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Structural and Spectroscopic Characterization of a Metal−Metal Bonded Ruthenium Porphyrin Dimer Cation

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Introduction

Although the porphyrin ligand has proven extremely useful in the study of unsupported multiple metal−metal bonds between transition metal atoms,[1] a long-standing criticism of M_2(porphyrin)$_2$ systems has been the lack of single-crystal X-ray diffraction studies. For this reason researchers have had to rely on less direct methods[2] to obtain structural information and metal−metal bond length data for these systems. We report here the X-ray structure determination, ESR, and solution magnetic susceptibility for a metal−metal bonded Ru_2^{5+} porphyrin dimer. The structural information is compared with that obtained from EXAFS[2a] and resonance Raman[2b] studies of analogous porphyrin complexes, while the ESR and magnetic properties are used to support a molecular orbital diagram which differs from that reported for isoelectronic Ru−Ru metal−metal bonded systems having bridging ligands.

Experimental Section

Materials. The syntheses of $[Ru(TPP)]_2$[3] and $[Ru(TPP)]_2PF_6$[4] were performed as described in the literature. All solvents were purified according to conventional methods and handled in a glovebox under a dry N_2 atm with $[O_2] < 2$ ppm.

X-ray Analysis of $[Ru(TPP)]_2PF_6CH_2Cl_2$ (1). Crystals of the Ru−Ru dimer suitable for X-ray diffraction were obtained by vapor diffusion of benzene into a saturated dichloromethane solution over 3 days. A black block with dimensions 0.20 × 0.30 × 0.40 mm was chosen and mounted on a glass fiber in paratone N oil at −80 °C using an improvised cold stage. All measurements were made on a Siemens SMART diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 7481 carefully centered reflections with $I > 10\sigma(I)$ in the range $2.20 < 2\theta < 52.10°$ corresponded to a cell with dimensions $a = b = 18.5148(4)$ Å, $c = 26.4410(4)$ Å, $Z = 4$, $V = 9063.9(3)$ Å^3. The data were collected at −143 °C using the ω scan technique to a maximum 2θ value of 52.1°.

The structure was solved by direct methods (SHELXS-86) and expanded using Fourier techniques (DIRDIF92). Following anisotropic refinement of the Ru atoms and isotropic refinement of the C, N, P, F, and Cl atoms the final cycle of full-matrix least squares refinement (2039 observed reflections with $I > 3\sigma(I)$ and 198 variable parameters) converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.078$, $Rw = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2} = 0.100$.

Electron Paramagnetic Resonance Spectroscopy. X-band spectra at 77 K were recorded on a Bruker spectrometer in frozen 1:1 toluene/dichloromethane. Microwave frquency, 9.516 GHz; gain, 8×10^4; modulation, 10 G; and power, 13 dB for a sweep of 2600−4400 G.

Magnetic Susceptibility. Magnetic susceptibility of a CD_2Cl_2 solution of **1** was determined by NMR spectroscopy according to equations in ref 14. Tetramethylsilane was used as a reference. A solution of 5.35 mg of **1** in 0.60 mL of CD_2Cl_2 produced a frequency shift of 4.8 Hz at an operating frequency of 400 MHz. A diamagnetic correction of -481×10^{-6} cgs emu/mol was applied to account for the porphyrin ligands.[5]

Results and Discussion

The structure of $[Ru(TPP)]_2PF_6$ (**1**) (TPP, tetraphenylporphyrinato dianion; OEP, octaethylporphyrinato dianion) is depicted in Figure 1. The important features are summarized below: (1) a Ru−Ru separation of 2.293(2) Å, which is within the range 2.24−2.30 seen for all other structurally characterized Ru_2^{5+} metal−metal bonded complexes.[6] (2) A twist angle of 29.4° between porphyrin macrocycles; the observed angle may result from competition between steric repulsions and intramolecular $\pi-\pi$ interactions from the *meso*-phenyl rings of one porphyrin to the *meso*-phenyl rings of the opposed porphyrin. (3) Each porphyrin is slightly domed, with Ru−N4 plane displacements of 0.378 Å. (4) Average Ru−N bond lengths of 2.06(2) Å, and (5) an N4−N4 separation of 3.049 Å are observed.

