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Self-Assembly of Predesigned Trimetallic Macrocycles Based on Benzimidazole as Nonlinear Bridging Motifs: Crystal Structure of a Luminescent Platinum(II) Cyclic Trimer[**]

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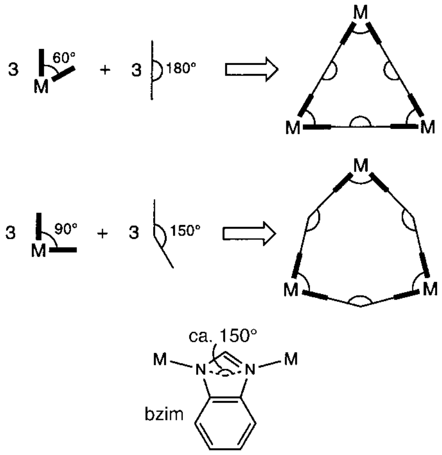
Self-assembly of mono- and polycyclic supermolecules is a challenging yet prolific area of research.[1] In the context of metallomacrocycles with internal cavities, efforts have focused on the design and construction of molecular squares,[2] while triangular arrays have remained relatively unexplored. In theory, if the building blocks are sufficiently rigid, the alternating combination of three subunits extending 60° bite angles with three linear linkers would constitute a equilateral triangle (Scheme 1). In practice, the former is difficult to attain at metal centers but is available in a number of bidentate ligands, and thus trimeric assemblies are formed in tandem with linear two-coordinate or *trans*-configured metallic bridges.[3] Triangular macrocycles bearing metal vertices and supported by 4,4′-bipyridine,[4] 2,2′-bipyrazine,[5] 1,3-bis(1-methylbenzimidazol-2-yl)benzene,[6] and various nucleobases[7] have been synthesized. However, only moderate selectivities are encountered in these reactions due to the presence of multiple chelating sites and other geometrical factors (ligand flexibility, angle strain at metal center), and mixtures of products are often afforded.



Scheme 1. Strategies for the syntheis of trimeric macrocycles with metal vertices.

We propose a *ligand-directed* strategy for the fabrication of trimetallic macrocycles by using bzim (bzim = N-anion of benzimidazole) as a rigid nonlinear bridging motif. Coupling of three edges exhibiting 150° angles with right-angled vertices (i.e. *cis* binding sites at metal centers residing in square-planar and octahedral environments) is anticipated to yield a cyclic trimer,[8] and based on this premise, the predefined geometry and unambiguous binding mode of the bidentate bzim ligand is ideal (Scheme 1). We report herein the highly efficient syntheses of luminescent platinum(II) trimeric assemblies directed by N-deprotonated benzimidazole.

Treatment of the luminescent cyclometalated Pt^{II} precursors [Pt(thpy)(Hthpy)Cl][9a] (Hthpy = 2-(2′-thienyl)pyridine) and [nBu$_4$N][Pt(bzqn)Cl$_2$][9b] (Hbzqn = 7,8-benzoquinoline) with sodium benzimidazolate afforded [Pt(thpy)(bzim)]$_3$ (**1**) and [Pt(bzqn)(bzim)]$_3$ (**2**) as orange and yellow crystalline solids, respectively, in high yields (80–90 %). In the FAB mass spectra, the anticipated molecular ion clusters for **1** and **2** are observed at m/z 1417 and 1471, respectively. The trimeric nature of **1** was confirmed by X-ray crystallography.[10]

The molecular structure of **1** (Figure 1) consists of alternating [(thpy)Pt] vertices and benzimidazolate edges. The slightly distorted square-planar geometry around each platinum center comprises the N and *ortho*-C atoms of thpy and

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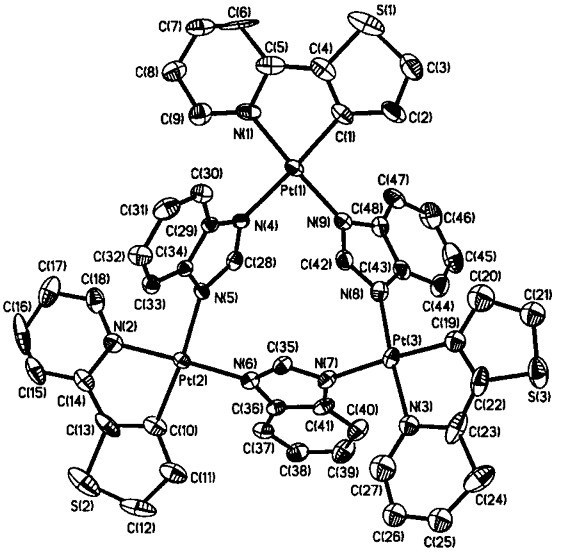

