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Synthesis and Characterization of Trinuclear Metal Complex Showing Helical Chirality

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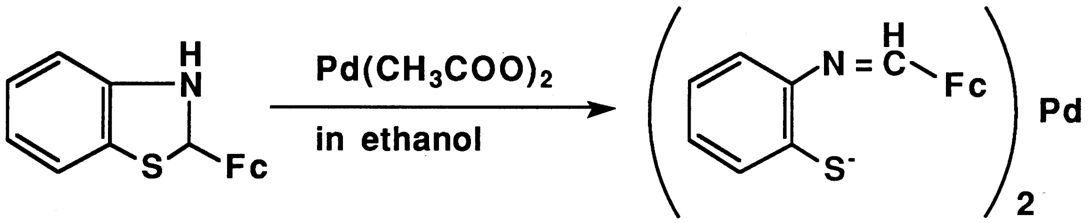
The reaction of 2-(ferrocenyl)benzothiazoline and palladium(II) acetate forms a trinuclear complex which reveals a monohelical arrangement. The X-ray crystal structure of such monohelical metal complex is reported, together with ^{1}H NMR investigations and the electrochemical properties.

Helicity is a widespread phenomenon in natural systems and are essential to life itself. To date, chemists have described the preparation and characterization of several multicomponent helical and double-helical compounds and pointed out an importance of ligand-ligand interactions for helical structures.1) However, monohelical compound, which is the most simple and basic in molecular helicity, is extremely rare in inorganic compounds.2) Here we wish to report the first example of spontaneously resolved square-planar monohelical complex.

The synthesis started from 2-(ferrocenyl)benzothiazoline, febz, which was obtained from ferrocencarboxaldehyde and 2-aminothiophenol.3) Deep red powder of *cis*-bis[2-N-(ferrocenylmethylideneamine)benzenethiolato]palladium(II), [Pd(fabt)$_2$], was prepared by heating at 70 °C for 30 min febz of 0.72 g (2.24 mmol) with palladium(II) acetate of 0.25 g (1.11 mmol) in dry ethanol of 15 ml under argon (Eq. 1).4) Deep red crystals of [Pd(fabt)$_2$] suitable for X-ray diffraction studies were obtained from 1:1 mixed solution of chloroform and methanol.



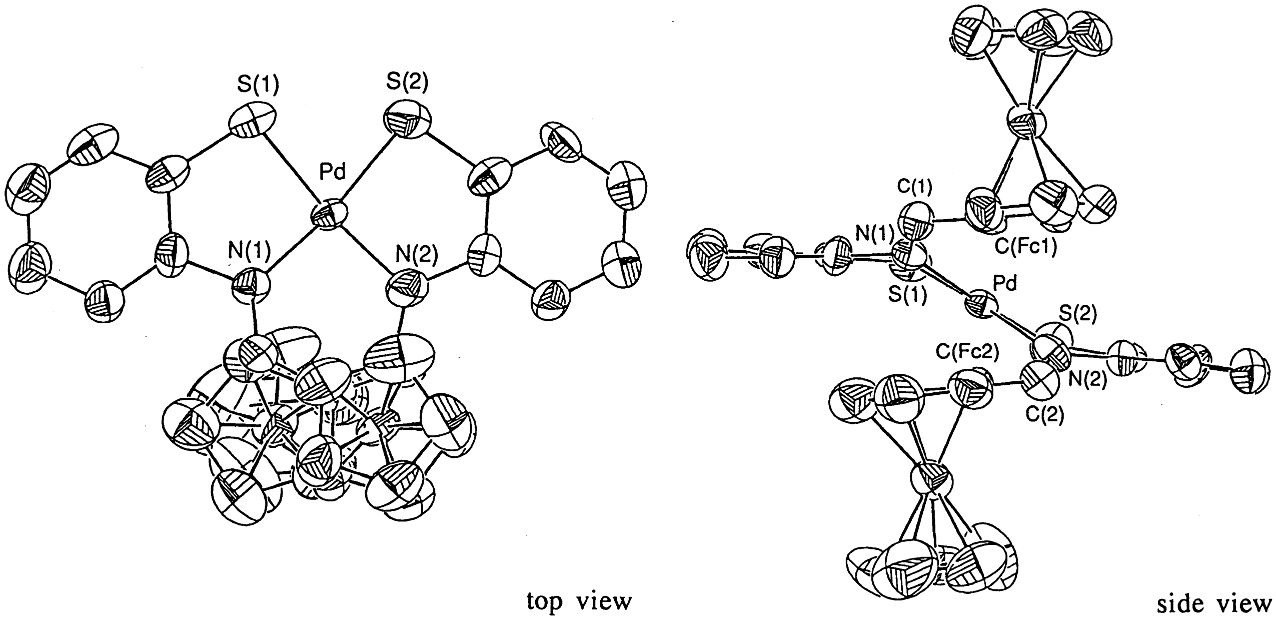
(1)