These parameters may be compared (Table 1) with those previously estimated from EXAFS and resonance Raman studies of $[Ru(OEP)]_2^{n+}$ ($n = 0$, 1, 2).[2] The excellent agreement between Ru−Ru bond lengths as calculated from the earlier EXAFS[2a] study of $[Ru(OEP)]_2^+$ and the current X-ray crystallographic study of $[Ru(TPP)]_2^+$ demonstrates that substitution of TPP for OEP has little effect on the metal−metal bond. The earlier resonance Raman investigation utilized empirical correlations to estimate Ru−Ru and Ru−N bond distances. Comparison of these with the crystallographic results shows that such correlations are remarkably accurate.

The molecular orbital diagram for Ru_2^{5+} metal−metal bonds with bridging ligands has been repeatedly shown to be $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$.[6] The possibility that degeneracy of the π^* and δ^* orbitals is a result of orbital overlap associated with the bridging aspect of the ligands used in these studies has been supported by an SCF-X-SW calculation,[7] and preliminary studies of an unbridged $[Ru(tmtaa)]_2^+$ ($tmtaa^{2-}$ = tetraza[14]annulene) metal−metal bonded dimer are consistent with a spin-doublet $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$ description.[8] Thus, we became interested in investigating the corresponding MO diagram for our unsupported Ru_2^{5+} metal−metal bond with porphyrin ligands.

Recently, our group reported solid-state evidence for a $^3A_{2g}$ ($\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$) ground state in the neutral $[Ru(OEP)]_2$ and $[Ru(OETAP)]_2$ (OETAP = tetrazaoctaethylporphyrinato dianion) porphyrin dimers.[9] The metal−metal bond length in $[Ru(OEP)]_2$ has been previously determined by X-ray crystallography to be

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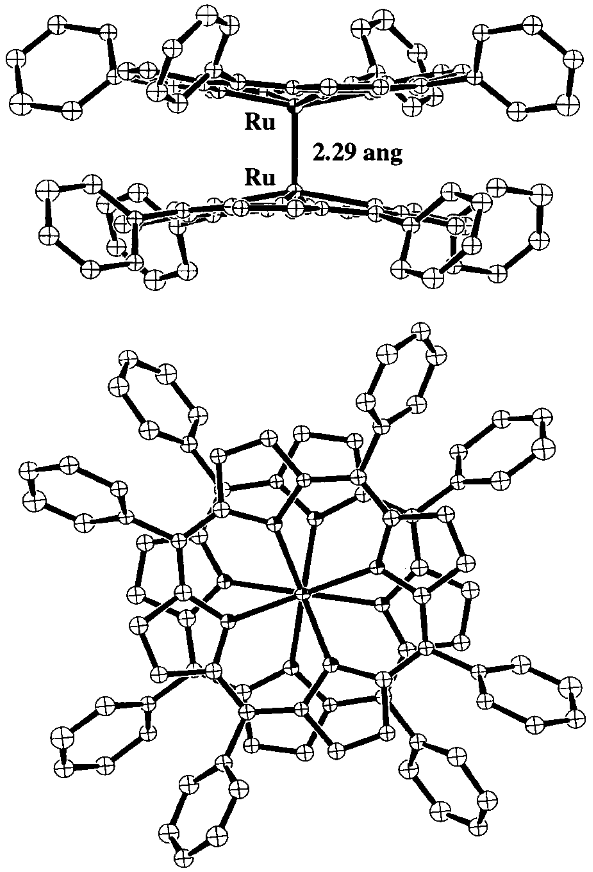

Figure 1. ORTEP plots of $[Ru(TPP)]_2PF_6$ at the 50% probability level. Hydrogen atoms have been omitted for clarity. (a) Ru−Ru distance is 2.293(2) Å; (b) torsion angle between porphyrin planes is 29.4°.

