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Syntheses and Structures of Dinuclear Palladium(II) and Platinum(II) Complexes with (2*S*,3*S*)-2,3-Diaminobicyclo[2.2.1]heptane

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Synopsis. Dinuclear complexes bridged by optically active diamines, $[Pd_2Cl_2(SS\text{-nbn})_3]Cl_2 \cdot 4H_2O$ (**1**) and $[Pt_2(en)_2(SS\text{-nbn})_2]Cl_4$ (**2**) (*SS*-nbn=(2*S*,3*S*)-2,3-diaminobicyclo[2.2.1]heptane, en=ethylenediamine) were prepared and characterized by X-ray crystallography for **1**. Pd(II) centers are square-planarly coordinated by Cl and three N of three bridging *SS*-nbn. Molecule **2** has been suggested to have two μ-*SS*-nbn and two chelating en.

The syntheses and X-ray structural analyses of various dinuclear Pt(II)[1)] and Pd(II)[2)] complexes with bidentate ligands have been extensively studied. In recent years, some Pt(II) dimers have proved to be excellent antitumor drugs.[3)] Farrell and co-workers first synthesized a series of complexes $[\{PtX_2Y\}_2(\text{diamine})]$ which have two units of the anticancer drug "cisplatin" linked by one molecule of bidentate diamine ligand.[3b,3c,4)] Except for their work, dimeric Pt(II) complexes bridged by diamines, particularly those with optically active diamines, have not been reported so far. Dinuclear Pd(II) complexes with bridging diamine have never been known. On the other hand, most well-known Pt(II) or Pd(II) dimers are of the type $[M_2(\mu\text{–}L)_mX_n]$ {M=Pt, Pd, L=bridging ligand, (m=2, n=2) or (m=4, n=0)}. To our knowledge, little is known about triply bridged Pt(II) or Pd(II) dimers. In this paper we report on the preparation and X-ray structural analysis of a novel dimer, $[Pd_2Cl_2(SS\text{-nbn})_3]Cl_2 \cdot 4H_2O$ (**1**) (*SS*-nbn=(2*S*,3*S*)-2,3-diaminobicyclo[2.2.1]heptane), together with a preliminary characterization of $[Pt_2(en)_2(SS\text{-nbn})_2]Cl_4$ (**2**).

Experimental

Preparation of Complexes. $Pd_2Cl_2(SS\text{-nbn})_3Cl_2 \cdot 4H_2O$ (1). An aqueous solution of *SS*-nbn·2HCl[5)] (1.2 mmol in 6 cm^3 of water) was passed through a column containing Dowex 1-X8 (OH^- form) with an additional amount of water used to liberate an aqueous solution of the free diamine. To the combined eluents was added a solution of $K_2[PdCl_4]$ (0.75 mmol in 2 cm^3 of water). The resulting solution was slowly evaporated to give 120 mg of crude **1**, which was recrystallized three times from water as yellow crystals. Found: C, 31.31; H, 5.91; N, 10.12%. Calcd for $C_{21}H_{42}N_6Cl_4Pd_2 \cdot 4H_2O$: C, 31.32; H, 6.26; N, 10.44%.

$[Pt_2(en)_2(SS\text{-nbn})_2]Cl_4$ (2). An aqueous *SS*-nbn solution was obtained from *SS*-nbn·2HCl (1.4 mmol), as described above. To this solution, 1.2 mmol of $[Pt(en)Cl_2]$[6)] was added. The resulting suspension was stirred at 60—80 °C until the mother complex was dissolved. The solution was then slowly evaporated to afford nearly colorless crystals (350 mg). The product was recrystallized twice from water. Found: C, 23.65; H, 4.89; N, 12.24%. Calcd for $C_9H_{22}N_4Cl_2Pt$: C, 23.90; H, 4.90; N, 12.39%.

