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Self-Assembly of Ligand-Bridged Molecular Rectangles Containing *fac*-Re(CO)$_3$ Corners

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Inorganic cyclophane molecules based on transition metals are a new class of compounds that possess extraordinary promise in host−guest, inclusion, and molecular recognition chemistry.[1−12] Slone et al.[13,14] recently reported the first luminescent molecular squares containing a variety of nitrogen-containing heterocycles as bridging groups between rhenium(I) corners. Work in our laboratory has been directed toward the preparation of new luminescent complexes of this type and their application in molecular sensing. We report here the unexpected preparation of a series of molecular rectangles based on *fac*-Re(CO)$_3$ corners containing 4,4′-bipyridine (4,4′-bpy) bridges as one side and two η^2-alkoxy or hydroxy bridges as the other. The complexes represent an unusual example of a low valent rhenium(I) center containing both π-acid and strong π-base ligands that "self-assemble". The results in this communication are closely related to the companion paper in this issue that reports thiolato-bridged molecular rectangles.[15] Both studies present a new class of molecular parallelogram.

The novel complexes were isolated in the attempt to prepare structures of higher order (e.g., ligand-bridged molecular cubes) by reaction of the precursor Re(CO)$_5$(CF$_3$SO$_3$)[16] with 4,4′-bpy in polar media.[17−19] Use of alcohols or water as solvent afforded bright yellow microcrystalline materials in essentially quantitative yield based on the Re precursor as the limiting reagent (eq 1). A number of alcohols were used, ranging from low-boiling methanol to high-boiling ethylene glycol. The complexes were characterized by elemental analysis, ^{1}H NMR, UV−visible, and IR spectroscopies, and in a single case, cyclic voltammetry and X-ray crystallography. Table 1 presents a selection of these data.

$$4\mathrm{Re(CO)_5(CF_3\,SO_3)} + 6(4,4'\text{-bpy}) + 4\mathrm{ROH} \rightarrow [\mathrm{Re_2(CO)_6(RO)_2}(4,4'\text{-bpy})]_2 + 4[(4,4'\text{-bpyH}^+)(\mathrm{CF_3SO_3})] \quad (1)$$

X-ray crystallographic quality crystals of the methoxy-bridged complex [Re$_2$(CO)$_6$(CH$_3$O)$_2$(4,4′-bpy)]$_2$·4CH$_3$CN were grown from the methanol soluble portion of the preparation. The single-crystal data[20] was collected at 22 °C using a crystal of dimensions 0.48 × 0.30 × 0.12 mm sealed in a capillary to prevent solvent loss. The ORTEP represenatation of this molecule shows each unit contains four acetonitrile solvate molecules. Average bond distances are as follows: Re−C(CO), 1.90 Å; Re−N(4,4′-bpy), 2.20 Å; Re−O(OCH$_3$), 2.13 Å, which are similar to those found for a number of other Re(I) complexes.[21] Of interest in potential sensing applications, however, is the near coplanarity of the bipyridine ligands (dihedral angle of 8.1°), which are close enough (3.55 Å) for π-cloud interactions[22,23] to play a role in determining the structure. The Re(I) centers were found to be 3.38 Å apart, and when compared to the distance reported for Re$_2$(CO)$_{10}$ by Dahl et al.[24] of 3.02 Å, it is safe to assume that the Re(I) centers do not have a significant bonding interaction.

Examination of the infrared spectra of the complexes shows an unexpectedly complex pattern of absorptions in the carbonyl stretching region, 2200−1700 cm^{-1}. Complexes with C_s microsymmetry show one high-energy absorption (>2000 cm^{-1}) and

