A Novel Trinuclear Platinum(II) Complex with *C, N, S* Donor Ligands Containing Ferrocenyl Groups

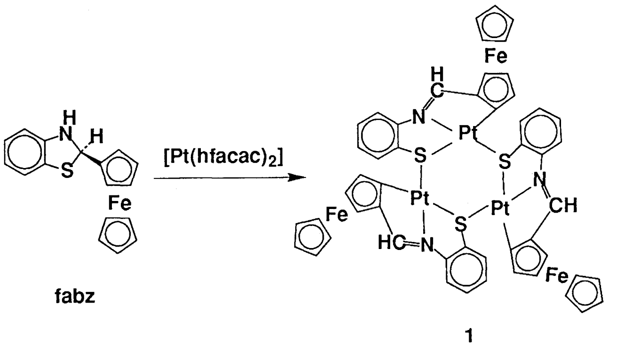
Isoroku Nagasawa, Tatsuya Kawamoto,* Hiro Kuma, and Yoshihiko Kushi*
Department of Chemistry, Graduate School of Science, Osaka University, 1-16 Machikaneyama, Toyonaka, Osaka 560

(Received July 2, 1996)

The reaction of [Pt(hfacac)$_2$] with 2-(ferrocenyl)-benzothiazoline affords a novel trinuclear platinum(II) complex, which has six-membered Pt$_3$S$_3$ ring with thiolate bridging, and three cyclometallated ferrocenyl groups have a less-symmetrical configuration.

Several metal ions induce rearrangement of benzothiazoline derivatives to yield the corresponding Schiff-base metal complexes with N,S chelates.[1] Indeed, the reactions of M^{2+} (M = Ni, Pd, Zn, and Hg) with 2-(ferrocenyl)benzothiazoline gave the Schiff-base metal complexes. Especially, Ni(II) and Pd(II) complexes showed the molecular helicity with *cis*-geometry of square planar configuration.[2] Furthermore, the reaction of M^{2+} (M = Pd and Pt) with 2-(1-naphthyl)benzothiazoline afforded the tetranuclear complexes with *C,N,S* donor atoms.[3] We present here a novel trinuclear platinum(II) complex **1** with *C,N,S* donor atoms which is obtained by cyclometallation of the ferrocenyl groups in 2-(ferrocenylmethyleneamino)benzenthiol.

To a solution of 2-(ferrocenyl)benzothiazoline (0.053 g, 0.16 mmol) in toluene (10 ml) was added an equimolar amount of [Pt(hfacac)$_2$] (0.100 g, 0.16 mmol)[4] and the solution was stirred at reflux for 5 h. The solvent was removed from the reaction mixture by using a rotary evaporator. The remaining black solid was washed with ether. The solid was dissolved in a minimum amount of dichloromethane and then purified on a silica gel column with dichloromethane as the eluent. The eluted main green band was collected and evaporated to dryness. The resulting dark green powder of **1** was recrystallized from dichloromethane-acetonitrile solution: Yield 11.8%. The suitable crystals for X-ray analysis were obtained from chloroform-methanol solution.



The molecular structure with a partial atoms labeling scheme of **1**, revealed by the X-ray analysis, is shown in Figure 1.[5] The coordination geometry around each of platinum atoms is square planar with *C,N,S$_2$* donor atoms and two sulfur atoms are located in *cis*- position. The platinum atoms are bridged by sulfur atoms. The bond distances between platinum atoms and the coordinated ones are normal.[6] It is interesting to note that the Pt-terminal S distances (av. 2.35 Å) are longer than the Pt-bridging S ones (av. 2.28 Å). This result indicates the strong *trans* influence of the coordinated carbon atoms of the cyclometallated ligands.[7]

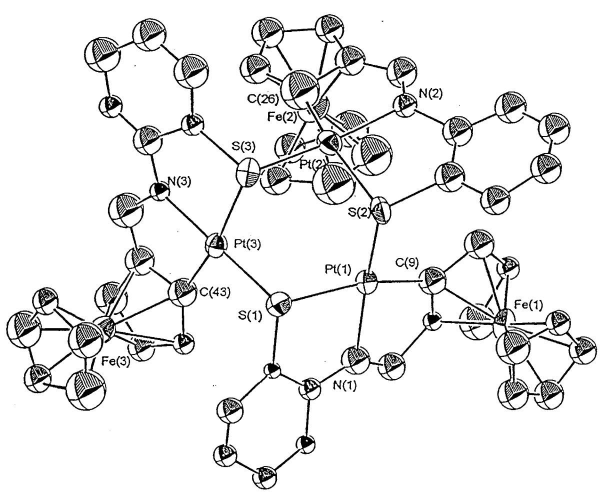


Figure 1. The molecular structure of **1**. Selected distances: Pt(1)-S(1) 2.37(4), Pt(1)-S(2) 2.28(4), Pt(1)-N(1) 2.22(13), Pt(1)-C(9) 2.06(17), Pt(2)-S(2) 2.33(4), Pt(2)-S(3) 2.27(5), Pt(2)-N(2) 2.14(12), Pt(2)-C(26) 2.00(27), Pt(3)-S(1) 2.29(4), Pt(3)-S(3) 2.35(4), Pt(3)-N(3) 2.00(10), Pt(3)-C(43) 1.99(16), Pt(1)-Pt(2) 3.535(9), Pt(1)-Pt(3) 3.685(8), Pt(2)-Pt(3) 3.698(9) Å. Selected angles: S(1)-Pt(1)-S(2) 93(1), S(1)-Pt(1)-N(1) 86(4), S(1)-Pt(1)-C(9) 161(5), S(2)-Pt(1)-N(1) 173(4), S(2)-Pt(1)-C(9) 106(5), N(1)-Pt(1)-C(9) 77(6), S(2)-Pt(2)-S(3) 92(1), S(2)-Pt(2)-N(2) 89(3), S(2)-Pt(2)-C(26) 163(8), S(3)-Pt(2)-N(2) 172(3), S(3)-Pt(2)-C(26) 100(8), N(2)-Pt(2)-C(26) 80(8), S(1)-Pt(3)-S(3) 91(1), S(1)-Pt(3)-N(3) 171(3), S(1)-Pt(3)-C(43) 103(5), S(3)-Pt(3)-N(3) 83(3), S(3)-Pt(3)-C(43) 166(5), N(3)-Pt(3)-C(43) 84(5)°.

