Formation of a Novel *μ*-Tetrasulfido-Bridged Dimer of a Dinuclear Platinum Complex

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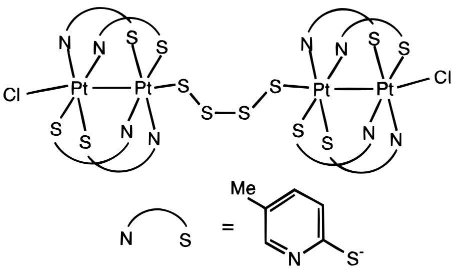
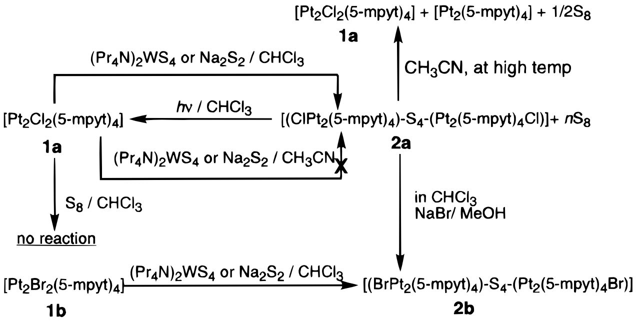
Transition metal polysulfides have been attracting much attention owing to their possible relevance to the catalytic activity of enzymes and usefulness as heterogeneous catalysts.[1] One of the most interesting features of such systems is that both the metal and sulfur may undergo redox reactions. In some cases, these systems show unique redox reactivity such as induced internal electron transfer.[2] Most of the synthetic procedures of transition metal polysulfides include elemental sulfur, hydrogen sulfide, ammonium polysulfide, or lithium disulfide as a polysulfide source. Recently, a report has shown that tetrathiometalate anion acts as a disulfide source.[3] Thus tetrathiometalate anions attract attention as new polysulfide sources. However, the mechanism of the formation of disulfide from the tetrathiometalate anion is still unclear. We wish to report herein a new tetrasulfido-bridged dimer of a dinuclear platinum(III) complex. The new complex [{XPt$_2$(5-mpyt)$_4$}$_2$(μ-S$_4$)] (5-mpyt = 5-methylpyridine-2-thiolate anion), **2** (X = Cl, **2a**; X = Br, **2b**), was formed by the reaction of [Pt$_2$X$_2$(5-mpyt)$_4$], **1** (X = Cl, **1a**; X = Br, **1b**),[4] with WS$_4^{2-}$. The involvement of elemental sulfur, S$_8$, in the crystals of **2a**·0.5S$_8$·2CHCl$_3$ and **2b**·0.5S$_8$·2CHCl$_3$ indicates that a μ-S$_4^{2-}$ group may be an intermediate to S$_8$.



Treatment of **1** with an equimolar amount of (Pr$_4$N)$_2$WS$_4$ in CHCl$_3$ in the dark at room temperature immediately gave a deep red solution, from which deep red crystals of **2** were isolated in 40−50% yield (Scheme 1).[5] However, the reaction of **1** with (Pr$_4$N)$_2$WS$_4$ in CH$_3$CN afforded a yellow precipitate of the platinum(II) dimer, [Pt$^{II}_2$(5-mpyt)$_4$], and an unidentified orange-brown W species which is soluble in CH$_3$CN. The reaction in CH$_3$CN was completed within several hours. The use of Na$_2$S$_2$ instead of (Pr$_4$N)$_2$WS$_4$ in CHCl$_3$ also gave **2** in similar yield.

Scheme 1



Elemental sulfur did not react with **1**. Thus, **1**, WS$_4^{2-}$ or S$_2^{2-}$, and solvent CHCl$_3$ are essential for the formation of **2**. The initial step of the reaction of **1** with WS$_4^{2-}$ or S$_2^{2-}$ would be the reduction of **1** by WS$_4^{2-}$ or S$_2^{2-}$ ions, since we observed partially reduced blue Pt species except for the reaction of **1** with WS$_4^{2-}$ in CHCl$_3$. The partially reduced species may be oxidized by solvent CHCl$_3$ to reproduce **1**.[6] The oxidation of a platinum(II) dimer, [Pt$_2$(5-mpyt)$_4$], by CHCl$_3$ has been demonstrated previously.[4] The reproduced **1** would again react with WS$_4^{2-}$ or intermediate polysulfide species. The S$_4^{2-}$ ion formed during the redox cycle acts as a bridge to give **2**. The redox cycle would further proceed to give eventually some elemental sulfur as evidenced from the involvement of S$_8$ molecules in the crystal of **2**. The CHCl$_3$ solution of **2** is very sensitive toward light. The CHCl$_3$ solution of **2a**, for instance, loses its deep color within 1 min to give **1a** by exposing the solution to a room light. This means that the light induces the rupture of Pt−S$_4$−Pt bonds. Although **2a** in CH$_3$CN is more stable than in CHCl$_3$, refluxing of the CH$_3$CN solution of **2a** afforded [Pt$^{II}_2$(5-mpyt)$_4$], [Pt$^{III}_2$Cl$_2$(5-mpyt)$_4$], and S$_8$.

