Table III. Interatomic Distances (Å) and Angles (Deg) for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$

| atoms | M = Mn | M = Re |
|---|---|---|
| (A) Metal-Metal Bond Length | | |
| M-M′ | 2.9038 (6) | 3.0413 (11) |
| (B) M-CO(axial) Distances | | |
| M-C(1) | 1.811 (3) | 1.929 (7) |
| M···O(1) | 2.945 (3) | 3.075 (7) |
| (C) M-CO(equatorial) Distances | | |
| M-C(2) | 1.854 (2) | 1.981 (6) |
| M-C(3) | 1.850 (2) | 1.987 (6) |
| M-C(4) | 1.853 (2) | 1.973 (6) |
| M-C(5) | 1.865 (2) | 2.007 (6) |
| M···O(2) | 2.988 (2) | 3.116 (5) |
| M···O(3) | 2.981 (2) | 3.119 (5) |
| M···O(4) | 2.975 (2) | 3.096 (5) |
| M···O(5) | 2.993 (2) | 3.128 (4) |
| (D) C-O Distances | | |
| C(1)-O(1) | 1.134 (4) | 1.146 (10) |
| C(2)-O(2) | 1.134 (4) | 1.136 (7) |
| C(3)-O(3) | 1.131 (3) | 1.132 (8) |
| C(4)-O(4) | 1.124 (3) | 1.124 (8) |
| C(5)-O(5) | 1.128 (3) | 1.122 (7) |
| (E) M′-M-CO(axial) Angle | | |
| M′-M-C(1) | 177.03 (9) | 176.34 (21) |
| (F) M′-M-CO(equatorial) Angles | | |
| M′-M-C(2) | 86.25 (7) | 86.70 (17) |
| M′-M-C(3) | 84.61 (7) | 84.21 (17) |
| M′-M-C(4) | 89.16 (7) | 89.71 (17) |
| M′-M-C(5) | 85.51 (7) | 84.88 (16) |
| (G) OC(axial)-M-CO(equatorial) Angles | | |
| C(1)-M-C(2) | 95.50 (11) | 95.52 (27) |
| C(1)-M-C(3) | 93.71 (11) | 93.65 (27) |
| C(1)-M-C(4) | 93.29 (12) | 93.29 (27) |
| C(1)-M-C(5) | 92.08 (11) | 92.19 (26) |
| (H) OC-M-CO(diequatorial) Angles | | |
| C(2)-M-C(3) | 170.67 (10) | 170.75 (24) |
| C(2)-M-C(4) | 88.16 (10) | 87.76 (24) |
| C(2)-M-C(5) | 89.98 (10) | 90.08 (24) |
| C(4)-M-C(5) | 174.46 (10) | 174.29 (24) |
| C(3)-M-C(4) | 89.84 (10) | 90.49 (24) |
| C(3)-M-C(5) | 91.17 (10) | 90.80 (23) |
| (I) M-C-O Angles | | |
| M-C(1)-O(1) | 179.21 (27) | 177.54 (65) |
| M-C(2)-O(2) | 178.14 (20) | 178.10 (52) |
| M-C(3)-O(3) | 178.54 (20) | 179.46 (53) |
| M-C(4)-O(4) | 176.34 (22) | 176.60 (54) |
| M-C(5)-O(5) | 178.53 (30) | 177.86 (51) |

value of 2.923 (3) Å. (Interestingly, the change in this distance arises principally from changes in the measured unit-cell dimensions rather than from major shifts in the fractional atomic coordinates.) The newly determined Re–Re bond length is 3.0413 (11) Å, somewhat *longer* than the previously accepted distance of 3.02 Å.[13]

(2) The axial manganese–carbonyl distance of 1.811 (3) Å is 0.045 Å shorter than the average equatorial manganese–carbonyl distance of 1.856 [7] Å.[14] Similarly, the Re–CO(axial) bond length of 1.929 (7) Å is 0.058 Å shorter than the average Re–CO(equatorial) bond length of 1.987 [15] Å. This result is in accordance with the accepted model for M–CO bonding and is the net result of competition for $d_\pi$ electron density between mutually trans pairs of equatorial carbonyl ligands.

