

Construction of the Tetranuclear Complex with Inter- and Intramolecular Stacking-Like Arrangement Composed of Planar Palladium(II) Units

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The reaction of a square-planar S-donating metalloligand $[\text{Pd}(\text{aet})_2]$ (aet = 2-aminoethanethiolate) with $[\text{Pd}(\text{NO}_3)_2(\text{bpy})]$ (bpy = 2,2'-bipyridine) gave a new type of S-bridged tetranuclear complex $[\text{Pd}_4(\text{aet})_4(\text{bpy})_2]^{4+}$ (**1**), in which two $\{\text{Pd}(\text{bpy})\}$ moieties are aligned so as to overlap each other by bridging with two $[\text{Pd}(\text{aet})_2]$ units.

The square-planar d^8 metal complexes with aromatic α -diimine ligands such as bpy, 1,10-phenanthroline (phen), and their derivatives have been attracted for their specific spectral, structural, and electrochemical properties.¹ These complexes have occasionally existed in stacking forms in crystals due to the π - π interactions of the pyridyl rings.² This suggests that the construction of polynuclear complexes with plural $\{\text{M}(\text{bpy})\}$ ($\text{M} = \text{Pd}^{\text{II}}$, Pt^{II} , or Au^{III}) moieties would be brought about by the stacking arrangement based on the inter- and / or intramolecular interactions for the resulting complexes. Therefore, such kinds of polynuclear complexes are very important and attractive in providing significant information on linear-chain structures and metal-metal interactions.² However, there is no example for the above types of polynuclear complexes, except for the planar dinuclear complexes, which can be synthesized with simple bridging ligands.³ The S-donating metalloligands such as $[\text{M}(\text{aet})_2]$ ($\text{M} = \text{Ni}^{\text{II}}$, Pd^{II} , etc.)⁴ are considered to be useful for the constructions of such types of polynuclear complexes with higher dimensional conformation, because of their spacer ability between the square-planar units. In the case of the reaction between $[\text{Ni}(\text{aet})_2]$ and $[\text{PtCl}_2(\text{bpy})]$, however, $[\text{Ni}(\text{aet})_2]$ does not act as a spacer between the square-planar $\{\text{Pt}(\text{bpy})\}$ moieties.⁵ As a result, unexpected dinuclear complex $[\text{Pt}(\text{bpy})\{\text{Ni}(\text{aet})_2(\text{H}_2\text{O})_2\}]^{2+}$, in which the Ni^{2+} ion has converted from the square-planar coordination geometry to the octahedral one, is formed. In this letter, we will describe the synthesis and crystal structure of a new type of tetranuclear complex **1**, which is formed by the reaction between two square-planar building-blocks, $[\text{Pd}(\text{aet})_2]$ and $[\text{Pd}(\text{NO}_3)_2(\text{bpy})]$.

To a yellow suspension containing 0.26 g (1.0 mmol) of $[\text{Pd}(\text{aet})_2]^{4-}$ in 20 cm^3 of water was added 0.40 g (1.0 mmol) of $[\text{Pd}(\text{NO}_3)_2(\text{bpy})]$.⁶

The mixture was stirred at 50 $^\circ\text{C}$ for 1 d, whereupon the mixture became a yellowish orange solution. After removing any unreacted materials by filtration, a few drops of a saturated NaNO_3 solution was added to the yellowish orange filtrate. The mixture was allowed to stand at 4 $^\circ\text{C}$ for several days, and the resulting yellowish orange $[\text{Pd}_4(\text{aet})_4(\text{bpy})_2](\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ crystals were collected by filtration.⁷ A well formed crystal was used for the X-ray analysis.⁸