$$2[\{\mathrm{ClPt_2(5\text{-}mpyt)_4}\}_2\mathrm{S_4}] \xrightarrow[\Delta]{\mathrm{CH_3CN}} [\mathrm{Pt^{III}{}_2Cl_2(5\text{-}mpyt)_4}] + [\mathrm{Pt^{II}{}_2(5\text{-}mpyt)_4}] + \mathrm{S_8}$$

Thus it appears that **2** is a kinetically favored intermediate. The axial Cl$^-$ ligands of **2a** can be substituted by an excess amount of Br$^-$ ion in CHCl$_3$/MeOH solution to give **2b**.

The X-ray structure analyses of **2a**,**b** disclosed that they are isomorphous and consist of a complex molecule in which {Pt$_2$(5-mpyt)$_4$X} units are linked by an S$_4^{2-}$ group (Figure 1), a disordered S$_8$ molecule (site occupancy = 0.5), and two CHCl$_3$ molecules in an asymmetric unit.[7] The Pt−Pt single bond

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(1) (a) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934. (b) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742. (c) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89. (d) Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1613. (e) Isobe, K.; Ozawa, Y.; Vázquez de Miguel, A.; Zhu, T.-W.; Zhao, K.-M.; Nishioka, T.; Ogura, T.; Kitagawa, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1882. (f) Bianicini, C.; Jiménez, M. V.; Mealli, C.; Meli, A.; Moneti, S.; Patinec, V.; Vizza, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1706. (g) Liao, J.-H.; Varotsis, C.; Kanatzidis, M. G. *Inorg. Chem.* **1993**, *32*, 2453.

(2) Murray, H. H.; Wei, L.; Sherman, S. E.; Greaney, M. A.; Eriksen, K. A.; Carstensen, B.; Halbert, T. R.; Stiefel, E. I. *Inorg. Chem.* **1995**, *34*, 841.

(3) Mizobe, Y.; Hosomizu, M.; Kubota, Y.; Hidai, M. *J. Organomet. Chem.* **1996**, *507*, 179.

(4) Umakoshi, K.; Kinoshita, I.; Ichimura, A.; Ooi, S. *Inorg. Chem.* **1987**, *26*, 3551.

(5) Experimental procedures and the physical properties of **2a**,**b** are described in the Supporting Information.

(6) For example, the tetranuclear mixed-valence compound [Pt$_2$(NH$_3$)$_4$(α-pyridonato)$_2$]$_2^{5+}$ is known to possess an intense blue color.

(7) Crystallographic data for **2a**·0.5S$_8$·2CHCl$_3$: C$_{50}$H$_{50}$Cl$_8$N$_8$Pt$_4$S$_{16}$, deep red crystal, monoclinic, space group $P2_1/a$ (No. 14), a = 17.226(5) Å, b = 32.762(5) Å, c = 16.157(11) Å, β = 111.00(3)°, V = 8513(7) Å^3, Z = 4, D_c = 1.83 g cm^{-3}, μ = 72.04 cm^{-1}, R (R_w) = 0.065 (0.073), GOF = 3.43. Crystallographic data for **2b**·0.5S$_8$·2CHCl$_3$: C$_{50}$H$_{50}$Br$_2$Cl$_6$N$_8$Pt$_4$S$_{16}$, deep red crystal, monoclinic, space group $P2_1/a$ (No. 14), a = 17.261(2) Å, b = 33.061(5) Å, c = 16.430(4) Å, β = 111.64(1)°, V = 8715(3) Å^3, Z = 4, D_c = 1.85 g cm^{-3}, μ = 78.96 cm^{-1}, R (R_w) = 0.073 (0.086), GOF = 3.02. Selected bond lengths (Å) and angles (deg) for **2b**: Pt1−Pt2 2.560(2), Pt3−Pt4 2.552(2), Pt1−Br1

