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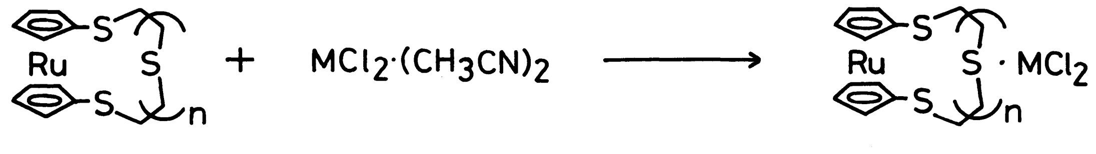
ISOLATION AND X-RAY CRYSTAL STRUCTURES OF THE 1:1 COMPLEXES OF Pt(orPd)Cl_2 WITH POLYTHIA[n](1,1')RUTHENOCENOPHANES AND RELATED COMPOUNDS

Sadatoshi AKABORI,* Sadao SATO,*,+ Takehiko TOKUDA, Yoichi HABATA,
Kayoko KAWAZOE,+ Chihiro TAMURA,+ and Masaru SATO++
Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274
+Analytical and Metabolic Research Laboratories, Sankyo Co., Lt., 1-2-58 Hiromachi, Shinagawaku, Tokyo 140
++Chemical Analysis Center, Saitama University, Urawa, Saitama 338

Platinum or Palladium dichloride coordinated to polythia[n]-(1,1')ruthenocenophanes, forming the crystalline 1:1 adducts. X-Ray crystallography of the complexes of the 1,4,7,10-tetrathia[n]-ruthenocenophane with $PtCl_2$ and $PdCl_2$ revealed that the Pt(or Pd)Cl_2 bonded selectively to the two S atoms among four S atoms of the ligand with a slightly distorted cis square-planer configuration.

Since the pioneering work by Pedersen,1) the excellent ion-binding properties of macrocyclic polyethers, polythiaethers, polyamines, and the related compounds have received much attention. While macrocyclic polyethers can form complexes with only alkali and alkaline earth metal ions, macrocycles with sulfur and nitrogen atoms as a coordinating donor are also capable of forming transition-metal complexes.2) Although a number of complexes of transition metals (Cu, Ni, Co, etc.)



1 2 3

1a: n=2
1b: n=3

2a: MCl_2 = cis-$PtCl_2$
2b: MCl_2 = trans-$PdCl_2$

3a: n=2, M=Pt
3b: n=2, M=Pd
3c: n=3, M=Pt
3c: n=3, M=Pd

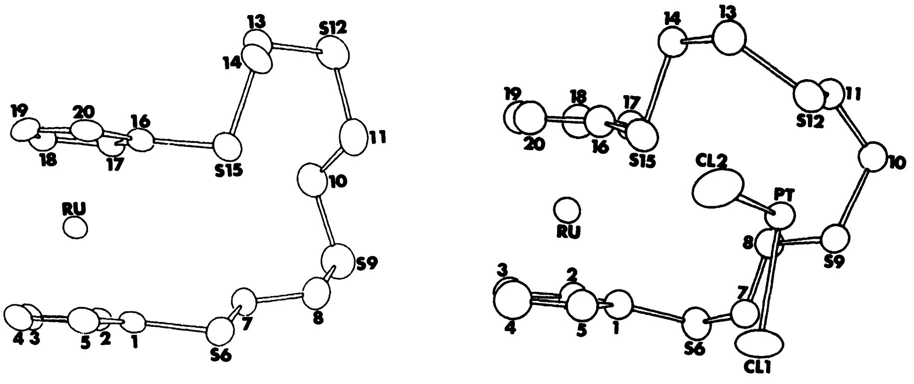
Table 1. Formation of Complex of **3a**-**3d**

Complexes	Yield/%	θ_m/°C
3a	51	257.0(dec.)
3b	89	248.0(dec.)
3c	79	211.0-212.0
3d	49	218.0-218.5

with thiacrown ethers and/or azacrown ethers have already been reported,[2)] few complexes of platinum group metals with these macrocyclic compounds are known.[3,4)] In the previous paper,[5)] we have reported the preparation of the polythia[n]-(1,1')ruthenocenophanes (**1**) by the reaction of 1,1'-bis(2-chloroethylthio)-ruthenocene with disodium 1,2-ethanedithiolate. In this paper, we report (i) the isolation of crystalline complexes (**3**) by the reaction of **1** with $MCl_2(CH_3CN)_2$ (**2**), (ii) the X-ray crystal structures of **1a**, **3a**, and **3b**, and (iii) the spectroscopic evidence for the existence of these complexes in a solution.

