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Carbon-Carbon Bond Formation in Helical Nickel(II) Complex, *cis*-Bis[2-N-(phenylmethylideneamine)benzenethiolato]nickel(II)

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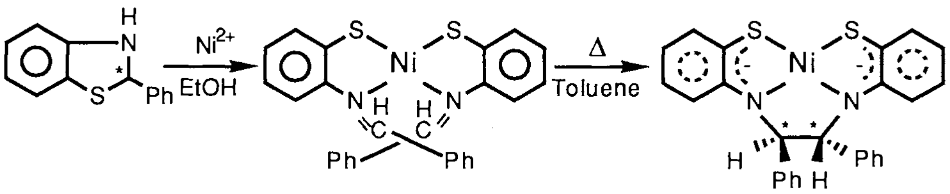
The reaction of 2-phenylbenzothiazoline with nickel(II) acetate tetrahydrate leads to *cis*-bis[2-N-(phenylmethylideneamine)benzenethiolato]nickel(II) (**1**) and two ligands in **1** are joined through a C-C bond to form a complex having two chiral centers (**2**). The X-ray structural analysis of **2** establishes the bond patterns of the delocalized ligand.

Helical structures are ubiquitous in nature and molecular helicity is well-known in double-helical compounds.1) Although monohelical inorganic compounds are rare,2) we have recently described the preparation and structural characterization of a trinuclear complex showing monohelical chirality.3) In an attempt to quantify the formation of helical complexes, we have found that the heating of nickel(II) complex with the monohelical chirality leads to the formation of a C-C bond between two ligands.

An ethanol solution of 2-phenylbenzothiazoline reacting with nickel acetate tetrahydrate under reflux for 10 min afforded deep brown crystals of **1**.4) X-Ray quality crystals were obtained from chloroform and methanol mixed solution. Complex **2** was formed by heating of **1** at reflux in toluene for 1 h, giving a black solution, and was purified by the use of a Silica Gel column (Scheme 1).5) Slow recrystallization from chloroform and methanol mixed solution is necessary to obtain X-ray quality crystals.



1 **2**

Scheme 1.

The structure of **1** with crystallographically imposed C_2 symmetry is a distorted square planar, since the dihedral angle between the NiNS planes is 23.4(2)°.6) The Ni-S and

Ni-N distances (2.180(1) and 1.926(2) Å) fall in the range found for NiN_2S_2-type thiolate complexes.[7,8] The imino bond distances (1.288(4) Å) also fall in the usual range.[8,9] The most significant information in this molecular structure is that this complex shows an unusual helical chirality (Fig. 1).

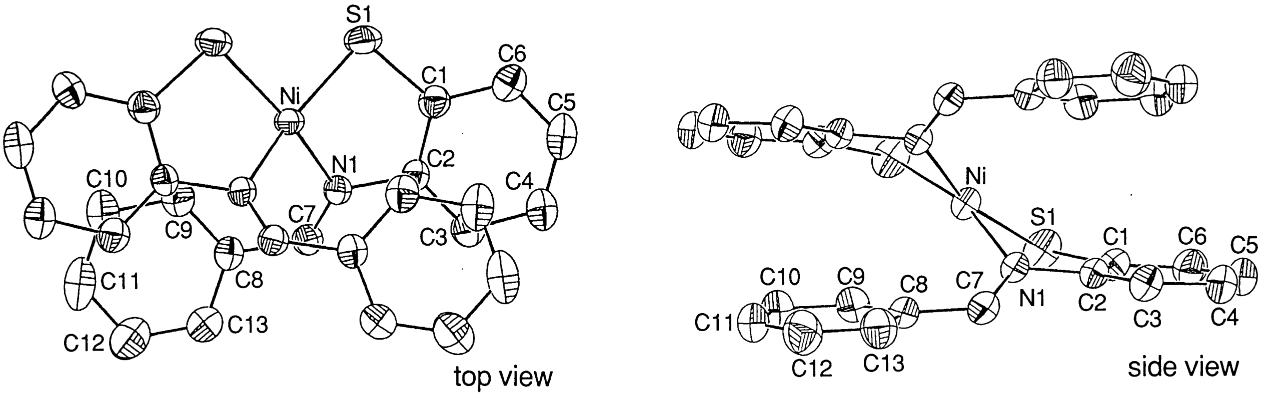


Fig. 1. Molecular structure of complex **1**. Selected bond and short contact distances (Å) and angles (°): Ni-S1, 2.180(1); Ni-N1, 1.926(2); S1-C1, 1.755(3); N1-C2, 1.436(3); N1-C7, 1.288(4); C7-C8, 1.455(4); C2···C9*, 3.140(5); C7···C7*, 3.852(4); S1-Ni-N1, 85.9(1); S1-Ni-S1*, 94.5(1); N1-Ni-N1*, 98.2(1).

