Self-assembly of Pd(II) and Pt(II) complexes with 2,2'-bipyridine-3,3'-16-crown-4 containing porous channels through anion···π interactions

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Abstract

Two complexes, [M(bpy-CE)(NO₃)₂] [M = Pd(II), Pt(II); bpy-CE = 2,2'-bipyridine-3,3'-16-crown-4], were synthesized and characterized by the X-ray diffraction study, and their isomorphous crystal structures confirm the formation of interesting porous frameworks with channel diameters of ca. 6.0 Å possibly through anion···π interactions.

Keywords: Self-assembly; Isomorphous; Porous; Channel; Anion···π interactions

Supramolecular noncovalent interactions are weak intermolecular forces that play a crucial role in both chemical and biological recognition [1], and these weak interactions involving hydrogen bonding, π···π, and other weak interactions have been widely exemplified. In addition, their combinations have been recently recognized as a very powerful and versatile strategy in material synthesis [2]. Thus, the main focus of crystal engineering has been focused on the design and synthesis of supramolecular networks or functional materials by means of noncovalent interactions [3], and their applications including chemical sieving, sensing, and catalysis based on these supramolecular systems have been examined and some have shown exciting progress [4].

Hydrogen bonding and cation···π interactions are of great importance for many biological systems and have been known for a long time [5], but in contrast, anion···π interactions are relatively less explored [6]. This is most likely due to the electron-donating character of anions, which is expected to lead to repulsive interactions with aromatic π electron clouds [7]. However, theoretical studies have demonstrated that they are energetically favorable interactions between electron deficient π systems (i.e., hexafluorobenzene, 1,3,5-triazine- and pyrazine-based derivatives) and anions (i.e., halides, N₃⁻, and NO₃⁻) [8]. In 2004, Meyer et al. reported a novel crystal structure showing anion···π interactions between Cl⁻ and the 1,3,5-triazine ring in a Carousel Cu(II)-triazine complex [9]. Later, Reedijk and co-workers have designed a series of 1,3,5-triazine-based derivatives toward anion···π studies, and many crystal structures have really indicated the existence of anion···π interactions based on crystallographic evidences and theoretical results [10]. In this context, the chemistry of anion···π interactions has recently become a growing interest as a branch of supramolecular chemistry. We report herein synthesis, structural, and spectroscopic properties of the self-assembled products, [M(bpy-CE)-(NO₃)₂] [M = Pd(II) 1, Pt(II) 2; bpy-CE = 2,2'-bipyridine-3,3'-16-crown-4].

2,2'-bipyridine-3,3'-16-crown-4 has been used in selective ion transport and metal-ion binding studies, where the allosteric effects were demonstrated by transition-metal-ion binding occurring in the bipyridyl moiety or...
alkali-metal-ion binding occurring in the crown-ether cavity, respectively [11]. Very recently, its Ru(II) complexes are also used to sense Pb(II) ions by taking advantage of luminescence properties and crown-ether cavities, and their studies show that the conformational restriction imposed upon \([\text{Ru(bpy)}_2(\text{bpy-CE})]^2^+\) (bpy = 2,2'-bipyridine) by metal-ion binding led to enhanced luminescence.[12] In relation to the bpy-CE ligand, only the crystal structures of \([\text{PtCl}_2(\text{bpy-CE})]\) [13] and \([\text{Ru(bpy)}_2(\text{bpy-CE})]\)(\text{PF}_6)_2 [12b] have been reported so far.

Upon reacting \(\text{Pd(NO}_3\text{)}_2\) or \(\text{Pt(NO}_3\text{)}_2\) with equimolar bpy-CE, 1 and 2 can be isolated as pale-yellow solids with ca. 78% and 65% yields, respectively [14]. Single crystals of 1 and 2 were grown from CH\(_3\)OH/diethyl ether, and both are isomorphous and crystallized in the space group of \(R\overline{3}c\), containing one disordered methanol and 2/3 water molecules in an asymmetric unit [15]. As shown in Fig. 1a and b, 1 and 2 form mononuclear complexes with square-planar geometries of Pd(II) and Pt(II) ions, where two nitrate anions are in an \textit{anti} conformation and two pyridyl groups are twisted by 26.0\(^\circ\) and 25.2\(^\circ\) for 1 and 2, respectively, slightly smaller than that of \([\text{PtCl}_2(\text{bpy-CE})]\) (31.1\(^\circ\)) [13].

