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Molecular Triangle from enPt^{II} and 2,2′-Bipyrazine**

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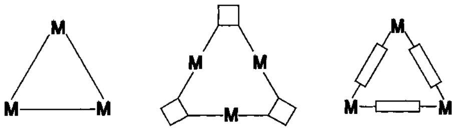
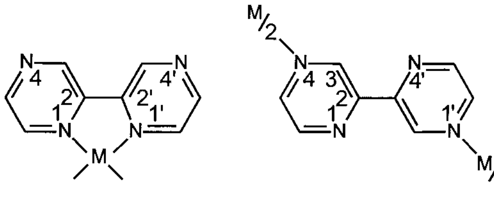
Cyclic trimetallic complexes with metal–metal bonds[1] or bridging ligands[2,3] are known in large numbers (Scheme 1), but examples containing bridging heterocycles arranged approximately perpendicular to the metal triangle are relatively rare.[3] Here we report on a trinuclear Pt^{II} complex containing 2,2′-bipyrazine ligands (bpz) which fulfills the latter requirement and forms spontaneously in a self-assembly process. The compound is of interest with respect to the formation and stability of "molecular squares"[4] from 4,4′-bipyridine ligands and rectangular, square-planar metal units. However, the impression that combining these building blocks always leads to squares and rectangles is misleading. As first indicated by Fujita and co-workers,[5] *cis*-Pd^{II}en (en = ethylenediamine) can be used with 4,4′-bipy to form both molecular squares and triangles or both in a concentration-dependent equilibrium.



Scheme 1.



Scheme 2.

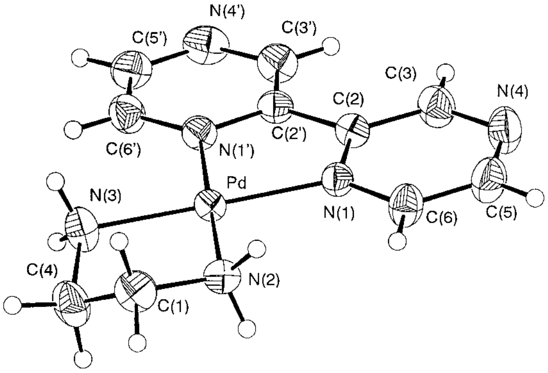


Figure 1. Structure of cation of **1**. Selected bond lengths [Å] and angles [°]: Pd–N(1) 2.034(3), Pd–N(1′) 2.025(3), Pd–N(2) 2.026(3), Pd–N(3) 2.023(3); N(1)-Pd-N(1′) 80.7(1), N(1)-Pd-N(2) 98.8(1), N(1)-Pd-N(3) 178.2(1), N(1′)-Pd-N(2) 179.4(1), N(1′)-Pd-N(3) 97.6(1), N(2)-Pd-N(3) 83.0(1), N(4)-Pd-N(4′) 73.0(1).

As demonstrated here, the heterocyclic ligand 2,2′-bipyrazine reacts with square-planar enM^{II} units (M = Pd or Pt) either with chelate or bridge formation (Scheme 2). In the first case bpz is practically coplanar with the coordination plane of M, whereas in the second case, following cyclization to the trinuclear complex, it is virtually perpendicular to the metal triangle. Compound **1** forms in 40% yield upon reaction of $[(en)Pd(H_2O)_2](NO_3)_2$ with bpz[6] and recrystallization of the crude product from water in the presence of $NaClO_4$. Figure 1 depicts the cation of **1**. The results of the X-ray structure determination[7–9] reveal that the N(1)-Pd-N(1′) angle of 80.7(1)° deviates markedly from 90° and is in

$[(en)Pd(bpz)](ClO_4)_2$ **1**

$[(en)Pt(bpz)](NO_3)_2$ **1′**

the range found for related complexes containing 2,2′-bipyridine[10] or *o*-phenanthroline.[11] In the case of a Ru^{II} compound containing a chelating bpz ligand, this value is 78.92(6)°.[12] The geometry of the Pd(en) unit is normal.[13] Attempts to use cation **1** as a corner stone in the preparation of a molecular square in the true sense[14]—that is, cyclization through the 4 and 4′ positions via linear metal units—have been unsuccessful as yet. We assume that the low basicity[15] of these positions rather than the nonideal N(4)-Pd-N(4′) angle

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(73.0(1)°) is responsible. However, we feel that metal units with a pronounced ability for π backdonation (e.g. Ru^{II})[16] might in principle be capable of forming such squares. There are many examples of complexes containing bridging pyrazine ligands[4e,f,17] for which similar criteria apply.

