When Is an Odd-Electron Dinuclear Complex a Mixed-Valent Species? Tuning of Ligand-to-Metal Spin Shifts in Diruthenium(III,II) Complexes of Noninnocent Bridging Ligands OC(R)NNC(R)O

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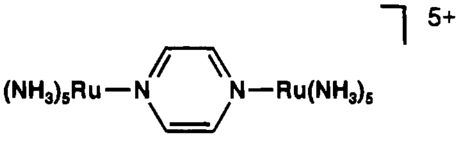
The complexes $\{(\text{adc-R})[\text{Ru(bpy)}_2]_2\}^n$ with bpy = 2,2′-bipyridine and adc-R = azodicarbonyl ligands O=C(R)−N=N−C(R)=O, R = NR'_2 (piperidyl), OC_2H_5, $OCH_2C_6H_5$, CH_3, C_6H_5, 4-C_6H_4COOH, and 4-$C_6H_4COOCH_3$, can exist in several oxidation states (n = 2−, 0, 2+, 3+, 4+) of which the stable (comproportionation constant $K_c > 5 \times 10^7$) and isolable paramagnetic intermediates (n = 3+) exhibit a considerable and remarkably tunable degree of metal/ligand/metal orbital mixing. The occurrence of intense ($\epsilon > 7000$ M^{-1} cm^{-1}) and hardly solvatochromic absorption bands at about 1500 nm, the temperature-dependent magnetic moment ($\mu_{\text{eff}} = 1.6-2.1\ \mu_B$) determined for one derivative, and the IR vibrational spectra did not allow us to make a conclusive determination of metal oxidation states; however, the EPR spectra observable only below 50 K reveal a strongly substituent- (R-) dependent degree of metal contribution to the singly occupied MO. XPS measurements of two 3+ ions which show Ru(II) *and* Ru(III) signals also exhibit a marked substituent effect on the electronic structure. Whereas the 4+ ions formed at rather positive potentials also seem to possess strongly mixed frontier orbitals, the stable 2+ ions clearly contain two Ru(II) centers and fully reduced, i.e. 1,2-dicarbonylhydrazido(2−) bridging ligands, $[\text{O=C(R)−N−N−C(R)=O}]^{2-}$. The results are interpreted within a hole vs electron transfer scheme, based on a three-site MO model for the metal/metal communication in ligand-bridged mixed-valent dimers according to which the intermediates $\{(\text{adc-R})[\text{Ru(bpy)}_2]_2\}^{3+}$ are best described as delocalized systems with varying contributions from $\text{Ru}^{\text{II}}/(\text{adc-R})^{\bullet-}/\text{Ru}^{\text{II}}$ and $\text{Ru}^{\text{II}}/(\text{adc-R})^{2-}/\text{Ru}^{\text{III}}$ resonance forms.

Introduction

The study of symmetrical d^5/d^6 mixed-valent complexes and of dinuclear ruthenium(III/II) species in particular has contributed significantly to the understanding of bonding and electron transfer in and between metal complexes.[2] Classical examples are the molecule-bridged Creutz–Taube ion **1**[3] and halide ion-bridged dimers such as **2**.[4]



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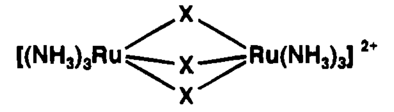

2 X = Cl, Br

In the search for bridging molecules which support effective communication between two metal centers, we focused our attention recently on the azodicarbonyl/1,2-dicarbonylhydrazido(2−) two-step redox system (Scheme 1),[5] which is distinguished by several remarkable features: (i) the comparably high electron affinities of carbonyl and azo functions[6] support a facile two-step reduction of the conjugated azodicarbonyl (adc-R) molecules; (ii) the singly[5c,7] and doubly reduced forms of (adc-R) are stabilized by resonance, similar to the aromatic stabilization of semiquinones and catecholates in the *o*-quinone redox series;[8] (iii) in the *cis/trans/cis* ("S frame")[9] conformation, the members of the redox system in Scheme 1 can serve as symmetrical bis-chelate ligands which are able to bind two metal centers at rather

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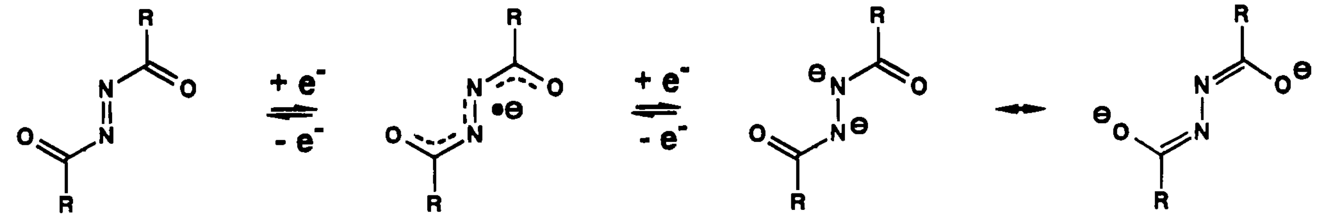
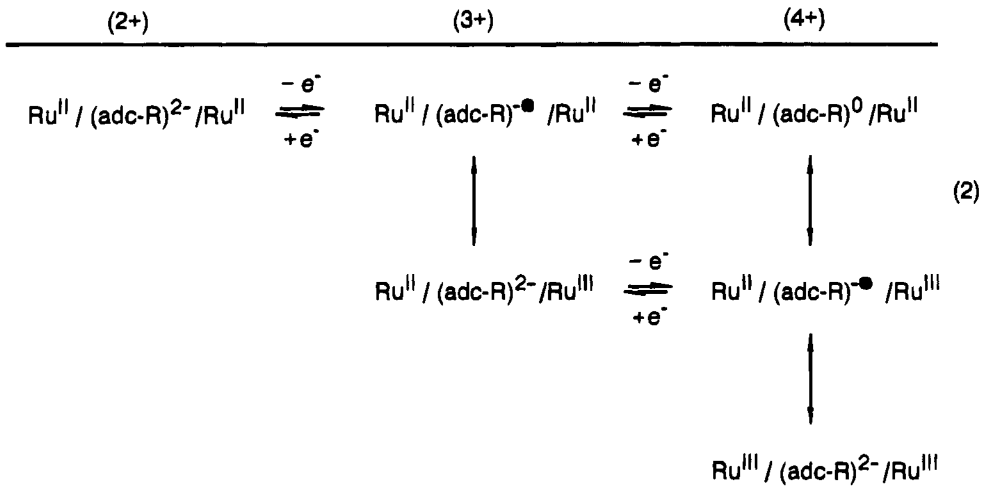
Scheme 1



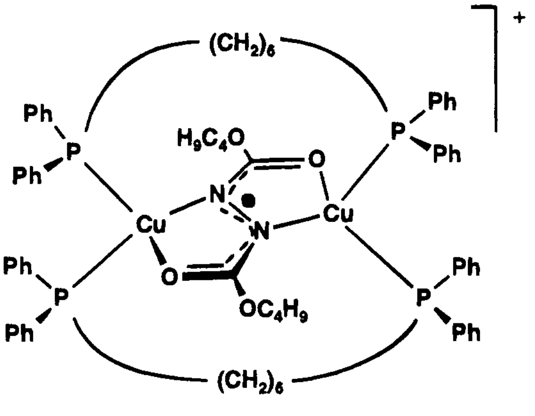
Scheme 2



close M−M distances of less than 5 Å in a stable arrangement with two edge-sharing five-membered chelate rings;[5c,9] (iv) four out of the six π centers of the redox system in Scheme 1 are potentially coordinating while the remaining two centers can be influenced by substituents R.

