DALTON COMMUNICATION

A dimer-to-dimer metal–metal linear aggregate from a (μ-1,3-NO_3)$_2$ double-bridged *cis*-(2,2′-bipyridine)palladium(II) cofacial dimer

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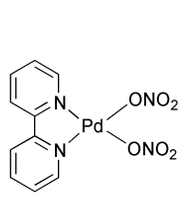
The first example of a (μ-1,3-NO_3)$_2$ double-bridged cofacial dimeric complex of a platinum group metal, {*cis*-[(2,2′-bipyridine)palladium(II)]$_2$(μ-1,3-NO_3)$_2$}(NO_3)(PF_6)·2CH_3CN·2H_2O was synthesized by reaction of silver(I) nitrate with *cis*-(2,2′-bipyridine)palladium(II) chloride in water and by recrystallization with NH_4PF_6 in acetonitrile; X-ray crystallographic analysis reveals that the cationic dimer is built upon (μ-1,3-NO_3)$_2$ double-bridging coordination to the two *cis*-(2,2′-bipyridine)Pd(II) units in a cofacial arrangement.

Recently, we have become interested in using *cis*-(2,2′-bipyridine)Pd(II) nitrate as an alternative to *cis*-(ethylenediamine)-Pd(II) nitrate in a coordinative array in molecular self-assembly,[1] which prompted us to understand its properties in solid state and in solution. To our knowledge, its solid structure is usually proposed as a monomer, (*cis*-2,2′-bipyridine)-Pd(NO_3)$_2$ (**1**), and its aqueous solution properties have been intensively investigated with very complex conclusions due to its hydrolysis.[2] Herein we report the synthesis and structure of a non-hydrolyzed dimer, {*cis*-[(2,2′-bipyridine)palladium(II)]$_2$(μ-1,3-NO_3)$_2$}$^{2+}$ (**2**). X-Ray crystallographic analysis reveals that the dimerized *cis*-(2,2′-bipyridine)Pd(II) units aggregate into a dimer-to-dimer linear conformation through direct metal–metal interaction[3] and π–π stacking.[4] Notably, the dimer was first reported to be linked by double nitrato-bridges (μ-1,3-NO_3)$_2$ in a cofacial arrangement, similar to the amido- or carboxylato-bridged "platinum blue"-type dimeric or polymeric Pt and Pd complexes.[5] It has been mentioned that there is a coordination mode of (μ-1,3-NO_3)$_2$ bonded to two metals,[6] which is scarcely seen in platinum group metals.[5–7]



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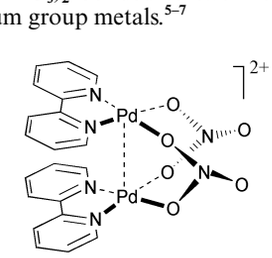

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Reaction of *cis*-(2,2′-bipyridine)Pd(II) chloride with two equivalents of silver nitrate in water resulted in the formation of a yellow solution after stirring for 8 h at room temperature. After removal of water, a yellow solid was obtained. Recrystallization in acetonitrile by layering ethyl ether gave yellow crystals in 80% yield based on a formula of (2,2′-bipyridine)Pd(NO_3)$_2$·0.5H_2O. According to the cationic dimer crystal structure reported in this communication, a formula for the yellow crystals was proposed as {*cis*-[(2,2′-bipyridine)-palladium(II)]$_2$(μ-1,3-NO_3)$_2$)}(NO_3)$_2$·H_2O, *i.e.*, [**2**](NO_3)$_2$·H_2O. Unlike the previously suggested unidentate nitrate coordinated monomer **1**,[2] the dimer [**2**](NO_3)$_2$·H_2O has two types of nitrate, the free and the bidentate bridging coordinated nitrates. Selected IR bands (solid, KBr pellet) were tentatively assigned,[6] 1384vs, 825m, 720m (NO_3^-); 766s cm^{-1} [(μ-1,3-NO_3)$_2$]. The free NO_3^- has D_{3h} symmetry, the totally symmetric N–O stretching mode is not IR active, but the doubly degenerate N–O stretching mode causes the strong band at about 1390 cm^{-1} and IR-active deformation modes give rise to medium bands at 830 and 720 cm^{-1}. The IR spectra clearly show characteristics of the free NO_3^- at 1384vs, 825m and 720m cm^{-1}. As for the (μ-1,3-NO_3)$_2$ doubly-bridged coordination mode, the case is quite complicated due to overlap with the absorptions of 2,2′-bipyridine ligand,[2] but the strong band at 766s cm^{-1} may be likely due to the (μ-1,3-NO_3)$_2$ coordination mode. Solution ^{1}H NMR spectra (300 MHz, CD_3CN, 298 K, TMS as internal standard) of [**2**](NO_3)$_2$·H_2O show two unique group peaks at 8.23–8.37 (br m, 12 H) and 7.68–7.72 (br t, 4 H) ppm, probably due to the stacking 2,2′-bipyridine ligands. The ESI MS spectra (saturated acetonitrile solution) gave important signals at *m*/*z* 324.1 (base), 711.5 (intense) and 1481.7 (weak), assigned to half of the dimer [½**2**]$^+$, dimer [**2** + NO_3]$^+$ and dimer-to-dimer aggregate [(**2** + 2NO_3)·(**2** + NO_3)]$^+$, respectively. It seems that cofacial dimerization and aggregates exist not only in the solid but also in solution.

