[(Cyclen)₄Ru₄(pz)₄]⁹⁺: A Creutz−Taube Square

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The Creutz−Taube ion, $[(NH_3)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$ (pz = pyrazine),[1] has played a pivotal role in the development of our understanding of electron delocalization in mixed-valence systems. This fascinating molecule is rather tentatively regarded as exhibiting Class III[2] behavior, in which an electron delocalizes between the two metal centers to give an apparent oxidation state of $Ru^{2.5+}$ on the vibrational time scale.[3] The work stimulates the interesting question of whether pyrazine can facilitate electron delocalization over more than just two metal centers. To a certain extent, this issue has been addressed for linear chains containing up to six ruthenium centers;[4] however, the nonequivalence of the metal sites in such a geometry disfavors complete delocalization. In an effort to study delocalization in more symmetric pyrazine-bridged systems, we have adopted a synthetic approach akin to that employed in assembling high-nuclearity metal−cyanide clusters.[5] Herein, we report the synthesis of a mixed-valence square complex, $[(\text{cyclen})_4\text{-}Ru_4(pz)_4]^{9+}$ (cyclen = 1,4,7,10-tetraazacyclododecane), in which electron delocalization occurs between four equivalent Ru centers.

Cyclen was selected as a tetradentate blocking ligand owing to its conformational preference for the cis coordination geometry required in assembling a square. A solution of $[(\text{cyclen})\text{RuCl}_2]\text{Cl}$[6] (1.0 g, 2.6 mmol) and pyrazine (0.21 g, 2.6 mmol) in a mixture of 12 mL of ethanol and 8 mL of water was stirred and heated at reflux for 12 h under a dinitrogen atmosphere. The resulting purple solution was evaporated to dryness to give a red-green solid. Diffusion of THF vapor into a concentrated aqueous solution of this solid afforded dichroic red-green needle-shaped crystals. The crystals were collected by filtration, washed with successive aliquots of acetone (3 × 5 mL) and ether (3 × 5 mL), and dried in air to give 1.2 g (97%) of $[(\text{cyclen})_4\text{Ru}_4(pz)_4]\text{Cl}_9\cdot17\text{H}_2\text{O}$ (**1**).[7]

X-ray analysis of a crystal of $[(\text{cyclen})_4\text{Ru}_4(pz)_4]\text{Cl}_9\cdot24\text{H}_2\text{O}$ (**1**·7H₂O) verified the structure of the anticipated square complex.[8] As shown in Figure 1, the molecule consists of four Ru centers linked through pyrazine ligands to form a regular square with an edge dimension of 6.956(4) Å.[9,10] The asymmetric unit of the crystal structure features two distinct Ru atoms with essentially identical coordination environments. The Ru−N$_{pz}$ distances[8] of 2.020(13) and 2.049(12) Å are slightly longer than the corresponding distances in the Creutz−Taube ion, which fall in the range 1.972(4)-2.002-(2) Å.[11] Note, however, that—consistent with an average oxidation state of $Ru^{2.25+}$—these distances are intermediate to the Ru^{II}−N$_{pz}$ and Ru^{III}−N$_{pz}$ separations of 2.013(3) and 2.115(1) Å observed for the one-electron reduced and oxidized forms of the Creutz−Taube ion, respectively.[11] All four pyrazine rings in the square are equivalent by symmetry, and each is canted away from the Ru₄ plane by an angle of 55.9°. Note that opposing pairs of pyrazine ligands cant toward each other on alternate faces of the square, such that, overall, the complex approximates D_{2d} symmetry. Interestingly, the squares stack in a perfectly eclipsed fashion via
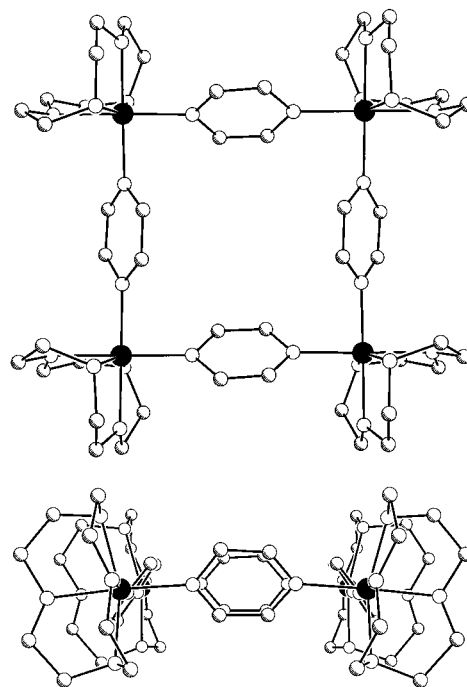

