complex was probably tetrahedral like the NiL_2^0 complex (Bechgaard, 1977). In this study we reconfirm both tetra-
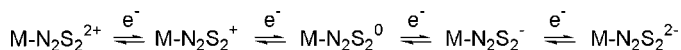
hedral structures, and we also identify the more conventional (square) planar structure of PdL_2^0 and PtL_2^0 that is usually found for Me-bis-dithiolene-like compounds (Eisenberg, 1970). Forbes et al. (1971) have suggested a square-planar structure for the N,N-dimethylphenylazothioformamide platinum complexes.

2. Experimental

The ligand L and the three metal complexes: PdL_2^0, PtL_2^0, NiL_2^0 were synthesized as described in the literature (Jensen et al., 1972). The

$$M\text{-}N_2S_2{}^{2+} \xrightleftharpoons{e^-} M\text{-}N_2S_2{}^{+} \xrightleftharpoons{e^-} M\text{-}N_2S_2{}^{0} \xrightleftharpoons{e^-} M\text{-}N_2S_2{}^{-} \xrightleftharpoons{e^-} M\text{-}N_2S_2{}^{2-}$$

Figure 2
Electron-transfer series containing five members.

M=Pd, Pt, Cu, Ni

Figure 3
The structure of N,N-diethylphenylazothioformamide (L) and the corresponding electron-transfer complexes of the type $M\text{-}N_2S_2^z$.

Table 2
The key angles (°) for the four complexes.

	NiL_2^0	CuL_2^0	PdL_2^0	PtL_2^0
S—M—S	119.50 (3)	123.62 (2)	180.00 (3)	180.00 (2)
N1—M—N1	144.53 (9)	144.84 (7)	180	180
N1—M—S	85.62 (4)	85.48 (4)	82.5 (1)	82.11 (7)
Plane†	75.39 (3)	71.26 (3)	0	0
Plane–phenyl‡	28.08 (7)	26.55 (6)	51.0 (1)	52.01 (8)

† Angle between ligand planes. ‡ Angle between ligand plane and phenyl group.

Table 3
The key distances (Å) for the four complexes.

	NiL_2^0	CuL_2^0	PdL_2^0	PtL_2^0
M—S	2.2085 (4)	2.2753 (4)	2.293 (1)	2.2932 (3)
S—C1	1.723 (2)	1.723 (2)	1.740 (4)	1.743 (2)
C1—N2	1.356 (2)	1.369 (2)	1.339 (5)	1.326 (3)
N2—N1	1.336 (2)	1.323 (2)	1.339 (5)	1.349 (3)
M—N1	1.873 (1)	1.922 (2)	1.994 (3)	1.9647 (2)

CuL_2^0 complex was prepared by immersion of a copper wire in a concentrated tetrahydrofuran (THF) solution of L. L dissolves the metal after which single crystals of CuL_2^0 grow on the wire. These crystals can be used directly for X-ray diffraction measurements (see Fig. 4; Nielsen *et al.*, 2006).

Crystals of the PdL_2^0 and NiL_2^0 complexes were grown by a slow evaporation of a CH_2Cl_2 solution in a round-bottomed flask equipped with a glass funnel. The crystals of PtL_2^0 were very tricky to grow, since slow evaporation from many different solvents led to twinned crystals or clusters of needle-like crystals, which looked like a Christmas tree. By applying the sitting-drop vapor-diffusion technique, known from protein crystallography, we succeeded in growing single crystals. The equipment for the sitting-drop technique consists of glass sitting-drop rods placed in a stender dish in glass sealed with vacuum grease. The reservoir solution consisted of 1 ml toluene and 0.5 ml THF, while the solvent for the drop was THF. The drops were 40 µl in size.

Single-crystal X-ray diffraction data were collected using a Bruker SMART Apex diffractometer with a CCD area detector. Further experimental details can be seen in Table 1.[1]

^{1}H NMR spectra of the PdL_2^0 complex and pure L were recorded on a 250 MHz Bruker NMR spectrometer in a $CDCl_3$ solution with tetramethylsilane (TMS) as an internal reference. The ^{1}H spectrum of the PdL_2^0 complex was investigated as a function of the temperature (from 300 to 210 K in $CDCl_3$ and from 300 to 450 K in 1,2-dichlorobenzene-d_4).