The Pt analogue of the cation in **1**, **1'**, was isolated as the nitrate salt and characterized by ^{1}H NMR spectroscopy. The sensitivity of crystals of **1'** has thus far prevented an X-ray crystal structure analysis.

A second Pt complex, which proved to be the cyclic species **2**, displays a markedly different ^{1}H NMR spectrum from **1'**. The cation of **2**[18] has C_2 symmetry (Figure 2). The three Pt atoms form an approximately equilateral triangle with Pt(1)−Pt(1)^i and Pt(1)−Pt(2) distances of 9.404(3) and 9.422(1) Å, respectively. The C_2 axis runs through Pt(2). In contrast to **1**, the bpz ligand in **2** is in a transoid orientation following rotation about the central C(2)−C(2') bond. The three metal atoms are therefore linked through N(4) atoms. The N(4)-Pt-N(4') angles at the Pt atoms are 87.1(5)° for Pt(1) and Pt(1)^i and 93.3(9)° for Pt(2).

$[\{(en)Pt(bpz)\}_3](NO_3)_6$ **2**

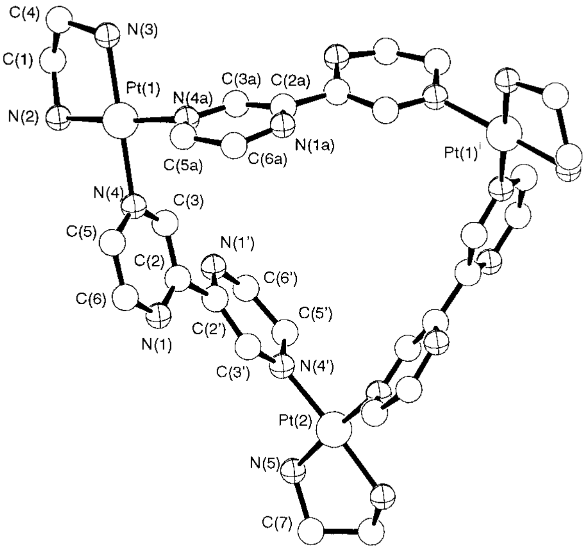

Figure 2. Structure of cation of **2**. Selected bond lengths [Å] and angles [°]: Pt(1)−N(4a) 2.017(13), Pt(1)−N(4) 2.075(14), Pt(1)−N(2) 1.97(2), Pt(1)−N(3) 2.043(13), Pt(2)−N(4') 1.98(2), Pt(2)−N(5) 1.982(13); N(4a)-Pt(1)-N(4) 87.1(5), N(1)-Pt(1)-N(2) 175.5(5), N(4a)-Pt(1)-N(3) 93.8(5), N(4)-Pt(1)-N(2) 95.7(7), N(4)-Pt(1)-N(3) 178.6(7), N(2)-Pt(1)-N(3) 83.4(6), N(4')-Pt(2)-N(4')^i 93.3(9), N(5)-Pt-N(5)^i 84.6(7), N(4')-Pt(2)-N(5) 91.1(6), N(4')-Pt-N(5)^i 175.7(6).

The two pyrazine rings of each bpz ligand in **2** are markedly twisted with respect to each other (21 and 27°), which appears to be crucial for formation of the triangle. Considering the fact that similar twist angles have been observed for 2,2'-bipyridine in the gas phase and in solution,[19] it appears likely that formation of **2** and possibly even of the (en)Pd/4,4'-bipyridine triangle[5] is facilitated by this feature.

Formation of the chelate complex **1'** and of the molecular triangle **2** from $[(en)Pt(H_2O)_2]^{2+}$ and bpz apparently takes place from two different linkage isomers: bonding through N(1) for **1'** and through N(4) for **2**. Following the reactions with NMR spectroscopy (^{1}H, ^{195}Pt) confirms this assumption. In the ^{1}H NMR spectra the number of resonances decreases as the reactions proceed, as expected for formation of **1'** from $[(en)Pt(H_2O)(bpz\text{-}N(1))]^{2+}$ and of **2** from $[(en)Pt(H_2O)(bpz\text{-}N(4))]^{2+}$.