Structure Determination. An Enraf-Nonius CAD4 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å) was used for data-collection experiments. The cell dimensions were accurately determined using 25 reflections over the range

Table 1. Fractional Atomic Coordinates and Isotropic Equivalent Thermal Parameters for $[Pd_2Cl_2(SS\text{-nbn})_3]_2{}^{4+}$ (**1**)

Atom	x	y	z	B_{eq}/Å^2
Pd(1)	−0.0338(1)	1/2	0.3467(1)	2.18(4)
Pd(2)	−0.1618(1)	0.5098(1)	0.4989(1)	2.31(4)
Pd(3)	0.1589(1)	0.2091(1)	0.0020(1)	2.66(5)
Pd(4)	0.0408(1)	0.21872(7)	0.1613(1)	2.62(5)
Cl(1)	0.0077(5)	0.6124(3)	0.3467(4)	3.5(2)
Cl(2)	−0.1575(4)	0.6260(3)	0.4996(4)	3.5(1)
Cl(3)	0.1316(5)	0.0937(3)	−0.0233(4)	3.7(2)
Cl(4)	0.0125(5)	0.1038(3)	0.1667(4)	4.0(2)
N(1)	0.123(1)	0.4883(7)	0.471(1)	3.2(4)
N(2)	−0.059(1)	0.3968(6)	0.3324(9)	2.5(3)
N(3)	−0.181(1)	0.5171(1)	0.212(1)	3.6(4)
N(4)	−0.0125(9)	0.5119(6)	0.6313(9)	2.6(3)
N(5)	−0.175(1)	0.409(1)	0.509(1)	2.7(4)
N(6)	−0.319(1)	0.5149(9)	0.373(1)	3.4(4)
N(7)	0.193(1)	0.315(1)	0.013(1)	3.2(5)
N(8)	0.310(1)	0.1864(9)	0.134(1)	3.3(5)
N(9)	0.007(1)	0.222(1)	−0.143(1)	2.7(4)
N(10)	−0.117(1)	0.224(1)	0.027(1)	2.8(5)
N(11)	0.054(1)	0.324(1)	0.166(1)	2.6(5)
N(12)	0.188(1)	0.207(1)	0.301(1)	2.7(4)
C(1)	0.146(1)	0.4784(9)	0.587(1)	2.8(5)
C(2)	0.088(1)	0.5333(8)	0.620(1)	2.6(4)
C(3)	0.186(1)	0.566(1)	0.722(1)	3.4(6)
C(4)	0.225(2)	0.508(1)	0.807(1)	5.4(6)
C(5)	0.284(1)	0.461(1)	0.767(1)	4.5(6)
C(6)	0.274(1)	0.486(1)	0.668(1)	3.7(5)
C(7)	0.277(1)	0.564(1)	0.688(1)	4.4(6)
C(11)	−0.145(1)	0.3630(8)	0.356(1)	3.2(5)
C(12)	−0.104(1)	0.3637(8)	0.483(1)	2.6(4)
C(13)	−0.109(1)	0.2861(8)	0.510(1)	3.9(6)
C(14)	−0.220(2)	0.259(1)	0.458(2)	5.0(7)
C(15)	−0.148(2)	0.2830(8)	0.336(2)	5.0(7)
C(16)	−0.251(2)	0.260(1)	0.342(2)	6.5(9)
C(17)	−0.048(2)	0.253(1)	0.453(2)	7(1)
C(21)	−0.273(1)	0.553(1)	0.225(1)	2.9(5)
C(22)	−0.341(1)	0.505(1)	0.258(1)	2.9(4)
C(23)	−0.464(2)	0.528(1)	0.174(2)	5.5(7)
C(24)	−0.478(2)	0.503(3)	0.073(2)	12(1)
C(25)	−0.412(2)	0.544(2)	0.031(2)	9(1)

Table 1. (Continued)

