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Dinuclear Palladium(II) Complex of Pyridine-2-thiol

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A number of Pt(III) complexes synthesized recently have been attracting much interest from the viewpoint of tervalent platinum chemistry [1–8]. All of them are dinuclear [1–8], and some of them are obtained by oxidation of the corresponding dinuclear Pt(II) complexes [3–6]. Although no palladium(III) complex has been synthesized as yet, palladium(II) complex, structurally similar to the dinuclear Pt(II) complex, has been synthesized by use of 6-substituted 2-hydroxypyridine [9]. Most of these Pd(II) complexes have two *trans*-PdN_2O_2 coordination squares which face each other at a distance of *ca.* 2.5 Å. Although in $[Pd_2(6\text{-mhp})_4]_5 \cdot 6CHCl_3$ the *cis* isomer was found to coexist with the *trans* isomer in a 1:4 ratio, Cotton and coworkers pointed out that the *cis* isomer may be an unstable species in such a complex [9b]. In this communication we report the synthesis and characterization of the *cis* isomer of tetrakis(pyridine-2-thiolato)dipalladium(II), $[Pd_2(pyt)_4]$.

Reaction of palladium(II) acetate with twice as many mols of pyridine-2-thiol (pytH) in dioxane at room temperature initially gave a brownish precipitate which then dissolved to give a red solution, from which an orange solid began to separate out after a few minutes. The orange compound, washed with dioxane and ethanol and dried *in vacuo*, was analyzed to be $Pd(pyt)_2$ (*Anal.* Found: C, 36.85; H, 2.46; N, 8.42. Calc. for $C_{10}H_8N_2PdS_2$: C, 36.76; H, 2.47; N, 8.58%.) Yield, 96%.

The orange single crystals obtained by recrystallization from chloroform were unstable in air and pulverized to give $Pd(pyt)_2$. The single-crystal X-ray analysis disclosed that the crystal is formulated as $[Pd_2(pyt)_4] \cdot 2CHCl_3$. Crystal data: $C_{22}Cl_6H_{18}N_4Pd_2S_4$, monoclinic, space group $P2_1/c$, $a = 12.518(2)$, $b = 6.587(1)$, $c = 18.878(3)$ Å, $\beta = 99.09(1)°$, $Z = 2$, $D_c = 1.93$ g cm^{-3}, μ(Mo Kα) = 19.5 cm^{-1}. Intensities were measured on an automated diffractometer by use of graphite-monochromated Mo Kα radiation. Of 2130 unique reflections collected in the $2\theta \leqslant 46.0°$ range, 1495 with $I > 3\sigma(I)$ were used for the structure analysis. The structure was solved by the heavy-atom method and refined by least-squares to $R = 0.043$.

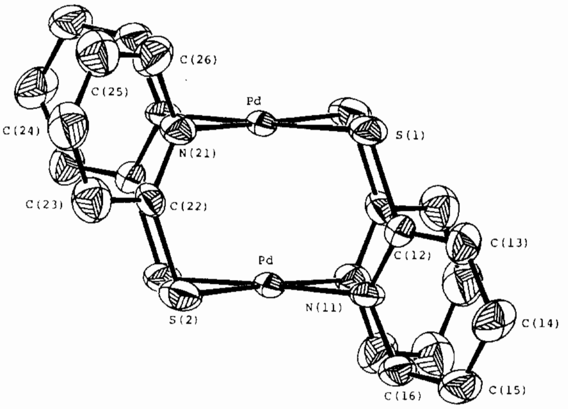

Fig. 1. A perspective view of $[Pd_2(pyt)_4]$. Thermal ellipsoids are drawn at 50% probability level.

Figure 1 shows the X-ray structure of $[Pd_2(pyt)_4]$. The dimer has a center of symmetry at the midpoint of Pd•••Pd, the virtual symmetry being C_{2h}. The S atoms lie at the *cis* position in either coordination square. Two PdS_2N_2 square slightly twist to each other about the Pd•••Pd axis, the average N–Pd–Pd–S torsion angle being 1.5°. The Pd atom slightly deviates (0.027(3) Å) from the coordination plane defined by the four donor atoms to another Pd atom. The Pd•••Pd distance (2.677(1) Å) is longer than those in the Pd(II) dimer of 6-methyl- and 6-chloro-2-hydroxypyridinates (2.547–2.570 Å) [9b] but less than that in $[Pd_2(CH_3CSS)_4]$ (2.754 or 2.738 Å) [10].

As some of $[Pt^{II}(bridge)_4Pt^{II}]$ type complexes are known to undergo an oxidative addition of iodine to give $[IPt^{III}(bridge)_4Pt^{III}I]$ [3, 4], an attempt was made to oxidize the dinuclear palladium(II) complex by iodine. The reaction in a 1:1 molar ratio in chloroform yielded a dark brown precipitate. However, characterization has not been successful as yet. On the other hand the reaction in the molar ratio of $[Pd_2(pyt)_4]:I_2 = 2:1$ gave a red compound in 90% yield. Recrystallization from dimethylformamide afforded thin plate-like crystals. The chemical and X-ray structure analyses* disclosed that the compound is formulated as $[Pd_4(pyt)_6I_2] \cdot DMF$. Figure 2 shows the tetranuclear structure which has a two fold axis perpendicular to Pd(1)•••

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*Crystal data: $C_{33}H_{31}I_2N_7OPd_4S_6$, monoclinic, space group $P2/c$; $a = 14.335(9)$, $b = 9.030(5)$, $c = 17.401(9)$ Å, $\beta = 108.30(8)°$; $Z = 4$, $D_c = 2.25$ g cm^{-3}. μ(Mo Kα) = 34.0 cm^{-1}. Intensity data were collected on an automated diffractometer by use of graphite-monochromated Mo Kα radiation. No correction was made for absorption. Of 6637 reflections collected in the $2\theta \leqslant 60.0°$ range, 2513 with $I > 3\sigma(I)$ were used for the structure analysis. The current R value is 0.059.

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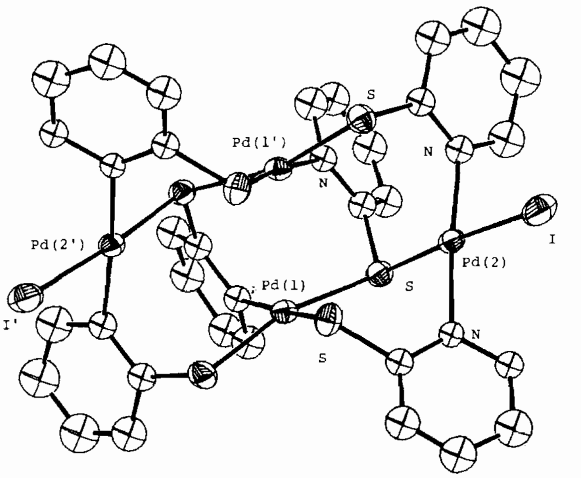

Fig. 2. Structure of [$Pd_4(pyt)_6I_2$]. Pd(1)···Pd(1') = 3.011(2) Å, Pd(1)···Pd(2) = 3.892(2) Å.

Pd(1') axis, the detail of which will be described elsewhere. This compound presumably results from the reaction $2[Pd_2(pyt)_4] + I_2 \rightarrow [Pd_4(pyt)_6I_2]$ + bis(2-pyridyl)disulfide. Thus iodine does not serve as oxidant to the metal atom in [$Pd_2(pyt)_4$].

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