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

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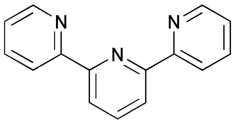
The cation $[Rh_2(\mu\text{-}O_2CMe)_2(MeCN)_6]^{2+}$ reacts with the bis-terpyridine ligand 2,3,5,6-tetra-2-pyridylpyrazine (tppz) to yield the reduced compound $[Rh_4(\mu\text{-}O_2CMe)_2(tppz)_2(MeOH)_4]^{4+}$ whose structure is that of molecular rectangle with edges defined by short Rh–Rh and long Rh–tppz–Rh units.

Metal complexes with nitrogen heterocyclic ligands are important players in the field of supramolecular chemistry.[1] The broad interest in these molecules stems, in large part, from their fascinating electron-transfer, magnetic and conducting properties.[2] One of the more active applications of nitrogen heterocyclic ligands in recent years is the self-assembly of mononuclear transition metal ions into molecular grids and other cyclic molecules.[3] Recent work in our laboratories hints at a parallel chemistry for multiply bonded dimetal units, as illustrated by our isolation of a molecular square consisting of alternating $Re_2^{II,II}$ and Pt^{II} corners bridged by isonicotinate anions.[4] The rich redox chemistry associated with multiply bonded dimetal complexes coupled with their high coordination numbers (up to 10) render them ideal building blocks for the construction of new types of molecular architectures.[5]

One class of compounds in our laboratories being used to construct metal-based assemblies is dirhodium polypyridyl complexes. A number of years ago we[6] and others[7] discovered that $Rh_2(O_2CR)_4$ and related molecules react with N–N chelates such as 2,2′-bipyridine (bpy) and 2,2′:6′,2″-terpyridine (tpy) to yield stable dinuclear products. Among the compounds isolated in this chemistry is the unusual cation $[Rh_2(\mu\text{-}O_2CPh)(tpy)_2(MeCN)_2]^{3+}$ which contains two tpy ligands in the equatorial plane. A logical extrapolation of this chemistry is to use a bridging bis-terpyridine ligand such as 2,3,5,6-tetra-2-pyridylpyrazine (tppz) in place of terpyridine to connect two Rh_2 units together. Indeed, we have found that it is possible to prepare a new type of metal–metal bonded molecular rectangle, *viz.*, $[Rh_4(\mu\text{-}O_2CMe)_2(tppz)_2(MeOH)_4][PF_6]_4$, by applying this strategy.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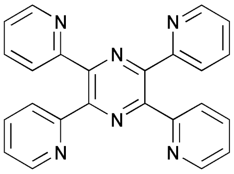
tppz

A methanol solution of $[Rh_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ (**1**)[8] was added to a CH_2Cl_2 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 $[n\text{-}Bu_4N][PF_6]$ yielded crystals of $[Rh_4(\mu\text{-}O_2CMe)_2(tppz)_2(MeOH)_4][PF_6]_4$ **2**·2MeOH.‡ The molecular cation in **2**·2MeOH 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 $[Rh_4(\mu\text{-}O_2CMe)_2(tppz)_2(MeOH)_4]^{4+}$ is 2.6060(11) Å, which is longer than the corresponding distance of 2.534(1) Å found in $[Rh_2^{II,II}(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$, but slightly shorter than the metal–metal distance observed in the mixed-valence chain compound $\{Rh_2^{I,II}(\mu\text{-}O_2CMe)_2(bpy)_2][BF_4]\cdot H_2O\}_n$ (2.666(2) Å).[9] Evidently, dirhodium distances in the reduced compounds are highly variable, as illustrated by the fact that the unsupported Rh^I–Rh^{II} bonds in $[Rh(MeCN)_4(BF_4)_{1.5}]_x$ are 2.8442(8) and 2.9277(8) Å).[10]

The immediate coordination sphere of the individual Rh_2 units consists of six nitrogen atoms from the two tppz ligands, two oxygen atoms from the bridging acetate group, and the two