Based on model studies, it appears that the pyrazine rings of the bpz ligand in **2** can undergo rather facile rotation about the C(2)−C(2') bond to produce different rotational isomers. The dynamics of this process and properties of the hydrophobic cavity of the cation of **2** with regard to possible host–guest interactions are subjects of ongoing work.

Experimental Section

1: $(en)PdCl_2$ (214 mg, 0.90 mmol) was suspended in water (30 mL) and stirred for 2 h at room temperature (RT) with $AgNO_3$ (297 mg, 1.75 mmol). After removal of AgCl by filtration and addition of bpz (138 mg, 0.87 mmol) to the filtrate, the mixture was stirred for 24 h at RT. The solution (pH 3.0) was then filtered and concentrated to 5 mL under vacuum. $NaClO_4$ (275 mg, 2.25 mmol) was then added to the yellow solution. Yellow **1** was obtained in 40% yield within two days at 4 °C. Satisfactory elemental analysis for $PdC_{10}H_{14}N_6O_8Cl_2$. ^{1}H NMR (200 MHz, D_2O, TSP): $\delta = 3.10$ (s, 4H, CH_2), 8.53 (dd, $^3J = 3.2$ Hz, $^5J = 1.1$ Hz, 2H, aromatic), 9.07 (d, $^3J = 3.2$ Hz, 2H, aromatic), 9.78 (d, $^5J = 0.9$ Hz, 2H, aromatic).

1' and **2**: $(en)PtCl_2$ (325 mg, 0.99 mmol) was suspended in water (30 mL), $AgNO_3$ (323 mg, 1.90 mmol) added, and the mixture stirred for 1 h at 80 °C. After the mixture was cooled and AgCl removed by filtration, bpz (150 mg, 0.95 mmol) was added, and the mixture stirred for three days at 45 °C. The reaction mixture was filtered and concentrated to 5 mL under vacuum. $NaNO_3$ (170 mg, 2.0 mmol) was then added to the yellow solution (pH 4.5). Yellow $\mathbf{2} \cdot n\,H_2O$ was isolated in 35% yield after 6–10 d at 4 °C. Satisfactory elemental analysis for $Pt_3C_{30}H_{54}N_{24}O_{24}$) (for $n = 6$, the X-ray structure analysis gave $n = 4$). ^{1}H NMR (200 MHz, D_2O, TSP): $\delta = 2.85$ (s, 4H, CH_2), 8.84 (dd, $^3J = 3.2$ Hz, $^5J = 1.1$ Hz, 2H, aromatic), 9.10 (d, $^3J = 3.2$ Hz, 2H, aromatic), 9.33 (s, 2H, aromatic); ^{195}Pt NMR (43 MHz, D_2O): $\delta = -2753$ (PtN_4). Needles of **1'** are formed as a side product (5%) in the synthesis of **2** if the reaction time is shortened by two days and the reaction temperature kept at 25 °C. ^{1}H NMR (200 MHz, D_2O, TSP): $\delta = 2.88$ (s, 4H, CH_2), 8.90 (dd, $^3J = 3.2$ Hz, $^5J = 0.8$ Hz, 2H, aromatic), 9.15 (d, $^3J = 3.2$ Hz, 2H, aromatic), 9.79 (d, $^5J = 0.8$ Hz, 2H, aromatic); ^{195}Pt NMR (43 MHz, D_2O): $\delta = -2749$ (PtN_4).

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[7] Crystal structure analysis of **1**: $C_{10}H_{14}N_6Cl_2O_8Pd$ ($M_r = 523.57$); orthorhombic, space group *Pbca*; $a = 13.612(1)$, $b = 14.899(1)$, $c = 17.258(1)$ Å, $V = 3500.0(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.987$ g cm^{-3}, $F(000) = 2080$, $\mu = 1.42$ mm^{-1}, 3430 observed reflections with $F_o > 4\sigma(F_o)$, $R_1 = 0.0370$, $wR_2 = 0.0957$, $S = 1.079$, max./min. residual electron density 0.77/−0.73 e Å^{-3}, Enraf-Nonius-CAD4 diffractometer, Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), graphite monochromator, absorption correction, Ψ scan, correction for Lorentzian and polarization effects. The structure was solved with the Patterson method[8] and refined with the least-squares method.[9] Oxygen atoms of ClO_4^- anions were disordered (occupancy factors 0.7 and 0.3).[18]