Atom	x	y	z	$B_{eq}/\text{Å}^2$
C(26)	−0.365(1)	0.589(1)	0.122(2)	4.8(7)
C(27)	−0.445(3)	0.604(2)	0.169(3)	9(1)
C(41)	0.075(1)	0.3628(8)	0.089(1)	2.9(5)
C(42)	0.195(1)	0.3536(8)	0.101(1)	3.2(5)
C(43)	0.227(2)	0.430(1)	0.095(2)	5.4(7)
C(44)	0.248(3)	0.457(1)	0.204(2)	6.4(9)
C(45)	0.134(3)	0.464(1)	0.195(2)	8(1)
C(46)	0.057(2)	0.440(1)	0.087(2)	4.7(7)
C(47)	0.111(2)	0.464(1)	0.021(2)	5.2(7)
C(51)	−0.124(1)	0.1937(9)	−0.078(1)	3.4(5)
C(52)	−0.096(1)	0.2408(8)	−0.141(1)	2.7(5)
C(53)	−0.190(2)	0.240(1)	−0.248(2)	6.2(7)
C(54)	−0.294(2)	0.278(1)	−0.257(2)	8(1)
C(55)	−0.327(2)	0.227(1)	−0.190(2)	7.4(8)
C(56)	−0.248(2)	0.173(1)	−0.155(2)	5.5(7)
C(57)	−0.235(2)	0.163(1)	−0.258(2)	6.4(7)
C(61)	0.297(2)	0.2076(9)	0.311(1)	3.7(5)
C(62)	0.305(1)	0.1565(8)	0.234(1)	3.7(5)
C(63)	0.416(2)	0.116(1)	0.315(2)	7.5(9)
C(64)	0.513(2)	0.163(2)	0.362(2)	11(1)
C(65)	0.499(2)	0.210(1)	0.439(2)	8(1)
C(66)	0.392(2)	0.188(1)	0.424(2)	5.8(8)
C(67)	0.386(2)	0.105(1)	0.411(2)	6.5(8)
Cl(5)	0.2085(5)	0.3448(4)	0.4361(4)	4.3(2)
Cl(6)	−0.2072(5)	0.3737(4)	0.0728(5)	4.5(2)
Cl(7A)	0.054(2)	0.362(1)	−0.235(2)	5.9(6)[a]
Cl(7B)	0.000(2)	0.375(1)	−0.236(2)	5.5(5)[a]
Cl(8A)	0.470(2)	0.329(2)	0.187(3)	5.9(6)[a]
Cl(8B)	0.452(3)	0.312(2)	0.149(3)	11(1)[a]
O(w1)	0.455(2)	0.813(1)	−0.985(2)	15(1)
O(w2)	0.311(2)	0.693(1)	0.933(1)	15(1)
O(w3)	0.199(2)	1.255(2)	0.736(3)	27(2)
O(w4)	0.214(4)	0.959(1)	0.152(2)	30(2)
O(w5)	0.557(2)	0.424(3)	0.725(3)	23(2)
O(w6)	−0.440(1)	0.3896(9)	0.386(1)	6.4(6)
O(w7)	0.643(3)	0.765(2)	0.325(3)	10(1)[a,b]
O(w8)	0.501(4)	0.844(3)	0.158(4)	16(2)[a,b]
O(w9)	0.497(4)	0.214(3)	0.061(4)	16(2)[a,b]
O(w10)	0.318(4)	0.288(2)	0.872(4)	14(2)[a,b]

a) Occupancy factors were 0.5. b) Refined isotropically.

$17° < 2\theta < 24°$. A total of 5238 reflections for **1** was obtained over the range $3° < 2\theta < 50°$, as observed ($F_o > 3\sigma(F_o)$), and was used for the structure determination. In addition to the usual data reduction, an absorption correction was made by an empirical method. The crystal data for **1** are as follows: **1**: $Pd_2Cl_4C_{21}H_{42}N_6 \cdot 4H_2O$; $F.W. = 805.3$; Space group $P2_1$; $a = 13.487(1)$, $b = 19.788(3)$, $c = 14.007(2)$ Å; $\beta = 117.83(1)°$; $V = 3306(14)$ Å^3; $Z = 4$; $D_c = 1.618$ g cm^{-3}; $D_m = 1.63$ g cm^{-3}; $R = 0.055$, $R_w = 0.049$ ($R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w(F_o)^2]^{1/2}$, $w = 1$); Crystal size $0.12 \times 0.27 \times 0.27$ (mm^3). The structures were solved by the Patterson analysis and subsequent difference Fourier syntheses, and refined by full-matrix least-squares techniques.[7] Scattering factors were taken from Ref. 8. For **1** all of the non-H atoms except for disordered water oxygens were refined anisotropically. The hydrogen atoms bound to carbon and nitrogen were included in the calculated positions as fixed parameters. The atomic coordinates and B_{eq} for **1** are given in Table 1.[9]

Measurements. The electronic absorption and circular dichroism (CD) spectra were recorded on a Shimadzu UV-210A spectrophotometer and a JASCO J-600 spectropolarimeter, respectively.