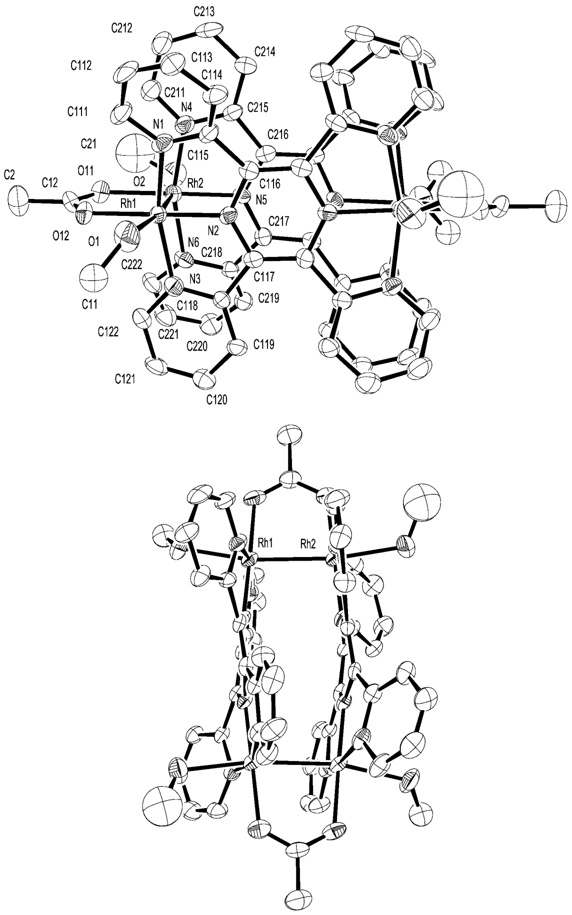

Fig. 1 Thermal ellipsoid plots of the cation in **2** from two different perspectives with important atoms labeled. Selected bond distances (Å) and angles (°): Rh1–Rh2 2.6060(11), Rh1–N1 2.042(8), Rh1–N2 1.934(7), Rh1–N3 2.019(8), Rh2–N4 2.007(7), Rh2–N5 1.930(7), Rh2–N6 2.044(7), Rh1–O12 2.058(6), Rh1–O1 2.219(7), Rh2–O2 2.252(7), Rh2–O11 2.054(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).

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axial MeOH molecules. 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 (A/B = 1.2, ΔH = 12.8 Oe) is observed at g = 2.003(1). At lower temperatures, the resonance becomes more anisotropic (A/B = 2.9 at 4.2 K) and slightly broader (ΔH = 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 ($|J| < 1$ K). A cyclic voltammogram study of **2** performed in 0.1 M TBAPF$_6$/MeCN displays two broad irreversible reduction processes at $E_{p,c} = -0.10$ 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 polypyridine 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

† [Rh$_2$(μ-O$_2$CMe)$_2$(MeCN)$_6$][BF$_4$]$_2$ (0.077g, 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 diethyl ether (3 × 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 $Rh_4P_4F_{24}C_{56}N_{12}O_8H_{51}$: C, 33.44; H, 2.56; N, 8.36. Found: C, 33.74; H, 2.51; N, 7.68%.

‡ *Crystal data* for **2**·2MeOH: $Rh_4P_4F_{24}C_{58}N_{12}O_{10}H_{59}$, 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_c = 1.892 g cm^{-3}, μ = 1.115 mm^{-1}, 32054 reflections (6107 unique, R_{int} = 0.0788) with 2θ = 50.0°, 483 variables, R = 0.076 [4569 data, $I > 2\sigma(I)$], $wR(F_o^2)$ = 0.1734, GoF = 1.098. CCDC 192036. See http://www.rsc.org/suppdata/cc/b2/b208164b/ for crystallographic files in CIF or other electronic format.

Crystals of [Rh$_4$(O$_2$CMe)$_2$(tppz)$_2$(MeOH)$_4$][PF$_6$]$_4$·2MeOH were obtained by slow diffusion of a toluene solution saturated with [n-Bu$_4$N][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,[11] and corrected for absorption using the SADABS program.[12] The structure was solved by direct methods and refined using the programs in the Bruker SHELXTL v5.1 software package.[13] 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.

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