

A Novel Biferrocene Trinuclear Complex with *Cis*-Configuration

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Abstract: A novel biferrocene trinuclear complex for Schiff base ligand *S*-methyl-*N*-(ferrocenyl-1-methyl -methylidene) dithiocarbazate (hereafter abbreviated as HL) is described. X-ray diffraction studies established the structure of the palladium complex, PdL₂. The geometry of Pd (II) in the complex is close to square planar and in novel *cis*-configuration with two ferrocene moieties on the same side. Degenerate four-wave mixing (DFWM) measurements show that the complex exhibit obvious nonlinear optical response.

Keywords: Palladium complex, *cis*-configuration biferrocene, third-order nonlinear optical property.

Recently, organometallic materials have been attracting a great deal of attention in the field of nonlinear optics^{1,2}. Sandwich-type compounds, like ferrocene, are examples of organometallic systems of potential interest because they contain aromatic cyclopentadienyl rings interacting with a metal atom through their π -electron systems³. Intuitively, such an interaction might lead to marked distortion of the π -electron system and thus influence optical nonlinearity of a metallocene molecule. Therefore, it seemed worthwhile to perform a systematic study of the feasibility of using a ferrocene moiety as a unit in π -conjugated structures of optimized third-order nonlinear properties. In this letter, we report a novel biferrocene trinuclear complex (PdL₂) with *cis*-configuration, which exhibits obvious third-order nonlinear optical response.

Preparation

Five drops of acetic acid were added to a mixture of *S*-methyl-dithiocarbazate (1.22 g, 10 mmol) and acetylferrocene (2.28 g, 10 mmol) in refluxing ethanol (50 cm³). The solution was further refluxed for 2h and on cooling a red-brown solid was formed. The solid was collected by filtration and washed with ethanol and dried *in vacuo*. Yield 0.28 g (85%) for the free ligand (HL). Ethanol solutions (25 cm³) of the ligand (0.66 g, 2 mmol), and PdCl₂(CH₃CN)₂ (0.26 g, 1 mmol) were mixed. The brown crystalline solid

Figure 1. The atomic numbering of the biferrrocene palladium complex. Pd (1) -S (1) 2.257 (1), S (1) -C (1) 1.738 (4), Pd (1) -N (1) 2.110 (3), S (2) -C (1) 1.747 (4), N (1) -N (2) 1.420 (4), N (1) -C (2) 1.295 (4) Å, S (1) -Pd (1) -N (1) 82.8 (1), S (1) -Pd (1) -S (1a) 89.0 (1), N (1) -Pd (1) -S (1a) 169.3 (1), N (1) -Pd (1) -N (1a) 106.1 (1) °

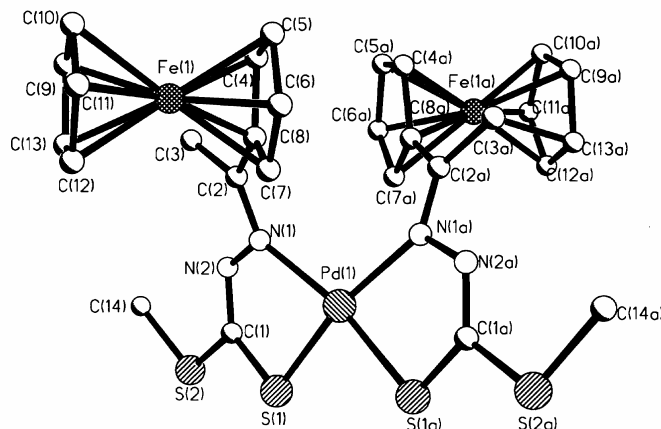
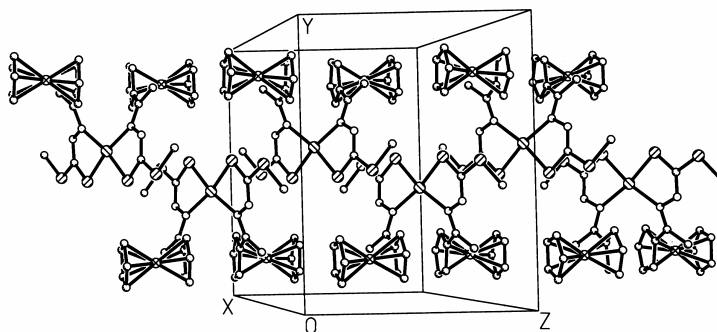


Figure 2. Packing of the title complex in a unit cell



formed after refluxing for 4h was collected by filtration, washed with ethanol and dried *in vacuo*. Yield 0.56 g (73%) of the palladium complex. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of a dichloromethane solution containing isopropanol.

