Formation of a nickel(II) complex with a new N_2S_2 macrocyclic ligand by C–Cl bond cleavage and C–S bond formation

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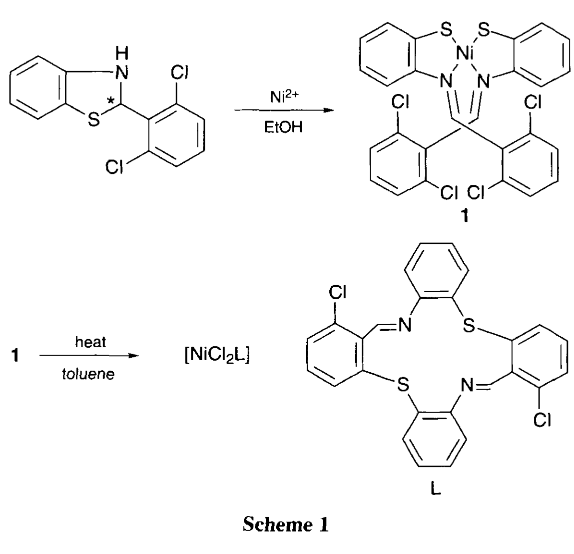
Heating a monohelical square-planar nickel(II) complex containing chlorine atoms in the side arms gives a distorted octahedral nickel(II) complex containing the *trans*-N_2S_2 macrocyclic ligand by carbon–chlorine bond cleavage and carbon–sulfur bond formation.

We have demonstrated recently that orthometallation of the side arm in a monohelical palladium(II) complex affords a sulfur-bridged tetranuclear palladium(II) complex.[1] As part of a project to find new chemical reactions in metal complexes caused by metal–ligand interactions, the monohelical square-planar nickel(II) complex **1**, in which the two *ortho* positions of the side arms are occupied by chlorines, has been prepared (Scheme 1). Here, we report that the activation of an aromatic C–Cl bond in **1** leads to a six-coordinate nickel(II) complex [$NiCl_2L$], with the new macrocyclic ligand L and the cleaved chlorine atoms bound to the metal centre.

Complex **1** was prepared by a well known ring opening reaction of benzothiazoline derivatives,[2] and characterized by IR, NMR and UV–VIS spectroscopies, elemental analysis† and X-ray diffraction methods.‡ The molecular structure of **1** together with the adopted numbering scheme is shown in Fig. 1. The coordination sphere around nickel is approximately square-planar with a dihedral angle between the S–Ni–N planes of 15.3° and the gross structure of **1** shows monohelical geometry. The Ni–S and Ni–N bond distances cover the same range as found for other analogous nickel(II) complexes.[3] The chlorine atoms of the side arms and the nickel centre show short contacts of Ni(1)···Cl(1) 3.000(2) and Ni(1)···Cl(4) 2.945(2) Å. Although these distances can be regarded as nonbonding, they are substantially shorter than the sum of the van der Waals radii (*ca* 3.4 Å).[4]

As shown in Scheme 1, heating of **1** in toluene under reflux afforded [$NiCl_2L$]. Elemental analysis showed that [$NiCl_2L$] had the same chemical composition as **1** and UV–VIS spectroscopic analysis of [$NiCl_2L$] revealed the characteristic octahedral coordination of the nickel complex.§ To elucidate the detailed structure of [$NiCl_2L$], single crystals were obtained from EtOH–diethyl ether and were subjected to X-ray diffraction analysis.¶ A perspective drawing with the adopted numbering scheme is shown in Fig. 2. The nickel atom occupies a distorted octahedral environment, formed by two N and two S atoms of the new macrocyclic ligand and two Cl atoms in *cis* geometry. The observed Ni–S and Ni–N distances correspond closely to those in similar complexes where the *trans*-N_2S_2 macrocyclic ring is folded such that the S donor atoms occupy *trans* positions.[5] In addition, the five-membered chelate bite angles, S(1)–Ni(1)–N(1) [82.3(2)°] and S(2)–Ni(1)–N(2) [84.3(2)°], and the six-membered chelate bite angles, S(1)–Ni(1)–N(2) [87.1(2)°] and S(2)–Ni(1)–N(1) [87.8(2)°], in the macrocyclic ligand are significantly smaller than for the ideal octahedral angle of 90°, while the bond angles around the nickel atom formed by the chlorine atoms (S–Ni–Cl, N–Ni–Cl and Cl–Ni–Cl) are $>90°$. It is presumed that the cavity of the macrocyclic ligand is too small for effective square-planar chelation of the nickel atom.