(3) The axial manganese···oxygen and rhenium···oxygen distances (2.945 (3) and 3.075 (7) Å, respectively) are shorter than the appropriate equatorial metal···oxygen distances (Mn···O(equatorial, average) = 2.984 [8] Å and Re···O(equatorial, average) = 3.115 [13] Å).

(4) The Mn′–Mn–CO(equatorial) angles are all acute, ranging from 84.61 (7) to 89.16 (7)° and averaging 86.38°. The Re′–Re–CO(equatorial) angles show similar trends, ranging from 84.21 (17) to 89.71 (17)° and averaging 86.38°.

(5) The OC(axial)–M–CO(equatorial) angles are all obtuse, ranging from 92.08 (11) to 95.50 (11)° in $Mn_2(CO)_{10}$ and 92.19 (26) to 95.52 (27)° in $Re_2(CO)_{10}$.

(6) The carbon–oxygen distances are all equivalent within the limits of experimental error. Ranges are 1.124 (3)–1.134 (4) Å in $Mn_2(CO)_{10}$ and 1.122 (7)–1.146 (10) Å in $Re_2(CO)_{10}$.

(7) All M–C–O systems are close to linear; individual values range from 176.34 (22) to 179.21 (27)° in $Mn_2(CO)_{10}$ and 176.60 (54) to 179.46 (53)° in $Re_2(CO)_{10}$.

(8) The molecules have approximate $D_{4d}$ symmetry in the solid state (see Figure 3). There are, however, numerous small deviations that are common to the two structures and presumably result from intermolecular interactions.

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**Registry No.** $Mn_2(CO)_{10}$, 10170-69-1; $Re_2(CO)_{10}$, 14285-68-8.

**Supplementary Material Available:** Tables of observed and calculated structure factor amplitudes for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ and table of data-processing formulas (17 pages). Ordering information is given on any current masthead page.

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[13] An electron diffraction study of $Re_2(CO)_{10}$ has revealed a Re–Re distance of 3.040 (5) Å: Gapotchenko, N. J.; Struchkov, Yu. T.; Alekseev, N. V.; Ronova, I. A. *J. Struct. Chem.* **1973**, *14*, 383.

[14] Esd's of average distances are enclosed in square brackets. They are calculated via the scatter formula $[\sigma]^2 = \sum_N (d_i - \bar{d})^2/(N - 1)$.

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Contribution from the Department of Chemistry,
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# Mixed-Valence Pyrazine-Bridged Complexes of Ruthenium-Containing Substituted Phenanthrolines

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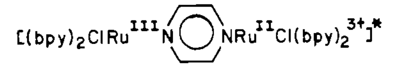
Mixed-valence transition-metal complexes continue to be of special interest, primarily because of the insight they provide into metal–metal interactions.[1] With the Hush model for mixed-valence complexes,[2] the extent of metal–metal interaction can be derived from the properties of the intervalence-transfer (IT) band (e.g., eq 1 for $[(bpy)_2ClRu(pyz)RuCl(bpy)_2]^{3+}$ (bpy = 2,2′-bipyridine).[3] Although several studies have focused on the effect of systematic changes in the *bridging* ligand on metal–metal interactions in these complexes,[4] few have examined the effect of a systematic change in the *nonbridging* ligands around the metal centers. Changes in the electronic environment about the metal could presumably lead to dramatic changes in the extent of metal–metal interaction. An understanding of such effects is essential if systems are to be designed in which the degree of metal–metal



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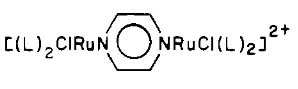
interaction is to be systematically controlled.

Our interest in studying metal–metal interactions in mixed-valence complexes resulted from a comparison of the properties of the previously reported $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ [5] (**1**) and $[(bpy)_2ClRu(pyz)RuCl(bpy)_2]^{3+}$ [3] (**2**) mixed-valence ions (pyz = pyrazine). Metal–metal interactions were observed to be considerably stronger in **1** than in **2**. One suggested explanation for the difference lay in the ability of the bipyridine ligands to "rob" the ruthenium centers of electron density via back-bonding. The effect should lead to a reduced interaction by the ruthenium ion with the $\pi$ system of the bridging pyrazine, presumably the pathway for metal–metal interaction. The observation suggested that, by varying the electron density around the metal centers, the extent of metal–metal interaction could be controlled. Specifically, increasing the electron density might lead to stronger interactions and vice versa.