Coordination compounds of mono- or dinucleating adc-R ligands, mostly in the doubly reduced hydrazido(2−) form, have been reported;[5,10] a recent electrochemical and structure analysis demonstrated the rather short distance between molecule-bridged metal centers and the potentially enormous stabilization of the radical intermediate state (adc-R)$^{\bullet-}$ by dicopper(I) coordination.[5c]

While the EPR data of complexes such as **3** have unambiguously shown the Cu(I)/(adc-R)$^{\bullet-}$/Cu(I) formulation of the ground state,[7b] first reports on corresponding dinuclear bis(2,2′-bipyridine)ruthenium complexes pointed to an ambivalence (Scheme 2) concerning the alternative between the Ru(II)/(adc-R)$^{2-}$/Ru(III) mixed-valent formulation and the radical complex alternative Ru(II)/(adc-R)$^{\bullet-}$/Ru(II).[5a,b]



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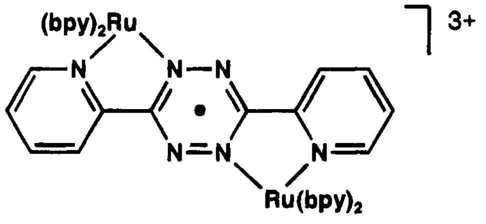

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In this work we present a comprehensive study of the electronic structures of the complexes {(adc-R)[Ru(bpy)$_2$]$_2$}^{n}

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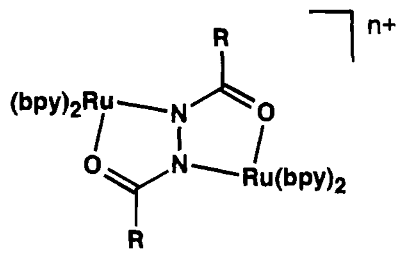
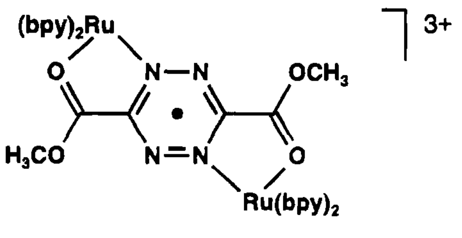
Chart 1



R = dialkylamino, alkoxy, alkyl, aryl

n = (2-), (0), 2+, 3+, (4+)

(Chart 1) with bpy = 2,2′-bipyridine and adc-R = azodicarbonyl ligands O=C(R)—N=N—C(R)=O, R = NR′$_2$ (piperidyl), OC$_2$H$_5$, OCH$_2$C$_6$H$_5$, CH$_3$, C$_6$H$_5$, 4-C$_6$H$_4$COOH, 4-C$_6$H$_4$COOCH$_3$. The methods used were cyclic voltammetry and UV/vis/near-IR, IR, and XPS spectroscopy of the neighboring 2+ and 3+ oxidation states as well as EPR spectroscopy and magnetic susceptibility studies of the paramagnetic 3+ intermediate form. The results are compared to those of related compounds with clear-cut radical complex (**4**,[11] **5**) or Ru(III)/Ru(II) mixed-valent character[2,3,12,13] (**1**, **6**) and will be interpreted within the hole vs electron transfer mechanistic scheme[5b] that is based on the three-site MO model for ligand-bridged mixed-valent dimers.[5b,14]



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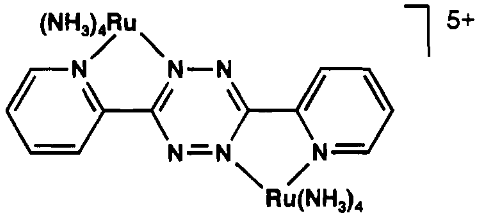

6

Experimental Section

General Procedures. Reactions involving ruthenium compounds were carried out under argon in order to avoid uncontrolled oxidation to the Ru(II,III) states by air. Solvents for recrystallization, spectroscopy, and electrochemistry were rigorously dried before use; satisfactory C,H,N analyses were obtained in all instances.

Syntheses. Ligands. The commerically unavailable ligands 3,5-bis(carbomethoxy)-1,2,4,5-tetrazine, bctz[15] (for compound **5**), 1,2-diacetylhydrazine, H$_2$adc-CH$_3$,[5b] 1,2-dibenzoylhydrazine, H$_2$adc-Ph,[16a] and 1,2-bis(1-piperidylcarbonyl)hydrazine, H$_2$adc-NR′$_2$,[16b] were prepared by literature procedures. Other ligands such as H$_2$adc-CF$_3$ or H$_2$adc-4-C$_6$H$_4$COOCH$_3$ were obtained accordingly[5b,16] by carefully reacting hydrazine hydrate and BrC(O)CF$_3$ or ClC(O)-4-C$_6$H$_4$COOCH$_3$, respectively.

(*μ*-1,2-Dicarbonylhydrazido(2−))tetrakis(2,2′-bipyridine)diruthenium(II,II) Bis(hexafluorophosphates), $\{(adc\text{-}R)[Ru(bpy)_2]_2\}(PF_6)_2$, R = CH$_3$, C$_6H_5$, 4-C$_6H_4$COOH, 4-C$_6H_4$COOMe. A 100 mg (0.19 mmol) sample of *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O and 0.095 mmol of the appropriate hydrazine derivative H$_2$adc-R were heated with 20 mg (0.5 mmol) of sodium hydroxide in 40 mL of a water/ethanol mixture (5/1) for 24 h under reflux. After cooling to room temperature and addition of 1 g of ammonium hexafluorophosphate dissolved in 40 mL of water, the precipitated complex was filtered off and dried under vacuum. Dissolution of this material in 15 mL of acetone, reprecipitation with 70 mL of diethyl ether, and drying under vacuum afforded the following complexes as dark purple materials: R = CH$_3$, 106 mg (91%);[5b] R = C$_6$H$_5$, 90 mg (69%); R = 4-C$_6$H$_4$COOH, hydrolyzed product obtained in 80% yield (110 mg) when H$_2$adc-C$_6$H$_4$COOCH$_3$ and the procedure described above were used; R = 4-C$_6$H$_4$COOCH$_3$, nonhydrolyzed complex obtained in 64% yield (90 mg) when the reaction time of H$_2$adc-C$_6$H$_4$COOCH$_3$ was reduced to 30 min and when column chromatography in acetone on neutral alumina was used to separate from hydrolyzed and nonconverted material.

$\{(adc\text{-}OC_2H_5)[Ru(bpy)_2]_2\}(PF_6)_2$. A suspension of 100 mg (0.19 mmol) of *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O, 20 mg (0.115 mmol) of H$_2$adc-OC$_2$H$_5$, and 74 mg (0.4 mmol) of KPF$_6$ was heated in 50 mL of 1,2-dichloropropane for 48 h under reflux. After cooling to room temperature, the solvent was removed under vacuum, the residue was dissolved in acetone, and the solution was filtered for column chromatography in acetone on neutral alumina. The purple fraction was collected, dried, and recrystallized several times from acetone/diethyl ether (1/4) to yield 20 mg (16%) of product.