3. Results and discussion

3.1. Crystal structures

For all four ML_2^0 complexes the coordination sites in L are the S and the N1 atoms (see Fig. 2), so that each metal ion is participating in two five-membered rings.

To quantitatively describe the structural conformations of the ML_2^0 complexes, and conclude whether the coordination should be characterized as square-planar or flattened tetrahedral, we have listed the relevant bond angles and distances in Table 2 and 3. These include the coordination distance to the central metal ion and the corresponding

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK5045). Services for accessing these data are described at the back of the journal.

angles involving the central metal ion. To describe the overall geometry we have determined the dihedral angle between the two ligand planes and the dihedral angle between the plane of the phenyl ring and the plane of the ligand. To shed light on the electronic configuration of the ligand and the metal we have listed all the bond lengths in the five-membered chelate rings.

From Tables 2 and 3 it is seen that both the Ni and Cu complexes adopt the flattened tetrahedral coordination, as already discovered by Hazell (1976) for the Ni complex. The structure of these two complexes is shown in Fig. 5. The crystals belong to the tetragonal space group $P4_12_12$. The in-ring N1—M—S angles are 85.61 (4) and 85.48 (4)°, for the Ni and Cu complexes respectively, which are below the value of 109° in a regular tetrahedron, and the N—M—N angles
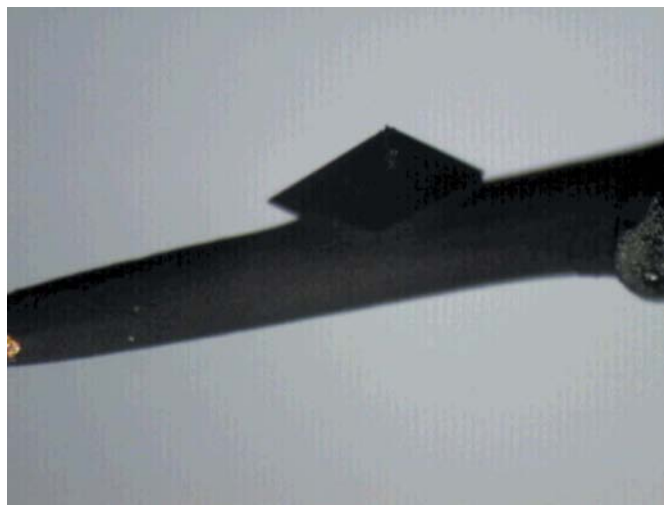
Figure 4
Picture of a crystal of the CuL_2^0 complex growing on a copper wire. The crystal consumes metallic copper when growing. The wire has been immersed in a concentrated THF solution of L.
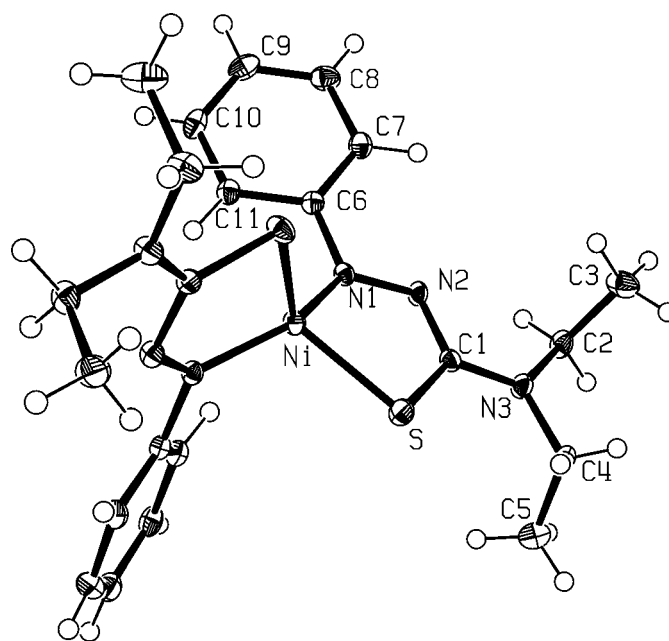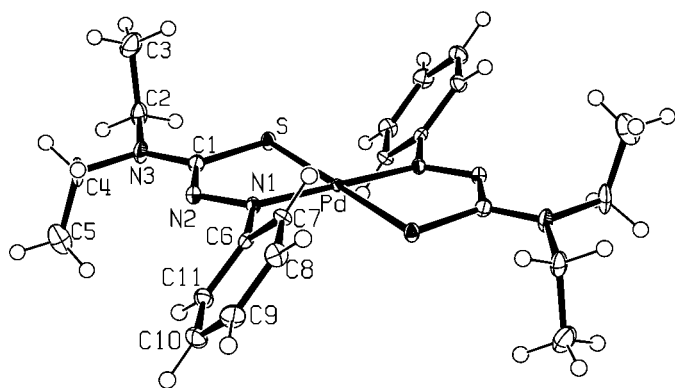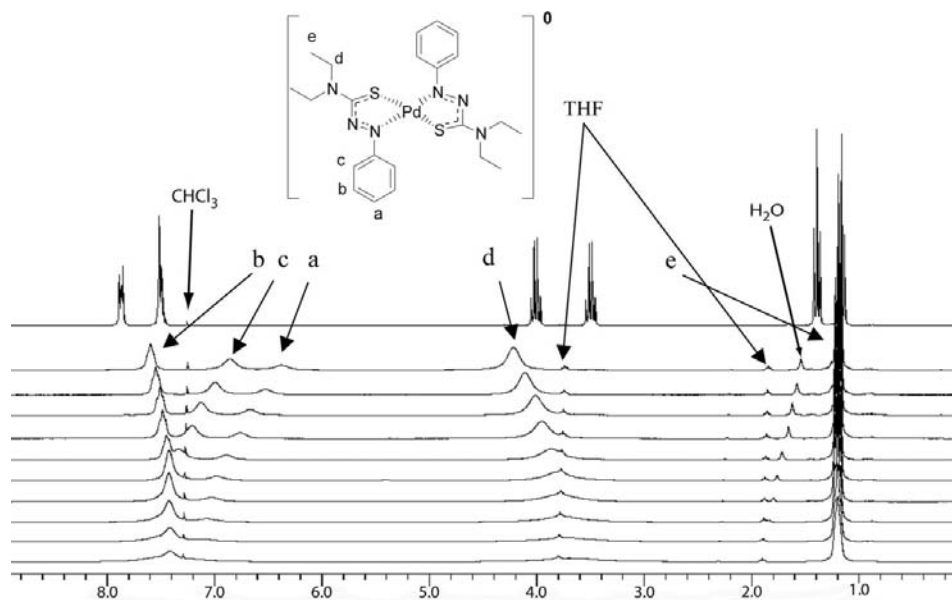