It is the purpose of this paper to examine a series of dimeric mixed-valence complexes where electron density around the metal centers is varied through substitution of a variety of 1,10-phenanthroline ligands. Initially, complexes of Ru(II) of the type



[2,2]

(L= 5-nitro-1,10-phenanthroline (nitrophen), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (dimethylphen), 3,4,7,8-tetramethyl-1,10-phenanthroline (tetramethylphen)) were prepared, followed by preparation of the fully oxidized Ru(III) analogues ([3,3]). Then, taking advantage of the comproportionation reaction (eq 2), the

$$[2,2] + [3,3] \rightleftharpoons 2[2,3] \qquad (2)$$

mixed-valence complexes ([2,3]) were generated in situ and examined.

## Experimental Section

1,10-Phenantholine and the substituted 1,10-phenanthrolines were commercially available. $[(1,10\text{-phenanthroline})_2RuCl_2]\cdot 3H_2O$ and $[(3,4,7,8\text{-tetramethyl-}1,10\text{-phenanthroline})_2RuCl_2]\cdot 3H_2O$ were prepared as previously described.[6] $[(5\text{-nitro-}1,10\text{-phenanthroline})_2RuCl_2]\cdot 3H_2O$ and $[(4,7\text{-dimethyl-}1,10\text{-phenanthroline})_2RuCl_2]\cdot 3H_2O$ were prepared in an identical manner. A solution of cerium(IV) perchlorate (~0.5 M) in 6 M $HClO_4$ was obtained from G. F. Smith and Co.

Electrochemical measurements were made vs. the saturated sodium chloride calomel electrode (SSCE) with a platinum-bead electrode at 25 ± 2 °C with use of a PAR Model 174A polarographic analyzer. Near-infrared spectra were recorded with use of a Cary Model 14 spectrophotometer. Elemental analyses were performed by Integral Microanalytical Labs (Raleigh, NC), by Galbraith Laboratories (Knoxville, TN), and by Mr. David Stammerjohn of this department.

**Preparations.** All procedures involving the preparations of the following compounds were carried out in the absence of light. All compounds gave satisfactory elemental analyses. *Caution! Some of the perchlorate salts of Ru(II) and Ru(III) were subject to detonation. It is suggested that the materials be handled only in small quantities.*

Table I. Electrochemical Data for Phenanthroline Complexes of Ru(II) in Acetonitrile[a]

| L | $E_{1/2}(1)$ | $E_{1/2}(2)$ |
|---|---|---|
| $[(L)_2ClRu(pyz)]^+$ [b] | | |
| nitrophen | 0.99 | |
| phen | 0.86 | |
| dimethylphen | 0.77 | |
| tetramethylphen | 0.73 | |
| $[(L)_2ClRu(pyz)RuCl(L)_2]^{2+}$ [c] | | |
| nitrophen | 1.00 | 1.10 |
| phen | 0.88 | 0.98 |
| dimethylphen | 0.79 | 0.89 |
| tetramethylphen | 0.73 | 0.85 |

[a] Potentials are in volts vs. SSCE at 25 ± 2 °C in 0.1 M TEAP (tetraethylammonium perchlorate). The estimated error is ±0.01 V. [b] Potentials refer to the reaction $[(L)_2ClRu(pyz)]^{2+} + e^- \rightarrow [(L)_2ClRu(pyz)]^+$. [c] Potentials refer to the reactions $[(L)_2ClRu(pyz)RuCl(L)_2]^{4+} + e^- \rightarrow [(L)_2ClRu(pyz)RuCl(L)_2]^{3+}$ ($E_{1/2}(2)$) and $[(L)_2ClRu(pyz)RuCl(L)_2]^{3+} + e^- \rightarrow [(L)_2ClRu(pyz)RuCl(L)_2]^{2+}$ ($E_{1/2}(1)$).