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(17) Preparation of [Re$_2$(OH)$_2$(CO)$_6$(4,4′-bpy)]$_2$. To a 250 mL purged round-bottom flask containing doubly distilled water (150 mL), 1.27 g (2.68 mmol) of Re(CO)$_5$(CF$_3$SO$_3$) and 1.6 equiv of 4,4′-bipyridine (0.672 g, 4.29 mmol) were added giving a clear solution. After about 5 min of heating, the solution turned a faint yellow. The resulting solution was heated at reflux and magnetically stirred for 3 h, yielding a bright yellow crystalline precipitate. The precipitate was filtered and washed multiple times with diethyl ether. Yield: 0.932 g, 95%. Anal. Calcd for Re$_4$C$_{32}$H$_{20}$O$_{16}$N$_4$: C, 26.30; H, 1.38; N, 3.83. Found: C, 26.35; H, 1.41; N, 3.78.
(18) Preparation of [Re$_2$(OCH$_3$)$_2$(CO)$_6$(4,4′-bpy)]$_2$. To a 100 mL N$_2$ purged round-bottom flask containing absolute methanol (50 mL), 0.513 g (1.08 mmol) of Re(CO)$_5$(CF$_3$SO$_3$) and 1.6 equivalents of 4, 4′-bipyridine (0.272 g, 1.73 mmol) were added giving a clear solution. The resulting yellow solution was heated at reflux. The precipitate that formed was filtered and washed multiple times with diethyl ether. The yellow filtrate was removed on a rotary evaporator and washed multiple times with diethyl ether yielding additional product. Yield: 0.396 g, 97%. Anal. Calcd for Re$_4$C$_{36}$H$_{28}$O$_{16}$N$_4$: C, 28.50; H, 1.86; N, 3.69. Found: C, 28.63; H, 1.84; N, 3.63.
(19) All rectangle compounds were analytically pure.
(20) [Re$_2$(OCH$_3$)$_2$(CO)$_6$(4,4′-bpy)]$_2$·4CH$_3$CN crystallized in the monoclinic space group $P2_1/c$, with a = 15.132(3) Å, b = 9.118(2) Å, c = 20.811(4) Å, a = 90°, b = 109.72(3)°, γ = 90°, V = 2703.1(9) Å^3, Z = 2, fw = 1681.64, d_{calc} = 2.066 g/cm^3, μ = 8.998 mm^{-1}. Intensity data were collected at 22 °C on a Siemens P3 diffractometer with Mo tube using Kα radiation and a graphite monochromator using the Wyckoff scan method in the 2θ range 4−55°. A total of 6191 independent reflections were measured with 3868 having $I > 2\sigma(I)$. Final R indices, R1 = 0.0499, wR2 = 0.0953, GoF = 1.09; R indices for all data, R1 = 0.1062, wR2 = 0.1216. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using structure solution programs form the SHELXTL system (version 5.03/Iris).
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Table 1. Spectral Properties of the Complexes[a]

complex	IR frequencies[b] (cm^{-1})	^1H NMR shifts for 4,4′-bpy (ppm)[c]	UV−visible[b] $\lambda_{max,nm}$ (ϵ, M^{-1} cm^{-1})
$[Re_2(OH)_2(CO)_6(4,4'\text{-bpy})]_2$	2018, 2004, 1904, 1881	8.50 (d) (3,5 and 3′,5′ of 4,4′-bpy) 7.43 (d) (2,6 and 2′,6′ of 4,4′-bpy)	240 (4.84×10^4) 370 (1.11×10^4)
$[Re_2(OCH_3)_2(CO)_6(4,4'\text{-bpy})]_2$	2020, 2008, 1909, 1889	8.45 (d) (3,5 and 3′,5′ of 4,4′-bpy) 7.50 (d) (2,6 and 2′,6′ of 4,4′-bpy)	242 (4.67×10^4) 390 (9.77×10^3)
$[Re_2(OCH_2CH_3)_2(CO)_6(4,4'\text{-bpy})]_2$	2019, 2007, 1907, 1888	8.65 (d) (3,5 and 3′,5′ of 4,4′-bpy) 7.85 (d) (2,6 and 2′,6′ of 4,4′-bpy)	242 (4.86×10^4) 380 (1.00×10^4)
$[Re_2(OCH_2CH_2OH)_2(CO)_6(4,4'\text{-bpy})]_2$	2020, 2008, 1908, 1888	9.01 (d) (3,5 and 3′,5′ of 4,4′-bpy) 7.88 (d) (2,6 and 2′,6′ of 4,4′-bpy)	240 (5.15×10^4) 380 (1.03×10^4)
$[Re(CO)_3(4,4'\text{-bpy})_3](CF_3SO_3)$	2038, 1931	8.76 (d), 8.68 (d) 7.86 (d), 7.72 (d)	244 (4.10×10^4) 300 (2.09×10^4)
$Re(CO)_3(4,4'\text{-bpy})_2Cl$[d]	2027, 1926, 1890	8.85 (m), 8.73 (m) 7.77 (m), 7.68 (m)	245 (3.59×10^4) 317 (1.32×10^4)
$[((2,2'\text{-bpy})(CO)_3Re)_2(4,4'\text{-bpy})](CF_3SO_3)_2$[e]	2037, 1937, 1931	8.54(d)[f] 7.76 (d)	246 (4.08×10^4) 340 (1.76×10^4)

[a] Abbreviations: 2,2′-bpy, 2,2′-bipyridine; 4,4′-bpy, 4,4′-bipyridine. [b] In CH_3CN. [c] In CD_3CN except for $Re_4(OCH_2CH_3)(CO)_{12}(4,4'\text{-bpy})_2$ which was done in $(CD_3)_2O$ for solubility reasons. [d] See refs 13, 14, and 21. [e] See refs 28−31 for ^1H-NMR and UV−visible data. Solution IR data collected at University of Wyoming. [f] In DMSO-d_6, see ref 28.