Figure 5
The X-ray structure of the NiL_2^0 complex. The structure is viewed normal to (100). The structure of the CuL_2^0 complex is similar.

---

of 144.55 (9) and 144.84 (7)° are larger. Furthermore, the dihedral angles between the two planes, defined by the five atoms in the two five-membered ligand rings, are 75.39 (3) and 71.26 (3)°, which are smaller than the expected 90° for perfect tetrahedral coordination. It should be mentioned that Hazell determined the dihedral angle in the Ni complex to be 70.4°. The difference could be due to the different data-collection temperatures (298 *versus* 118 K in the present study). The dihedral angles between the plane of the phenyl ring and the plane of the ligand (the five-membered ring) are 28.08 (7) and 26.55 (6)°, respectively, which means that the phenyl ring is twisted out of the plane of the five-membered ring.

The smaller dihedral angles in the CuL_2^0 complex compared with the NiL_2^0 shows that the CuL_2^0 complex has an even more flattened tetrahedral coordination than the NiL_2^0 complex. The smaller angle between the phenyl group and the ligand plane combined with the more flattened coordination imply that the distance between the two C11 atoms (the two closely spaced atoms in the phenyl groups) are longer than in the NiL_2^0 complex, 4.522 and 4.405 Å, respectively. This

Figure 6
The X-ray structure of the PdL_2^0 complex. It can be seen that the coordination about the metal ion is square planar. The structure of the PtL_2^0 complex is similar.

Figure 7
The ^{1}H NMR of the PdL_2^0 complex as a function of temperature. At the bottom the temperature is 210 K and at the top 300 K (in steps of 10 K). The spectrum of pure *L* is shown at the top.

indicates that the intermolecular packing forces are stronger in the NiL_2^0 compared with the CuL_2^0 complex.