**$[(L)_2Ru(pyz)Cl](ClO_4)$.** In a typical preparation, $[(1,10\text{-phenanthroline})_2RuCl_2]\cdot 3H_2O$ (342.3 mg, 0.584 mmol) was suspended in a 2:1 acetone–methanol solution. $AgClO_4$ (0.1256 g, 0.606 mmol) and pyrazine (0.7188 g, 8.97 mmol) were added, and the mixture was stirred under nitrogen between 30–50 °C for ~2 h. The reaction mixture was filtered to remove AgCl, and the filtrate was added to stirring ether (300 mL) to produce a red-orange precipitate. The product was purified by column chromatography on neutral alumina using acetonitrile for elution. The pure product was the first band to elute from the column. The product was isolated by adding the acetonitrile solution to stirring ether to produce a red-orange solid which was collected, washed with ether, and dried under vacuum. Yields for compounds ranged from 20% to almost 100%.

**$[(L)_2ClRu(pyz)RuCl(L)_2](ClO_4)_2$.** In a typical preparation, $[(1,10\text{-phenanthroline})_2RuCl_2]\cdot 3H_2O$ (488.9 mg, 0.834 mmol) was suspended in a 5:1 acetone–methanol solution (~60 mL), and $AgClO_4$ (173.0 mg, 0.835 mmol) was added. The mixture was heated at reflux under nitrogen for ~3 h. The resulting purple-red solution of $[(L)_2Ru(solvent)Cl]^+$ was filtered to remove AgCl. To the filtrate was added $[(1,10\text{-phenanthroline})_2Ru(pyz)Cl](ClO_4)$ (0.5640 g, 0.834 mmol), and the resulting solution was heated to reflux for ~48 h under nitrogen. The black-red product which precipitated from the solution was collected, washed with ether, and dried under vacuum. Yields for compounds ranged from 40% to 63%.

**$[(L)_2ClRu(pyz)RuCl(L)_2](ClO_4)_4$.** In a typical preparation, $[(1,10\text{-phenanthroline})_2ClRu(pyz)RuCl(1,10\text{-phenanthroline})_2](ClO_4)_2\cdot 5H_2O$ (107.4 mg, 0.0788 mmol) was suspended in stirring acetonitrile (~5 mL), and 0.1 N Ce(IV) in 1.2 N $HClO_4$ was added dropwise (1.6 mL, 0.16 mmol) to produce a green-brown suspension. Additional 0.1 N Ce(IV) was added (~1 mL) to ensure complete oxidation. A sample of 1.0 N $HClO_4$ (~25–50 mL) was then added to complete precipitation of the product. The precipitate was collected, washed with 1.0 N $HClO_4$, and dried under vacuum. The yield was 80%.

The purity of the compounds was checked spectrophotometrically by reduction of a dilute solution of the compounds in acetonitrile with $N_2H_4$ and comparison of the resulting spectrum with the one expected for the pure reduced complex.[3]

## Results and Discussion

Prior to preparation and study of the dinuclear complexes, the parent monomeric complexes, $[(L)_2ClRu(pyz)]^+$, were examined. All of the complexes undergo a reversible oxidation in acetonitrile from Ru(II) to Ru(III) (Table I). The $E_{1/2}$ values for the process (expressed as reduction potentials) have a range of 260 mV, suggesting significant differences in the amount of electron density about the metal center in the various complexes.

In addition, there exists an essentially linear relationship between the p$K_a$'s of the free phenanthroline (Figure 1) ligands and the $E_{1/2}$ values for the monomeric complexes. The rela-

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(1) For recent reviews, see: (a) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. (b) Taube, H. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 481. (c) Meyer, T. J. *Ibid.* **1978**, *313*, 496.

(2) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.

(3) Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064.

(4) See, for example: (a) Felix, F.; Ludi, A. *Inorg. Chem.* **1978**, *17*, 1782. (b) Powers, M. J.; Salmon, D. J.; Callahan, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 6731. (c) Fischer, H.; Tom, G. M.; Taube, H. *Ibid.* **1976**, *98*, 5512.

(5) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.

(6) Giordano, P. J.; Bock, C. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 6960.