X-ray structural analysis of the nitrate salts of **1** revealed the presence of a discrete tetravalent complex cation, four nitrate anions, and five water molecules.⁸ As shown in Figure 1, the complex cation contains two square-planar $\{\text{Pd}(\text{bpy})\}$ moieties and two $[\text{Pd}(\text{aet})_2]$ units. Each square-planar $\{\text{Pd}(\text{bpy})\}$ moiety is coordinated by the two bridging S atoms from the different $[\text{Pd}(\text{aet})_2]$ units, and the two bpy moieties are aligned so as to overlap each other. The PdN_2S_2 planes in the $\{\text{Pd}(\text{aet})_2\}$ units are almost perpendicular to those in the $\{\text{Pd}(\text{bpy})\}$ moieties, and the Pd-S-Pd bridging angles (average $115.50(4)^\circ$) in **1** are similar to those observed in $[\text{Pd}_2\{\text{Pd}(\text{aet})_2\}_4]^{4+}$.⁹ The N-Pd-N angles (average $79.3(1)^\circ$) in the two $\{\text{Pd}(\text{bpy})\}$ moieties are relatively acute, and the Pd-N distances (average $2.086(3)$ Å) are longer than those observed in the other Pd^{II} complexes with bpy.¹⁰ These seem to be attributable to the influence of the bridging S atoms on the trans positions. The Pd-S distances (average $2.2925(9)$ Å) in the $[\text{Pd}(\text{bpy})\text{S}_2]$ units are slightly longer than those (average $2.2734(9)$ Å) in the $[\text{Pd}(\text{aet})_2]$ units, and the S-Pd-S angles (average $86.76(3)^\circ$) in former are more acute than those ($94.21(3)^\circ$) in latter. This implies that the Pd atoms in the $\{\text{Pd}(\text{bpy})\}$ moieties have more distorted square-planar geometries, compared with those in the $[\text{Pd}(\text{aet})_2]$ units. The averaged distance and dihedral angle between the least squares planes of the two $\{\text{Pd}(\text{bpy})\}$ moieties are 3.477 Å and 9.88° , respectively, and seem to indicate the presence of some interactions between the two $\{\text{Pd}(\text{bpy})\}$ moieties.

The electronic absorption spectrum of **1** in water consists of the bands at 25.0, 30.3, 33.28, 41.84, and $49.75 \times 10^3 \text{ cm}^{-1}$,⁷ and remains unchanged for periods exceeding 1 week. Among these absorption bands, the band at $33.28 \times 10^3 \text{ cm}^{-1}$ is assigned as the π - π^* transition localized on the bpy skeleton, and located on relatively higher energy side than $[\text{Pd}(\text{NO}_3)_2(\text{bpy})]$.^{6, 11} Furthermore, the value of the molar absorptivity for the band is not twice as large as that for the corresponding band of the mononuclear Pd^{II} complex with only one bpy ligand.¹¹ These facts suggest the existence of the π - π interaction between the two bpy skeletons.

In the crystalline state, most of the bands observed in water are located at lower energy sides, but the band due to the transition localized on the bpy skeleton is shifted toward the higher energy side.⁷ This suggests that another interactions, except for the intra-molecular interactions, such as intermolecular interactions are present. In the crystalline state as shown in Figure 2, the complex **1** exists in the dimer-like structure with a coplanar stacking arrangement, in which the bpy moieties of the two distinct complex cations are antiparallel to each other. The intermolecular bpy-bpy distance is almost the same value (ca. 3.5 Å) as the intramolecular bpy-bpy distance, which is within the range of the π - π stacking contact.² Accordingly, these facts imply that, in the crystalline state, intermolecular π - π interaction between the bpy skeletons can exist as well as intramolecular interaction.

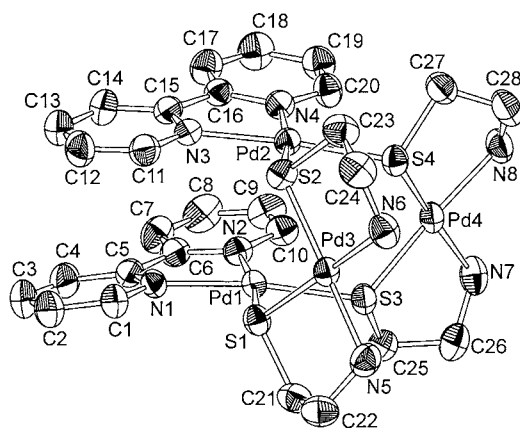


Figure 1. Perspective view of the complex cation **1**.