febz

[Pd(fabt)$_2$]

Fc = ferrocenyl group

The molecular structure of the $[Pd(fabt)_2]$ is shown in Fig. 1.5) $[Pd(fabt)_2]$ forms a slightly distorted square-planar *cis*-type coordination by 2S and 2N atoms. The Pd-S 2.258(4), 2.264(4) and the Pd-N 2.059(10), 2.085(11) Å are in normal range.6) The chelate angles S-Pd-N are 83.5(3) and 84.2(3)°. The S-Pd-S and N-Pd-N angles are 86.8(2) and 105.7(4)° respectively. The dihedral angle between two Pd, S, N planes is only 5.2°. In each fabt ligand, a cyclopentadienyl ring, a C=N double bond, and a benzenethiolato moiety lie on the nearly same plane,7) and a conjugated link is formed. Further, the dihedral angle between two cyclopentadienyl planes, jointed to C(1) and C(2) respectively, is 8.0°. Thus two ferrocene moieties are in nearly parallel. The most remarkable feature of the molecular structure is that this complex shows a helical chirality which is a consequence of ligand-ligand interactions causing a conformation of the ligands similar to that of the helicenes.8) Furthermore, the space group, $P2_12_12_1$ and $Z = 4$, indicates that the crystals are spontaneously resolved.



top view side view

Fig. 1. ORTEP drawings of molecule $[Pd(fabt)_2]$. Selected interatomic distances (Å) and angles (°); Pd-S(1) 2.258(4), Pd-S(2) 2.264(4), Pd-N(1) 2.059(10), Pd-N(2) 2.085(11), C(1)-C(2) 3.86(2), C(1)-C(Fc2) 3.43(2), C(2)-C(Fc1) 3.35(2), C(Fc1)-C(Fc2) 3.22(2), S(1)-Pd-S(2) 86.8(2), S(1)-Pd-N(1) 83.5(3), S(2)-Pd-N(2) 84.2(3), N(1)-Pd-N(2) 105.7(4).

Addition of *Pirkle*'s reagent to $[Pd(fabt)_2]$ leads to a drastic change in its ^1H NMR spectrum (Fig. 2): surprisingly large splitting of peaks are observed in the ferrocenyl region (δ = 4.0 - 5.7 ppm).9) This indicates no racemization of the compound in solution on the NMR time scale.

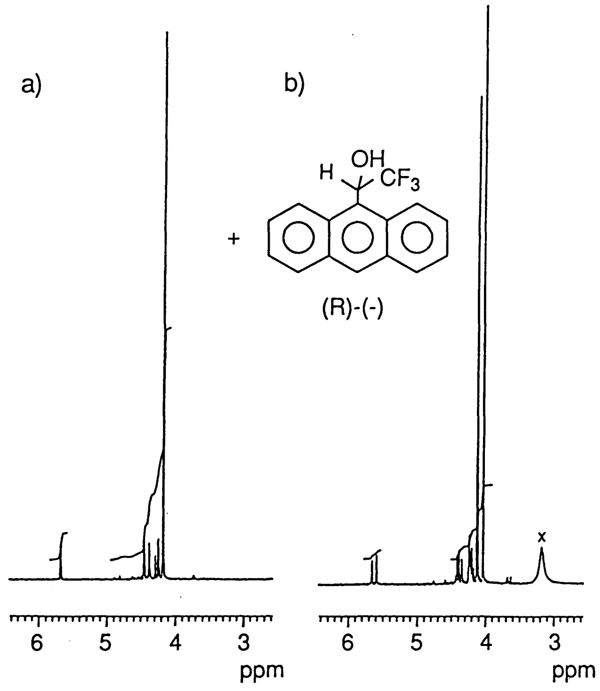


Fig. 2. The ^{1}H NMR spectra (400 MHz, $CDCl_3$) for cyclopentadienyl rings of a) $[Pd(fabt)_2]$ and b) $[Pd(fabt)_2]$ in the present of *Pirkle*'s reagent.