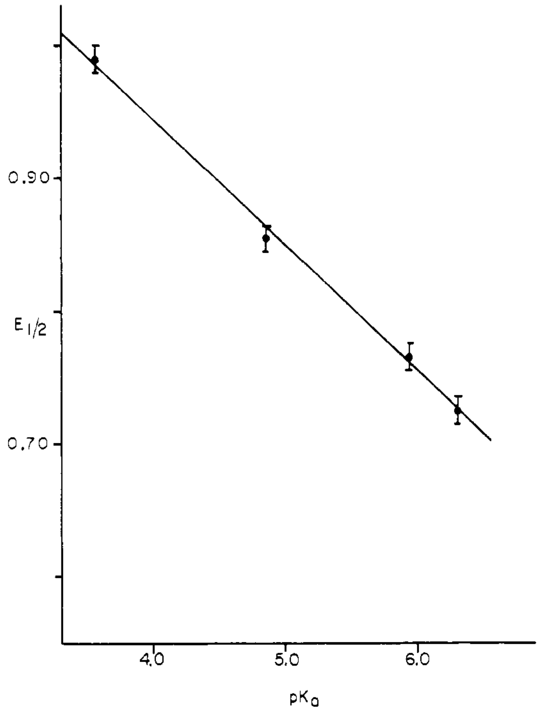

**Figure 1.** $E_{1/2}$ (V) for $[(L)_2Ru(Cl)(pyz)]^{2+/+}$ couples vs. p$K_a$ for L ligands. p$K_a$ values are taken from: (a) Day, P.; Sander, N. *J. Am. Chem. Soc. A* **1967**, 1530. (b) Brandt, W. W.; Gullstrom, D. K. *J. Am. Chem. Soc.* **1952**, *74*, 3532. (c) Yasada, M.; Sone, K.; Yamasaki, K. *J. Phys. Chem.* **1956**, *60*, 1667.

**Table II.** $\pi \rightarrow \pi^*$ Transitions of Phenanthroline Ligands in Acetonitrile[a]

| L | $\lambda_{max}(1)$ | $\lambda_{max}(2)$ |
|---|---|---|
| nitrophen | 263 | 230 |
| phen | 263 | 229 |
| dimethylphen | 263 | 236 |
| tetramethylphen | 269 | 243 |

[a] $\lambda_{max}$ values are expressed in nanometers (nm) with an estimated error of ±1 nm.

tionship is a reflection of the classical electron-donating ability of methyl groups and electron-withdrawing ability of nitro groups. Donation of electron density to the metal center makes oxidation of Ru(II) to Ru(III) more facile while withdrawal of electron density from the metal center makes oxidation more difficult. Generally, p$K_a$ values are thought to reflect the $\sigma$-donor abilities of the free ligand and the strength of the resulting $\sigma$ bond between the ligand and the metal.[7] The observed linear relationship suggests that the variation of the $E_{1/2}$ values in the monomeric series is due primarily to changes in $\sigma$-electron density around the ruthenium ions. If the $\pi$-acceptor abilities of the ligands were also changing dramatically (at least, in comparison with the $\sigma$-donor abilities), deviations in the p$K_a$ vs. $E_{1/2}$ plot would be suspected.[7] In addition, the $\pi \rightarrow \pi^*$ transitions[8] in the free phenanthroline ligands (Table II) all occur at essentially the same energies. With the assumption that these transitions correctly relate to the orbitals employed by the metal for back-bonding, the observation also is consistent with small deviations in the $\pi$-acceptor properties of the ligands.

The analogous dinuclear [2,2] complexes undergo an initial reversible oxidation to produce the mixed-valence [2,3] ions followed by a second reversible oxidation to give the fully oxidized [3,3] ions (Table I). This behavior is expected given the similarity between these systems and other pyrazine-bridged ruthenium systems.[3,5]

**Table III.** Intervalence Transfer (IT) Bands for Mixed-Valence $[(L)_2ClRu(pyz)RuCl(L)_2]^{3+}$ Complexes in Acetonitrile[a]

| L | IT $10^{-3}\lambda_{max}$,[b] cm$^{-1}$ | $\epsilon$,[c] M$^{-1}$ cm$^{-1}$ | $10^2 f$[d] |
|---|---|---|---|
| nitrophen | 7.9 | 458 | 0.937 |
| phen | 7.6 | 650 | 1.48 |
| dimethylphen | 7.5 | 735 | 1.59 |
| tetramethylphen | 7.7 | 589 | 1.27 |

