What Determines the Comproportionation Constant in Molecule-Bridged Mixed-Valence Complexes? Evidence for the Crucial Role of the Ligand LUMO in Four Ru^II Ru^III Dimers

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Electrochemical data of four bis chelate bridged complexes $\{[Ru(bpy)_2]_2(\mu,\eta^4\text{-L})\}^{n+}$, bpy = 2,2′-bipyridine, show conclusively that the electron density at the coordination centers in the LUMO of the bridging π ligand determines the comproportionation constant of the Ru^II Ru^III mixed-valence state ($n = 5$). Neither the number of mediating π centers nor the distance or the orientation of the two metal centers plays a significant role. The presence of two equivalent chiral metal centers in these complexes leads to formation of meso and DL diastereomers, as shown for one example by ^{1}H NMR.

An essential requirement for the isolability of mixed-valence complexes is a sufficiently large comproportionation constant K_c. The comprehensive studies in the field of ruthenium(II, III) pentaammine mixed-valence systems,[1-5] which had commenced with the synthesis of the pyrazine-bridged Creutz–Taube ion ($K_c = 4 \times 10^6$),[1,2] have suggested some answers as to what factors can contribute to K_c; however, these factors frequently showed variation in the same direction. For example, the large K_c of $\sim 10^8$ for the N$_2$-bridged complex[2,4] can have its origin in the short metal–metal distance ($d_{\text{M-M}} \approx 500$ pm)[3] and the possibility for direct d/d overlap (orientation), in the small π system of the bridge, or in the high electron density at N in the possibly interacting π^* LUMO of the ligand. Conversely, the small $K_c = 2 \times 10^1$ in the 4,4′-bipyridine-bridged system[2,5] can result from the opposite of either of these reasons; the metal–metal distance and the bridging π system are large, whereas the LUMO electron density at the coordinating centers is relatively small because of delocalization within the ligand.[6]

We can now present and compare K_c values of four complexes[7,8] of $[Ru(bpy)_2]^{n+}$ fragments (bpy = 2,2′-bipyridine) with bis chelate ligands (Chart I); despite rather positive oxidation potentials, these complexes clearly show which of the above-mentioned effects is responsible for K_c. A detailed characterization of the ligands (Chart I) has shown[10] that they should be very useful to distinguish between "direct" and ligand-mediated metal–metal interaction.

Experimental Section

Cyclic voltammetry was performed with ca. 10^{-3} M solutions of the complexes in CH$_3$CN/0.1 M Bu$_4$N$^+$ClO$_4^-$; all materials were rigorously dried. A three-electrode configuration, including a glassy-carbon working electrode and SCE or Ag/AgCl reference electrode, was used; equipment consisted of a PAR Model 363 potentiostat and a Wenking Model VSG 72 scan generator. ^{1}H NMR spectra (270 MHz) were recorded on a Bruker WH 270 system; electronic absorption spectra were taken on a Pye Unicam SP 1800 spectrometer.

The ligands bppz, bptz, and abpy were prepared according to literature procedures.[8,9] The dinuclear complex of bppz was obtained as the mono(acetonitrile) tetrakis(hexafluorophosphate) compound by reacting the ligand with 2 equiv of cis-Ru(bpy)$_2$Cl$_2$ for 20 min in ethanol/water (1:10) under reflux. Precipitation with a saturated aqueous solution of NH$_4$PF$_6$ and recrystallization from acetonitrile/ether yielded 85% of the dark green compound ($\nu_{\text{MLCT}} = 17\,120$ and $23\,150$ cm^{-1} in CH$_3$CN). Anal. Calcd for C$_{56}$H$_{45}$F$_{24}$N$_{13}$P$_4$Ru$_2$ (M_r 1682.1): C, 39.98; H, 2.70; N, 10.83. Found: C, 39.77; H, 2.97; N, 10.99.