To a hot solution of **1a** ($7.9\text{x}10^{-5}$ mol) in acetonitrile (5 ml) was added a solution of **2a** ($7.9\text{x}10^{-5}$ mol) in acetonitrile (10 ml) and the solution was then cooled to room temperature. After 1 h, crystals of the complex **3a**[6)] were isolated. Other complexes **3b**-**3d**[6)] were also prepared essentially by the same method. These complexes were confirmed by microanalysis to be 1:1 complexes. These results are summarized in Table 1. Their ^{1}H-NMR and IR spectra and X-ray analyses provided further information about the structure of the complexes. The ^{1}H-NMR spectrum of **1a** in $CDCl_3$ showed a pair of triplets corresponding to the α- and β-ring protons of the ruthenocene nucleus at δ 4.62 (J=1.8 Hz, 4H) and 4.77 (J=1.8 Hz, 4H), in addition to a singlet at δ 3.10 (4H, CH_2) and a multiplet at δ 2.75-3.21 (8H, CH_2). On the other hand, in the ^{1}H-NMR spectrum (in DMSO-d_6) of **3a**, the signals of the methylene protons were shifted down-field about 0.2-0.4 ppm, compared with those of **1a**. In addition, even more remarkable differences were observed in the chemical shifts of the cyclopentadienyl (Cp) ring protons of **3a**. That is, the α- and β-ring protons of the ruthenocene nucleus of **1a** resonated as two symmetrical triplets, but in **3a** the signal of the α-ring protons split into two broad multiplets at δ 4.85 (2H)-5.02 (4H) together with multiplets of the β-ring protons at δ 4.66-4.76 (4H). These results suggest an unsymmetrical structure for **3a** in the solution. In the IR spectrum (CsI disk) of **3a**, the absorptions at 325 and 312 cm^{-1}, are assignable to ν(Pt-Cl) of cis-$PtCl_2$ moiety. The results well agree with the configuration of the starting material, cis-$PtCl_2(CH_3CN)_2$.7) An interesting result was found in the formation of the palladium complex. The IR spectrum of the Pd--complex (**3b**) showed the peaks at 325 and 316 cm^{-1}, which are also assignable as ν(Pd-Cl) of the cis-$PdCl_2$ moiety, neverthless the trans-$PdCl_2(CH_3CN)_2$ was used as the starting material.7) The above results are supported by the X-ray crystallographic analysis of **3a**.

The conformation of **3a** is illustrated in Fig. 1, together with the molecular structure of the corresponding free ligand **1a**.8) The Pt atom, which is complexed by two S atoms of the tetradentate thiacrown ether part, has a slightly distorted cis square-planer environment; the two S atoms at the 9- and 12-positions of the ligand occupy two cis positions and two Cl atoms occupy the other two cis positions. The bond angles around the Pt atom vary from 89.3(2)° to 91.4(3)°, and the bond angles and the Pt-Cl and Pt-S bond lengths are within the expected range for such bonds.9) The interesting selective coordination of the Pt atom on the two S atoms among the coordinatable four S atoms is attributable to the steric hindrance of the two cyclopentadienyl rings to the two S atoms of the 6- and 16-positions. Moreover, the conformation of the organic ligand moiety differs greatly between the metal-free ligand (**1a**) and the complex (**3a**). Main conformational changes are reflected in the torsion angles of the macrocyclic moiety and overlapping patterns between cyclopentadienyl (Cp) rings. The three torsion angles of the S-C-C-S are remarkably changed by the complexation, compared with those of the corresponding free ligand **1a**.10) The two Cp rings take the eclipsed conformation, in which the dihedral angles between them are 5.3° and 2.9° for **1a** and **3a**, respectively. However, the torsion angle (69.1°) between the S(6)-C(1) bond and the S(15)-C(16) bond around the z-axis of the ruthenocene nucleus in **3a** is much larger than the corresponding one (5.3°) in the free ligand **1a**. That is, the Cp-rings of a ruthenocene nucleus in **3a** rotate each other by about (2π/5)° in the complexation with $PtCl_2$. Also, the X-ray crystal data showed the two compounds (**3a** and **3b**) to be isomorphous.



(a) (b)

Fig. 1. ORTEP drawings of molecules with atomic numbering scheme of (a) **1a** and (b) **3a**.

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6) All new complexes gave satisfactory microanalytical results and spectral data consistent with the assigned structure.
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8) Crystal Data. **1a**: F.W.=441.7, triclinic, space group P1, a=13.828(2), b=11.890(2), c=5.587(2)Å, α=95.93(2), β=105.39(2), γ=102.22(1)°, V=853.1(3) Å^3, Z=2, Dx=1.72 g cm^{-3}, μ(MoKα)=1.4 mm^{-1}, R=3.1%. **3a**: F.W.=707.7, monoclinic, P2$_{1/n}$, a=9.912, b=28.142(9), c=7.521(3) Å, β=102.08(4)°, V=2053.3(16) Å^3, Z=4, Dx=2.29 g cm^{-3}, μ(MoKα)=8.3 mm^{-1}, R=7.0%.
9) G. K. Worfgang, K. B. Dietlich, and B. Gerd, Acta Crystallogr., Sect. B, 36, 2545 (1980).
10) Torsion angles (°). **1a**: S(6)-C(7)-C(8)-S(9) -175.7(1), S(9)-C(10)-C(11)-S(12) 173.6(1), S(12)-C(13)-C(14)-S(15) -96.3(4). **3a**: S(6)-C(7)-C(8)-S(9) -170.5(0), S(9)-C(10)-C(11)-S(12) 55.0(2), S(12)-C(13)-C(14)-S(15) 57.0(2).

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