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Synthesis and Dimeric Structure of a Palladium(II) Complex with Bis(benzoylacetoneimine)-1,3-propan-2-ol

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A palladium(II) complex with 2-hydroxy-*N*,*N′*-bis(1-methyl-3-hydroxy-3-phenol-2-propene-1-ylidene)-1,3-propanediamine (H_3L), $[Pd(HL)]_2$, was synthesized and characterized by measurements of the magnetic moment and the electronic spectra. The X-ray crystal structure shows that the compound has a dimeric structure with two planar N_2O_2 coordination environments, which is formed by hydrogen-bonds between the alkoxy groups and the coordinating keto groups.

Bis(benzoylacetoneimine)-1,3-propan-2-ol (2-hydroxy-*N*,*N′*-bis(1-methyl-3-hydroxy-3-phenol-2-propene-1-ylidene)-1,3-propanediamine, abbreviated as H_3L) is a unique ligand, which affords oligonuclear metal species as well as dinuclear metal complexes.[1–4] The ligand has five donor atoms consisting of two keto-oxygen and one alkoxy-oxygen, and two imino-nitrogen atoms. Usually, the central alkoxy group is deprotonated to bridge two metal atoms in a tridentate fashion for each metal atom, giving a square-planar environment with an exogenous ligand. This is the case for 3d-block metal ions, such as nickel(II) ion, and no one knows what species is formed for larger 4d-block metal ions, such as palladium(II) ion. Thus, pursuing our interest in palladium chemistry with polydentate ligands, we have started a study of this system, and have obtained the first example of a palladium(II) complex with the ligand H_3L, $[Pd(HL)]_2$ (**1**). Here, we report on the synthesis and structural characterization of **1**.

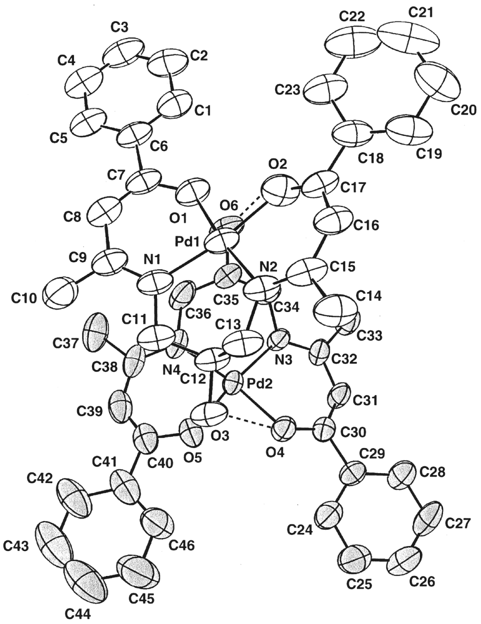

Fig. 1. Perspective view of the structure of **1** showing the atom labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–Pd2 5.133(1), Pd1–O1 1.987(4), Pd1–O2 2.003(4), Pd1–N1 2.008(5), Pd1–N2 2.004(5), Pd2–O4 1.997(5), Pd2–O5 1.975(5), Pd2–N3 2.012(6), Pd2–N4 2.019(6), O2–O6 2.819(7), O3–O4 2.763(6); O1–Pd1–O2 81.4(2), O1–Pd1–N1 91.9(2), O1–Pd1–N2 172.2(2), O2–Pd1–N1 173.3(2), O2–Pd1–N2 90.9(2), N1–Pd1–N2 95.8(2), O4–Pd2–O5 80.9(2), O4–Pd2–N3 90.3(2), O4–Pd2–N4 173.1(2), O5–Pd2–N3 171.0(2), O5–Pd2–N4 92.2(2), N3–Pd2–N4 96.6(2).

The treatment of H_3L with $Na_2[PdCl_4]$ in methanol containing triethylamine afforded reddish-orange crystals of **1**. An X-ray crystallographic study revealed that the ligand is not fully deprotonated and coordinated to one metal center with a N_2O_2 donor set in the HL form, giving a mononuclear [Pd(HL)] unit (Fig. 1). Each palladium atom has an essentially square-planar coordination environment within the deviations from the best plane of 0.02 Å. The Pd–N and Pd–O distances are 2.004(5)–2.019(6) Å and 1.975(5)–2.003(4) Å, respectively. These values are comparable to those observed for palladium amine complexes and palladium *β*-diketonates.[5] It is noteworthy that the two [Pd(HL)] units are held together by hydrogen bonds between the keto groups and the central alkoxy groups, which are not deprotonated [O2···O6 2.819(7) Å, O3···O4 2.763(6) Å], as shown in Fig. 2. The Pd1···Pd2 distance is 5.133(1) Å, which is too long for any metal-metal interaction. This is a unique example of stacked dinuclear complexes with head-to-tail arranged HL ligands [Pd1···O6 3.632(5), Pd1···C35 3.577(7), Pd2···O3 3.757(5), Pd2···C12 3.635(7), N2···C34 3.845(9) Å]. This situation may be encountered by the pres-