Yellow prism crystals suitable for X-ray analysis† were obtained by slow diffusion of ethyl ether into a mixture of the crystalline nitrate product and NH_4PF_6 in acetonitrile. As shown in Fig. 1, the crystal structure has been established for the dimeric cation {*cis*-[(2,2′-bipyridine)palladium(II)]$_2$(μ-1,3-NO_3)$_2$}$^{2+}$ (**2**), crystallizing with the counter anions, one NO_3^- and one PF_6^-, and solvent molecules (two molecules of CH_3CN and two molecules of H_2O).

Fig. 1 depicts the dimer-to-dimer aggregate from dimer **2**. In each dimeric cation {*cis*-[(2,2′-bipyridine)palladium(II)]$_2$-(μ-1,3-NO_3)$_2$}$^{2+}$, both Pd(II) atoms are coordinated by a 2,2′-bipyridine and bridged by two NO_3^- ligands in a cofacial arrangement.[5] The geometry around Pd(II) is square planar, composed of two nitrogen atoms from the bipyridine and two oxygen atoms from two bridging nitrates. The two bridged coordinated squares are arranged in an offset face-to-face stacking mode by a dihedral angle of 17°, conforming to an approximate π–π interaction.[4] The resulting Pd1 ··· Pd2 distance of 2.848(3) Å is significantly shorter than that in the *cis*-(2,2′-bipyridine)Pd(II) dimeric complex of two head–tail triazolopyrimidinate (μ-1,3-NCN)$_2$ bridges [3.034(1) Å][5c] and some double-carboxylato-bridged (μ-1,3-OCO)$_2$ palladium complexes {[Pd(CH_3COO)$_2$]$_3$, 3.105(1)–3.203(1);[8a] [(π-C_3H_5)-Pd(CH_3COO)]$_2$, 2.94 Å[8b]} but is similar to that in other *cis*-(2,2′-bipyridine)Pd(II) analogues.[5d,e] The (μ-1,3-NO_3)$_2$ double-nitrato-bridged Pd–O bonds are significantly shorter [1.991(8)–

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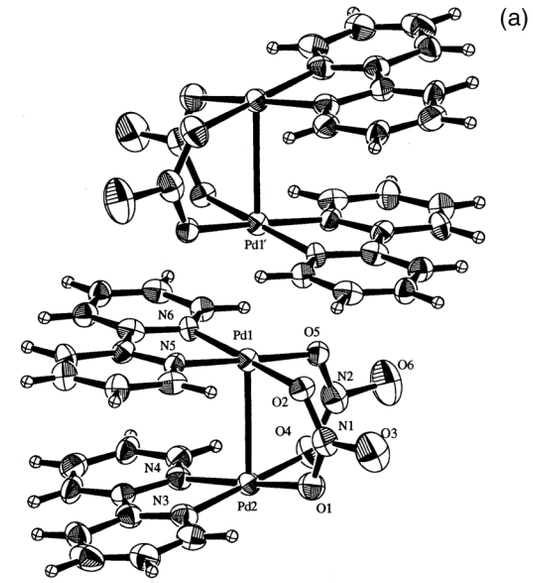