Figure 1. Structure of the square $[(\text{cyclen})_4\text{Ru}_4(pz)_4]^{9+}$ complex in **1**·7H₂O, as viewed parallel (upper) and perpendicular (lower) to the *a*-axis of the crystal. Black, shaded and white spheres represent Ru, C, and N atoms, respectively; H atoms are omitted for clarity. The molecule exhibits crystallographically imposed D_2 symmetry, with two-fold rotation axes running along (and perpendicular to) the diagonals of the Ru₄ square. Selected mean interatomic distances (Å) and angles (deg): Ru−N$_{pz}$ 2.03(2), Ru−N$_{cyclen}$ 2.08(4), Ru⋯Ru 6.956, N$_{pz}$−Ru−N$_{pz}$ 89.0, N$_{pz}$−Ru−N$_{cyclen}$ 89.5(2), 95.1(7), 100.9(5), N$_{cyclen}$−Ru−N$_{cyclen}$ 82(1), 92.2(6), Ru−N$_{pz}$⋯N$_{pz}$ 176(1), Ru⋯Ru⋯Ru 90(2).

intermolecular N−H⋯Cl⋯H−N interactions, forming one-dimensional columns that run along the *a*-axis of the crystal.

Compound **1** is soluble in water, methanol, and to a more limited extent, DMF. Its electronic absorption spectrum in aqueous solution[7] matches the diffuse reflectance spectrum of the solid, indicating that the square complex remains intact in solution. In the visible region, the absorption spectrum is dominated by a very intense band centered at 506 nm, with shoulders arising at 438 and 588 nm. Presumably, each of these features corresponds to an MLCT band in which a Ru^{II} d electron is promoted into a π^* orbital of a pyrazine ligand.[12] Surprisingly, no strong absorption bands occur in the near-infrared region of the spectrum; however, a manifold of low-intensity ($\epsilon_M < 10$) narrow-width peaks seemingly appears in the range 1550−1800 nm.[13]

Clean electrochemical behavior was not observed for **1** in any of the aforementioned solvents. Consequently, the solubility properties of the square complex were adjusted by partially exchanging the associated counteranions. A saturated aqueous solution of

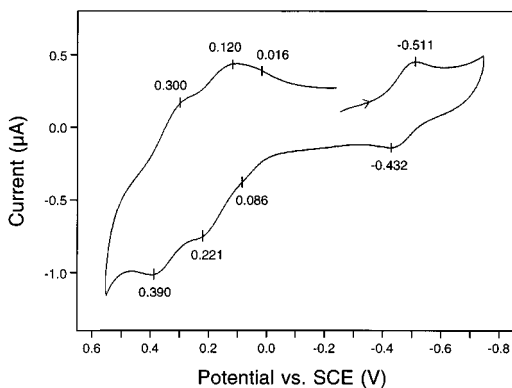* Corresponding author. E-mail: jlong@cchem.berkeley.edu.

Figure 2. Cyclic voltammogram of **2** in acetonitrile. The measurement was performed on a platinum electrode at a scan rate of 100 mV/s with 0.1 M (Bu$_4$N)PF$_6$ as the supporting electrolyte. Ferrocene was employed as an internal standard.

Na(BPh$_4$) was added to a saturated aqueous solution of **1**, prompting precipitation of a red-purple solid. The solid was collected by filtration, and washed with successive aliquots of water and ether to give an essentially quantitative yield of [(cyclen)$_4$Ru$_4$(pz)$_4$]-(BPh$_4$)$_6$Cl$_3$·4H$_2$O (**2**).[14] Compound **2** is soluble in polar organic solvents, such as acetone, acetonitrile, and DMF.

Figure 2 depicts the cyclic voltammogram for a saturated solution of **2** in acetonitrile. A quasireversible reduction wave corresponding to the [(cyclen)$_4$Ru$_4$(pz)$_4$]$^{9+/8+}$ couple is centered at $E_{1/2} = -0.472$ V ($\Delta E_p = 79$ mV) versus SCE.[15] A series of irreversible reduction processes occur at potentials beyond -0.8 V (not shown), and most likely correspond to reduction of the pyrazine ligands.[10d] One poorly resolved and two fairly distinct oxidation events are evident at $E_{1/2}$ = 0.051 V ($\Delta E_p = 70$ mV), 0.171 V ($\Delta E_p = 101$ mV), and 0.345 V ($\Delta E_p = 90$ mV) versus SCE. Assuming that the poorly resolved wave—which appears as a shoulder in differential pulse voltammograms—is indeed due to the square complex, these are reasonably assigned to the 9+/10+, 10+/11+, and 11+/12+ couples, respectively.[15] Further oxidation beyond 0.6 V leads to decomposition of the compound.