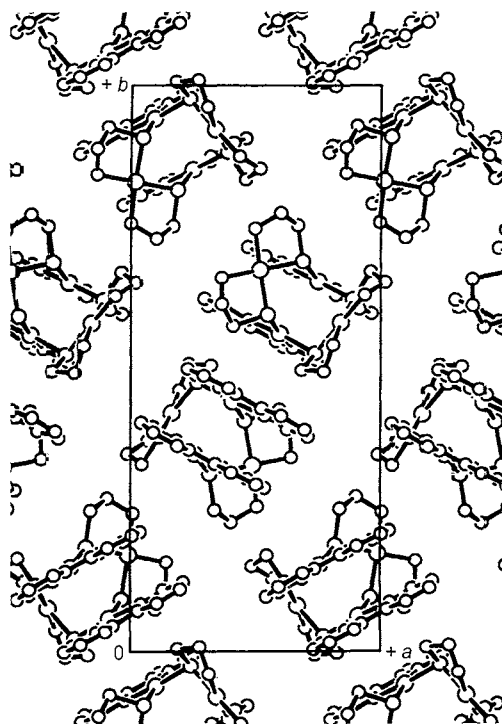


Figure 2. Projection of crystal packing for 1 viewed along c axis.

Further study on the synthesis and some properties of a series of the present tetranuclear Pd^{II} complexes is in progress.

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References and Notes

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- 7 Anal. Found: C, 24.46; H, 3.55; N, 12.11%. Calcd for $[\text{Pd}_4(\text{aet})_4(\text{bpy})_2](\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$: C, 24.36; H, 3.65; N, 12.17%. Visible-UV spectrum in H_2O [ν_{max} , 10^3 cm^{-1} (ϵ , $10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 25.0 (3.29)^{sh}, 30.3 (12.44)^{sh}, 33.28 (26.96), 41.84 (61.82), 49.75 (101.3). Diffuse reflection spectrum in the crystalline state [ν_{max} , 10^3 cm^{-1}]: 24.54, 28.0^{sh}, 33.6^{sh}, 37.74, 46.5^{sh}.
- 8 Crystal data for $[\text{Pd}_4(\text{aet})_4(\text{bpy})_2](\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$: $FW = 1380.61$, monoclinic, $P2_1/n$ (#14), $Z = 4$, $a = 12.295(2)$, $b = 28.358(2)$, $c = 13.350(1) \text{ \AA}$, $\beta = 99.970(9)^\circ$, $V = 4584.3(7) \text{ \AA}^3$, $D_{\text{calc}} = 2.000 \text{ g cm}^{-3}$, $\mu = 1.808 \text{ mm}^{-1}$, for $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Measurements were carried out on a Rigaku AFC7S diffractometer. The structure was solved by a direct method and refined by a full-matrix least square. Final $R = 0.028$ and $R_w = 0.046$ for 8217 observed reflections ($I > 2.00\sigma(I)$). Selected bond distances (\AA) and angles ($^\circ$): Pd1-S1 = 2.2934(8), Pd1-S3 = 2.3023(9), Pd1-N1 = 2.094(3), Pd1-N2 = 2.073(3), Pd2-S2 = 2.2871(9), Pd2-S4 = 2.2872(9), Pd2-N3 = 2.085(3), Pd2-N4 = 2.091(3), Pd3-S1 = 2.2773(9), Pd3-S2 = 2.2832(9), Pd3-N5 = 2.066(3), Pd3-N6 = 2.079(3), Pd4-S3 = 2.2711(9), Pd1-S4 = 2.2620(9), Pd4-N7 = 2.066(3), Pd4-N8 = 2.086(3), S1-Pd1-S3 = 87.13(3), N1-Pd1-N2 = 79.5(1), S2-Pd2-S4 = 86.38(3), N3-Pd2-N4 = 79.1(1), S1-Pd3-S2 = 94.62(3), N5-Pd3-N6 = 93.0(1), S3-Pd4-S4 = 93.80(3), N7-Pd4-N8 = 93.9(1), Pd1-S1-Pd3 = 117.32(4), Pd2-S2-Pd3 = 111.12(4), Pd1-S3-Pd4 = 121.08(4), Pd2-S4-Pd4 = 112.46(4).
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