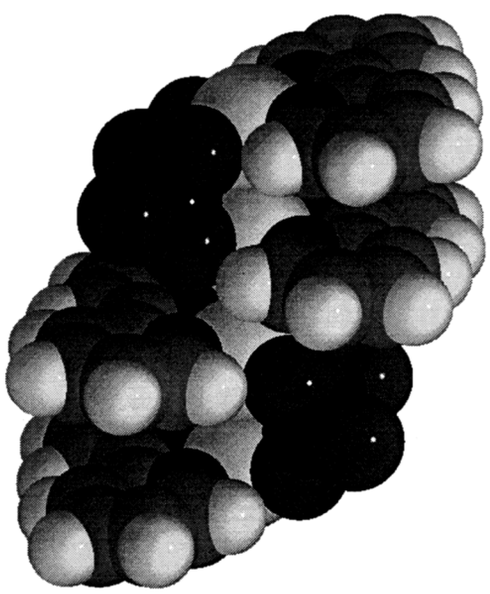

Fig. 1 (a) A thermal ellipsoid plot of **2** and the dimer-to-dimer aggregate, counter anions and solvents are omitted for clarity. (b) A space-filling diagram. Selected distances (Å) and bond angles (°): Pd1 ··· Pd2, 2.848(3); Pd1 ··· Pd1′, 3.117(3); Pd1–O2, 2.027(6); Pd1–O5, 1.998(6); Pd1–N5, 1.974(7); Pd1–N6, 2.016(8); Pd2–O1, 1.991(8); Pd2–O4, 2.019(8); Pd2–N3, 2.035(9); Pd2–N4, 2.023(8). O2–Pd1–O5, 90.1(3); O2–Pd1–N5, 94.4(3); O2–Pd1–N6, 175.1(3); O5–Pd1–N5, 175.6(3); O5–Pd1–N6, 94.3(3); N5–Pd1–N6, 81.3(3); O1–Pd2–O4, 88.7(3); O1–Pd2–N3, 93.9(3); O1–Pd2–N4, 173.9(3); O4–Pd2–N3, 177.4(3); O4–Pd2–N4, 96.2(3); N3–Pd2–N4, 81.3(4).

2.027(6) Å] than those of the unidentate coordination between Pd(II) and O of NO_3^- ligands (2.066 Å)[8c] but are very close to those of $[Pd(CH_3COO)_2]_3$ [1.973(9)–2.014(9) Å].[8a]

Interestingly, the two dimers aggregate alternatively along the linear chain consisting of the four Pd(II) atoms with Pd ··· Pd distances of 2.848(3) (intradimer) and 3.117(3) Å (interdimer), showing quite strong metal–metal interactions. The dimer-to-dimer aggregates do not extend infinitely but arrange in a zigzag orientation along crystal axis *a* through a normal π–π interaction (Fig. 2).

It should be noted that the strong π-acidic ligand, 2,2′-bipyridine, may play an important role in increasing the metal–

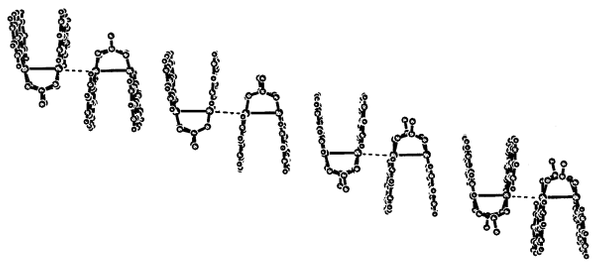

Fig. 2 A packing diagram of **2**.

metal interaction and stabilizing $(\mu\text{-}1,3\text{-}NO_3)_2$ bridging, since a cofacial dimeric Pd comlex with a π-acidic ligand, $[(\pi\text{-}C_3H_5)Pd(CH_3COO)]_2$, was reported very early.[8b] Further experiments will be directed toward extending this synthesis to other π-acidic ligands and to other platinum group metals. In addition, the $(\mu\text{-}1,3\text{-}NO_3)_2$ bridging cofacial dimeric complex does not show isomerization (head–head or head–tail) and the bridge is less sterically hindered than those previously reported,[5] hence the dimer **2** may be employed as a building block to construct functional coordination polymer possessing metal–metal interaction and π–π stacking.[3] From its cofacial geometry, this metal–metal contacted dimer could be regarded as an extended coordinative array with 90° coordination angle[1] to be employed in further molecular self-assembly.

Notes and references

† Crystal data for **2** was collected at 110.2 K on a Rigaku Raxis-II Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. $\mathbf{2}(NO_3)(PF_6)\cdot 2CH_3CN\cdot 2H_2O$, $C_{24}H_{26}N_9Pd_2PF_6O_{11}$, M = 974.29, triclinic, $P\bar{1}$, a = 13.18(1), b = 13.64(1), c = 11.68(1) Å, α = 113.32(6), β = 97.29(4), γ = 69.43(3)°, V = 1805(3) Å^3, Z = 2. D_c = 1.792 g cm^{-3}, $F(000)$ = 964, 2θ = 52.7° ($0 \ll h \ll 15$, $-15 \ll k \ll 16$, $-14 \ll l \ll 14$). A total of 5388 reflections was collected. The final cycle of full-matrix least-squares refinement was based on 4415 observed reflections [$I > 3.50\sigma(I)$] and 479 variable parameters and converged with final residuals of $R1$ = 0.072 and $wR2$ = 0.092. CCDC reference number 170480. See http://www.rsc.org/suppdata/dt/b1/b108470b/ for crystallographic data in CIF or other electronic format.

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