(*μ*-1,2-Dicarbonylhydrazido(2−))tetrakis(2,2′-bipyridine)diruthenium(III,II)Tris(hexafluorophosphates). The mixed-valent form of the diethyl ester complex could be obtained via two different routes:

$\{(adc\text{-}OC_2H_5)[Ru(bpy)_2]_2\}(PF_6)_3$. Route A. A 100 mg (0.19 mmol) amount of *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O was heated under reflux together with 17 mg (0.095 mmol) of H$_2$adc-OC$_2$H$_5$ and 20 mg (0.5 mmol) of NaOH in 50 mL of water/ethanol (4/1) for 12 h. After cooling to room temperature and addition of 1 g NH$_4$PF$_6$ in 40 mL of water, a purple material was precipitated, oxidized with 10 mL of H$_2$O$_2$ (30%), filtered off, washed with small amounts of water, and dried under vacuum to yield a brown complex in 88% yield (120 mg).

Route B. Alternatively, 100 mg (0.077 mmol) of the bis(hexafluorophosphate) complex, dissolved in 20 mL of 1,2-dichloroethane, could be oxidized using 20 mg (0.08 mmol) of AgPF$_6$, which caused a color change from purple to light brown. Elemental silver was removed by filtration and the oxidized product precipitated by addition of 60 mL of diethyl ether. After washing with diethyl ether and drying under vacuum, the yield of the mixed-valent complex was 95 mg (86%).

Route A was also used to obtain the complexes **$\{(adc\text{-}R)[Ru(bpy)_2]_2\}(PF_6)_3$**, R = NR′$_2$ and OCH$_2$C$_6$H$_5$, with the exception that the intermediate product was oxidized with AgPF$_6$ in 1,2-dichloroethane solution to give the brown mixed-valent complexes in about 80% yield.

Route B was used to synthesize the following **$\{(adc\text{-}R)[Ru(bpy)_2]_2\}(PF_6)_3$**: R = CH$_3$, 85% yield; R = C$_6H_5$, 92% yield.

(*μ*-1,2-Azodicarboxylate)tetrakis(2,2′-bipyridine)diruthenium Tetrakis(hexafluorophosphates), $\{(adc\text{-}R)[Ru(bpy)_2]_2\}(PF_6)_4$, R = NR′$_2$, OC$_2H_5$, OCH$_2C_6H_5$. These complexes were prepared from the isolated bis- or tris(hexafluorophosphate) forms via oxidation with AgPF$_6$ in DCE. While isolation of the pure complexes failed due to their facile reduction in contact with nucleophiles, including most solvents, they could be generated *in situ* for absorption spectroscopy in DCE.

(*μ*-3,6-Bis(carbomethoxy)-1,2,4,5-tetrazine(1−))tetrakis(2,2′-bipyridine)diruthenium(II,II) Tris(hexafluorophosphate) Dihydrate, $\{(bctz)[Ru(bpy)_2]_2\}(PF_6)_3 \cdot 2H_2O$. A suspension of 100 mg (0.19 mmol)

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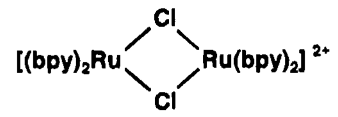
of *cis*-$Ru(bpy)_2Cl_2{\cdot}2H_2O$, 19 mg (0.096 mmol) of bctz, and 140 mg (0.76 mmol) KPF_6 was heated in 40 mL of 1,2-dichloroethane for 48 h under reflux. After cooling to room temperature, the solution was filtered, the residue was washed with DCE and redissolved in acetone, and resultant solution was filtered. Precipitation of the product from the filtrate by addition of diethyl ether and recrystallization from acetone/diethyl ether (10/1) yielded 18 mg (12%) of dark red material.

Instrumentation. Cyclic voltammetry: PAR Model 363 potentiostat, Bank Model VSG 72 or POS 73 function generator; three-electrode configuration with glassy carbon working electrode, Pt wire counter electrode, and saturated calomel (SCE) reference. Susceptibility measurements: SQUID SHE 905 magnetometer, diamagnetic correction. EPR: Varian E 109 and Bruker ESP 200 spectrometers (X band); Oxford Instruments ESR 900 cryostat, EPI 548A frequency counter, and Varian NMR gaussmeter. IR: Perkin-Elmer 283 and 684 spectrometers. UV/vis/near-IR: Shimadzu UV 160 and Bruins Instruments Omega 10 spectrophotometers. XPS: A.E.I.-ES-200 B spectrometer, photoionization by Al K_α radiation (1486.6 eV, 12 kV/10 mA, C 1s as reference at 286.0 eV). The compounds were deposited on gold foil from acetone solutions.

Results

Synthesis. Depending on the redox potential $E(2+/3+)$ (Table 1), the dinuclear complexes **1** could be obtained as purplish dications, as orange-brown trications, or as mixtures thereof. The mixtures could be separated by column chromatography or recrystallization; however, the preparation of pure oxidation states was also possible using reductants such as dithionite for the isolation of pure 2+ ions or oxidants such as H_2O_2 or $AgPF_6$ in acetone for the synthesis of pure trications. In all instances, the complexes were precipitated as hexafluorophosphates.

Employing *cis*-$Ru(bpy)_2Cl_2$ as starting material, we found that the oxidation and protonation state of the adc-R ligand was crucial for a successful synthesis. The use of nonreduced, i.e. azodicarbonyl, ligands, adc-R, was successful with limited yields only in the case of adc-OC_2H_5 in 1,2-dichloroethane (DCE) solution. The isolated dicationic complex had apparently been reduced by fractions of the Ru(II)-containing starting material. Other nonreduced ligands such as adc-NR'_2 did not give any of the desired product; the use of the bulky di-*tert*-butyl ester adc-$O^tC_4H_9$ resulted only in formation of the doubly chloride-bridged dimer **7**.[17]



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The best synthetic procedure for the complexes in Chart 1 involved heating of $Ru(bpy)_2Cl_2$ with reduced, i.e. 1,2-dicarbonylhydrazine ligands, H_2adc-R, in the presence of NaOH in H_2O/EtOH (5/1). The use of H_2adc-$C_6H_4COOCH_3$ resulted in partial hydrolysis of the methyl ester function on prolonged reaction; nevertheless, ester and free acid species could be separated by column chromatography. No product was observed in corresponding reactions of $Ru(bpy)_2Cl_2$ with H_2adc-OC_6H_5, H_2adc-H, and H_2adc-CF_3. Attempts to obtain a mononuclear complex $[(\text{adc-}OC_2H_5)Ru(bpy)_2]^{n+}$ were not successful; only dinuclear species were obtained even after using a 4-fold excess of the ligand.

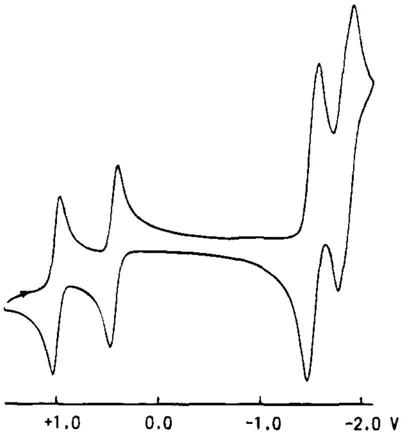
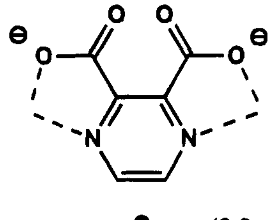


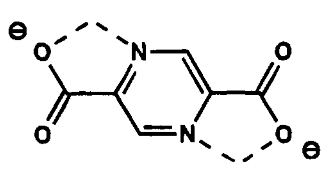
Figure 1. Cyclic voltammogram of $[(bpy)_2Ru(\text{adc-}CH_3)Ru(bpy)_2]^{n+}$ in CH_3CN/0.1 M Bu_4NClO_4 (100 mV/s).