Crystal Structure Determination

The intensities of the biferrrocene palladium complex were collected at 294K on a Rigaku RAXIS-IIC imaging plate diffractometer using Mo-K α ($\lambda = 0.71073 \text{ \AA}$) from a rotating-

anode generator operating at 50KV and 90mA ($2\theta_{\max} = 55^\circ$). The structure of the palladium complex was solved by direct method. The crystal structure belongs to monoclinic, space group C2/c with cell dimensions, $a=18.859$ (1), $b=14.400$ (1), $c=11.203$ (1) Å, $\beta=105.97^\circ$, $V=2925\text{Å}^3$, $Z=4$. All non-hydrogen atoms were refined anisotropically by full-matrix least squares to final $R=0.0391$, $R_w=0.051$ ($w^{-1}=\sigma^2(F)$) for 2862 reflections with $F_o > 4.0\sigma(F)$. All calculations were carried out on a PC-586 computer using the SHELXL-PC program package. The maximum shift was 0.03 and $S=1.80$. In the final difference map, the residuals are 0.58 and -1.18eÅ^{-3} , respectively.

Results and Discussion

The crystal structure and stereogram of the complex packing in a crystal unit cell are shown in **Figure 1** and **Figure 2**, respectively. The Pd (II) atom is coordinated in slightly distorted square-planar configuration with two equivalent Pd-N bonds (2.110 (3) Å) and Pd-S bonds (2.257 (1) Å). The dihedral angle between the two coordination planes is 4.0° . The ligand, as expected, lost a proton from the tautomeric thiol form and as a single negatively charged bidentate ligand coordinating to the palladium ion *via* the mercapto sulphur and β -nitrogen atoms, forming delocalized plane⁴. The complex has a quite surprising *cis*-configuration (N (1) -Pd (1) -N (1a), 106.1 (1), S (1) -Pd (1) -S (1a), 89.0 (1)°, symmetry code: a: -x, y, 0.5-z) with two ferrocene moieties on the same side. The structure is very rare, to our knowledge, this might be the first example for the negatively charged bidentate thiocarbazates coordinated in *cis*-configuration. It was suggested that, the *cis*-configuration was stabilized by the interactions between the two substituted cyclopentadienyl planes associated with different ion atoms. Least-square planarity analysis shows that, the two acetylcyclopentadienyl planes are almost planar (dihedral angle of 2.9°). The bond distances in the side chain are intermediate between formal single and double bonds, pointing to electron delocalization over the entire moiety. However, the obviously double characters of the four C-N bonds might suggest that the electron delocalization might be weakened by the twist structure of the ligands caused by the *cis*-positioning of the ferrocene moieties. The long Fe-Fe separation suggests that the interaction between the two ferrocene moieties might be quite weak, and must be through the bridge, if there exists interaction.

Third-order nonlinear optical susceptibility ($\chi^{(3)}$) for the complex was determined in DMF solution using the DFWM technique. The results showed that the biferrocene trinuclear complex exhibits obvious third-order nonlinear optical (NLO) response, the third-order nonlinear optical susceptibility is about 4.5×10^{-12} esu (CS₂ as a reference sample). We considered that NLO response of the complex came from the conjugated plane and donor electron of the ferrocene moiety of the system.

Acknowledgments

This work is supported by the National Natural Science Foundation of China, Natural Science Foundation of Anhui Province and Open Foundation of State Key Laboratory of Coordination Chemistry, Nanjing University.

References

1. J. Long, *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 21.
2. J. H. Si, Q. G. Yang, Y. G. Wang, *Opt. Commun.*, **1996**, *132*, 311.
3. J. L. Bredas, C. Adant, Tackx and A. Persoons, *Chem. Rev.*, **1994**, *94*, 243.
4. Y. P. Tian, C. Y. Duan, X. Z. You, *Transition Met. Chem.*, **1998**, *23*, 17.

Received 6 October 1998