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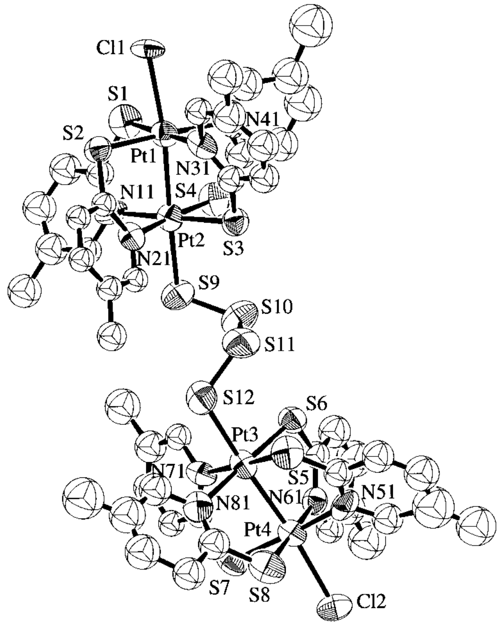

Figure 1. ORTEP drawing of [{$ClPt_2$(5-mpyt)$_4$}$_2S_4$] (**2a**). Selected bond distances (Å) and angles (deg): Pt1−Pt2 2.556(2), Pt3−Pt4 2.558(2), Pt1−Cl1 2.603(7), Pt4−Cl2 2.567(8), Pt2−S9 2.435(8), Pt3−S12 2.424(9), S9−S10 1.96(1), S10−S11 2.04(1), S11−S12 1.99(1); Cl1−Pt1−Pt2 172.5(2), Pt1−Pt2−S9 174.7(2), Pt2−S9−S10 111.3(5), S9−S10−S11 107.2(6), S10−S11−S12 108.8(6), S11−S12−Pt3 109.7(5), S12−Pt3−Pt4 174.9(3), Pt3−Pt4−Cl2 173.4(2).

distances in **2**, which are affected by the bite distance of the bridging ligand and σ-donor strength of axial ligands,[8] are only 0.02 Å longer than that of **1a** (2.532(1) Å), while those are much shorter than that of [Pt^{II}_2(4-mpyt)$_4$].[4] The Pt−Cl distance in **2a** is, however, 0.11−0.15 Å longer than that of **1a** (2.458(2) Å), which is ascribed to stronger coordination of S_4 ligand to Pt_2 units.[9] The difference between Pt−Cl and Pt−Br distances is ascribed to the difference between ionic radii of Cl^- and Br^- ions.[10] The S_4 ligands in **2** have approximately C_2 symmetry. The inner S−S distances in **2** are longer than or almost the same as the outer S−S distances, which is contrast with the tendency found in [PtS_4(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane) and related complexes where the S_4 ligand acts as a chelating ligand.[11] According to the recent molecular orbital calculation for the free S_4^{2-} dianion, the nonplanar gauche C_2 structure is the most stable form compared with D_{2h}, C_{2v}, and C_{2h} structures, where the inner S−S distance is longer than the outer S−S distances.[12] Thus the structures of the S_4 ligands in **2** are in stable conformations as in the theoretical prediction.

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Supporting Information Available: Text describing experimental procedures for the synthesis and reaction of **2a** with NaBr with spectral data for **2a**,**b** and crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters and ORTEP diagrams for **2a**,**b** (19 pages). Ordering information is given on any current masthead page.

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2.705(5), Pt4−Br2 2.660(6), Pt2−S9 2.42(1), Pt3−S12 2.41(1), S9−S10 2.00(2), S10−S11 1.99(2), S11−S12 1.99(2), Br1−Pt1−Pt2 171.1(1), Pt1−Pt2−S9 174.4(3), Pt2−S9−S10 111.0(6), S9−S10−S11 109.6(7), S10−S11−S12 109.1(7), S11−S12−Pt3 109.9(6), S12−Pt3−Pt4 174.3(3), Pt3−Pt4−Br2 173.2(1). Full details for the crystallographic analysis of **2a**,**b** are described in the Supporting Information.

(8) Umakoshi, K.; Sasaki, Y. *Adv. Inorg. Chem.* **1993**, *40,* 187.

(9) The in-plane Pt−Cl and Pt−S(av) distances in [$PtCl_4$]$^{2-}$ (2.310(1) Å)[13] and [Pt(4-mpytH)$_4$]$^{2+}$ (2.325 Å)[14] are very similar, while the Pt−S_{axial} distances in **2a** are shorter than the Pt−Cl distance in **1a**.

(10) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32,* 751.

(11) Briant, C. E.; Calhorda, M. J.; Hor, T. S. A.; Howells, N. D.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1983**, 1325.

(12) Mebel, A. M.; Morokuma, K.; Isobe, K. *Inorg. Chem.* **1995**, *34,* 1208.

(13) Ohba,S.; Sato, S.; Saito, Y. *Acta Crystallogr.* **1983**, *B39,* 49.

(14) Nishioka, T.; Kinoshita, I.; Kitano, K.; Ooi, S. *Chem. Lett.* **1992**, 883.