Complex **2**, which has the same chemical formula for **1**, is isolated as black crystalline solids. In **2**, two ligands in **1** are linked by a C-C bond (C7-C14) between the imino carbon atoms (Fig. 2).[10] This result shows that the proximity of the helical array's extremities allows electrons to move easily and cyclically through the array. In addition, it is also apparent that the helical geometry of **1** results in stacking interactions between Ph-C7=N1 moieties. A similar C-C bond formation has been described by C. Floriani et al.[11] However, their nickel(II)-alkali ion complexes are generated by the reductive dimerization using alkali metals, and both reactions are virtually distinct from each other. Although the hydrogen atoms on C7 and C14 are difficult to find from the difference map only, bond distances and angles around C7 and C14 clearly indicate an sp^3 hybridization for these atoms, which are chiral. As a consequence, chiral elements change from helical chirality P (or M) in **1** to two chiral centers R, R (or S, S) in **2**.

The structure of **2** is an approximate square planar, since the dihedral angle between the NiNS planes is 7.2(2)°. The Ni-N (1.830(5) and 1.826(4) Å) distances in **2** seem consistent with those in $[Ni(C_6H_4(NH)_2)_2]$ (av. 1.832(11) Å).[12] The N1-C2 and N2-C22 (1.352(7) and 1.351(7) Å) distances, which are shorter than the bond distances (av. 1.38(2) Å) found in $[Ni(C_6H_4(NH)_2)_2]$, demonstrate considarable double bond character in the two N-C(sp^2) bonds. The Ni-S (2.126(2) and 2.129(2) Å) and S-C (1.728(7) and 1.729(6) Å) distances are longer than the values (av. 2.101(2) Å for Ni-S and av. 1.71(1) Å for S-C) found in $[Ni(S_2C_2(C_6H_5)_2)_2]$.13) However, the difference of these bond lengths may be attributed to the difference between a benzene moiety in **2** and an ethylene one in $[Ni(S_2C_2(C_6H_5)_2)_2]$ and/or the difference between N_2S_2 and S_4 coordination. The complex **2** shows a redox property ($E_{1/2}$(V) = -0.96(-2/-1), -0.10(-1/0), 1.19(0/+1)) analogous to $[Ni(abt)_2]$, abt = amidobenzenethiolate, ($E_{1/2}$(V) = -0.93(-2/-1), -0.03(-1/0), 1.05(0/+1)).14,15) The result clearly indicates that **2** is quite similar to $[Ni(abt)_2]$ with highly delocalized ligands.14,16) To the best of our knowledge X-ray analysis of **2** gives the first structural characterization of nickel complex with N_2S_2 chelate, which is dithiolene-like.