The analogous syntheses of the dinuclear bptz[8a-c] and abpy complexes[8a] have been described; the yield of the latter could be improved[8a] to 27% by treating the red mononuclear complex [(abpy)Ru(bpy)$_2$]$^{2+}$ with
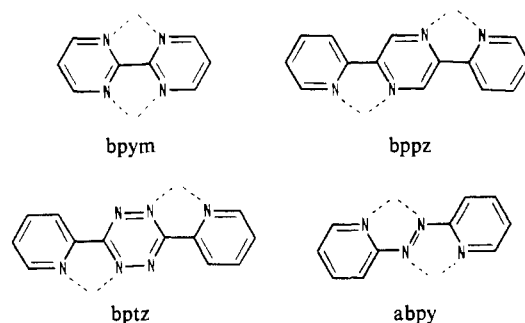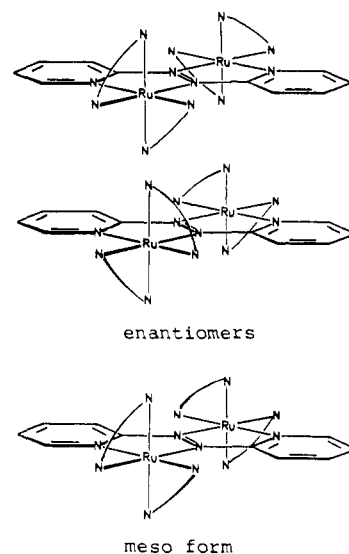
Chart I

bpym   bppz

bptz   abpy

Chart II. Meso Form (Bottom) and Pair of Enantiomers (Top) of the Dinuclear Abpy Complex with $[Ru(bpy)_2]^{n+}$ Fragments

enantiomers

meso form

a further 1 equiv of cis-Ru(bpy)$_2$Cl$_2$ for 6 h in boiling 1-butanol. Precipitation of the tetracation as the tetrakis(hexafluorophosphate) com-

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Table I. Oxidation Potentials E^a of Dinuclear [Ru(bpy)$_2$]$^{2+}$ Complexes with Symmetrically Bridging Ligands μ-L (Chart I) and Characteristics of These Ligands[b-e]

L	$E^{4+,5+}$	$E^{5+,6+}$	ΔE	K_c	$\sum c_N^{2\ b}$	$\sum a_N^c$	d_{M-M}	m^e
bpym[f]	1.53	1.69	0.16	5×10^2	0.380	0.912	550	3
bppz	1.39	1.58	0.19	2×10^3	0.419	1.072	700	4
bptz	1.52	2.02	0.50	3×10^8	0.532	1.280	700	4
abpy	1.67	2.22	0.55	2×10^9	0.668	1.680	490	2

[a] Electrochemical data in V vs SCE from cyclic voltammetry in CH$_3$CN/0.1 M Bu$_4$N$^+$ClO$_4^-$. $K_c = 10[\exp(\Delta E)/0.059$ V]. [b] Total sum of squared LUMO coefficients for coordinating N centers of the ligands from Hückel MO calculations; individual c_N^2 values are given in ref 10. Coulomb integral parameters $h_N = 0.75$ and $h_{N'} = 0.5$ for noncoordinating N centers of bptz; all resonance integral parameters $k = 1.0$. [c] Sum of ESR coupling constants a in mT (1 T = 10^4 G) for coordinating ^{14}N centers in corresponding dinuclear Mo(CO)$_4$ complexes of anion radical ligands L$^{•-}$ from ref 14. [d] Approximate metal–metal distances[3,8a,12,13] in pm. [e] Minimum number of N or C π centers between metals. [f] Electrochemical data from ref 7a.
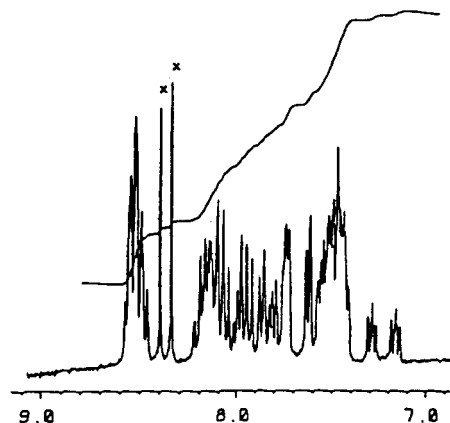