Indeed, this is a consequence of steric effects in the crown-ether moiety, especially between the two methylene groups bonded to the bipyridyl fragment. In solution, the two rings are expected to flip rapidly, and this has been investigated and followed by dynamic \(^1\text{H} \text{NMR spectroscopy in [PtCl}_2(\text{bpy-CE})]\) [13]. The above process proceeds through a transition state in which the aromatic ring systems are coplanar.

More importantly, 1 and 2 are stacked to form interesting porous frameworks in the solid state, which possibly contain anion\(\cdots\pi\) interactions of 3.102 Å between the oxygen atoms of nitrates and the midpoints of C(3)==C(4) bonds and a channel diameter of ca. 6.0 Å, filled with disordered solvent molecules as shown in Fig. 1c and d. Consequently, the anion\(\cdots\pi\) distances of 3.102 Å in 1 and 2 are generally comparable to those values of Zn(II) and Cu(II) triazine-based derivative complexes showing coordinated nitrate\(\cdots\pi\) interactions (3.006–3.202 Å) [10e], which is also supported by the theoretical calculations. In fact, most of the anion\(\cdots\pi\) interactions exist in the aromatic systems, but they are still found in the olefin-like system [7g] and our previous work [16]. The

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**Fig. 1.** (a) A perspective view of 1. Selected bond lengths (Å) and angles (\(^\circ\)): Pd–N(1) 1.977(4), Pd–O(3) 2.018(3), N(1)–C(1) 1.335(6), N(1)–C(5) 1.376(5), C(1)–C(2) 1.382(7), C(2)–C(3) 1.370(7), C(3)–C(4) 1.403(7), C(4)–C(5) 1.383(6); N(1)–Pd–O(3) 94.07(15), C(6)–O(1)–C(7) 113.8(3), N(2)–O(3)–Pd 112.9(3), C(1)–N(1)–Pd 123.2(3). ORTEP diagram shows 50% probability ellipsoids. (b) A perspective view of 2. Selected bond lengths (Å) and angles (\(^\circ\)): Pt(1)–N(1) 1.977(4), Pt(1)–O(3) 2.030(4), N(1)–C(1) 1.327(6), N(1)–C(5) 1.375(5), C(1)–C(2) 1.386(8), C(2)–C(3) 1.370(7), C(3)–C(4) 1.403(7), C(4)–C(5) 1.383(6); N(1)–Pt(1)–O(3) 175.39(15), C(6)–O(1)–C(7) 114.2(4), N(2)–O(3)–Pt(1) 115.7(3), C(1)–N(1)–Pt(1) 123.2(3). ORTEP diagram shows 50% probability ellipsoids. (c) The packing diagram shows anion\(\cdots\pi\) interactions drawn by green lines for 1 and 2. (d) The anion\(\cdots\pi\) directed assembly leads to the formation of interesting porous frameworks containing a channel diameter of ca. 6.0 Å for 1 and 2.
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Appendix A. Supplementary data


References

[14] [Pd(bpy-CE)(NO3)2]: The reaction of Pd(NO3)2 (23 mg (0.1 mmol)) with bpy-CE [33 mg (0.1 mmol)] in CH2Cl2 (20 ml) at room temperature for 4 h gave a pale-yellow solution. The solution was filtered off and the filtrate was concentrated to ca. 5 mL to give a pale-yellow...
precipitate with a 78% yield. \(^1\)H NMR (400 MHz, CD\(_2\)CN, 25 °C): \(\delta\)(ppm) 8.47 (d, 1H, \(J_{HH} = 7.9\) Hz, N–CHCH), 8.24 (s, 1H, N–CHCHCH), 7.73 (dd, 1H, \(J_{HH} = 5.7\) Hz, N–CHCHCH), 4.64 (s, 2H, CCH\(_2\)–O), 3.72 (s, 4H, O–C\(_2\)H\(_2\)C\(_2\)H–O), 3.61 (s, 2H, O–C\(_2\)H–O). Anal. Calcld (%) for C\(_{18}\)H\(_{22}\)N\(_4\)O\(_{10}\)Pd: C, 38.55; H, 3.95; N, 9.99. Found (%): C, 38.26; H, 3.74; N, 9.75.

\([\text{Pt(bpy-CE)}(\text{NO}_3)_2]\) \(\text{I}\): It was prepared in a similar way as that of \(\text{I}\) with a 65% yield except that Pt(NO\(_3\))\(_2\) was used instead of Pd(NO\(_3\))\(_2\).