Figure 1. Perspective view of **1** (30% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity). Selected bond lengths [Å] and angles [°]: Pt(2)–N(2) 2.03(1), Pt(2)–C(10) 2.01(1), Pt(2)–N(5) 2.100(9), Pt(2)–N(6) 2.016(9), N(4)–C(28) 1.33(1), N(5)–C(28) 1.35(1), N(6)–C(35) 1.34(1), N(7)–C(35) 1.32(1), N(8)–C(42) 1.34(1), N(9)–C(42) 1.33(1); N(2)-Pt(2)-C(10) 80.7(5), N(5)-Pt(2)-N(6) 89.0(3), N(7)-Pt(3)-N(8) 88.4(4), N(4)-Pt(1)-N(9) 87.8(3), Pt(1)-N(4)-C(28) 130.3(7), N(4)-C(28)-N(5) 114.6(9), Pt(2)-N(5)-C(28) 132.8(8).

two N atoms of different bzim bridges. The comparable interatomic distances within the N-C-N fragments of the bzim moieties (mean 1.33 Å) imply considerable delocalization after N-deprotonation. The three N-Pt-N angles within the macrocycle (range 87.8(3)–89.0(3)°) show minimal strain, in contrast to Fujita's proposed triangles containing 4,4′-bipyridine.[4] The Pt–N(bzim) interactions are out of the triplatinum plane (Figure 2) because the bidentate bite angles exhibited by the bzim anions (range 138–140°) deviate slightly from 150°. This inherent coordination geometry ensures the successful and efficient assembly of the trimeric macrocycles described here. Interestingly, the bzim groups are orientated in a *syn, anti, anti* (two-up, one-down) fashion to create an open cavity with different faces, which is reminiscent of the partial cone conformation in calixarenes.[11] From the mean plane through the platinum atoms, the angle to the *syn* bzim units is 60° (av), while the inclination of the unique bzim is 77°. The opening at the *syn* bzim rim is about 7.4 Å, which narrows considerably towards the core to about 4.7 Å at the imidazole centroids. The Pt···Pt distances are 6.1 Å (av), while the depth of the cavity is approximately 5 Å. This molecular pocket has lower symmetry than previously reported metallomacrocycles,[2e] and this may have important consequences for future work towards molecular hosts. In addition, $\pi-\pi$ interactions are evident between thpy systems in adjacent molecules, with interplanar separations of around 3.5 Å.

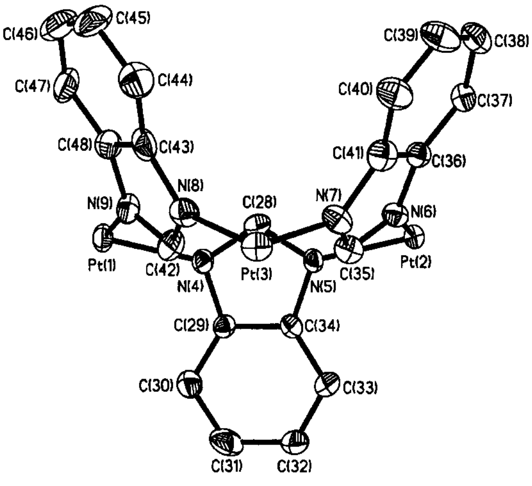

Figure 2. Perspective view of **1** showing orientations of benzimidazolate ligands (thpy groups are omitted for clarity).

The absorption spectrum of **1** in CH_2Cl_2 contains bands at 270–360, 400–430, and 480–560 nm, which can be assigned to spin-allowed ligand-centered (^{1}LC, $\pi_{thpy}\rightarrow\pi^*_{thpy}$ with metal perturbation) and spin-allowed and spin-forbidden metal-to-ligand charge transfer (^{1}MLCT and ^{3}MLCT, $d_{Pt}\rightarrow\pi^*_{thpy}$) transitions, respectively.[12] The UV/Vis spectrum of **2** is comparable to that of the bis(cyclometalated) derivative [Pt(bzqn)$_2$].[13] Complex **1** is emissive at 301 K in CH_2Cl_2, with peak maxima at 560 (sh, 580 nm) and 606 nm (sh, 636 and 661 nm; lifetime, $\tau = 8$ µs; quantum yield, $\Phi = 0.016$) that are slightly blue-shifted to 557 (sh, 575 nm) and 601 nm (sh, 633 and 656 nm) at 77 K. Based on previous studies[12, 13] and the observation of minor solvatochromic effects (< 10 nm), these emissions are tentatively assigned as MLCT transitions with LC character. In the crystalline form, multiple emission with λ_{max} at 571, 617, and 664 nm are apparent at 301 K. The substantial red shift of the 664 nm band relative to that observed in the solution state is attributed to excimeric emission arising from π-stacking in the solid state (see above).[14] In contrast, no emission is observed for **2** in CH_2Cl_2 or in the solid state at room temperature, although weak emission is evident at 77 K in solid state. Hence complex **1** has greater potential for photoinduced energy and electron transfer applications than **2**.