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[18] Crystal structure analysis of **2**: $C_{30}H_{42}N_{24}O_{18}Pt_3 \cdot 4H_2O$ ($M_r = 1684.11$); monoclinic, space group *C2/c*; $a = 18.936(3)$, $b = 15.056(1)$, $c = 20.136(5)$ Å, $\beta = 107.84(2)°$, $V = 5464.7(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.047$ g cm^{-3}, $F(000) = 3232$, $\mu = 7.76$ mm^{-1}, 3272 observed reflections with $F_o > 4\sigma(F_o)$, $R_1 = 0.0610$, $wR_2 = 0.1878$, $S = 1.379$, max./min. residual electron density 1.29/−1.58 e Å^{-3}, Enraf-Nonius-CAD4 diffractometer, Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), graphite monochromator, absorption correction, Ψ scan, correction for Lorentzian and polarization effects. The structure was solved with the Patterson method[8] and refined with the least-squares method.[9] The nitrate anions and water molecules were treated isotropically. It is possibe that there are still partially occupied water positions, but their refinement was impossible. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100386. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supramolecular Arrays of 4,7-Phenanthroline Complexes: Self-Assembly of Molecular Pd_6 Hexagons**

Jeffrey R. Hall, Stephen J. Loeb,* George K. H. Shimizu, and Glenn P. A. Yap

The formation of supramolecular arrays of metal ions and ligands is favored by a metal-directed, self-assembly mechanism, which allows for high-yield synthesis under thermodynamic control.[1] Rigid complexes can be synthesized in which the overall structure is dictated by a combination of the binding constraints of the ligand and the geometrical requirements of the metal ions.[2] For example, tetranuclear squares were first prepared by combining the approximately 90° angles of a square-planar palladium complex with the linearly oriented donor atoms of 4,4′-bipyridine.[3] In a similar fashion, polypyridine ligands and metal ions have produced a fascinating variety of squares,[4] boxes,[3b, 5] helicates,[6] catenanes,[7] rotaxanes,[8] racks,[9] grids,[10] and ladders.[11]

To increase the scope of such assemblies, we have begun to explore the use of predesigned organometallic fragments as building blocks.[12] A similar strategy was recently employed to prepare dendrimers[13] as well as nanoscale squares[14] and hexagons.[15] Here we report the self-assembly of a rigid, cyclic structure that contains 4,7-phenanthroline (**1**) and the linear organopalladium complex fragments **2a** or **2b** as building blocks. Self-assembly of these complimentary molecular building blocks with angular requirements of 60 and 180° results in a six-component [3+3] cyclic array.

Complexes **2a** and **2b** are readily prepared by palladation of the thioether ligands 1,2,4,5-tetrakis(*n*-butylthiomethyl)benzene and 1,2,4,5-tetrakis(phenylthiomethyl)benzene, respectively, with two equivalents of $[Pd(MeCN)_4][BF_4]_2$ in acetonitrile. Combining equimolar amounts of **1** and **2a**$[BF_4]_2$ or **2b**$[BF_4]_2$ in an appropriate solvent (**2a**, CH_2Cl_2; **2b**, $(CH_3)_2CO$) resulted in quantitative formation of the hexanuclear complexes **3a** and **3b** (Scheme 1). These complexes can be isolated as BF_4^- salts in the form of air- and moisture-stable, pale yellow, microcrystalline solids; their solubility depends on the R group attached to the sulfur center.

The ^{1}H NMR spectra of **3a** and **3b** are consistent with highly symmetrical structures and show large coordination shifts for the phenanthroline ring protons, in the range from $\Delta\delta = 0.65$ for H1 and H10 to $\Delta\delta = 1.63$ for H5 and H6. Integration of the signals indicates a 1:1 ratio of organometallic complex fragment to 4,7-phenanthroline, and this is supported by elemental analyses. In attempts to observe intermediates in the self-assembly process, experiments involving stepwise addition of metal to ligand and ligand to metal were monitored by ^{1}H NMR spectroscopy. In no case were species other than the cyclic product and the component in excess

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