The green tetracationic complexes could be obtained in the case of adc-NR'_2 and adc-OR' systems by oxidation of the 2+ or 3+ species with $AgPF_6$ in noncoordinating dichloromethane; however, the high lability of the 4+ complexes precluded isolation of pure materials. Complexes with adc-R ligands (R = alkyl, aryl) have higher oxidation potentials, $E(3+/4+) > 1$ V (Table 1), and could no longer be oxidized with $AgPF_6$.

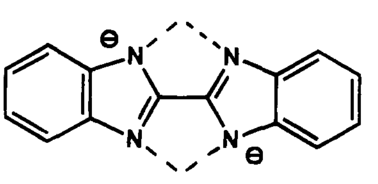
Cyclic Voltammetry. All isolated complexes show cyclic voltammograms in chlorinated hydrocarbons as illustrated in Figure 1. There are two reversible one-electron processes in the positive potential range and two two-electron processes beyond −1.5 V vs SCE. The data, some obtained also in other solvents, are summarized in Table 1 together with comproportionation constants K_c[18] and some results which were reported for dinuclear $Ru(bpy)_2$ complexes of the related ligands **8**–**10**.



8 $(2,3\text{-pzdc}^{2-})$



9 $(2,5\text{-pzdc}^{2-})$



10 (bibzim^{2-})

Infrared Vibrational Spectroscopy. The positions of some major IR vibrational bands in the very complex spectra were determined as a function of the oxidation state in order to obtain

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[17] (a) Johnson, E. C.; Sullivan, B. P.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 2211. (b) See also recently reported bis(alkoxy)-bridged derivatives: Bardwell, D.; Jeffery, J. C.; Joulie, L.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1993**, 2255.

[18] Calculated from $K_c = [Ru_2^{II,III}]^2/[Ru_2^{II}][Ru_2^{III}] = 10^{\Delta E/0.059V}$; $\Delta E(3+) = E(3+/4+) - E(2+/3+)$.

Table 1. Electrochemical Data[a] for the Bridged Complexes $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{n+}$

L	solvent[b]	$E(4+/3+)$	$E(3+/2+)$	$E(2+/0)$[c]	$\Delta E(3+)$[d]	$K_c(3+)$[e]
adc-NR'$_2$[f]	DCE	0.64(70)	0.18(80)		0.46	0.62×10^8
adc-OC_2H_5	DCE	0.89(70)	0.38(60)	−1.55(160)	0.51	4.4×10^8
adc-$OCH_2C_6H_5$	DCE	0.88(80)	0.40(90)	−1.55(190)	0.48	1.4×10^8
adc-CH_3	DCE	1.03(140)	0.51(100)	−1.48(160)	0.52	6.4×10^8
	AN	0.99(70)	0.43(70)	−1.52(100)[g]	0.56	31×10^8
adc-C_6H_5	DCE	1.18(90)	0.61(90)	−1.46(130)	0.57	46×10^8
	AN	1.10(70)	0.53(60)	−1.51(110)[g]	0.57	46×10^8
adc-C_6H_4COOH	DCE	1.13(100)	0.59(70)	−1.52(130)	0.54	14×10^8
	AN	1.13(60)	0.56(60)		0.57	46×10^8
adc-$C_6H_4COOCH_3$	DCE	1.16(170)	0.65(110)	−1.45(180)[g]	0.51	4.4×10^8
	AN	1.15(80)	0.59(60)	−1.48(100)	0.56	31×10^8
bctz (complex **5**)	DCE	0.06(60)[k]	−1.2(irr)		≈1.2	$\approx 10^{20}$
2,3-pzdc,[h] **8**	AN	1.11	0.97		0.14	2.3×10^2
2,5-pzdc,[i] **9**	AN	0.92	0.74		0.18	1.1×10^3
bibzim,[j] **10**	AN	1.06	0.77		0.29	8.2×10^4

[a] From cyclic voltammetry at 100 mV/s scan rate. Potentials E in V vs SCE, peak potential differences in mV (in parentheses). [b] DCE = 1,2-dichloroethane, AN = acetonitrile; each with 0.1 M Bu_4NClO_4 as electrolyte. [c] Two-electron waves. [d] $\Delta E(3+) = E(4+/3+) - E(3+/2+)$. [e] According to ref 18. [f] NR'$_2$ = 1-piperidyl. [g] Additional two-electron wave at −1.85 V. [h] Pyrazine-2,3-dicarboxylate (see ref 24b). [i] Pyrazine-2,5-dicarboxylate (see ref 24a). [j] 2,2'-Bis(benzimidazolate) (see ref 24c). [k] The free ligand has $E(0/1-) = -0.40$ V vs SCE.

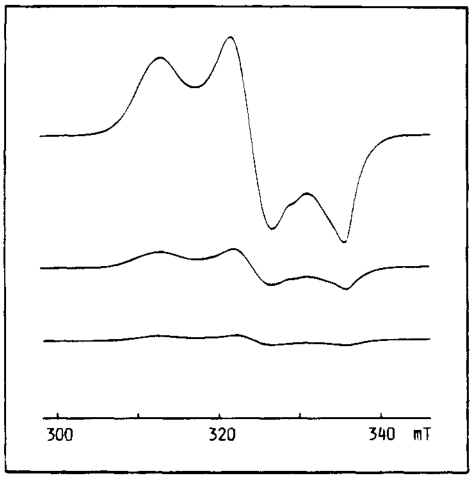

Figure 2. EPR spectra of $[(bpy)_2Ru(adc\text{-}OC_2CH_5)Ru(bpy)_2]^{3+}$ in frozen acetone solution at 3.6 K (top), 7 K (center), and 20 K (bottom) with constant instrument settings.

Table 2. EPR Data[a] for the Complexes $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{3+}$

L	g_1	g_2	g_3	$\langle g\rangle_{cal}$[b]	$g_1 - g_3$
adc-NR'$_2$[c]	2.107	2.030	1.981	2.040	0.126
adc-OC_2H_5	2.108	2.035	1.963	2.036	0.145
adc-$OCH_2C_6H_5$	2.132	2.036	1.957	2.043	0.175
adc-CH_3	2.224	2.016	1.911	2.054	0.313
adc-C_6H_5	2.344	2.003	1.895	2.089	0.449
adc-C_6H_4COOH	2.355	2.008	1.875	2.089	0.480
adc-$C_6H_4COOCH_3$	2.364	1.982	1.853	2.078	0.511
bctz[d]	2.020	1.999	1.989	2.0027	0.031

[a] Measurements at 3.8 K in frozen acetone solutions. [b] According to ref 27. [c] NR'$_2$ = 1-piperidyl. [d] Resolved spectrum at 298 K: $a(^{14}N)$ = 0.54 ± 0.12 mT (4 N), $a(^{99,101}Ru)$ = 0.37 mT (2 Ru). The free ligand radical anion bctz$^{\bullet-}$ has $a(^{14}N)$ = 0.502 mT and $\langle g\rangle$ = 2.0041.