The separation between the first oxidation and reduction waves in the cyclic voltammogram of **2** indicates a comproportionation constant of $K_c = 10^{8.9}$ associated with the following equilibrium:

$$[Ru^{II}_4]^{8+} + [Ru^{II}_2Ru^{III}_2]^{10+} \rightleftharpoons 2[Ru^{II}_3Ru^{III}]^{9+} \qquad (1)$$
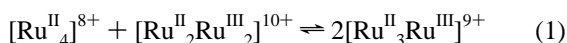
This is larger than the value of $K_c = 10^{6.6}$ reported for the Creutz—Taube ion,[1b] suggesting a greater degree of electron delocalization between the four metal centers in [(cyclen)$_4$Ru$_4$(pz)$_4$]$^{9+}$. Interestingly, subsequent oxidation waves are more closely spaced, implying a lesser degree of delocalization in the [Ru$^{II}_2$Ru$^{III}_2$]$^{10+}$ and [Ru^{II}Ru$^{III}_3$]$^{11+}$ squares, with $K_c = 10^{2.0}$ and $10^{3.0}$, respectively. Note that the decrease in extent of delocalization upon oxidation of the [Ru$^{II}_3$Ru^{III}]$^{9+}$ species is consistent with the diminished metal—pyrazine orbital interactions expected upon raising the average Ru oxidation state.

The foregoing results support assignment of the [(cyclen)$_4$Ru$_4$-(pz)$_4$]$^{9+}$ square as a class III mixed-valence complex;[3a] however, additional physical measurements are necessary to make this assertion with confidence.[16] Future research will attempt to probe the effects of further extending electron delocalization in such systems through the synthesis and characterization of a cubic Ru$_8$-(pz)$_{12}$ complex.

Supporting Information Available: Tables of crystallographic information for the structure of **1** (PDF), and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) This compound was synthesized using a procedure analogous to that reported for the preparation of [(cyclam)RuCl$_2$]Cl (cyclam = 1,4,8,11-tetraazacyclotetradecane): Sakai, K.; Yamada, Y.; Tsubomura, T. *Inorg. Chem.* **1996**, *35*, 3163.
(7) Characterization of **1**: Absorption spectrum (D$_2$O): λ_{max} (ϵ_M) 263 (24700), 331 (8900), 438 (sh, 21800), 506 (57100), 588 (sh, 22000) nm. μ_{eff} = 1.72 μ_B at 295 K. Anal. Calcd for C$_{48}$H$_{130}$Cl$_9$N$_{24}$O$_{17}$Ru$_4$: C, 28.27; H, 6.43; Cl, 15.65; N, 16.48; Ru, 19.83. Found: C, 28.39; H, 6.11; Cl, 15.31; N, 16.54; Ru, 19.47. The water content of this compound was confirmed by thermogravimetric analysis.
(8) Crystal and structure refinement parameters for **1**·7H$_2$O: C$_{48}$H$_{144}$Cl$_9$N$_{24}$O$_{24}$-Ru$_4$, T = 129 K, *Fddd*, Z = 8, a = 8.660(6) Å, b = 38.79(3) Å, c = 56.28(4) Å, V = 18904(21) Å^3, d_{calc} = 1.522 g/cm^3, R1 = 0.0794, wR2 = 0.1908. Data were collected on a Siemens SMART diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation, and were corrected for Lorentz, polarization, and absorption effects. The structure was refined against all data using SHELXTL 5.0. The chloride anions and solvate water molecules are severely disordered in the structure. The large esds associated with the interatomic distances and angles for the structure are a consequence of the extremely narrow diameter of the crystal, which limited the data to a resolution of only 1.00 Å.
(9) To our knowledge, the only other pyrazine-bridged square assemblies that have been structurally characterized are [(CO)$_{12}$X$_4$Re$_4$(pz)$_4$] (X = Cl, Br): (a) Slone, R. V.; Hupp, J. T.; Stern, C. L.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **1996**, *35*, 4096. (b) Rajendran, T.; Manimaran, B.; Lee, F.-Y.; Chen, P.-J.; Lin, S.-C.; Lee, G.-H.; Peng, S.-M.; Chen, Y.-J.; Lu, K.-L. *J. Chem. Soc., Dalton Trans.* **2001**, 3346.
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(13) Efforts to verify these features and monitor their solvent dependence are ongoing.
(14) Characterization of **2**: Absorption spectrum (MeCN): λ_{max} (ϵ_M) 265 (31200), 340 (8510), 433 (sh, 22600), 470 (sh, 33700), 514 (40000), 578 (sh, 24300) nm. Anal. Calcd for C$_{192}$H$_{224}$B$_6$Cl$_3$N$_{24}$O$_4$Ru$_4$: C, 65.75; H, 6.44; N, 9.58. Found: C, 65.98; H, 6.65; N, 9.22. The water content of this compound was confirmed by thermogravimetric analysis.
(15) For comparison, the 5+/4+ and 5+/6+ couples for the Creutz—Taube ion in aqueous solution occur at 0.13 and 0.52 V versus SCE, respectively.[1b]
(16) Thus far, our interpretations of infrared spectra have proven inconclusive in this regard. Weak bands arising from a symmetric pyrazine stretching mode (ν_{8a})[17] are apparent at 1589 and 1579 cm^{-1} in the spectra of solids **1** and **2**, respectively; however, given the symmetry of the square complex, the presence of these bands is not necessarily indicative of electron localization. Sharp features corresponding to the cyclen N—H stretching modes could not be discerned in either spectrum.
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