Table 1. Structural Parameters Calculated for $[Ru(Por)]_2^+$ Dimers

spectroscopic technique	ref	Ru−Ru length, Å	Ru−N length, Å
X-ray crystallography[a]	this work	2.293(2)	2.06(2)
EXAFS[b]	2a	2.29(2)	2.03(2)
resonance Raman[b]	2b	2.33(3)	2.06(1)

[a] Molecule studied was $[Ru_2(TPP)_2]PF_6$; TPP, tetraphenylporphyrin dianion. [b] Molecule studied was $[Ru_2(OEP)_2]PF_6$; OEP, octaethylporphyrin dianion.

2.408(1) Å.[10] A decrease of 0.12 Å in this bond length to the value we have observed for **1** is consistent with removal of an electron from the π^* orbital.[11] This implies a solid-state MO diagram, $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$, which is not the same as that observed for isoelectronic Ru_2^{5+} cores with bridging ligands.

ESR provides a diagnostic tool for distinguishing between ground states of either one or three unpaired electrons. A quartet ground state would be subject to Kramer's rule and thus exhibit a $\Delta M_s = 1$ allowed transition in the microwave region (Kramer's doublet, $M_s = \pm^1/_2$). For an $S = {}^3/_2$ system with $D \gg gBH$,

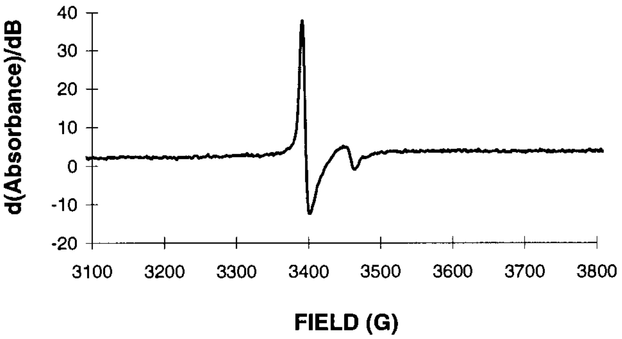

Figure 2. ESR spectrum of $[Ru(TPP)]_2PF_6$ at 77 K showing both the parallel ($g_\parallel = 1.953$) and perpendicular ($g_\perp = 1.993$) regions. Solvent system is 1:1 dichloromethane/toluene, and microwave frequency is 9.516 GHz.

Weltner has shown that the experimentally observed $g_\perp^e$ ($g_\perp$ effective) value may be estimated as $2g_\perp[1 - (3/16)(g_\perp BH/D)^2]$.[12] Thus, $g_\perp^e 2g_\perp$ and resonance should be observed in the range 3.8−4.5. Indeed, Drago and Telser have located the Kramer's doublet transition for $[Ru_2(C_3H_7COO)_4]Cl$ at $g_\perp^e = 4.40$.[13]

The ESR signal from **1** at 77 K is shown in Figure 2. The observed values, $g_\parallel = 1.953$ and $g_\perp = 1.993$, imply that $[Ru(TPP)]_2PF_6$ exhibits a single unpaired electron and is best described by an $S = {}^1/_2$ ground state. Hyperfine splitting due to $I = {}^5/_2$ ^{99}Ru (12.72% natural abundance) and $I = {}^5/_2$ ^{101}Ru (17.07% natural abundance) was not observed.

Solution magnetic susceptibility of **1** by the Evans method[14] is also consistent with the presence of a single unpaired spin. A value of 1.85 μ_B was obtained at 292 K in CD_2Cl_2. Analogous studies of carboxylate and amido bridged Ru_2^{5+} cores all gave magnetic moments between 3.7 and 4.3 μ_B.[15] Thus, the combination of ESR, Ru−Ru bond length, and magnetic moment all indicate that the $[Ru(TPP)]_2PF_6$ dimer exhibits a bonding scheme which is different from that seen for homologous systems with bridging ligands. For the unbridged porphyrin dimer, we have assigned this MO diagram as $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$.

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Supporting Information Available: Structural parameters and additional ORTEP diagrams (15 pages). Crystal information, in CIF format, is also available on the Internet only. Ordering and access information is available on any current masthead page.

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