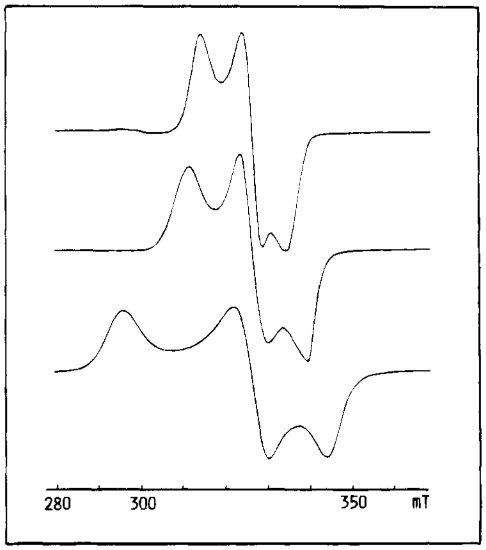

Figure 3. EPR spectra of $[(bpy)_2Ru(adc\text{-}R)Ru(bpy)_2]^{3+}$ at 3.8 K in frozen acetone solutions. R = NR'$_2$ (top), OC_2H_5 (center), CH_3 (bottom).

information on the effective oxidation states of the ligands in the complexes (Chart 1). Following identification of those bonds belonging to the $Ru(bpy)_2$ groups and to the PF_6^- counterions, the main change observed upon oxidation of the 2+ forms was a shift of (adc-R)-based bands at 1530 and 1400 cm^{-1} (2+) to 1410 and 1310 cm^{-1} for the 3+ ions.

Electron Paramagnetic Resonance. As odd-electron complex ions, the 3+ forms display EPR signals albeit only at rather low temperatures in the frozen state. For instance, the EPR intensity of the complex $\{(adc\text{-}OC_2H_5)[Ru(bpy)_2]_2\}^{3+}$ decreases markedly upon warming from 4 to 20 K (Figure 2). The spectra show pronounced rhombicity, however, with a distinct variation depending on the substituents R (Table 2). Figure 3 shows the changes within such a series, and Figure 4 gives a graphical representation of the g component values as a function of the electron donor effect of these substituents. For comparison, Figure 4 also contains the g component splitting of the typical Ru(II,II) radical complexes **5** and of the Ru(III)/Ru(II) mixed-valent dimer **1**.[12]

Magnetic Susceptibility. The temperature-dependent magnetic susceptibility of the complex $\{(adc\text{-}OC_2H_5)[Ru(bpy)_2]_2\}(PF_6)_3$ was studied because of the unusual EPR intensity behavior as shown in Figure 2. The results show a μ_{eff} value of about 1.7 μ_B at 3 K, increasing slowly but steadily to 2.2 μ_B at 300 K without reaching a saturation level. Curie–Weiss behavior was observed at low temperatures with a Θ value of −1.15 K; deviations from the linear relation $1/\chi_m$ vs T are obvious at higher temperatures (Figure 5).

X-ray Photoelectron Spectroscopy. For two redox pairs, i.e. complexes $\{(adc\text{-}R)[Ru(bpy)_2]_2\}^{2+/3+}$, R = OC_2H_5 and C_6H_5, we have determined the energies of the $3d_{3/2}$ and $3d_{5/2}$ ionizations by XPS (ESCA) spectroscopy. Figure 6 shows the spectra in which the metal features are partially obscured by the carbon 1s ionizations; Table 3 summarizes the data of these

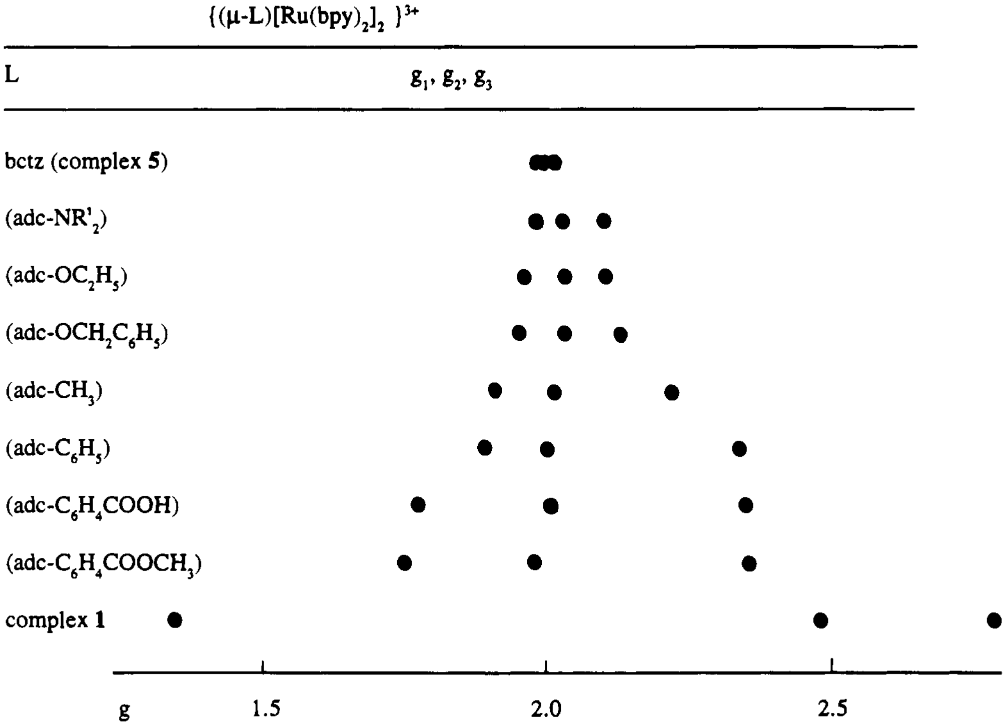

Figure 4. Graphic representation of g anisotropies of $[(bpy)_2Ru(adc\text{-}R)Ru(bpy)_2]^{3+}$ at 3.8 K in frozen acetone solutions. g factors of complexes **1** (Creutz–Taube ion) and **5** are given for comparison.

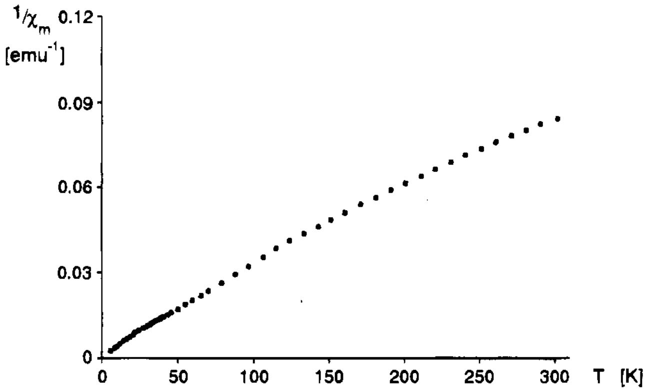

Figure 5. Temperature dependence of $1/\chi_m$ for $[(bpy)_2Ru(adc\text{-}CH_3)Ru(bpy)_2](PF_6)_3$.

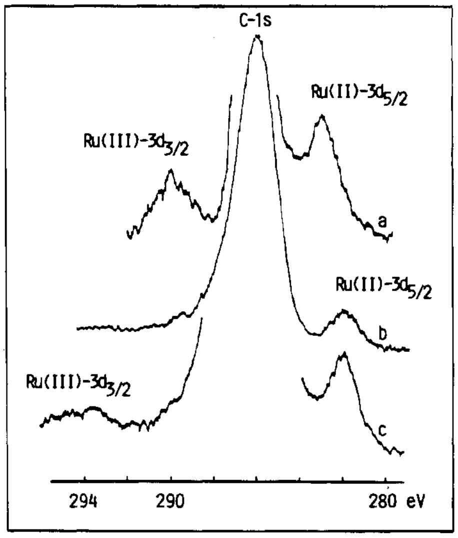

Figure 6. XPS spectra of $[(bpy)_2Ru(adc\text{-}R)Ru(bpy)_2](PF_6)_n$: R = OC_2H_5, $n = 3$ (top, a); R = OC_2H_5, $n = 2$ (center, b); R = C_6H_5, $n = 3$ (bottom, c).

and reference compounds which were analyzed assuming a constant spin–orbit splitting Δ_{so} of 4.2 eV.[19]

UV/Vis/Near-IR Spectroscopy. In all three ionization states 2+ to 4+ the complexes in Chart 1 show intense absorptions in the visible region. Typical features are long-wavelength absorption maxima at about 520 nm for the 2+ form, around 1500 nm for the 3+ state, and at 880 nm for the 4+ ions (Figure 7). The data and their solvent dependence (solvatochromism) are summarized in Table 4. The variability of what could be viewed as metal-to-metal charge transfer (MMCT) or intervalence transition (IT)[2a,20] of the various 3+ ions is shown in Figure 8.