Results and Discussion

Although reports concerning the synthesis of nbn have appeared,[10,11] this diamine has not yet been optically resolved, and has not attracted any interest as its potential complexing agent. We have found that a reaction of *rac*-nbn with (2*R*,3*R*)-2,3-*di*-*O*-benzoyltartaric acid (*R*,*R*-BA) affords a R^*R^*-nbn·*R*,*R*-BA complex having a formula of $C_{25}H_{28}N_2O_8 \cdot 2H_2O$ diastereoselectively, from which an optically active (+)-R^*R^*-nbn has been obtained.[5] The absolute configuration of the diamine was determined by X-ray crystallography of the complex, and the *SS*-configuration was confirmed on the basis of the asymmetric carbon in the *R*,*R*-BA moiety.[5] A mixture of $K_2[PdCl_4]$ and *SS*-nbn in an approximately 2 : 3 molar ratio afforded bright-yellow crystals **1** together with a small amount of a white crystalline by-product, probably a quadrupolly bridged dinuclear complex having a formula of $[Pd_2(SS\text{-nbn})_4]Cl_4 \cdot 2H_2O$ based on an elemental analysis. When K_2PtCl_4 was treated with 1.5 equiv of the *SS*-nbn ligand, similarly to the Pd(II) case, an intense yellow color appeared, suggesting the formation of an analogous Pt(II) dimer as **1**, which could not yet be isolated as pure crystals. Compound **2** was easily obtained from an equimolar reaction of $[PtCl_2(en)]$ with *SS*-nbn. Since *SS*-nbn adopts a fully eclipsed conformation with respect to the C1–C2 bond, the torsion angle N1–C1–C2–N4 is opened to ca. 120°. Due to this fact and the very rigid framework, this ligand would be generally considered to act as a bridging bidentate ligand rather than a chelating ligand.

An X-ray structural analysis of **1** revealed the presence of two crystallographically independent dimeric cations (**1a** and **1b**) per an asymmetric unit. Since the uncoordinated Cl anions and water solvents of crystallization were found to be partially disordered, these were located adequately consistent with the chemical stoichiometry and crystallography. Both **1a** and **1b** complexes adopt quite a similar geometry. Figure 1 shows the structure of one of the cations (**1a**) with the numbering scheme. In both dimers, each palladium(II) ion is in the center of a quasi-square-planar arrangement formed by a coordinated Cl atom and three N atoms of three bridging *SS*-nbn molecules. The two square planes of each Pd(II) center are almost parallel; the dihedral angle between the two mean coordination planes (Pd, Cl, three N) is as small as 3.1—3.3°. *SS*-nbn adopts a configuration with an *exo*-(head) and an *endo*-(tail) oriented amino group. If we follow a sequence of ligating N1–N2–N3 atoms for the **1a** moiety around the Pd2–Pd1 axis, it can be said that this molecule possesses a head-to-head-to-tail arrangement as to the orientation of the amino group. (see Fig. 2a) The same is

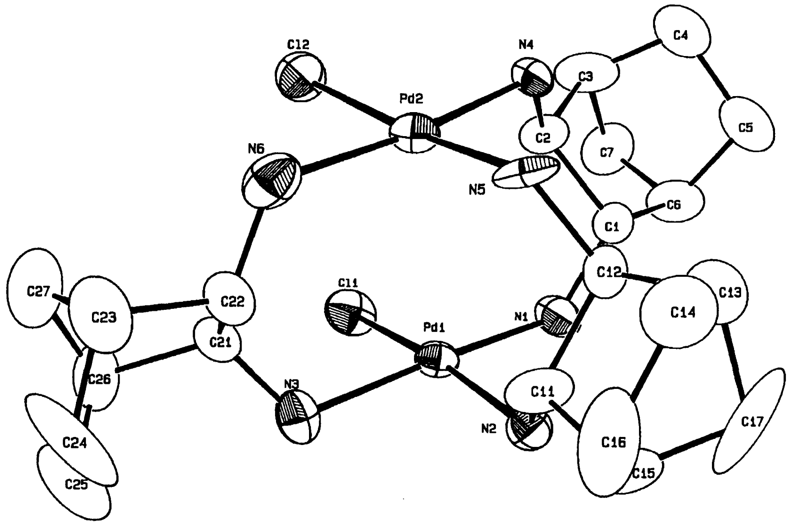
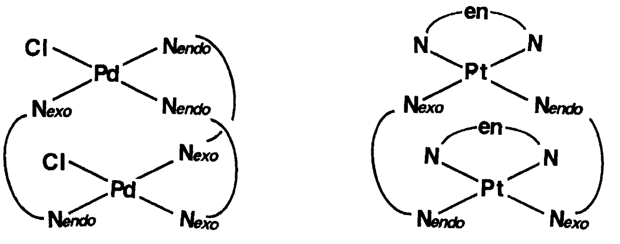


Fig. 1. Structure of **1a** cation determined by an X-ray analysis.