Reaction of **1** to give [$NiCl_2L$] is an example of the activation of C–Cl bonds and the short contacts for Ni(1)···Cl(1) and Ni(1)···Cl(4) in **1** suggest the possibility of an intramolecular Ni···Cl interaction.[6] The macrocyclic ligand is generated by the cleavage of C–Cl bonds in **1**, which is followed by C–S bond formation. Thus the novel reaction of aromatic C–Cl bonds with the metal centre (Cl^- addition) and the sulfur atom (oxidation) results in the synthesis of the macrocyclic ligand. A similar reaction in bis(*N*-2-iodoethylsalicylaldiminato)nickel(II) has been reported by Kluiber and Sasso.[7] Their complex rearranges from *trans*-N_2O_2 square-planar to *trans*-iodo octahedral with a planar macrocyclic ligand.[8] In contrast, the present complex



Scheme 1

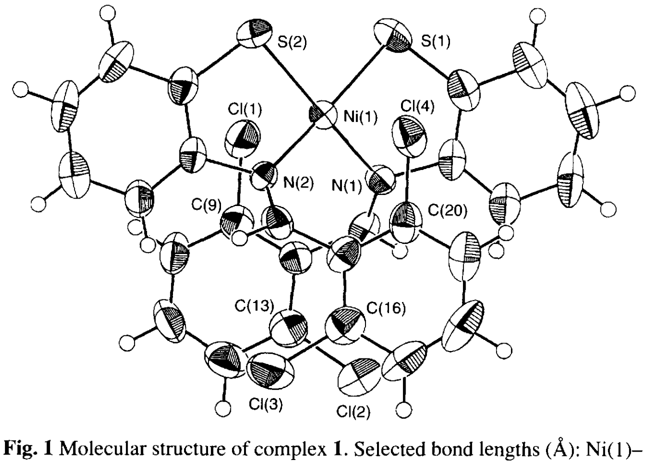


Fig. 1 Molecular structure of complex **1**. Selected bond lengths (Å): Ni(1)–S(1) 2.182(2), Ni(1)–S(2) 2.163(2), Ni(1)–N(1) 1.950(3), Ni(1)–N(2) 1.933(3), Cl(1)–C(9) 1.733(5), Cl(2)–C(13) 1.723(5), Cl(3)–C(16) 1.736(5), Cl(4)–C(20) 1.738(5), Ni(1)···Cl(1) 3.000(2), Ni(1)···Cl(4) 2.945(2). Selected bond angles (°): S(1)–Ni(1)–S(2) 87.3(1), S(1)–Ni(1)–N(1) 87.3(1), S(2)–Ni(1)–N(2) 87.2(1), N(1)–Ni(1)–N(2) 100.1(2), Ni(1)···Cl(1)···C(9) 90.1(2), Ni(1)···Cl(4)···C(20) 94.2(2).

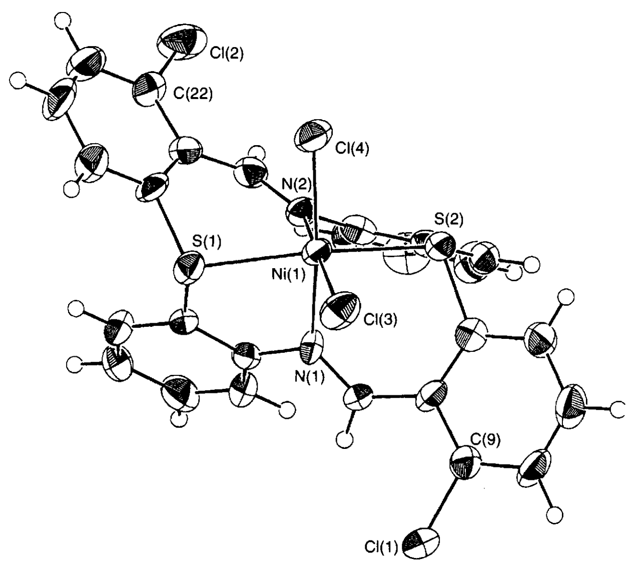


Fig. 2 Molecular structure of [NiCl$_2$L]. Selected bond lengths (Å): Ni(1)–S(1) 2.386(2), Ni(1)–S(2) 2.355(2), Ni(1)–N(1) 2.103(5), Ni(1)–N(2) 2.104(5), Ni(1)–Cl(3) 2.337(2), Ni(1)–Cl(4) 2.335(2), Cl(1)–C(9) 1.732(7), Cl(2)–C(22) 1.715(7). Selected bond angles (°): S(1)–Ni(1)–N(1) 82.3(2), S(1)–Ni(1)–N(2) 87.1(2), S(1)–Ni(1)–Cl(3) 95.1(1), S(1)–Ni(1)–Cl(4) 94.4(1), S(2)–Ni(1)–N(1) 87.8(2), S(2)–Ni(1)–N(2) 84.3(2), S(2)–Ni(1)–Cl(3) 92.2(1), S(2)–Ni(1)–Cl(4) 94.3(1), N(1)–Ni(1)–N(2) 79.6(2), N(1)–Ni(1)–Cl(3) 92.4(2), Cl(3)–Ni(1)–Cl(4) 97.3(1).

rearranges from *cis*-N$_2$S$_2$ square-planar to *cis*-chloro octahedral with the folded macrocyclic ligand.