Figure 1. Section of the 270-MHz ^{1}H NMR spectrum of the dinuclear complex {[Ru(bpy)$_2$]$_2$(bppz)}(PF$_6$)$_4$ in CD$_3$CN. Among numerous overlapping signals of 2-pyridyl groups, two characteristic singlets (X) of the equivalent pyrazine protons H(3,6) are visible in a 1:1 ratio for the meso and DL diastereomers.

pound in water and recrystallization from acetonitrile/ether yielded the emerald green compound ($\nu_{MLCT} = 13\,230$ and $25\,580$ cm^{-1} in CH$_3$CN) in the hydrated form.

Reduction potentials and electron spectroscopic data of the complexes will be discussed in detail in a forthcoming publication.[11]

Results and Discussion

Since all symmetrical dinuclear complexes contain two equivalent chiral metal centers, they should probably be formed as 1:1 mixtures of meso and DL diastereomers, as illustrated for the abpy system in Chart II. This aspect had not been addressed in previous studies of {[Ru(bpy)$_2$]$_2$(μ-bpym)}$^{4+}$ or related systems;[7,8,13] clear evidence for such a situation has now been obtained for the dinuclear bppz complex, which exhibits *two* characteristic[10] singlet signals for the equivalent 3,6-protons of the pyrazine ring at 8.34 and 8.40 ppm in the 270-MHz ^{1}H NMR spectrum (Figure 1). Differences in the overall electronic structure, e.g. in the redox properties of the stereoisomeric complexes, are expected to be very small; in fact, no such effects have been noted during electrochemical or electron spectroscopic studies.[7,8,11]

In the series of the four individual bridging ligands (Chart I), azo-2,2'-bipyridine (abpy) has very Hückel MO coefficients c_N^2(LUMO) and induces a very small metal–metal distance d_{M-M} of ∼500 pm,[8,10,12] 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) has large c_N^2(LUMO) coefficients yet gives rise to a larger d_{M-M} of about 700 pm,[10,12] 2,5-bis(2-pyridyl)pyrazine (bppz) induces a similar d_{M-M} but has small c_N^2(LUMO) coefficients,[10] and, finally, 2,2'-bipyrimidine (bpym) also has small c_N^2(LUMO) coefficients but forms bis chelate complexes with rather small d_{M-M} values of ∼550 pm.[10-13] Furthermore, the metal d$_{yz}$ orbitals are pointing toward each other in binuclear bpym complexes, thus allowing direct overlap of metal d orbitals;[10] all the other ligands used here
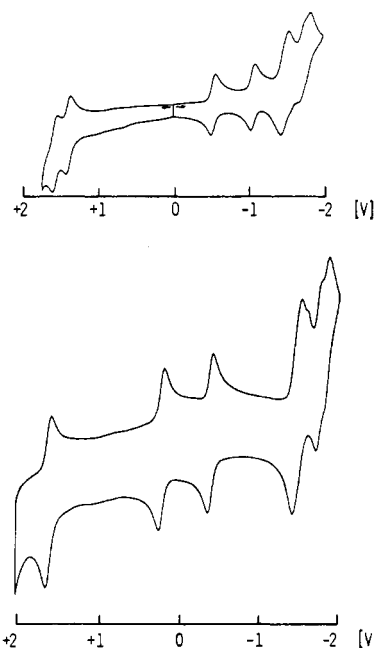

Figure 2. Cyclic voltammograms of the dinuclear bppz (top) and abpy complexes (bottom) with [Ru(bpy)$_2$]$^{2+}$ fragments. Comparison with the two one-electron-reduction waves[8a,d] of the latter system illustrates the one-electron nature of the first oxidation signal at 1.70 V.

have these metal orbitals oriented in a "staggered" fashion,[10] precluding virtually any direct overlap.