The structure determinations of the neutral Pd and Pt complexes show that both adopt the more conventional square-planar structure with the metal ion placed on a crystallographic inversion centre (see Fig. 6). This is in agreement with predictions made by Forbes *et al.* (1971) based on a combination of electrochemical, EPR and electronic spectral studies. As seen in Table 1 the key angles N—*M*—N and S—*M*—S are both 180° by symmetry, as is characteristic for square-planar coordination. The in-ring N1—*M*—S angles are 82.49 (9) and 82.11 (7)°, for the Pd and Pt complexes, respectively. Furthermore, the dihedral angle between the two ligand planes is exactly 0°. The angles between the phenyl group and the ligand plane are 51.0 (1) and 52.01 (8)° for the PdL_2^0 and the PtL_2^0 complexes, respectively.

Blanchard *et al.* (2005) demonstrated that X-ray crystallography can be used as a tool to assign the given oxidation level of the ligand. They have shown that for complexes with 1-phenyl- and 1,4-diphenyl-substituted *S*-methylisothiosemicarbazides as the ligands, the bond lengths of the N—N and C—N bonds are characteristic for the oxidation level of the ligand, *e.g.* if the N—N bond is rather short (1.34 ± 0.01 Å) the ligand can be regarded as a π-radical anion, $L^{\bullet-}$, but if the bond lengths are significantly shorter (1.24 ± 0.01 Å), then the ligand can be regarded as being in its oxidized level (L^{ox}). From our data (see Tables 2 and 3) it can be seen that the NiL_2^0, PdL_2^0 and PtL_2^0 complexes all have N—N bond lengths of 1.34 ± 0.01 Å and therefore can be rationalized as M^{II} complexes with two π-radical anion ligands antiferromagnetically coupled, $[Ni^{II}(L^{\bullet-})_2]$, $[Pd^{II}(L^{\bullet-})_2]$ and $[Pt^{II}(L^{\bullet-})_2]$.

Blanchard *et al.* (2005) calculated the values of the bond lengths N=C, C—S, C—N, N—N in $(HN-N=C(SH)NH^{\bullet-})$ to be 1.294, 1.897, 1.342 and 1.343 Å, respectively. Furthermore, the average S—C and C—N distances in dithiocarbamate structures are 1.70 and 1.34 Å (Eisenberg, 1970). By comparing these bond lengths with the bond lengths in the five-membered ring in the ligand described in this work, we find an indication for a large delocalization of the π electron density over the five-membered ring.

The CuL_2^0 complex has a slightly smaller N—N bond length (1.32 Å) and a slightly larger C—N bond length compared with the other three complexes. This can be rationalized if one assumes that the CuL_2^0 complex consists of Cu^I, one π-radical anion ligand and one neutral ligand, $[Cu^I(L^{\bullet-})(L)]$, as proposed by Bechgaard (1977). Which of these two configurations, $[Cu^0(L^{\bullet-})_2]$ (antiferromagtically coupled) or $[Cu^I(L^{\bullet-})(L)]$, that is the more reasonable for the $Cu(L)_2^0$ complex, cannot be decided on the X-ray data alone.