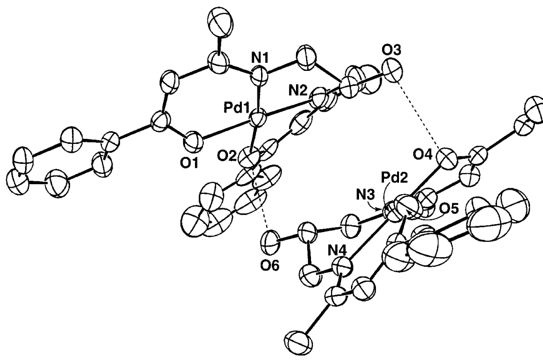

Fig. 2. Another view of the structure of **1**. Hydrogen atoms are omitted for clarity.

ence of alkoxy groups, which are not deprotonated. This is understandable, since alkoxo-bridged complexes have very rarely been isolated in palladium chemistry.[5]

The magnetic moment of **1** is 0.59 B.M. at room temperature. Because the residual paramagnetism can be ascribed to the temperature-independent paramagnetism of the palladium atom, we can thus conclude that the complex is diamagnetic with low-spin d^8 in accord with the square-planar geometry of the Pd(II) ion. The diffuse reflectance spectrum of **1** shows bands at 237, 325, 375, and 430 nm. The electronic spectrum of **1** in CH_2Cl_2 resembles the diffused reflectance spectrum. Judging from the transition energies and intensities, the former three bands in the ultraviolet region may be ascribed as being due to intraligand transitions, and the latter band may be assigned to a charge-transfer transition.

Experimental

Synthesis of 1. After H_3L (38 mg, 0.10 mmol) and sodium tetrachloropalladate(II) (29 mg, 0.10 mmol) were dissolved in methanol (10 cm^3), triethylamine (130 mg, 1.28 mmol) was added. The solution was kept at room temperature for several days. Reddish-orange plates were deposited and collected by filtration and dried in vacuo over P_2O_5: Yield, 22 mg (46%). Found: C, 57.03; H, 5.06; N, 5.70%. Calcd for $C_{23}H_{24}N_2O_3Pd$: C, 57.21; H, 5.01; N, 5.80%. IR (KBr) ν (OH) 3452, ν (C=C) 1588, 1563, ν (C=N) 1508 (s) cm^{-1}. μ_{eff} (286 K) 0.59 B.M. λ_M (CH_2Cl_2) 0 S mol^{-1} cm^2. Electronic spectrum in CH_2Cl_2: λ_{max} (ε dm^3 mol^{-1} cm^{-1}) 314 (9640), 352 (14600), 440 (2560) nm. Diffuse reflectance spectrum: 237, 325, 375, and 470 nm.

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin–Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO Infrared Spectrometer Model IR700 in the 4000–400 cm^{-1} region. The electronic conductivities were measured on a Horiba conductivity meter (DS-14). The magnetic susceptibilities were measured by the Faraday method. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[6] The effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility.

X-ray Crystal Structure Analysis. The crystal was sealed in a glass capillary together with the mother liquor and mounted on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation at 25±1 °C. The unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20 \le 2\theta \le 30°$. Intensitiy data were corrected for Lorentz-polarization effects. An absorption correction was performed using the Ψ-scan method. The structures were solved by direct methods and refined by full-matrix least-squares methods using the weighting scheme $w = 1/[\sigma^2(|F_0|) + (0.02|F_0|)^2 + 1.0]$. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to the alkoxy-oxygen atoms were located from the difference Fourier map and the other hydrogen atoms were inserted at their calculated positions. These hydrogen atoms were fixed at their positions. All of the calculations were carried out on a VAX station 4000 90A computer using a MolEN program package.[7]

Crystallographic data: for **1**; $C_{46}H_{48}N_4O_6Pd_2$, *F.W.* = 965.8, monoclinic, space group $P2_1/a$, $a = 14.464(3)$, $b = 18.276(2)$, $c = 16.662(3)$ Å, $\beta = 107.64(1)°$, $V = 4197(1)$ Å^3, $Z = 4$, $D_m = 1.54$, $D_c = 1.52$ g cm^{-3}, μ(Mo $K\alpha$) = 8.96 cm^{-1}, crystal dimensions 0.15 × 0.50 × 0.60 mm, 6797 reflections measured ($2\theta_{max} = 48°$), 5035 [$I \ge 2\sigma(I)$] used in the refinement, $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.044$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.052$. The X-ray analysis data have been deposited as Document No. 74013 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 152189.

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