The results from cyclic voltammetric oxidation of the complexes {[Ru(bpy)$_2$]$_2$(μ,η^4-L)}$^{4+}$ with the four individual ligands L are summarized in Table I. Figure 2 shows cyclic voltammograms of two complexes.

The data in Table I demonstrate conclusively that *only the electron density at the coordination centers in the LUMO of the bridging π ligand correlates with K_c*. Most importantly, neither the number of "mediating" π centers nor the distance or the orientation of the two metal centers seems to play a significant role, thus disfavoring "direct" metal–metal interaction as a major factor in determining K_c, at least for this type of mixed-valence complexes. Richardson and Taube have pointed out[3,4] that the increased π acidity on coordination of one Ru^{III} center should contribute to K_c; in fact, large LUMO coefficients at the coordinating nitrogen centers would exactly enhance such an effect in mixed-valence dimers with conjugated bridging ligands. As an experimental measure for the LUMO charge densities in the bridging ligands the sums of the ^{14}N ESR coupling constants $\sum a_N$ of corresponding dinuclear Mo(CO)$_4$ complex anion radicals[14] as included in Table I show a correlation with K_c similar to that of the $\sum c_N^2$ values. Unfortunately, anion radical complexes of the [Ru(bpy)$_2$]$^{2+}$ fragments show rather poor ESR resolution[8b] and cannot be used for correlation.

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Given the limits of Hückel MO calculations and the complexity of the compounds compared here, it is not surprising that the observed correlation between K_c and the LUMO charge densities is not clearly linear or exponential. Although the question of thermodynamic stability of mixed-valence systems is certainly complex[2-5,17] and requires thorough MO treatments, this study of mixed-valence complexes that exist at rather positive potentials does provide some guidelines for the design of novel conjugated bridging ligands[15] particularly capable of stabilizing mixed-valence oxidation states. In such ligands, the combined LUMO charge densities of all coordination centers should be as large as possible

(pyrazine of the Creutz–Taube ion[1] has $\sum c_N^2 = 0.55^{16}$) while other factors such as metal–metal distance seem to be of less importance.

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High-Pressure Kinetic Study of Formation and Dissociation of First- and Second-Row d¹⁰ Divalent Metal Ion Complexes with Bipyridine in Aqueous Solution: A Cation Size Dependent Reaction Mechanism[1]