Discussion

Synthesis. A first remarkable result of the reactions carried out between $Ru(bpy)_2Cl_2$ and adc-R or H_2adc-R is that no evidence was found for mononuclear species $[(adc\text{-}R)Ru(bpy)_2]^{n+}$, even when an excess of adc-R ligand was used. This result indicates a strong tendency of the singly $Ru^{II}(bpy)_2$-coordinated ligands (adc-R) to bind another metal center in what may be viewed as charge transfer-assisted polynucleation.[21] Accordingly, the best synthetic procedure involved the use of partly deprotonated 1,2-dicarbonylhydrazines H_2adc-R. The presence of two redox-active metal centers and of the two-step organic redox system adc-R/(adc-R)$^{\bullet-}$(adc-R)$^{2-}$ (Scheme 1) creates several accessible oxidation states and resonance formulations (Scheme 2) for the complexes $\{(adc\text{-}R)[Ru(bpy)_2]_2\}^{n+}$. According to the electrochemical results, the most stable oxidation states are the 2+ and, to some extent, the 3+ forms. The rather low values of the potentials $E(2+/3+)$ (Table

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[19] (a) Citrin, P. H. *J. Am. Chem. Soc.* **1973**, *95*, 6472. (b) Citrin, P. H.; Ginsberg, A. P. *J. Am. Chem. Soc.* **1981**, *103*, 3673.

[20] Blasse, G. *Struct. Bonding (Berlin)* **1991**, *76*, 153.

[21] Kaim, W.; Olbrich-Deussner, B.; Gross, R.; Ernst, S.; Kohlmann, S., Bessenbacher, C. In *Importance of Paramagnetic Organometallic Species in Activation, Selectivity and Catalysis*; Chanon, M., Ed.; Kluwer: Dordrecht, 1989; p 283.

Table 3. Photoionization Energies[a] of Ru(III)/Ru(II) Mixed-Valent Complexes

	Ru(II)		Ru(III)			
	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	C 1s	ref
$\{[Ru(bpy)_2]_2(\mu\text{-adc-}C_6H_5)\}(PF_6)_3$	282.0	*b*	*b*	293.5	286.0	this work
$\{[Ru(bpy)_2]_2(\mu\text{-adc-}OC_2H_5)\}(PF_6)_3$	283.0	*b*	*b*	290.5	286.0	this work
$\{[Ru(NH_3)_5]_2(\mu\text{-pz})\}(Br)_5$[c]	280.4	284.6	282.7	287.0	285.0	19b
$\{[Ru(bpy)_2Cl]_2(\mu\text{-pz})\}(Tos)_3$[c]	280.0	*b*	282.0	*b*	284.4	19a

[a] Values in eV (±0.2 eV); spin−orbit splitting 4.2 eV (see ref 19). [b] Obscured by C 1s ionization band. [c] pz = pyrazine, Tos = tosylate.

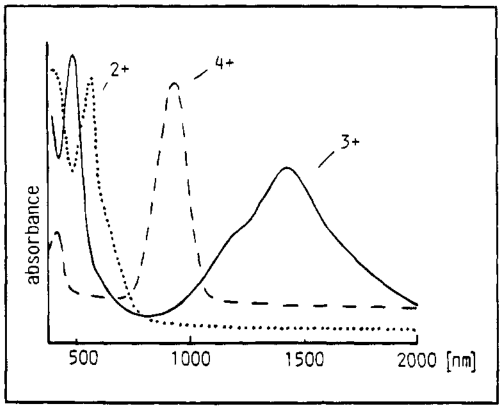

Figure 7. Absorption spectra of the three oxidation states of $[(bpy)_2Ru(adc\text{-}OC_2H_5)Ru(bpy)_2]^{n+}$ in acetone. Absorption scales are different for each spectrum.

1) explain the frequent occurrence of mixtures of 2+ and 3+ ions in the initially isolated products. The highly oxidizing 4+ ions could be generated in three instances where $E(3+/4+) < +1.0$ V, using $AgPF_6$; however, their lability precluded isolation as pure solids.

We recently pointed out the possible existence of two diastereoisomers (meso form and pairs of enantiomers) for symmetrical bis(tris-chelate) complexes such as **3**.[5a,b,22,23a] Unfortunately, all attempts to obtain useful NMR spectra of the 2+ ions failed, presumably due to the presence of small amounts of line-broadening paramagnetic 3+ ions.

Cyclic Voltammetry. In the region between −1.4 and −1.9 V vs SCE all dinuclear complexes exhibit a pair of two-electron waves which can be unambiguously attributed to the stepwise reduction of the metal-bound bpy coligands.[5a,b,22−24]

The pair of reversible one-electron processes observed between +0.1 and +1.2 V can be attributed either to the ligand-based two-step redox system (Scheme 1)[5c] or to two separated Ru(II)/Ru(III) transitions.[2,3,17,22,24] While there is a shift of both these potentials $E(2+/3+)$ and $E(3+/4+)$ to higher values upon replacing donating substituents R with acceptor groups, the differences ΔE between these two potentials of about 0.5 V and thus the comproportionation constants K_c of about 10^8 for the 3+ intermediates are not significantly affected by changing the groups R (Table 1). When compared to values of dinuclear adc-R complexes such as **3**, where the intermediate was definitely established to be an anion radical complex,[5c] the K_c values of about 10^8 for the 3+ forms of the complexes in Chart 1 are relatively small; K_c amounts to $10^{19.7}$ for complex **3**.[5c]

If both one-electron waves are thus tentatively attributed to metal-centered electron transfer processes, the splitting would reflect the ligand-mediated interaction between metal centers. Within this assumption, a comparison to related dinuclear bis(bipyridine)ruthenium complexes of dianionic ligands **8**−**10** or similar species[24] reveals that the adc-R complexes described here have much higher K_c values (Table 1).

Summarizing, the use of both extreme alternatives from Scheme 2 in the interpretation of the 2+/3+/4+ electron transfer series of the (adc-R)-bridged complexes **3** suggests an unusual situation in these complexes. The failure to fully understand the behavior using either one of these alternatives thus points to a delocalized electronic structure with strong metal−metal coupling and partial contributions from the ligand to the ground state of the 3+ ions.

Infrared Vibrational Spectroscopy. The major changes in the mid-infrared spectra of complexes $\{(adc\text{-}R)[Ru(bpy)_2]_2\}^{2+/3+}$ involve a low-energy shift of strong OCNNCO backbone stretching bands between 1400 and 1600 cm^{-1} for the 2+ species by about 150 cm^{-1} upon oxidation to the 3+ forms. In view of the results for related ruthenium−dioxolene redox systems[8] where oxidation from the catecholate via the *o*-semiquinone to the *o*-quinone states is accompanied by high-energy shifts in the IR spectra, the opposite effect observed here rather suggests a predominantly metal-based oxidation, which would cause a strengthening of metal−ligand but weakening of intraligand bonds.