\(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C): \(\delta\)(ppm) 8.76 (d, 1H, \(J_{HH} = 5.5\) Hz, N–CHCH), 8.49 (d, 1H, \(J_{HH} = 9.0\) Hz, N–CHCHCH), 7.68 (dd, 1H, \(J_{HH} = 5.6\) Hz, N–CHCHCH), 4.72 (s, 2H, CCH\(_2\)–O), 3.80 (s, 4H, O–C\(_2\)H\(_2\)C\(_2\)H–O), 3.68 (s, 2H, O–C\(_2\)H–O). Anal. Calcld (%) for C\(_{18}\)H\(_{22}\)N\(_4\)O\(_{10}\)Pt: C, 33.29; H, 3.41; N, 8.63. Found (%): C, 33.46; H, 3.14; N, 8.95.

Crystal data for \(\text{I}\) • 3CH\(_3\)OH • 2H\(_2\)O: C\(_{57}\)H\(_{82}\)N\(_{12}\)O\(_{35}\)Pd\(_3\), \(M = 1814.55\), rhombohedral, space group \(R\bar{3}c\), \(a = 20.2351(9)\) Å, \(b = 20.2351(9)\), \(c = 30.5885(14)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 120^\circ\), \(V = 10846.7(8)\) Å\(^3\), \(Z = 18\), \(\mu = 0.839\) mm\(^{-1}\), \(F(000) = 5556\), 14,323 reflections collected. 2782 independent, \(R_{int} = 0.035\), final residuals \(R_1 = 0.035\), \(wR_2 = 0.051\) \([I > 2\sigma(I)]\); \(R_1 = 0.057\), \(wR_2 = 0.156\) (all data). Crystal data for \(\text{II}\) • 3CH\(_3\)OH • 2H\(_2\)O: C\(_{57}\)H\(_{82}\)N\(_{12}\)O\(_{35}\)Pt\(_3\), \(M = 2080.71\), rhombohedral, space group \(R\bar{3}c\), \(a = 20.4196(8)\) Å, \(b = 20.4196(8)\), \(c = 30.8786(17)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 120^\circ\), \(V = 11150.2(9)\) Å\(^3\), \(Z = 18\), \(\mu = 5.732\) mm\(^{-1}\), \(F(000) = 6202\), 31,514 reflections collected. 3078 independent, \(R_{int} = 0.036\), final residuals \(R_1 = 0.035\), \(wR_2 = 0.092\) \([I > 2\sigma(I)]\); \(R_1 = 0.042\), \(wR_2 = 0.098\) (all data).

[15] Crystal data for \(\text{I}\) • 3CH\(_3\)OH • 2H\(_2\)O: C\(_{57}\)H\(_{82}\)N\(_{12}\)O\(_{35}\)Pd\(_3\), \(M = 1814.55\), rhombohedral, space group \(R\bar{3}c\), \(a = 20.2351(9)\), \(b = 20.2351(9)\), \(c = 30.5885(14)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 120^\circ\), \(V = 10846.7(8)\) Å\(^3\), \(Z = 18\), \(\mu = 0.839\) mm\(^{-1}\), \(F(000) = 5556\), 14,323 reflections collected. 2782 independent, \(R_{int} = 0.035\), final residuals \(R_1 = 0.035\), \(wR_2 = 0.051\) \([I > 2\sigma(I)]\); \(R_1 = 0.057\), \(wR_2 = 0.156\) (all data). Crystal data for \(\text{II}\) • 3CH\(_3\)OH • 2H\(_2\)O: C\(_{57}\)H\(_{82}\)N\(_{12}\)O\(_{35}\)Pt\(_3\), \(M = 2080.71\), rhombohedral, space group \(R\bar{3}c\), \(a = 20.4196(8)\) Å, \(b = 20.4196(8)\), \(c = 30.8786(17)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 120^\circ\), \(V = 11150.2(9)\) Å\(^3\), \(Z = 18\), \(\mu = 5.732\) mm\(^{-1}\), \(F(000) = 6202\), 31,514 reflections collected. 3078 independent, \(R_{int} = 0.036\), final residuals \(R_1 = 0.035\), \(wR_2 = 0.092\) \([I > 2\sigma(I)]\); \(R_1 = 0.042\), \(wR_2 = 0.098\) (all data).