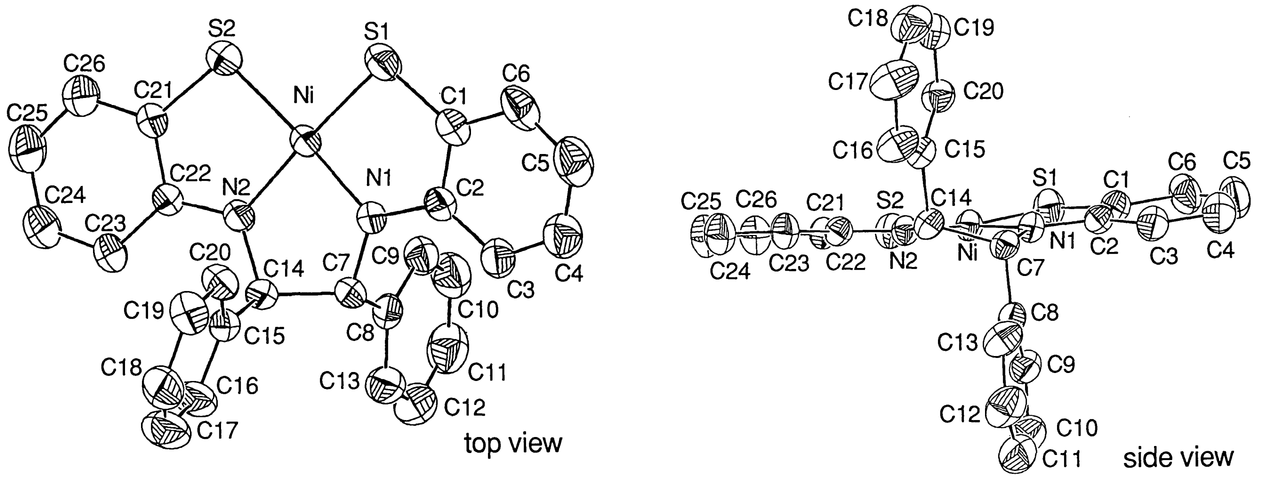


Fig. 2. Molecular structure of complex **2**. Selected bond distances (Å) and angles (°): Ni-S1, 2.126(2); Ni-S2, 2.129(2); Ni-N1, 1.830(5); Ni-N2, 1.826(4); S1-C1, 1.728(7); S2-C21, 1.729(6); N1-C2, 1.352(7); N2-C22, 1.351(7); N1-C7, 1.464(7); N2-C14, 1.464(8); C7-C14, 1.561(8); C7-C8, 1.513(9); C14-C15, 1.520(9); C1-C2, 1.421(8); C2-C3, 1.414(9); C3-C4, 1.372(9); C4-C5, 1.399(10); C5-C6, 1.356(12); C1-C6, 1.420(9); C21-C22, 1.427(9); C22-C23, 1.421(8); C23-C24, 1.371(10); C24-C25, 1.415(11); C25-C26, 1.366(9); C21-C26, 1.412(9); S1-Ni-N1, 89.5(2); S2-Ni-N2, 89.8(2); S1-Ni-S2, 95.4(1); N1-Ni-N2, 85.7(2).

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4) The complex **1** gave a satisfactory elemental analysis. Found: C, 64.98; H, 4.34; N, 5.89%. Calcd for complex **1**, $C_{26}H_{20}N_2S_2Ni$: C, 64.61; H, 4.17; N, 5.80%. Visible-UV spectrum, $CHCl_3$ solvent [ν_{max}, 10^3 cm^{-1} (log ε; ε in mol^{-1} dm^3 cm^{-1})]: 11.90 (1.69), 21.84 (3.49). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.78 (d, J = 7 Hz, 4H), δ 7.78 (s, 2H), δ 7.41 (t, J = 7 Hz, 2H), δ 7.40 (d, J = 8 Hz, 2H), δ 7.23 (t, J = 8 Hz, 4H), δ 7.02 (t, J = 8 Hz, 2H), δ 6.67 (t, J = 8 Hz, 2H), δ 6.21 (d, J = 8 Hz, 2H); ^{13}C NMR, δ 166.38, 150.01, 146.58, 134.56, 131.33, 129.58, 128.81, 128.75, 121.19, 116.71.

5) The complex **2** gave a satisfactory elemental analysis. Found: C, 64.60; H, 4.21; N, 5.52%. Calcd for complex **2**, $C_{26}H_{20}N_2S_2Ni$: C, 64.61; H, 4.17; N, 5.80%. Visible-UV spectrum, $CHCl_3$ solvent [ν_{max}, 10^3 cm^{-1} (log ε; ε in mol^{-1} dm^3 cm^{-1})]: 8.75 (3.43), 10.13 (3.36), 11.98 (4.56), 17.07 (3.15), 18.54 (3.14), 21.16 (3.09), 30.96 (3.77). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.71 (qd, J = 8 and 1 Hz, 2H), δ 7.34 - 7.22 (m, 12H), δ 7.14 (dt, J = 6 and 1 Hz, 2H), δ 7.02 - 6.99 (m, 2H), δ 6.34 (s, 2H); ^{13}C NMR, δ 211.50, 162.03, 160.36, 143.39, 131.54, 129.00, 127.99, 127.80, 126.71, 122.86, 119.82, 83.24.

6) Crystal data for [$C_{26}H_{20}N_2NiS_2$], M = 483.27, Monoclinic, $C2/c$, a = 23.065(4), b = 6.924(2), c = 13.809(2) Å, β = 102.64(1)°, V = 2152.0(9) $Å^3$, Z = 4, Dc = 1.49 g cm^{-3}, Dm = 1.48 g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 11.1 cm^{-1}, R = 0.052, Rw = 0.050 for 2242 reflections ($|Fo| > 3\sigma(|Fo|)$).

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10) Crystal data for [$C_{26}H_{20}N_2NiS_2$], M = 483.27, Monoclinic, $P2_1/n$, a = 8.631(10), b = 24.365(19), c = 10.798(4) Å, β = 102.69(6)°, V = 2215.2(33) $Å^3$, Z = 4, Dc = 1.45 g cm^{-3}, Dm = 1.44 g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 11.1 cm^{-1}, R = 0.078, Rw = 0.075 for 3465 reflections ($|Fo| > 3\sigma(|Fo|)$).

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15) Cyclic voltammetry was performed in a three-electrode cell with a glassy carbon disk as working electrode, platinum wire as counter electrode, and a Ag/AgCl reference electrode and was measured in CH_2Cl_2 containing 0.1 M tetra-n-butylammonium tetrafluoroborate. The scan rate is 200 mV/s. $E_{1/2}$ (quasi-reversible) is the average of the anodic and cathodic peak potentials vs Ag/AgCl.

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