Coupling dirhodium units through terpyridine bridges: synthesis and structure of a novel molecular rectangle

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The cation \([\text{Rh}_2((\mu-O_2CMe)_2(\text{MeCN})_6)]^{2+}\) reacts with the bis-terpyridine ligand 2,3,5,6-tetra-2-pyridylpyrazine (tppz) to yield the reduced compound \([\text{Rh}_2((\mu-O_2CMe)_2(tppz)_2(MeOH)_4)]^{2+}\) whose structure is that of molecular rectangle with edges defined by short Rh–Rh and long Rh–tppz–Rh units.

Metal complexes with nitrogen heterocyclic ligands are important players in the field of supramolecular chemistry.¹ These molecules possess fascinating electron-transfer, magnetic and conducting properties.² One of the more active applications of nitrogen heterocyclic ligands is the self-assembly of multinuclear transition metal ions into molecular grids and other cyclic molecules.³ Recent work in our laboratories hints at a strategy.⁴ A logical extrapolation of this chemistry is to use a bridging bis-terpyridine ligand such as 2,3,5,6-tetra-2-pyridylpyrazine (tppz) to construct metal-based assemblies is dirhodium polypyridyl complexes. One class of compounds in our laboratories being used to construct metal-based assemblies is dirhodium polyterpyridyl complexes. A number of years ago we⁶ and others⁷ discovered that \(\text{Rh}_2(O_2CMe)_2(\text{tppz})_2(\text{MeOH})_4\) reacts with the bis-terpyridine ligand 2,3,5,6-tetra-2-pyridylpyrazine (tppz) to prepare a new type of metal bonded molecular rectangle, –Rh–Rh–tppz–Rh units. Indeed, we have found that it is possible to prepare a new type of metal–metal bonded molecular rectangle, \(\text{Rh}_2(O_2CMe)_2(\text{tppz})_2(\text{MeOH})_4\) by applying this strategy.

A methanol solution of \([\text{Rh}_4((\mu-O_2CPh)(\text{tpy})_2(\text{MeCN})_6)]^{2+}\) was added to a CH₂Cl₂ solution of tppz and refluxed until the color changed to green.† Isolation of the product and subsequent crystallization from a methanol–toluene mixture in the presence of excess [n-Bu₄N][PF₆] yielded crystals of \([\text{Rh}_4((\mu-O_2CPh)(\text{tpy})_2(\text{MeOH})_4)][\text{PF}_6]_2\).² The molecular cation in 2 MeOH is a molecular rectangle that consists of alternating Rh–Rh and Rh–tppz–Rh edges (Fig. 1). The fact that the cation/anion ratio is 1:4 is an indication that the cation has been reduced by two electrons from the original oxidation states of the starting materials.⁹ In the event of no redox chemistry, the tetranuclear rhodium complex would bear a cationic charge of six rather than four. The unique Rh–Rh distance in \([\text{Rh}_4((\mu-O_2CPh)(\text{tpy})_2(\text{MeOH})_4)]^{4+}\) is 2.6060(11) Å, which is longer than the corresponding distance of 2.534(1) Å found in \([\text{Rh}_3^{I,II}((\mu-O_2CMe)_2(\text{MeCN})_6)][\text{BF}_4]_2\), but slightly shorter than the metal–metal distance observed in the mixed-valence chain compound \([\text{Rh}_3^{II,III}((\mu-O_2CMe)_2(bpy))_2][\text{BF}_4]\).² Six oxygen atoms from the bridging acetate group, and the two

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**Fig. 1** Thermal ellipsoid plots of the cation in 2 from two different perspectives with important atoms labeled. Selected bond distances (Å) and angles (°): Rh1–Rh2 2.6060(11), Rh1–N1 2.042(8), Rh1–N2 1.934(7), Rh1–N3 2.019(8), Rh2–N4 2.067(7), Rh2–N5 1.930(7), Rh2–N6 2.044(7), Rh1–O12 2.058(6), Rh1–O1 2.219(7), Rh2–O2 2.252(7), Rh2–O11 2.045(7); N2–Rh1–N3 80.8(3), N2–Rh1–N1 81.2(3), N3–Rh1–N1 160.6(3), N2–Rh1–O12 178.5(3), N3–Rh1–O12 100.1(3), N1–Rh1–O12 97.7(3).
The geometry of the Rh–tppz bonding is distorted, as evidenced by the fact that the Rh–N interactions to the central pyridyl nitrogen atoms (Rh(1)–N(2) and Rh(2)–N(5)) are ~0.1 Å shorter than the Rh–N bonds to the outer rings (Rh(1)–N(1), Rh(1)–N(3), Rh(2)–N(4) and Rh(2)–N(6)). The equatorial ligands are arranged in a nearly eclipsed geometry which is a requisite condition for the stabilization of a cyclic structure. It should be pointed out that, although the opposing tppz ligands are in a face-to-face disposition, the pyridyl rings are significantly distorted from the pyrazine plane, presumably due to steric interactions.

