Crystal Structure and Spectrochemical Properties of a Dinuclear Palladium(II) Complex with 2,3,5,6-Tetra(2-pyridyl)-pyrazine

Yasunori Yamada,* Yoshitaro Miyashita,

Kiyoshi Fujisawa, and Ken-ichi Okamoto*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571

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A dinuclear Pd(II) complex bridged with 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) was newly obtained by the reaction of Pd(II) ion with tppz. The crystal structure of the dinuclear complex was determined by X-ray structural analysis. The spectrochemical properties of the complex are also discussed in relation to the stereochemical behavior.

Polynuclear metal complexes with aromatic nitrogen heterocycles as bridging ligands have been attractive for a long time.[1] Among these bridging ligands, the polydentate ones are of current interest because of their availability for constructions of supramolecular complexes. Though many polynuclear complexes are prepared with such ligands, their coordination chemistry has not been sufficiently known, except for several ones. As for the bis(tridentate)-type ligands, for instance, the non-linear type ligand 6′,6″-bis(2-pyridyl)-2,2′ : 4,4″ : 2″,2‴-quaterpyridine (bpqp) is relatively popular, and is used for preparing dinuclear complexes.[2] As for the complexes with 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz), on the other hand, several types of mono- and dinuclear complexes including four-coordinated tetrahedral, five-coordinated trigonal bipyramidal or six-coordinated octahedral geometries have been prepared so far.[3—15] However, the crystal structure and properties of a dinuclear complex with two square-planar metal centers have not been clarified. In the present paper, we describe the stereochemistry and some spectrochemical properties of the dinuclear Pd(II) complex with tppz.

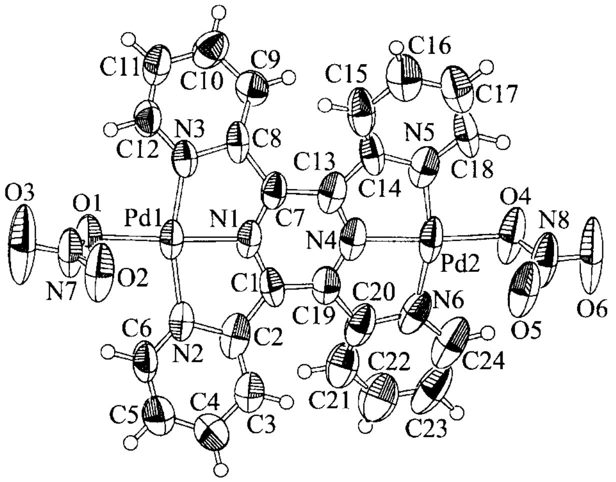

Fig. 1. Perspective view of $[Pd_2(NO_3)_2(tppz)]^{2+}$ with the atomic labeling scheme (ellipsoids at 50% probability).

An X-ray structural analysis for the dinuclear complex revealed the presence of a discrete divalent complex cation, two nitrate anions, and a half water molecule, $[Pd_2(NO_3)_2(tppz)]$-$(NO_3)_2 \cdot 0.5H_2O$. In this dinuclear complex, each of two Pd atoms is coordinated by three nitrogen atoms from tppz and one oxygen atom from nitrate (Fig. 1). Although the two Pd atoms take almost a square-planar geometry, there is a considerable deviation from planarity in the PdN_3O planes (max. dev. 0.063(5) Å). It is noteworthy that, furthermore, the central pyrazinyl moiety in tppz is significantly distorted from planarity, and the C(1)N(1)C(7) and C(13)N(4)C(19) planes form a dihedral angle of 10.4°. The $Pd–N_{\text{prazinyl}}$ distances (av 1.932(7) Å) are considerably shorter than the $Pd–N_{\text{pyridyl}}$ distances (av. 2.003(10) Å), which correspond well to those observed in other Pd(II) complexes with an aromatic imine.[16—18] Additionally, the intramolecular metal–metal distance is 6.4609(9) Å, indicating no direct interactions between the two metal ions, except for those through the π-electronic system of the central pyrazinyl moiety.

The electronic absorption spectrum of $[Pd_2(NO_3)_2$-$(tppz)]^{2+}$ exhibits four peaks at 456.0, 430.0, 400.5, and 308.0 nm, and two shoulders at 380^{sh} and 340^{sh} nm. Although all of the absorption bands are shifted toward the longer wavelength side in the solid state, both the absorption and reflection spectra are essentially consistent with each other. Among these bands, the 400.5, 380, 340, and 308.0 nm bands in the ultraviolet region are also observed in the case of other tppz complexes, and can be assigned as intraligand π–π^* transitions localized in tppz. Judging from the transition energies and intensities, on the other hand, the 456.0 and 430.0 nm bands are considered to be due to metal-to-ligand charge-transfer (MLCT) transitions. This indicates that the structure in solution is almost the same as that in the crystalline state.

