Synthesis and Characterization of Molecular Rectangles Based upon Rhenium Thiolate Dimers

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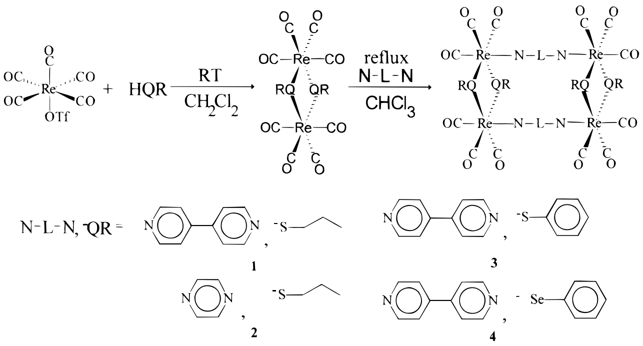
There has been substantial recent interest in the construction and characterization of transition-metal-containing macrocycles; particularly popular have been tetrametallic "molecular squares," i.e., macrocycles featuring cis-coordinated transition-metal corners and rigid or semirigid difunctional ligand edges. (Other known macrocycles, although not tetrametallic, include triangles[1,2] and hexagons.[3,4])[5−13] Notably, many of the squares have been shown to behave as hosts for small molecule guests[5−7,9,14] and some have been shown to function as solution phase sensors.[9,14] In addition, X-ray crystallographic studies have shown that the compounds tend to form aligned channel structures.[8,10,11] Exploitation of this solid-state feature may allow thin films of the squares to be used for sieving and separations.[11]

Scheme 1



To the best of our knowledge, all tetrametallic macrocycles reported to date have square or near-square cavities.[15] Of particular interest would be the synthesis of an assembly in which one side of the cavity is of a significantly different length than the other—a molecular rectangle. In a host/guest or molecular recognition context, such an arrangement should lead to altered chemical selectivity and might prove especially useful in achieving selective binding and/or enhanced binding of planar aromatic guest species. It should be noted that purely organic cyclophane-type rectangles have already been reported by several workers, and that binding of planar aromatic guests has been demonstrated.[16−19] We reasoned, however, that transition-metal-containing rectangles might display useful alternative redox, optical or molecular charge characteristics. Previous attempts to synthesize tetrametallic rectangles from mixtures of singly functional bridging ligands such as pyrazine (pz) and 4,4′-bipyridine (4,4′-bpy), together with $Re(CO)_5Cl$, exclusively yielded squares rather than mixed bridging ligand rectangles.[11] In this communication we report the synthesis and characterization of molecular rectangles based upon rhenium-thiolate dimers.

The dimeric complex $[(CO)_4Re(\mu\text{-SR})]_2$ has been known for some time,[20−22] synthesized by reaction of $HRe(CO)_5$ with HSR; we have found that it can also be formed by reaction of $Re(CO)_5OTf$[23] (OTf = trifluoromethanesulfonate) with various alkyl and aromatic thiols at room temperature in deoxygenated CH_2Cl_2. Purification of a rhenium-propanethiolate dimer by column chromatography (3:2 hexanes/CH_2Cl_2, silica), followed by reaction with 4,4′-bpy in refluxing $CHCl_3$ and under flow of N_2, gave the molecular rectangle **1** as a yellow precipitate in 80% yield. Rectangle **2** was prepared analogously to **1** by replacing 4,4′-bpy with pz. Addition of hexanes to the reaction mixture precipitated the pz-containing product as dark red crystals. The synthesis of the rectangles is summarized in Scheme 1.[24] Rectangles **1** and **2** were characterized by ^1H NMR, FAB-MS, elemental analysis, UV−vis absorption, FTIR, and X-ray crystallography.[25,26] No evidence was obtained for luminescence, either in the solid state or in solution.