The paramagnetic nature of 2 and therefore the oxidation state of the dirhodium units was confirmed by EPR measurements performed on a polycrystalline sample. At room temperature, a slightly anisotropic resonance line (\(\Delta I = 1.2\)) and slightly broader (\(\Delta H = 12.8\) Oe) is observed at \(g = 2.003(1)\). At lower temperatures, the resonance becomes more anisotropic (\(\Delta I = 2.9\) at 4.2 K) and slightly broader (\(\Delta H = 19.8\) Oe at 4.2 K). The magnetic susceptibility deduced from the integration of the resonance line and preliminary SQUID magnetometer measurement indicate that the coupling between the spins on the dirhodium units in the tetramer is most likely antiferromagnetic and very weak (\(\mathcal{J} < 1\) K). A cyclic voltamogram study of 2 performed in 0.1 M TBAPF\(_6\)/MeCN displays two broad irreversible reduction processes at \(E_{1/2} = -0.10\) V and \(-0.86\) V vs Ag/AgCl. The irreversible nature of the waves does not allow for an estimation of the comproportionation constant that would reflect the extent of coupling between the two Rh\(_2\) units.

The results of this study demonstrate the feasibility of preparing novel types of paramagnetic cyclic molecules based on the self-assembly of multiply-bonded dimetal units with poly(pyridine) building blocks. Further prospects for incorporating other electron-rich metal–metal bonded complexes into cyclic architectures with planar conjugated ligands are being pursued in our laboratories.

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Notes and references

\[\text{[Rh(μ-1,2-C\(_2\)Me\(_2\))\(_2\)MeCN\(_2\)](BF\(_4\))_2}(0.077 g, 0.10 mmol)\] was dissolved in 20 mL of MeOH and added to a CH\(_2\)Cl\(_2\) solution (5 mL) of tppz (0.045 g, 0.12 mmol) under nitrogen and heated for 1 h, during which time the purple solution changed to a pale brown-red color and finally to green. The solution was concentrated and treated with methanol ether (3 \(\times\) 5 mL) to yield a green solid which was collected by filtration and recrystallized from a MeOH–benzene solution. Yield: 82 mg (92%). Anal. Calc. for Rh\(_2\)(μ-tppz)\(_2\)(MeCN)\(_2\): C, 33.44; H, 2.56; N, 8.36. Found: C, 33.74; H, 2.51; N, 7.68%.

\[\text{Crystal data for 2-MeOH: Rh}_{2}\text{P}_{2}\text{F}_{2}\text{C}_{2}\text{N}_{2}\text{O}_{2}\text{H}_{20}, M = 2075.64, monoclinic, space group C2/c, a = 15.604(5), b = 23.279(5), c = 21.081(5) Å, β = 110.158(5)°, V = 7189(3) Å\(^3\), Z = 4, D\(_s\) = 1.892 g cm\(^{-3}\), μ = 1.115 mm\(^{-1}\), 32054 reflections (6107 unique, R\(_{int}\) = 0.078) with 20 \(\geq 50.0°\), 483 variables, R = 0.076 [4569 data, I \(\geq 2\sigma(I)]\), wR(F) = 0.1734, GoF = 1.098. CCDC 192036. See http://www.wrc.org/uk/pdfs/data/cc2629815648.pdf for crystallographic files in CIF or other electronic format. Crystals of [Rh(μ-1,2-C\(_2\)Me\(_2\))\(_2\)tppz(MeOH)]\(_2\)(PF\(_6\))\(_2\)MeOH were obtained by slow diffusion of a toluene solution saturated with [\(n\text{-Bu}_4\text{N}]\text{PF}_6\] into a solution of the title compound in methanol. Data were collected on a Siemens SMART CCD diffractometer at 110.2 K with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation and were corrected for Lorentz and polarization effects. The frames were integrated in the Siemens SAINT software package and corrected for absorption using the SADAB program. The structure was solved by direct methods and refined using the programs in the Bruker SHELXTL v5.1 software package. The disordered C11 atom was modeled over two positions with 60/40% occupancies. Restraints were applied in the refinement of one of the [PF\(_6\)]\(^-\) anions. All non-hydrogen atoms were refined anisotropically with the exception of atoms C11, C11A, P3, F31, F32 and F33. Hydrogen atoms were placed in calculated positions and constrained with isotropic thermal parameters.