Footnotes

† Complex **1**: 2-Aminothiophenol (0.29 g, 2.3 mmol) was added to an ethanol solution (20 ml) containing 2,6-dichlorobenzaldehyde (0.40 g, 2.3 mmol). The mixture was heated at reflux for 30 min and then nickel(II) acetate tetrahydrate (0.28 g, 1.1 mmol) was added. (The benzothiazoline derivative was not isolated.) The mixture was heated at reflux for 20 min and then cooled to room temp. The dark red–brown precipitate was isolated by filtration and dried *in vacuo*. Yield: 79%. Single crystals suitable for X-ray crystal structure analysis were obtained by diethyl ether diffusion of a chloroform solution. IR: ν(C=N) 1593 cm^{-1}, ν(arom. C=C) 1569 cm^{-1}. Anal. Calc. for C$_{26}$H$_{16}$Cl$_4$N$_2$NiS$_2$: C, 50.28; H, 2.60; N, 4.51. Found: C, 50.17; H, 2.82: N, 4.70%. NMR (CDCl$_3$, 23 °C): ^{1}H (270 MHz) δ 8.05 (s, 2 H), 7.44–7.23 (AB$_2$ system, 6 H), 7.30 (dd, 2 H), 7.03 (dt, 2 H), 6.69 (dt, 2 H), 6.33 (dd, 2 H); ^{13}C (67.8 MHz), δ 163.29, 153.19, 147.27, 134.80, 131.89, 130.09, 129.67, 129.10, 128.70, 121.38, 117.46. UV-VIS: ν_{max}(CHCl$_3$)/10^3 cm^{-1} [log(ε/dm^3 mol^{-1} cm^{-1})]: 15.0(sh) (2.67), 19.0(sh) (3.32), 21.6 (3.51).

‡ *Crystal data* for complex **1**, C$_{26}$H$_{16}$Cl$_4$N$_2$NiS$_2$, M = 621.04, monoclinic, space group *Cc*, a = 11.204(3), b = 16.584(3), c = 14.051(8) Å, β = 99.30(3)°, U = 2577(2) Å^3, Z = 4, D_c = 1.60 g cm^{-3}, μ(Mo-Kα) = 1.35 mm^{-1}. A total of 1750 reflections (3 < 2θ < 40°) were measured on a Mac Science MXC3 diffractometer using graphite-monochromated Mo-Kα radiation; 1459 with $F > 3\sigma(F)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least squares. The refinement converged at R = 0.027, R_w = 0.028.

§ Complex [NiCl$_2$L]: a suspension of **1** (0.104 g, 0.17 mmol) in toluene (30 ml) was heated at reflux for 1 h and then cooled to room temp. The resulting red–brown precipitate (0.072 g) was filtered off and dried *in vacuo*. The precipitate was recrystallised from methanol–diethyl ether yielding dark red crystals. Yield 12%. Single crystals suitable for X-ray crystal structure analysis were obtained by diethyl ether diffusion of an ethanol solution. **CAUTION**: We felt some pain in our skin after the treatment of this complex. IR: ν(C=N) 1598 cm^{-1}, ν(arom. C=C) 1564 cm^{-1}. Anal. Calc. for C$_{26}$H$_{16}$Cl$_4$N$_2$NiS$_2$: C, 50.28; H, 2.60; N, 4.51. Found: C, 50.45; H, 3.05; N, 4.45% UV-VIS ν_{max}(CHCl$_3$)/10^3 cm^{-1} [log(ε/dm^3 mol^{-1} cm^{-1})]: 10.8 (1.95), 21.8 (3.10), 30.7 (4.38).

¶ *Crystal data* for [NiCl$_2$L], C$_{26}$H$_{16}$Cl$_4$N$_2$NiS$_2$, M = 621.04, orthorhombic, space group $Pna2_1$, a = 20.369(11), b = 8.697(3), c = 14.161(15) Å, U = 2508(3) Å^3, Z = 4, D_c = 1.65 g cm^{-3}, μ(Mo-Kα) = 1.39 mm^{-1}. A total of 5103 reflections (3 < 2θ < 50°) were measured on a Mac Science MXC3 diffractometer using graphite-monochromated Mo-Kα radiation; 1766 with $F > 3\sigma(F)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least squares. The refinement converged at R = 0.036, R_w = 0.036. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/182.

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