The ^{1}H NMR spectrum of the dinuclear complex in diluted DNO_3 exhibits four signals (δ = 8.12, 8.46, 8.66, and 8.70) for sixteen hydrogen atoms. This implies that four pyridyl rings in the dinuclear complex are almost equivalent to each other. Although the ^{1}H NMR resonances are satisfactorily sharp and well-resolved, a broadening is observed only for the H atoms at the 3-positions of the pyridine rings. As can be seen in the crystal structure of $[Pd_2(NO_3)_2(tppz)]^{2+}$ (Fig. 1), a significant steric crowding exists between each of two sets of the neighboring H atoms at the 3-positions of the pyridine rings. This seems to result in the broadening observed for the signal of the H atoms at the 3-positions of the pyridine rings. No other peaks were found in the spectrum of the complex for periods exceeding 1 week. This indicates that the dinuclear complex is relatively stable in solution, as in the solid state.

Experimental

Preparation. To a methanol solution containing 0.49 g (2.2 mmol) of $Pd(CH_3COO)_2$ (Wako Pure Chemical Ind. Co., Ltd.) in 200 cm^3 of methanol was added 0.39 g (1.0 mmol) of tppz (Aldrich Chemical Co., Inc.); the mixture was then stirred at 50 °C for 24 h. After cooling to room temperature, 200 cm^3 of 0.1 mol dm^{-3} HNO_3 was added to the above reaction solution, and the mixture was evaporated to dryness. The obtained orange materials were dissolved in 0.1 mol dm^{-3} HNO_3, and the solution was left standing at 4 °C for a few days. The resulting $[Pd_2(NO_3)_2(tppz)](NO_3)_2 \cdot 0.5H_2O$ crystals (0.652 g, 76%) were collected by filtration. A well-formed crystal was used for an X-ray structural analysis. Calcd for $[Pd_2(NO_3)_2(tppz)](NO_3)_2 \cdot 0.5H_2O = C_{24}H_{17}N_{10}O_{12.5}Pd_2$: C, 33.59; H, 2.00; N, 16.32%. Found: C, 33.60; H, 1.89; N, 15.83%. Visible-UV spectrum in 0.1 mol dm^{-3} HNO_3 [ν_{max}, nm (ε 10^4 mol^{-1} dm^3 cm^{-1})]: 456.0 (2.92), 430.0 (3.12), 400.5 (4.46), 380 $(3.82)^{sh}$, 340 $(4.03)^{sh}$, 308.0 (4.81). Diffuse reflection spectrum in the crystalline state [ν_{max}, nm]: 463.5, 442.0, 420^{sh}, 390^{sh}, 355^{sh}, 330^{sh}. ^1H NMR (500 MHz, at 25 °C in 0.1 mol dm^{-3} DNO_3) $\delta = 8.12$ (t, 4H, H_4), 8.46 (t, 4H, H_5), 8.66 (br, 4H, H_3), 8.70 (d, 4H, H_6).

Measurement. The electronic absorption and diffuse reflection spectra were recorded with a JASCO Ubest V-560 and V-570 spectrophotometer, respectively. All of the measurements were carried out at room temperature. The ^1H NMR spectra were recorded with a Bruker AM-500 NMR spectrometer in DNO_3 diluted with D_2O (concentration: 0.1 mol dm^{-3}). The sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as an internal reference. An elemental analysis (C, H, N) was performed by the Analysis Center of the University of Tsukuba.

Crystallography. Intensity data were collected on a Rigaku RASA-7S four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.71069 Å). The structure was solved by a direct method using SIR92 and refined by a full-matrix least-squares method using the teXsan program package.[19] All calculations were performed on an Indigo II computer. Crystal data for $[Pd_2(tppz)(NO_3)_2](NO_3)_2 \cdot 0.5H_2O$: $C_{24}H_{17}N_{10}O_{12.5}Pd_2$, F.W. = 858.26, monoclinic, space group $P2_1/c$ (#14), a = 14.680(4), b = 13.224(3), c = 15.588(2) Å, β = 110.59(1)°, V = 2832(1) $Å^3$, Z = 4, D_{calc} = 2.012 g cm^{-3}, μ = 1.358 mm^{-1}, crystal size 0.38×0.35×0.30 mm, trans. factors 0.94—1.00, 5176 reflections measured ($2\theta_{max}$ = 55.0°), 2440 observed reflections [$I > 2.00\sigma(I)$] used in the refinement, R = 0.049, R_w = 0.062 and GOF = 1.54 for 442 parameters. The final atomic positional parameters are deposited in Tables S1—S3.[20] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 145231.

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20 Lists of final atomic coordinates and equivalent isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and bond distances and angles are deposited as Document No. 73045 at the Office of the Editor of Bull. Chem. Soc. Jpn.