In conclusion, we have described a simple yet efficient methodology for the synthesis of trimeric platinum(II) macrocycles, which are structurally related to calixarenes. We anticipate that this strategy will be applicable to other square-planar and octahedral metal complexes. In view of the established photoluminescence of cyclometalated Pt^{II} species,[15] this study paves the way for the design of molecular sensors with large cavities[16] based on suitable nonlinear bidentate ligands with rigid, predefined geometry.

Experimental Section

1: A mixture of benzimidazole (0.05 g, 0.39 mmol) and excess NaH in THF (10 mL) under a N_2 atmosphere was stirred for 20 min until the evolution of hydrogen ceased. The solution was filtered, added to [Pt(thpy)(Hthpy)Cl] (0.20 g, 0.36 mmol) in CH_2Cl_2 (15 mL), and stirred at reflux for 12 h. The resultant orange solution was concentrated to 5 mL and addition of diethyl ether afforded an orange solid. Slow evaporation of an acetone/benzene solution yielded orange crystals (yield 88%). Satisfactory elemental analysis was obtained; ^{1}H NMR (500 MHz, CD_2Cl_2, 27 °C, TMS): δ = 8.40–6.31 (m); ^{13}C NMR (126 MHz, [D$_6$]DMSO, 27 °C, TMS): δ = 162.6, 150.6–148.3, 144.2–140.3, 133.3–132.7, 128.8–128.1, 123.0–115.5, 110.5; IR (Nujol): $\tilde{\nu}$ = 1605 cm^{-1} (C=N); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 277 (47000), 337 (22000), 357 (18000), 409 (5200), 421 (4800), 480 (110), 494 (110), 512 (110), 535(80), 554 nm (70); FAB-MS: m/z (%): 1417 (100) [M^+], 1300 (30) [$M^+ -$ bzim].

2: As for **1** using benzimidazole (0.04 g, 0.33 mmol), excess NaH, and [$n\mathrm{Bu_4N}$][Pt(bzqn)$\mathrm{Cl_2}$] (0.20 g, 0.29 mmol). A yellow precipitate was afforded after reflux for 12 h. Slow evaporation of an acetone/benzene solution yielded yellow crystals (yield 84%). Satisfactory elemental analysis was obtained; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 27°C, TMS): $\delta = 9.26$-6.91 (m); ^{13}C NMR (126 MHz, [D$_6$]DMSO, 27°C, TMS): $\delta = 156.7$, 149.4–148.8, 144.2–138.4, 133.4–115.7, 110.5; IR (Nujol): $\tilde{\nu} = 1620$, 1610 cm^{-1} (C=N); UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ (ε) = 271 (70000), 278 (73000), 358 (14000), 372 (14000), 413 (4000), 469 nm (440); FAB-MS: m/z (%): 1471 (100) [M^+], 1354 (25) [$M^+ -$ bzim].

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A New Type of Glycosidic Linkage: An Open-Chain Acetal-Linked *N*-Acetylgalactosamine in the Core Part of the Lipopolysaccharides from *Proteus* Microorganisms**

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Monosaccharides in natural compounds are usually present in a cyclic hemiacetal form, in which the exocyclic hemiacetal oxygen atom is used for the connection to the aglycon. Herein we report the identification of a new type of linkage between monosaccharides found in the core part of the lipopolysaccharides (LPS) from two serotypes of *Proteus*. LPS is a component of the outer membrane of Gram-negative bacteria, and comprises three regions: the O-antigenic polysaccharide, the lipid A, and the core, a nonrepetitive oligosaccharide linking the O-antigenic polysaccharide to the lipid A.[1] Normally, core oligosaccharides have complex structures, relatively conserved for each type of bacteria. The biological

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