[a] 25 ± 2 °C. [b] Estimated error is ±100 cm$^{-1}$. [c] Estimated error in reproducibility is ±5%. The concentrations of the mixed valence species were calculated from the $\Delta G_{com}$ values given in Table IV. [d] Oscillator strength.[2]

**Table IV.** Stability of Mixed-Valence $[(L)_2ClRu(pyz)RuCl(L)_2]^{3+}$ Complexes[a]

| L | $\Delta G_{com}$ V | $\Delta G_{com}$ kcal/mol |
|---|---|---|
| nitrophen | 0.10 | −2.3 |
| phen | 0.10 | −2.3 |
| dimethylphen | 0.10 | −2.3 |
| tetramethylphen | 0.12 | −2.8 |

[a] Values are in 0.1 M TEAP/$CH_3CN$ at 25 ± 2 °C.

The mixed-valence [2,3] species were generated in situ by mixing equimolar quantities of the [2,2] and [3,3] ions in acetonitrile (eq 2). As observed with previous mixed-valence ruthenium systems, all the complexes displayed an IT band in the near-infrared region (Table III). The IT bands are all at approximately the same energy (~7.7 × 10$^3$ cm$^{-1}$). According to the Hush theory, this means that the activation energies ($E_{th}$) for thermal electron transfer

$$[2,3] \xrightarrow[E_{th}]{k_{et}} [3,2]$$

and the corresponding rates of thermal intramolecular electron transfer ($k_{et}$) in all the complexes are very similar (~5.5 kcal/mol and 5.7 × 10$^8$ s$^{-1}$, respectively[9]). Previous studies involving substituted phenanthroline complexes of ruthenium suggest that activation barriers to electron transfer should indeed be very similar for such complexes.[13]

It has been noted that the free energy change ($\Delta G_{com}$) for reaction 2 may give some indication as to the extent of metal–metal interaction in mixed-valence complexes.[1b,3] In a series of mixed-valence complexes where the size and charge remain essentially constant (as is true for the mixed-valence complexes under consideration), variations in $\Delta G_{com}$ presumably would reflect any effects of resonance delocalization energy on the stabilization of the mixed-valence species. As seen in Table IV, $\Delta G_{com}$ remains essentially constant for the phenanthroline mixed-valence complexes, suggesting that electronic delocalization in all the mixed-valence species is very similar.

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(7) Buckingham, D. A.; Sargeson, A. M. "Chelating Agents and Metal Chelates"; Dwyer, F. P., Mellor, D. P., Eds.; Academic Press: New York, 1964; pp 237–282.

(8) McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 135.

(9) The average activation energy, $E_{th}$, for intramolecular electron transfer was estimated from the average energy of the intervalence transfer band, $E_{op}$, with use of the Hush relationship for a symmetrical mixed-valence system: $E_{th} \approx E_{op}/4$. The rate constant for electron transfer, $k_{et}$, was then estimated by using $k_{et} = k_B T/h \exp(-E_{th}/RT)$. If the effects of delocalization are inclued in the estimates, $E_{th} \approx E_{op}/4 - H_{12}$, where $H_{12}$ arises through resonance interaction between the two metal sites.[3,10,11] Estimating $H_{12}$ as ~1.3 kcal/mol[3,11] gives $E_{th} \approx$ 4.2 kcal/mol and $k_{et} \approx 5.2 \times 10^9$ s$^{-1}$. Modification of the preexponential term ($k_B T/h$) can also lead to different estimates of $k_{et}$.[3,12]

(10) Creutz, C.; Kroger, P.; Matsubara, T.; Netzel, T. L.; Sutin, N. *J. Am. Chem.* Soc. **1979**, *101*, 5442.

(11) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

(12) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 752.

(13) Lin, C. T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.

Another measure of the extent of the metal–metal interaction in mixed-valence ions is the intensity of the IT band. With the Hush model, as the ground-state electronic interaction between the two metal ions increases, the intensity of the IT band should increase.[14] Given in Table III are the extinction coefficients for the IT bands and the corresponding oscillator strengths.