Although the frameworks of the tetranuclear Pd(II) and Pt(II) complexes with 1-naphthyl groups instead of ferrocenyl ones consist of eight-membered M$_4$S$_4$ (M = Pd(II) and Pt(II)) ring having $\bar{4}$ symmetry,[3] the framework of complex **1** consists of six-membered Pt$_3$S$_3$ ring in chair form.[5] This difference arises from the difference of substituent groups in benzothiazoline derivative. Three ferrocene units in **1** occupy general positions and the molecule **1** has no threefold axis C_3. The Pt(2)···Fe(2) distance being 3.49(3)Å is shorter than the other two Pt···Fe distances (Pt(1)···Fe(1) 3.69(3)Å, Pt(3)···Fe(3) 3.66(3)Å).

In CDCl$_3$, ^{1}H NMR spectrum of **1** gives three signals corresponding to the non-substituted cyclopentadienyl ring protons in cyclopentadienyl region and also three azomethine signals.[8] This result indicates that the low symmetry of the complex **1** without C_3 axis is also maintained in solution.

In general, platinum(II) and palladium(II) complexes with the N, S chelate ligands, which form square planar configuration, are yellow - red and actually the analogous tetranuclear Pt(II) and Pd(II) complexes with *C,N,S$_2$* donor atoms are dark red.[3] It is worthy of note that the present trinuclear Pt(II) complex **1** is green. The electronic absorption spectrum of **1** in dichloromethane solution has four bands at 13.6 (ε = 1600), 17.1 (4900), 21.3 (4000), 25.2 × 10^3cm^{-1} (7200 dm^3 mol^{-1} cm^{-1}). By comparing this spectrum with those of the tetranuclear Pt(II) complex[3] 12.5 (170), 15.7 (2290), 18.4 (6030) and 25.2 × 10^3cm^{-1} (21380 dm^3 mol^{-1} cm^{-1}), the intensity of the band around 13 × 10^3 cm^{-1} in complex **1** is about 10 times that in tetranuclear complex and this band causes the complex **1** to be colored green.

References and Notes

1 L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta,* **1**, 365 (1967); L. F. Lindoy and S. E. Livingstone, *Inorg. Chem.,* **7**, 1149 (1968); A. P. Koley, R. Nirmala, L. S. Prasad, S. Ghosh, and P. T. Manoharan, *Inorg. Chem.,* **31**, 1764 (1992).

2 T. Kawamoto and Y. Kushi, *J. Chem. Soc., Dalton Trans.*, **1992**, 3137.

3 T. Kawamoto, I. Nagasawa, H. Kuma, and Y. Kushi, *Inorg. Chem* ., **35**, 2427 (1996).

4 S. Okeya and S. Kawaguchi, *Inorg. Synth.*, **20**, 65 (1980).

5 Crystal data for **1**: $C_{51}H_{39}Fe_3N_3Pt_3S_3 \cdot CHCl_3$, M=1662.25, monoclinic, a = 21.439(7), b = 11.990(7), c = 20.919(4)Å, β = 90.79(2)°, U = 5376.7(37)Å^3, space group $P2_1/n$, Z = 4, F(000) = 3136, Mo-Kα radiation, Graphite monochromator, room temperature. All crystallographic measurements were made using a MAC science MXC3 diffractometer. Empirical absorption corrections (ψ-scan) were applied. Lattice parameters were determined by application of the automatic diffractometer indexing routine to the positions of 22 reflections. Data were measured in the range $3 \leq 2\theta \leq 50°$ in the ω-2θ scan with three check reflections being measured every 100 data. The structure was solved by direct methods(SIR92) and refined by full-matrix least squares analysis using 2596 unique reflections to final R factor = 0.0705, Rw = 0.0902. Refinement was anisotropic only for the platinum, iron, chlorine, and sulfur atoms.

6 J. -H. Chou and M. G. Kanatzidis, *Inorg. Chem.,* **33**, 5372 (1994). (chair form); M. Capdevila, W. Clegg, P. Gonzalez-Duarte, and I. Mira, *J. Chem. Soc., Dalton Trans.,* **1992**, 173. (twist-boat form).

7 S. Chattopadhyay, C. Sinha, P. Basu, and A. Chakravorty, *J. Organomet. Chem.,* **414**, 421 (1991); C. Arlen, M. Pfeffer, O. Bars, and D. Grandjeam, *J. Chem. Soc., Dalton Trans.,* **1983**, 1535; W. de Greaf, J. Boersma, W. J. J. Smeets, A. L. Spek, and G. von Koten, *Organometallics*, **8**, 2907 (1989).

8 Selected data for **1**: ^{1}H NMR(270 MHz, $CDCl_3$) δ 4.09, 4.11, 4.21 (s, 15H, free-Cp), 4.35-4.50 (m, 9H, substituted-Cp), 7.10-7.90 (m, 12H, phenyl ring), 8.63, 8.67, 8.74 (s, 3H, N=CH).