The M—N and M—S bond lengths are very similar to bond lengths of the same type observed in complexes such as $Ni(S_2CN(C_2H_5)_2)_2$, $Pd(S_2CC_6H_5)_2$ (Eisenberg, 1970), $Pd(ESDT)(PrNH_2)Cl$ (Faraglia *et al.*, 2001), Pd complexes with *ortho*-iminophenolate derivatives as the ligand (Kokatam *et al.*, 2005) and Ni
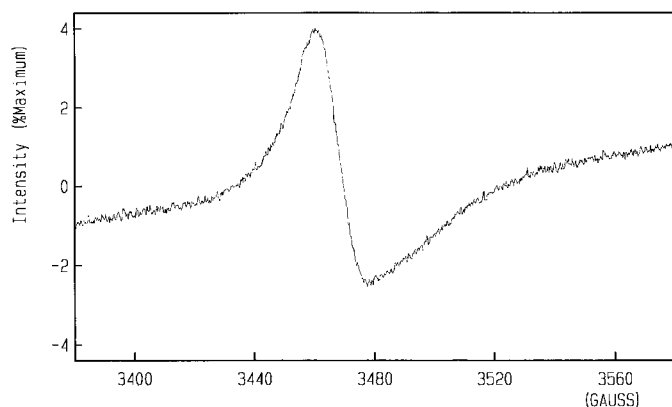
1,2-dichlorobenzene
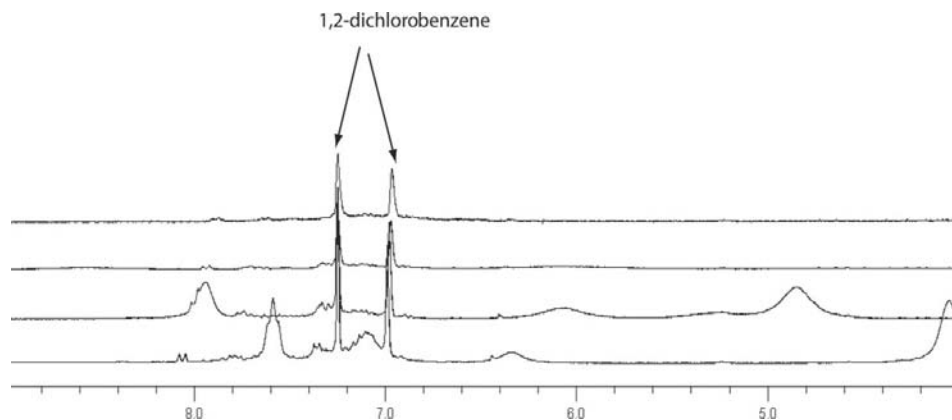
Figure 8
The ^{1}H NMR of the PdL$_2^0$ complex as a function of the temperature. At the bottom the temperature is 300 K and in the top 450 K (steps of 50 K).

complexes with 1-phenyl- and 1,4-diphenyl-substituted *S*-methyli-sothiosemicarbazides as the ligand (Blanchard *et al.*, 2005).

3.2. ^{1}H NMR studies of the complexes

The CuL$_2^0$ complex is strongly paramagnetic and, as was reported earlier (Bechgaard, 1973), it was not possible to record an ^{1}H NMR spectrum, while the other three complexes all give rather broad lines for the nuclei close to the metal ion (Nielsen *et al.*, 2006). These broad lines for the NiL$_2^0$, PdL$_2^0$ and PtL$_2^0$ complexes are particularly striking since Blanchard *et al.* (2005) did not observe broad lines for the nickel complexes with the 1-phenyl- and 1,4-diphenyl-substituted *S*-methyli-sothiosemicarbazides nor did Faraglia *et al.* (2001) for the Pd(ESDT)(PrNH$_2$)Cl complex. We have recorded ^{1}H NMR spectra as a function of the temperature (from 450 to 210 K) for PdL$_2^0$ (which is the complex with the largest line broadening) to investigate whether an equilibrium exists between two conformations. The ^{1}H NMR spectra are seen in Fig. 7 (temperature range 300–210 K), together with the spectrum of *L* at 300 K, and in Fig. 8 (temperature range 440–300 K). The position of the lines for the protons close to Pd move as a function of temperature. The experiment shows a clear coalescence indicative of some kind of equilibrium. However, the lines do not split up into two sets of lines upon cooling in the temperature range studied; neither do they become any sharper at higher temperatures. In CS$_2$ solutions, we have also investigated the

concentration dependence of the chemical shifts and the width of the lines. It was found that both the width and the chemical shifts of the lines were independent of the concentration, which eliminates a possible dimer or oligomer formation. Based on these experiments it is therefore not possible to decide what type of equilibrium is present.

From the fit of the ^{1}H NMR spectra of the PdL$_2^0$ complex the T_2 spin–spin relaxation time constant can be estimated to be shorter than 100 ms, which is much smaller than normal for small diamagnetic compounds. A short T_2 relaxation time constant gives broad lines in the spectrum and is indicative of paramagnetism. An ESR spectrum of the PdL$_2^0$ complex in the solid state at room temperature was recorded (see Fig. 9). Only a very weak signal tentatively assigned to a doublet state was observed, and is probably due to a small impurity in the form of the oxidized complex. This impurity could give rise to broader lines, but it would broaden all the lines equally and not broaden the lines originating from nuclei near the Pd, as was observed. At present, we suggest that the thermal population of low-lying magnetic states is at the origin of the apparent paramagnetic effects.