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The rate constants for the formation and dissociation of $Zn(H_2O)_4bpy^{2+}$ and $Cd(H_2O)_4bpy^{2+}$ as well as the stability constants of these two complexes have been studied as a function of temperature in aqueous solution. The kinetic and equilibrium parameters obtained are $k_f^{298}/M^{-1} s^{-1} = (2.3 \pm 0.2) \times 10^6$, $k_r^{298}/s^{-1} = 13 \pm 5$, log ($K^{298}/M^{-1}$) = 5.23 ± 0.05, $\Delta H_f^{\ddagger}/kJ\ mol^{-1}$ = 35.4 ± 0.6, $\Delta H_r^{\ddagger}/kJ\ mol^{-1}$ = 62.8 ± 0.9, and $\Delta H°/kJ\ mol^{-1}$ = -27.4 ± 0.9 for Zn^{2+} and $k_f^{298}/M^{-1} s^{-1} = (3.3 \pm 0.3) \times 10^6$, k_r^{298}/s^{-1} = 160 ± 20, log (K^{298}/M^{-1}) = 4.33 ± 0.06, $\Delta H_f^{\ddagger}/kJ\ mol^{-1}$ = 24.0 ± 2.3, $\Delta H_r^{\ddagger}/kJ\ mol^{-1}$ = 46.1 ± 2.8, and $\Delta H°/kJ\ mol^{-1}$ = -22.1 ± 2.4 for Cd^{2+}. The influence of pressure on the rate constants for formation of the complexes has also been studied. For Cd^{2+}, determination of the rate constant for the dissociation of the mono complex at variable pressure could be made by adding Cu^{2+} to form the $Cu(H_2O)_4bpy^{2+}$ complex quantitatively and measuring the rate-limiting dissociation of the Cd^{2+} complex. For the analogue Zn^{2+} system, the activation volume for the dissociation process had to be calculated as the difference between the reaction volume obtained from a variable-pressure equilibrium study and the activation volume for the formation step. For Zn^{2+}, the small negative activation entropies ($\Delta S_f^{\ddagger}/J\ K^{-1}\ mol^{-1} = -4 \pm 2$ and $\Delta S_r^{\ddagger}/J\ K^{-1}\ mol^{-1} = -12 \pm 3$) and positive activation volumes ($\Delta V_f^{\ddagger}/cm^3\ mol^{-1} = +7.1 \pm 0.4$ and $\Delta V_r^{\ddagger}/cm^3\ mol^{-1} = +3.6$) are interpreted in terms of a dissociative interchange mechanism. The negative values found for Cd^{2+} ($\Delta S_f^{\ddagger}/J\ K^{-1}\ mol^{-1} = -39.7 \pm 8.2$, $\Delta S_r^{\ddagger}/J\ K^{-1}\ mol^{-1} = -48.4 \pm 9.7$, $\Delta V_f^{\ddagger}/cm^3\ mol^{-1} = -5.5 \pm 1.0$, and $\Delta V_r^{\ddagger}/cm^3\ mol^{-1} = -6.9 \pm 1.2$) show that an associative interchange mechanism operates. This change in activation mode on going from the first to the second row is attributed to the large difference in ionic radius between the two cations.

Introduction

The interest in kinetic studies of simple substitution reactions on metal ions has been revived since variable-pressure techniques have become productive investigation tools to complement the traditional mechanistic criteria. The number of inorganic reactions for which volumes of activation have been measured is thus in constant progression, and confidence in the ability of this parameter to help in characterizing the mechanism of simple coordination reactions is also increasing regularly.[2] Some information has been collected for most first-row octahedral transition-metal cations, and it is now clear that the mechanisms are similar for solvent exchange and ligand substitution. It has also been learned that these mechanisms gradually change along the series from associative to dissociative activation mode, at least for the 2+ and 3+ oxidation states in water, methanol, and acetonitrile media.[3] Kinetics of solvent exchange and complex formation on second-row octahedral cations has received much

less interest, however, probably because of the more complex chemistry involved with these ions. Our study of $Mo(H_2O)_5NCS^{2+}$ formation from $Mo(H_2O)_6^{3+}$ seems in fact to be the only variable-pressure work in water reported to date.[4] In the present account, we extend our investigations to a later member on this row, the d¹⁰ divalent cadmium ion, and, for the sake of comparison, to its first-row parent Zn^{2+}. The rates for water exchange of these two cations are too fast to be measured at the present stage of NMR instrumentation, and one is forced to turn toward complex formation reactions that can be studied by other experimental techniques. In this context, we have chosen to study the formation, dissociation, and equilibrium of the mono complexes of Zn^{2+} and Cd^{2+} with the uncharged bidentate bipyridine ligand in aqueous solution, using stopped-flow and UV–visible spectroscopic techniques at variable temperature and pressure.

Experimental Section

Chemicals and Solutions. Hydrated $Zn(ClO_4)_2$ was prepared from ZnO (Merck, p.a.) dissolved in concentrated $HClO_4$ (Merck, p.a.), and it was recrystallized from water. $Cd(ClO_4)_2·6H_2O$ (Ventron, p.a.), $Cu(ClO_4)_2·6H_2O$ (Fluka, purum), and 2,2'-bipyridine (bpy, Fluka, p.a.) were used as supplied. Stock solutions were prepared volumetrically at room temperature with doubly distilled water. The pH of all sample solutions was set between 5.8 and 6.0 and measured with a combined

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