(a) (b)

Fig. 2. Schematic representation of the geometric arrangement of **1a** (a) and **2** (b), where N_{exo}–N_{endo} (N_{endo}–N_{exo}) and N-en-N, respectively, represent *SS*-nbn and the en ligand.

true for **1b**. Other possible geometric isomers with a head-to-head-to-head or a head-to-tail-to-head geometry could not be prepared under the examined conditions. The geometries about palladium(II) are slightly distorted square planar with diagonal Cl–Pd–$N_{opposite}$ and N–Pd–$N_{opposite}$ angles of 171.4(5)—173.1(6)° and 172.6(6)—173.6(7)°, respectively. The adjacent N–Pd–$N_{adjacent}$ angles (91.0(6)—93.4(6)°) are larger than the Cl–Pd–$N_{adjacent}$ angles (87.3(4)—88.4(4)°) due to a strain caused by the bulky ligand. The Pd–Pd bond distances range from 3.297(3) to 3.317(3) Å, indicating the lack of significant metal-metal bonding.[12] Both the Pd–Cl and Pd–N bond lengths were found to be normal.[13] Figure 2b illustrates the dinuclear cation of **2** which was found to be present by an X-ray analysis. The Pt(en) moieties resemble that for a structurally related complex $[Pt(en)(L)]_2$ (L=2-pyridone) reported so far.[14] The Pt–Pt separation (3.603(2) Å) is significantly greater compared with the direct Pt–Pt bond length.[12]

The electronic absorption and CD spectra of both complexes are shown in Fig. 3. Complex **1** showed a broad electronic spectrum in which only one peak at around 29900 $cm^{-1}$was found to be identical with the $^1A_{2g}\rightarrow{}^1A_{1g}$ transition band in $[PdCl(dien)]^+$.[15,16] For **2** the transition energies of the bands at 34700, ca. 39000 (sh), and 44300 cm^{-1} are roughly close to those of three bands for $[Pt(en)(S\text{-pn})]^{2+}$ which have been assigned to ^3E_g, $^1A_{2g}$, and $^1E_g\rightarrow{}^1A_{1g}$.[17] On the other hand, the CD pattern of **2** in the 22000—42000 cm^{-1} region was fairly different from that of monomeric Pt(II) complexes with N_4 donor atoms,[17,18] both in positions and intensities. This trend is more pronounced for **1**. These CD spectral feature may be due to an asymmetrically distorted structure, although a further discussion will be presented elsewhere.

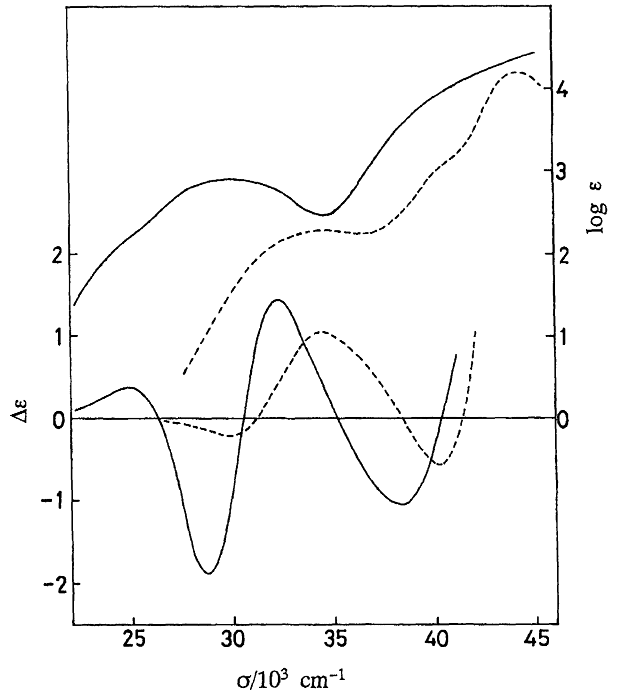


Fig. 3. Electronic absorption and CD spectra of **1** (—) and **2** (---) in an aqueous solution.

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