In contrast to the $\Delta G_{\mathrm{com}}$ measurements, the intensity measurements indicate that differences in metal–metal interaction do exist for the mixed-valence complexes. The trend of the increasing interaction with increasing electron density about the metal center is followed up to the 4,7-dimethyl-1,10-phenanthroline complex. The 3,4,7,8-tetramethyl-1,10-phenanthroline complex unexpectedly breaks the pattern. Models indicate a possible steric problem with crowding between the 3(8) methyl group on one ruthenium site and the 3(8) methyl group on the other ruthenium site in this complex. The difficulty, however, does not appear to be overly severe, specifically, not sufficiently severe to cause significant deviation from any ruthenium–pyrazine–ruthenium orientation that could exist for the other mixed-valence complexes.

Although the intensity studies suggest differences in the extent of metal–metal interaction in these complexes, the differences are apparently not of sufficient magnitude to be reflected in differences in $\Delta G_{\mathrm{com}}$. The contribution to $\Delta G_{\mathrm{com}}$ due to stabilization by electronic delocalization can be estimated with use of method developed by Taube and co-workers.[11] With this procedure, resonance stabilization of the [2,3] species can be estimated to be very small and to vary from 52 cal/mol (2.3 mV) for the $\mathrm{[(nitrophen)_2ClRu(pyz)RuCl(nitrophen)_2]^{3+}}$ complex to 89 cal/mol (3.9 mV) for $\mathrm{[(dimethylphen)_2ClRu(pyz)RuCl(dimethylphen)_2]^{3+}}$.[17] Such small differences in resonance interactions (~2 mV) would be undetectable in making determinations of $\Delta G_{\mathrm{com}}$ values.[18]

Although the amount of electron density on the ruthenium centers is being varied in the series of mixed-valence complexes, the variation does not cause overly dramatic increases or decreases in the extent of metal–metal interaction. The valence electrons on the ruthenium centers are in the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals. One, or more, of these orbitals is of appropriate symmetry to overlap with the $\pi$ system of the bridging pyrazine, which is thought to be the pathway for metal–metal interactions in these complexes. As discussed above, the variation in electron density in the series arises through variation in the $\sigma$-donor ability of the various phenanthroline ligands. To a reasonable approximation, the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals are not of appropriate symmetry to interact significantly with the $\sigma$ orbital on the nitrogen donating the pair of electrons from the ligand. Since the $\pi$-accepting abilities of the various ligands apparently are similar, the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals may be at very similar energies in all the complexes. If so, the interaction of the $d_{xy}$, $d_{yx}$, and $d_{xz}$ orbitals with the $\pi$ system of pyrazine will be similar for all complexes, resulting in only small differences in metal–metal interaction. Instead of using ligands which have a variable $\sigma$-donor ability, it may be more appropriate to use ligands which have a variable $\pi$-donor ability (such as dithiocarbamates)[20] to cause significant changes in ruthenium–ruthenium interaction in complexes like these.