Electron Paramagnetic Resonance. EPR spectroscopy is a superior method for determining effective oxidation states and electron distributions; however, it requires paramagnetic substrates such as the 3+ forms of the adc-R complexes. The alternative posed in Scheme 2 between a mixed-valent system $Ru^{II}/(adc\text{-}R)^{2-}/Ru^{III}$ and a radical complex $Ru^{II}/(adc\text{-}R)^{\bullet-}/Ru^{II}$ lends itself well to an EPR study: The latter type of paramagnetic compounds, including dinuclear complexes of azodicarbonyl anion radical ligands $(\mu\text{-adc-R})^{\bullet-}$,[7] should exhibit well-resolved EPR spectra at room temperature, isotropic *g* factors $\langle g \rangle$ close to 2.0023 (free electron value), and a small *g* anisotropy in frozen solution.[11,25] On the other hand, mixed-valent systems involving Ru(III) should exhibit large *g* anisotropies and $\langle g \rangle$ values deviating significantly from 2.00 because of the sizable spin−orbit coupling constant of the metal centers which are involved in spin accommodation.[12,13,26] Furthermore, the lines should be fairly broad, especially at higher temperatures in fluid solution. In fact, no $^{99,101}Ru$ isotope splitting was observed even in a single-crystal EPR study[12] of the Creutz−Taube ion **1** (^{99}Ru, 12.7%, $I = {}^5/_2$, $g_N = -0.249$; ^{101}Ru, 17.0%, $I = {}^5/_2$, $g_N = -0.279$).

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(23) (a) Ernst, S.; Hänel. P.; Jordanov. J.; Kaim W.; Kasack, V.; Roth, E. *J. Am. Chem. Soc.* **1989**, *111*, 1733. (b) Ernst, S. D.; Kaim, W. *Inorg. Chem.* **1989**, *28*, 1520.

(24) (a) Sedney, D.; Ludi, A. *Inorg. Chim. Acta* **1981**, *47*, 153. (b) Woitellier, S.; Launay, J. P.; Sowinska, M. *Nouv. J. Chim.* **1986**, *10*, 241. (c) Haga, M.; Matsumura-Inoue, T.; Yamabe, S. *Inorg. Chem.* **1987**, *26*, 4148. (d) Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 1442. (e) Haga, M.; Ano, T.; Ishizaki, T.; Kano, K.; Nozaki, K.; Ohno, T. *J. Chem. Soc., Dalton Trans.* **1994**, 263 and literature cited. (e) Haga, M.; Bond, A. M. *Inorg. Chem.* **1991**, *30*, 475. (f) Haga, M.; Ano, T.; Kano, K.; Yamabe, S. *Inorg. Chem.* **1991**, *30*, 3843. (g) Ohno, T.; Nozaki, K.; Haga, M. *Inorg. Chem.* **1992**, *31*, 4256. (h) Hage, R.; Haasnoot, J. G.; Reedijk, J.; Wang, R.; Vos, J. G. *Inorg. Chem.* **1991**, *30*, 3263. (i) Bruni, S.; Cariati, F.; Dei, A.; Gatteschi, D. *Inorg. Chim. Acta* **1991**, *186*, 157.

(25) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187.

(26) Cf.: (a) Raynor, J. B.; Jeliazkowa, B. G. *J. Chem. Soc., Dalton Trans.* **1982**, 1185. (b) Salmonsen, R. B.; Abelleira, A.; Clarke, M. J. *Inorg. Chem.* **1984**, *23*, 385. (c) Taqui Khan, M. M.; Srinivas, D.; Kureshy, R. I.; Khan, N. H. *Inorg. Chem.* **1990**, *29*, 2320.

Table 4. UV/Vis/Near-IR Absorption Data[a] for Complexes $[(bpy)_2Ru(\mu\text{-adc-R})Ru(bpy)_2]^{n+}$ in Different Solvents

		λ_{max} (log ϵ)					
R	*n*	H_2O	CH_3OH	$(CH_3)_2SO$	CH_3CN	$(CH_3)_2CO$	ClH_2CCH_2Cl
NR'_2[b]	2						367, 515[c]
	3					472	471
	4					866	861
OC_2H_5	2	350, 502[c]	359, 518	356, 523	363, 521	364, 523	360, 529 (4.25, 4.23)
	3	443	447	454	451	449	453(4.12)
				1457	1423	1444	1430(3.98)
	4						373, 893 (3.96, 4.39)
$OCH_2C_6H_5$	2	344, 502[c]	360, 520	348, 523	350, 520	361, 522	362, 527
	3	444	444		455	447	450
					1468	1480	1462
	4						375, 897
CH_3	2	340, 504[c]	346, 514	350, 529	353, 513	348, 528	350, 533 (4.25, 4.22)
	3	434	446			444	443 (4.13)
						1577	1550 (3.97)
C_6H_5	2	348, 498[c]	352, 506	360, 521	352, 516	360, 520	358, 524 (4.26, 4.20)
	3	427	443	430	431		430 (4.06)
				1631	1640		1603 (4.07)
C_6H_5COOH	2	340, 495[c]	353, 507	353, 517		355, 515	355, 518 (4.26, 4.18)
	3	428				438	450 (4.03)
						1652	1728 (3.84)
$C_6H_5COOCH_3$	2	346, 496[c]	352, 505	356, 516		354, 515	356, 518
	3	428				438	437
						1640	1620

[a] Wavelengths in nm; molar extinction coefficients ϵ in $M^{-1}\ cm^{-1}$. [b] NR'_2 = 1-piperidyl. [c] Weak long-wavelength shoulders at about 600 nm (in all solvents).

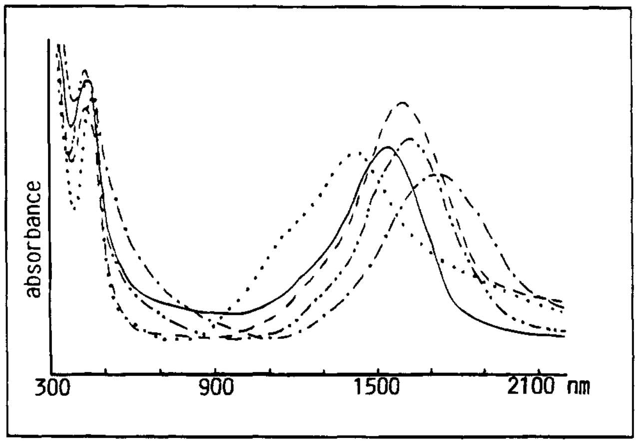

Figure 8. Absorption spectra of $[(bpy)_2Ru(adc\text{-}R)Ru(bpy)_2]^{3+}$ in 1,2-dichloroethane. R = OC_2H_5 (···), CH_3 (—), C_6H_5 (– –), 4-C_6H_4COOH (– · –), 4-$C_6H_4COOCH_3$ (– ·· –). Absorption scales are different for each spectrum.