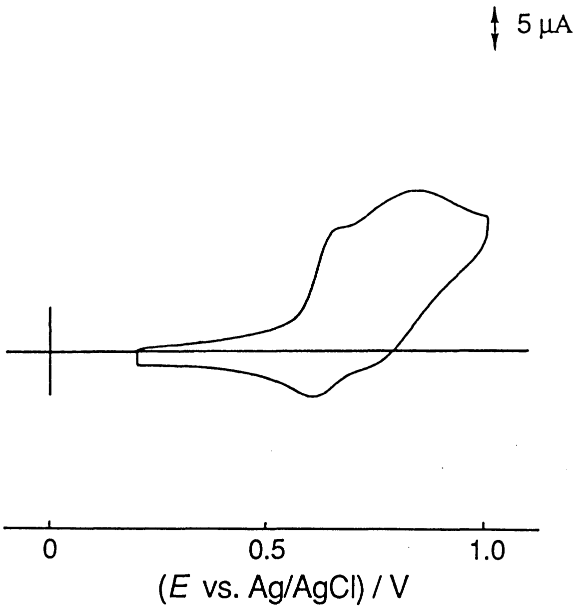


Fig. 3. Cyclic voltammogram of $[Pd(fabt)_2]$ at a GC electrode for scan rate 200 mV/s in acetonitrile solution (0.5 mM).

$[Pd(fabt)_2]$ contains two ferrocene units as a redox active center and the redox properties have been investigated by cyclic voltammogram technique.[10] This complex exhibits two oxidations (Ea = 0.65 and 0.84 V) attributable to a $Fe^{III/II}$ couple as shown in Fig. 3 while the ^{1}H NMR spectrum and ^{13}C NMR spectrum indicate the complex with C_2 symmetry.[9] This observation indicates that there is significant interaction between the two ferrocene units. We consider that this interaction plays a crucial role on the stability of monohelical geometry.

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4) The complex gave a satisfactory elemental analysis. Found: C, 54.25; H, 3.87; N, 3.74%. Calcd for $[Pd(fabt)_2]$: C, 54.68; H, 3.78; N, 3.75%.

5) Crystal data for $C_{34}H_{28}N_2PdS_2$: Orthorhombic, $P2_12_12_1$, a = 20.575(9) Å, b = 12.349(3) Å, c = 11.754(3) Å, V = 2986 Å^3, Z = 4, Dc = 1.66 g cm^{-3}, Dm = 1.6 g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 17.09 cm^{-1}, R = 0.064, Rw = 0.053 for 2349 reflections ($|Fo| > 3\sigma(|Fo|)$).

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7) Two benzene rings and four cyclopentadienyl rings are approximately parallel with interplanar angles in the range 0.3 - 13.9°.

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9) W. H. Pirkle and M. S. Hoekstra, *J. Am. Chem. Soc.*, **98**, 1832 (1976). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75(s, 2H), δ 7.40(d, 2H), δ 7.01(t, 2H), δ 6.82(t, 2H), δ 6.81(d, 2H), δ 5.67(m, 2H), δ 4.44(m, 2H), δ 4.37(m, 2H), δ 4.24(m, 2H), δ 4.17(s, 10H). The ^{1}H NMR spectrum shows four resonances (δ = 5.67, 4.44, 4.37, and 4.24) for monosubstituted cyclopentadienyl rings. Since monosubstituted cyclopentadienyl rings normally provide just two proton resonances, the observation of four such signals suggests that the ferrocenyl groups cannot rotate about C(1)-C(Fc1) or C(2)-C(Fc2) bond. ^{13}C NMR ($CDCl_3$, 400 MHz): (ppm) 162.68, 151.32, 146.18, 129.45, 127.84, 122.04, 117.58, 78.35, 73.49, 72.32, 71.48, 69.81, 69.10. The ^{13}C NMR spectrum indicates 13 magnetically distinct carbon resonances, strongly suggesting that the monohelical geometry results in C_2 symmetry about metal ion.

10) 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 acetonitrile containing 0.1 M tetra-n-butylammonium tetrafluoroborate.

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