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**Registry No.** $\mathrm{[(nitrophen)_2Ru(pyz)Cl](ClO_4)}$, 76529-22-1; $\mathrm{[(phen)_2Ru(pyz)Cl](ClO_4)}$, 76529-24-3; $\mathrm{[(dimethylphen)_2Ru(pyz)Cl](ClO_4)}$, 76514-56-2; $\mathrm{[(tetramethylphen)_2Ru(pyz)Cl](ClO_4)}$, 76514-58-4; $\mathrm{[(nitrophen)_2ClRu(pyz)RuCl(nitrophen)_2](ClO_4)_2}$, 76514-60-8; $\mathrm{[(phen)_2ClRu(pyz)RuCl(phen)_2](ClO_4)_2}$, 76514-62-0; $\mathrm{[(dimethylphen)_2ClRu(pyz)RuCl(dimethylphen)_2](ClO_4)_2}$, 76514-64-2; $\mathrm{[(tetramethylphen)_2ClRu(pyz)RuCl(tetramethylphen)_2](ClO_4)_2}$, 76514-66-4; $\mathrm{[(nitrophen)_2ClRu(pyz)RuCl(nitrophen)_2](ClO_4)_4}$, 76514-68-6; $\mathrm{[(phen)_2ClRu(pyz)RuCl(phen)_2](ClO_4)_4}$, 76514-70-0; $\mathrm{[(dimethylphen)_2ClRu(pyz)RuCl(dimethylphen)_2](ClO_4)_4}$, 76514-72-2; $\mathrm{[(tetramethylphen)_2ClRu(pyz)RuCl(tetramethylphen)_2](ClO_4)_4}$, 76514-74-4; $\mathrm{[(nitrophen)_2ClRu(pyz)RuCl(nitrophen)_2]^{3+}}$, 76549-97-8; $\mathrm{[(phen)_2ClRu(pyz)RuCl(phen)_2]^{3+}}$, 76549-98-9; $\mathrm{[(dimethylphen)_2ClRu(pyz)RuCl(dimethylphen)_2]^{3+}}$, 76549-99-0; $\mathrm{[(tetramethylphen)_2ClRu(pyz)RuCl(tetramethylphen)_2]^{3+}}$, 76550-00-0; $\mathrm{(phen)_2RuCl_2}$, 15453-59-5; $\mathrm{(tetramethylphen)_2RuCl_2}$, 68510-56-5; $\mathrm{(nitrophen)_2RuCl_2}$, 76514-75-5; $\mathrm{(dimethylphen)_2RuCl_2}$, 76514-76-6; nitrophen, 4199-88-6; phen, 66-71-7; dimethylphen, 3248-05-3; tetramethylphen, 1660-93-1; $\mathrm{[(nitrophen)_2Ru(pyz)Cl](ClO_4)_2}$, 76514-78-8; $\mathrm{[(phen)_2Ru(pyz)Cl](ClO_4)_2}$, 76514-80-2; $\mathrm{[(dimethylphen)_2Ru(pyz)Cl](ClO_4)_2}$, 76514-82-4; $\mathrm{[(tetramethylphen)_2Ru(pyz)Cl](ClO_4)_2}$, 76514-84-6.

**Supplementary Material Available:** Analytical data for the ruthenium phenanthroline compounds (1 page). Ordering formation is given on any current masthead page.

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[14] The Hopfield[15] and "PKS"[16] models for mixed-valence complexes also develop the same relationship.

[15] Hopfield, J. J. *Biophys. J.* **1977**, *18*, 311.

[16] (a) Piepho, S. B.; Krausz, E. R.; Schatz, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 2996. (b) Wong, K. Y.; Schatz, P. N.; Piepho, S. B. *J. Am. Chem Soc.* **1979**, *101*, 2793.

[17] Resonance stabilization of $\mathrm{[(phen)_2ClRu(pyz)RuCl(phen)_2]^{3+}}$ and $\mathrm{[(tetramethylphen)_2ClRu(pyz)RuCl(tetramethylphen)_2]^{3+}}$ were estimated as 81 cal/mol (3.5 mV) and 69 cal/mol (3.0 mV), respectively. The values were calculated from the data in Table III, on the assumption $d$ (the distance between the metal ions) = 6.9 $\text{Å}^3$ and the bandwidths ($\Delta\nu_{1/2}$) $4.5 \times 10^3$ (nitrophen complex,) $5.0 \times 10^3$ (phen complex), $4.7 \times 10^3$ (dimethylphen complex), and $4.7 \times 10^3$ cm$^{-1}$ tetramethylphen complex).

[18] $\Delta G_{\mathrm{com}}$ is determined from the relationship $\Delta G_{\mathrm{com}} = E_{1/2}(2) - E_{1/2}(1)$.[19] Since experimental error in determining the $E_{1/2}$ values may be as high as ±10 mV, differences in resonance interactions less than 10 mV would be difficult to accurately determine.

[19] See, for example: Gagne, R. R.; Koval, C. A.; Smith, T. J.; Cimolina *J. Am Chem. Soc.* **1979**, *101*, 4571.

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# X-ray Photoelectron Spectra of Inorganic Molecules. 28.[1] Sulfur 2p Binding Energies of Molybdenum Complexes Believed To Contain a Coordinated Partial Disulfide Bond

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From previous X-ray photoelectron spectra (XPS) measurements,[3-9] the binding of thioether and thiolate moieties to metal ions ($\mathrm{M{\leftarrow}SR_2}$ and M—SR coordination, respectively)

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[1] (a) Part 27: Walton, R. A. *Inorg. Chem.*, **1980**, *19*, 1100. (b) The present paper is Contribution No. 750 from the Charles F. Kettering Research Laboratory.

[2] (a) Purdue University. (b) Charles F. Kettering Research Laboratory.

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