two overlapping low-energy absorptions[25] which have been assigned to the expected a″ and 2a′ vibrations.[26−28] From the crystallographic data it might be expected that local C_s symmetry prevails for each corner unit. Assuming a perfect rectangle for the atom corner positions, the complex should have D_{2h} symmetry resulting in the symmetrical equivalence of each corner. The facial tricarbonyl motif will be preserved if coupling between the modes is negligible. Table 1 shows the IR stretching frequencies for four rectangles as well as two known molecules which should be excellent comparators: *fac*-$Re(CO)_3(4,4'\text{-bpy})_2Cl$[25] and the dimer $[((2,2'\text{-bpy})(CO)_3Re)_2(4,4'\text{-bpy})](CF_3SO_3)$.[29−32] The former resembles a corner, and the latter the 4,4′-bpy dimer bridge portion of the rectangle. As is shown in Table 1, symmetry-lowering is observed in the rectangles, since four resonances are observed

In contrast to the IR spectroscopic data, ^1H NMR spectroscopy reveals only two bpy resonances as would be seen in the free ligand and infers that each Re(I) center is equivalent (Table 1). Three resonances are seen for the comparator molecules, $[Re(CO)_3(4,4'\text{-bpy})_2](CF_3SO_3)$ and *fac*-$Re(CO)_3(4,4'\text{-bpy})_2Cl$ as might be expected for C_{3v} and C_s symmetry, respectively (assuming free rotation of the species in solution). One explanation to the conflicting spectrocopic interpretations of structure is the existence of a fluxional process[14,33] which is fast on the NMR time scale. Low-temperature ^1H NMR spectroscopy was unsuccessful, due to a lack of solubility of the complexes in suitable solvents. Since D_{2h} symmetry has five IR allowed modes, another possibility is strong coupling between corners. This point is still under investigation.

The UV−visible spectra of the rectangle complexes are similar in form to those of other monomeric and dimeric Re(I) species containing bpy ligands.[13,14,25,29−32,34] In all cases, the spectra are characterized by a sharp, intense $\pi-\pi^*$ transition and a broad, moderately intense band which has previously been assigned as a $d\pi(Re)-\pi^*(bpy)$ MLCT transition.[25] The molar absorptivity for the MLCT peak maxima are not easily determined since extensive spectral overlap occurs with the $\pi-\pi^*$ absorptions. In addition to the sharp $\pi-\pi^*$ absorption at ca. 240−250 nm, there is an additional peak around 380 nm that tails into the MLCT region. This feature is present in all of the rectangles, and has been previously assigned as a second $\pi-\pi^*$ transition by Tapolsky et al.[30−32] For all of the complexes, the $\pi-\pi^*$ maximum seems insensitive to structural change. The MLCT band maximum, on the other hand, is red-shifted for the rectangles compared to the complexes $[Re(CO)_3(4,4'\text{-bpy})_3](CF_3SO_3)$, $Re(CO)_3(4,4'\text{-bpy})_2Cl$, and $[((2,2'\text{-bpy})(CO)_3Re)_2(4,4'\text{-bpy})]$ $(CF_3SO_3)_2$. This red shift has two probable causes: the coordination of another metal center at the free nitrogen of the 4,4′-bypyridine thus lowering the π^* orbitals, and the electron donation of an alkoxide relative to chloride raising the relative energy of the $d\pi$ orbitals.

Cyclic voltammetry for $[Re_2(CO)_6(CH_3O)_2(4,4'\text{-bpy})]_2$ was obtained in N_2 saturated CH_3CN with 0.1 M *n*-tetrabutylammonium hexafluorophospate as supporting electrolyte with a Pt working, SCE reference, and Pt wire auxiliary electrodes with ferrocene as an internal standard. Two reversible one-electron 4,4′-bpy reductions were observed at $E_{1/2}$ values of −1.09 V (ΔE_p = 72 mV) and −1.28 V (ΔE_p = 74 mV). One essentially irreversible Re-based oxidation occurred at −1.34 V ($\Delta E_p \sim 0.21$ V).

The self-assembled rectangles luminesce in the solid state, but not in solution. The absence of solution luminescence may be from enhanced nonradiative decay via torsional motion about the 4,4′-bpy bridge[14,33] or may have its origin in a proximate emissively silent state, for example, a LLCT excited-state based on alkoxide donor and bpy acceptor orbitals. Although the lack of luminescence and small cavity size limit the usefulness of the complexes for sensor applications, the rectangular complexes themselves represent a new structural motif in supramolecular chemistry.

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Supporting Information Available: Tables of atomic coordinates, bond lengths, bond angles, and thermal parameters for $[Re_2(CO)_6(CH_3O)_2(4,4'\text{-bpy})]_2 \cdot 4CH_3CN$ (7 pages). Ordering information is given on any current masthead page.

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