4. Conclusion

We have presented a detailed structural analysis of the four *M*-N$_2$S$_2$ complexes: NiL$_2^0$, CuL$_2^0$, PdL$_2^0$ and PtL$_2^0$, where the ligand *L* is *N,N*-diethylphenylazothioformamide. All four complexes are the central members in four different five-membered electron-transfer series. We reconfirm the distorted tetrahedral coordination of the NiL$_2^0$ complex at 118 K, which was discovered by Hazell (1976) at 298 K and establish the distorted tetrahedral coordination of the CuL$_2^0$ complex envisaged by Bechgaard (1977). The square-planar coordinations of the PdL$_2^0$ and PtL$_2^0$ complexes envisaged by Forbes *et al.* (1971) are also established. We suggest that there is a high degree of delocalization of the π electron density in the ligand planes. We suggest that the unusually broad lines observed in the ^{1}H NMR spectra of the PdL$_2^0$ compound originate from the thermal population of low-lying magnetic states.

References

Bechgaard, K. (1973). Thesis. University of Copenhagen, Denmark.
Bechgaard, K. (1974). *Acta Chem. Scand. A*, **28**, 185–193.
Bechgaard, K. (1977). *Acta Chem. Scand. A*, **31**, 683–688.
Blanchard, S., Neese, F., Bothe, E., Bill, E., Weyhermüller, T. & Wieghardt, K. (2005). *Inorg. Chem.* **44**, 3636–3656.
Busch, M. & Ridder, H. (1904). *Ber. Dtsch. Chem Ges.* **29**, 843–849.
Davidson, A., Edelstein, N., Holm, R. H. & Maki, A. H. (1963). *J. Am. Chem. Soc.* **85**, 2029–2030.
Eisenberg, R. (1970). *Prog. Inorg. Chem.* **12**, 295–369.
Faraglia, G., Fregona, D., Sitran, S., Giovagnini, L., Marzano, C., Baccichetti, F., Casellato, U. & Graziani, R. (2001). *J. Inorg. Biochem.* **83**, 31–40.
Forbes, C. E., Gold, A. & Holm, R. H. (1971). *Inorg. Chem.* **10**, 2479–2485.

Figure 9
The ESR spectrum of the PdL$_2^0$ complex in the solid state at room temperature.

Garrett, C. E. & Prasad, K. (2004). *Adv. Synth. Catal.* **346**, 889–900.

Hazell, R. G. (1976). *Acta Chem. Scand. A*, **30**, 322–326.

Holm, R. H., Balch, A. L., Davison, A., Maki, A. H. & Berry, T. E. (1967). *J. Am. Chem. Soc.* **89**, 2866–2874.

Jensen, K. A., Bechgaard, K. & Pedersen, C. Th. (1972). *Acta Chem. Scand.* **26**, 2913–2922.

Kokatam, S., Weyhermüller, T., Bothe, E., Chaudhuri, P. & Wieghardt, K. (2005). *Inorg. Chem.* **44**, 3709–3717.

Kosower, E. M. & Miyadera, T. (1972). *J. Med. Chem.* **15**, 307–312.

Nielsen, K., Bechgaard, K. & Krebs, F. C. (2005). *Macromolecules*, **38**, 658–659.

Nielsen, K., Bechgaard, K. & Krebs, F. C. (2006). *Synthesis*, **15**, 1639–1644.

Pluijgers, C. W., Berg, J., Sijpesteijn, A. K., Tempel, A. & Verloop, A (1968). *Rec. Trav Chim. Pays-Bas*, **87**, 833–843.

Pyl, Von Th., Scheel, K. H. & Beyer, H. (1963). *J. Prakt. Chem. 4. Reihe*, **20**, 255–262.

Sasse, K. & Hammann, I. (1971). *Ger. Offen*, DT2145418.

Sonogashira, K., Thoda, Y. & Hagihara, N. (1975). *Tetrahedron Lett.* **50**, 4467–4470.