The infrared absorption spectra for both rectangles show four bands in the region associated with carbonyl stretches. Only three

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(24) The synthetic scheme was extended to two other rectangles. Rectangle **3** was formed from a benzenethiolate−rhenium dimer and a 4,4′-bpy bridge. Rectangle **4** used a benzeneselenolate−rhenium dimer and a 4,4′-bpy bridge. These compounds were characterized only by ^1H NMR, FTIR, and UV−vis absorption methods. (See Supporting Information.)
(25) ^1H NMR spectra for **1** (acetone-d_6), δ 1.18 (CH_3-, t, $J = 7.23$ Hz, 12H), 1.81 (-CH_2-, m, $J = 7.35$ Hz, 8H), 3.34 (-CH_2S, t, $J = 7.35$ Hz, 8H), 7.92 (H_m, d, $J = 6.81$ Hz, 8H), 9.15 (H_o, d, $J = 6.78$ Hz, 8H); **2** (acetone-d_6), δ 1.10 (CH_3-, t, $J = 7.41$ Hz, 12H), 1.73 (-CH_2-, m, $J = 7.41$ Hz, 8H), 3.25 (-CH_2S, t, $J = 7.35$ Hz, 8H), 9.22 (H_{pz}, s, 8H). Mass spectra for **1** (LRFAB), 1696.0 calcd, 1696.1 obsd; **2** (LRFAB), 1541.9 calcd, 1542.2 obsd. IR spectra in CH_2Cl_2 (CO region, cm^{-1}): **1**, 2019, 2006, 1919, 1900; **2**, 2021, 2013, 1932, 1912 cm^{-1}.

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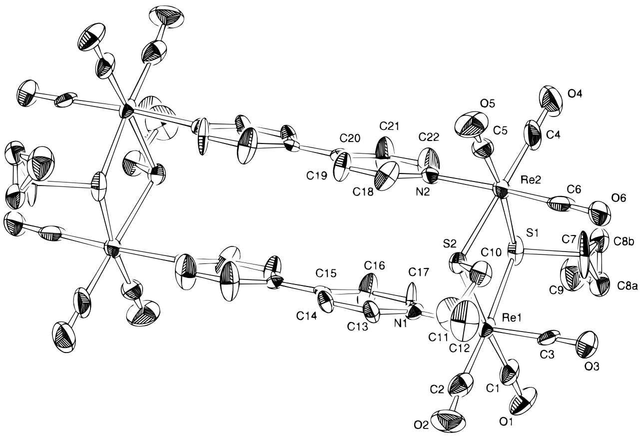

Figure 1. ORTEP drawing of **1** with hydrogens excluded for clarity. The molecule sits on an inversion center which is located at the center of the cavity. Thermal ellipsoids drawn to 50% probability.

would be expected if the rectangles were viewed simply as tetrametallic assemblies of $(CO)_3Re(SR)_2(L)$ subunits that independently possessed C_s symmetry. On the other hand, if each rectangle is viewed as a pair of $[(CO)_3Re(\mu\text{-}SR)L]_2$ subunits separately displaying aproximate C_{2v} symmetry, up to six carbonyl bands would be expected in both the IR and Raman spectra.[27,28] Preliminary FT Raman studies on rectangle **1** have shown six bands in the carbonyl region, with Raman shifts coincident with stretching frequencies encountered in the infrared spectrum.

Structures for rectangles **1** and **2** were determined by X-ray crystallography.[26] The crystals of **1** were grown by slow evaporation, while the crystals for **2** were grown by layering the reaction mixture ($CHCl_3$) with hexanes and then placing the vial in the freezer. The structure of **1** (Figure 1) shows a rectangular framework with dimensions of 3.81 × 11.57 Å, as defined by the rhenium centers. An interesting feature in the structure is the near-planarity of the pyridyl planes (dihedral angle between the planes of <1°) of the bridging 4,4′-bipyridines. Typically, the pyridyl planes in 4,4′-bpy ligands used as bridges are twisted by anywhere from 25 to 35°, so as to reduce interaction of the ligand's 3,3′ and 5,5′ protons.[8,10-12] There are examples, however, of coplanar rings in the crystal structures of such molecules as biphenyl[29] and several coordination polymers.[30-32] The planarity has been attributed to a variety of factors, from better packing in the solid state,[29] to H-bonding interactions with a counterion.[32] In the case of rectangle **1**, the planarity is presumably due primarily to steric interference which would occur between the two bipyridine bridges if the rings adopted their typical twist. The structure of **2** (Supporting Information) shows a framework with dimensions of 3.69 × 7.22 Å, based on rhenium atoms. Unfortunately, once van der Waals radii are taken into account, the interplanar spacing in **2**, like **1**, is too small to permit the resulting cavity to function as a receptor site, even for planar molecules such as benzene.

The molecular rectangles were also examined electrochemically: at a scan rate of 2 V/s, in CH_2Cl_2 as solvent, **1** displayed an overlapping pair of reversible waves centered at 0.48 V vs ferrocene. Given the overlap, these are perhaps most reasonably assigned to equivalent metal or metal/sulfur oxidations occurring at opposite ends of the rectangle. Compound **1** also displayed reversible waves at −1.60 and −1.81 V, tentatively assigned as bipyridine ligand reductions. At 100 mV/s, in butyronitrile as solvent (required for solubility), **2** exhibited a complicated, partially chemically irreversible, oxidative voltametric wave that peaked at +0.80 V vs ferrocene. The wave is speculatively assigned to $Re^{I/II}$, although an alternative assignment as oxidation of coordinated propanethiolate cannot be ruled out. The compound also exhibited reversible reductions at −1.23 and −1.64 V; these almost certainly are associated with pyrazine ligand reduction.

To conclude, we find that bridged, rectangular, tetrametallic molecules of varying length can be obtained from chalcogenolate-linked dirhenium precursors and appropriate difunctional ligands. While these molecules are not likely to be of use as hosts, they will likely serve as stepping stones for further work. First, the synthetic scheme suggests an approach which might be used to create molecular rectangles possessing larger cavities. Preformation of comparatively stable, doubly bridged rhenium thiolate dimer edges proved necessary to form rectangular cavities, since singly bridging imine- and azine-based ligands gave only squares; other high-stability edges could be envisioned. Second, extension of the synthetic chemistry to different pyridyl-functionalized bridging ligands might allow one to exploit the small gap between the bridges to study interesting cofacial ligand interactions, for example, porphyrin−porphyrin interactions.

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Supporting Information Available: UV−vis and elemental analyses for **1** and **2**, and an ORTEP for **2**; UV−vis, IR, and ^1H NMR data for **3** and **4** (2 pages). X-ray crystallographic files, in CIF format, for **1** and **2** are also available on the Internet only. Ordering and access information is given on any current masthead page.

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(26) Crystal data: **1**, monoclinic, space group $P2_1/n$ (No. 14), $a = 9.323(3)$ Å, $b = 17.644(4)$ Å, $c = 15.695(3)$ Å, $\beta = 92.92(2)°$, $V = 2580.9(10)$ Å^3, $Z = 2$, $D_c = 2.180$ g/cm^3, final R value 0.039 for 4735 unique reflections; **2**, monoclinic, space group $P2_1/n$ (No. 14), $a = 15.0237(8)$ Å, $b = 11.2476(6)$ Å, $c = 15.7302(9)$ Å, $\beta = 109.0264(16)°$, $V = 2512.9(4)$ Å^3, $Z = 2$, $D_c = 2.15$ g/cm^3, final R value 0.072 for 8800 unique reflections.

(27) The "dimer" interpretation has previously been invoked in a discussion of IR spectra for $[(CO)_4Re(\mu\text{-}X)]_2$ ($X = Cl^-, Br^-, I^-$) species where it clearly would be consistent with the existence of substantial metal−metal interaction across the bridging halides (El-Sayed, M. A.; Kaesz, H. D. *Inorg. Chem.* **1963**, *2*, 158).

(28) Also pertinent is a recent report on a hydroxy bridged Re dimer, $[Re_2(\mu\text{-}OH)(\mu\text{-}1,1'\text{-bis-(diphenylphosphino)ferrocene})(CO)_6]$, for which five IR-active carbonyl stretches were noted (Jiang, C.; Wen, Y.-S.; Liu, L.-K.; Hor, T. S. A.; Yan, Y. K. *Organometallics* **1998**, *17*, 173).

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