At first sight, the EPR results for most of the complexes $\{\text{-(adc-R)}[Ru(bpy)_2]_2\}^{3+}$ clearly suggest the mixed-valent formulation. The spectra are observable only at very low temperatures T < 50 K; both the g anisotropies and the calculated[27] average values $\langle g \rangle$ are closer to a Ru(III) situation[26] than to a radical complex formulation involving spin-paired, i.e. low-spin, Ru(II).[11] However, there are marked and systematic variations: With acceptor substituents R = C_6H_5, 4-$C_6H_4COOCH_3$, and 4-C_6H_4COOH, the g components are indeed similar to those of Ru(III) centers with low symmetry[26] albeit with a smaller total g anisotropy. With strong donor substituents R = OR′ and especially NR'_2, on the other hand, the 3+ ions exhibit a much diminished spread of the three g components and smaller $\langle g \rangle$ values (Table 2), the maintained rhombic symmetry being typical for such bis-chelated systems.[13,28] There is still a considerable difference from "true" Ru(II)-containing complexes of anion radical ligands such as **4**[11] or **5** or from dinuclear complexes with a strong semiquinone component;[8,23a] nevertheless, Figure 4 illustrates that decreasing donor and increasing acceptor effects of the ligands R result in a strongly increasing contribution from the mixed-valent formulation $\{(bpy)_2Ru^{II}[(adc\text{-}R)^{2-}]Ru^{III}(bpy)_2\}^{3+}$.

The interpretation of this variation (Figure 4) rests on the role of the bridging ligand adc-R. Donor substituents R destabilize the doubly reduced state $(adc\text{-}R)^{2-}$ and thus favor the radical anion complex formulation; acceptor substituents stabilize $(adc\text{-}R)^{2-}$ and with it the mixed-valent character of the 3+ ions. As a consequence, the significant substituent dependence of the g anisotropy indicates considerable participation of the bridging ligand in the spin distribution. This clear result stands in marked contrast to the almost exclusive metal character of the singly occupied MOs in Ru(III)/Ru(II) ammine mixed-valent dimers bridged by neutral acceptor ligands such as pyrazine (**1**)[12] or 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (**6**).[13] As we pointed out before,[5b] the difference can be accounted for by assuming an *electron transfer* formalism for the exchange interaction in the latter systems (involvement of the π^* LUMO of μ-L) and a *hole transfer* mechanism in the case discussed here, i.e. involvement of the π HOMO of $\mu\text{-}L^{2-}$. Consequences of this difference are the nonparticipation of the bridging ligand in the spin distribution for the 5+ ions because of a MO nodal region at the ligand bridge in the second orbital of the three-center model M–(μ-L)–M (allyl radical situation).[5b,14,23a,29] In contrast, the 3+ ions with two more electrons in the three-center model (Chart 2) should have a singly occupied MO with a rather high contribution from the bridging ligand, according to an allyl dianion situation; the results presented here (Table 2, Figure 4) clearly support such an interpretation.

While the EPR results presented here point to a sizable if variable contribution of the mixed-valent form to the ground state of the (adc-R)-bridged 3+ ions, the absence of any detectable $^{99,101}Ru$ hyperfine coupling[11] did not allow us to

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(27) Calculated from $\langle g \rangle = [(g_1^2 + g_2^2 + g_3^2)/3]^{1/2}$.

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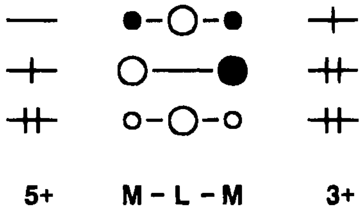
Chart 2



determine from EPR[30] whether the mixed-valent state is localized (Ru^{III}/Ru^{II}) or delocalized (Ru$^{2.5}$/Ru$^{2.5}$). The XPS and UV/vis/near-IR studies discussed further below should provide pertinent clues.

Magnetic Susceptibility. The magnetism of the complex $\{(adc\text{-}OC_2H_5)[Ru(bpy)_2]_2\}(PF_6)_3$ at low temperatures is as expected, indicating an $S = {}^1/_2$ ground state with a magnetic moment of 1.7 μ_B at 3 K. The slow but steady increase of μ_{eff} up to 2.2 μ_B at 300 K and the deviation from the Curie–Weiss behavior (Figure 5) suggest some additional contributions from low-lying excited states with higher multiplicity. Such states may also be invoked to explain the disappearance of the EPR signals on warming to still rather low temperatures (Figure 2).[31,32] At this stage, it would be speculative to define such low-lying states; however, the possibility of low-lying intermediate spin states for ions of the 4d element ruthenium may not be completely ruled out. Factors favoring such effects would be the low-symmetry environment of the metal centers with presumably one very weak bond[33] (here: Ru----O) as can be deduced from the related dicopper complex **3** ($d_{Cu-N} \approx 2.03$ Å, $d_{Cu--O} = 2.32$ Å).[5c]

X-ray Photoelectron Spectroscopy. The XPS method has been applied to the Creutz–Taube ion **1** and related species,[19] showing distinct Ru(II) and Ru(III) features despite the apparent delocalized nature of that prototypical mixed-valent complex.[2c] The high energy and very short spectroscopic time scale of about 10^{-17} s make XPS a somewhat controversial spectroscopy with respect to the question of electronic (de)localization in mixed-valent complexes; highly polarizable and not very strongly coupled systems may thus be influenced through the applied technique in terms of an apparently "localized" structure.[19]

The measurements performed for three selected complexes (Figure 6, Table 3) show solely the expected Ru(II) component for the $\{(adc\text{-}OC_2H_5)[Ru(bpy)_2]_2\}^{2+}$ ion whereas the corresponding 3+ species displays an additional component at higher energies in the region of Ru(III). As was described previously,[19] the C 1s band obscures one of the doublets ($3d_{3/2}$, $3d_{5/2}$) for each oxidation state, assuming a constant spin–orbit splitting of about 4.2 eV.[19] A study of $\{(adc\text{-}C_6H_5)[Ru(bpy)_2]_2\}^{3+}$ with its EPR spectroscopically-detected higher metal contribution to the ground state shows a larger splitting ("chemical shift difference") between Ru(II) and Ru(III) features. Such a correlation has similarly been obtained in the series of pyrazine-bridged complexes with $Ru(NH_3)_5$ and $Ru(bpy)_2Cl$ complex fragments;[19] the results shown here confirm the sizable contribution from the bridging ligand and do not straightforwardly confirm a fully delocalized situation with respect to the metal oxidation states.

While the situation for the (adc-R)-bridged complexes is thus similar to the one observed for the Creutz–Taube ion **1**, there are ligand-bridged Ru(II)/Ru(III) dimers[34] and tetramers[35] which exhibit complete valence averaging in the XPS experiment.

UV/Vis/Near-IR Spectroscopy. The assignment of long-wavelength bands of the 2+ forms with their unambiguous Ru(II)/$(adc\text{-}R)^{2-}$/Ru(II) oxidation state situation can be made in accordance with the results obtained for the related $(bpy)_2$Ru(cat) complexes (cat: catecholates).[8a] The intense and negatively solvatochromic absorptions at about 520 and 360 nm are attributed to Ru(II)-to-bpy transitions (d → $\pi^*_{1,2}$(bpy), metal-to-ligand charge transfer, MLCT); weak long-wavelength shoulders at about 600 nm are assigned to ligand-to-ligand charge transfer (LLCT) transitions: $\pi[(adc\text{-}R)^{2-}] \rightarrow \pi^*_1(bpy)$. The separations of about 2.0 V between the redox potentials $E(2+/3+)$ and $E(0/2+)$ (Table 1) correlate reasonably with the average MLCT absorption maxima at 2.35 eV (1 eV = 8066 cm^{-1}); the slightly higher differences at ca. 0.35 (e)V as compared to the typical values of 0.2 (e)V[23b,36] for exclusively polypyridine-coordinated systems are probably due to more extensive intramolecular reorganization at the presumably[5c] unsymmetrically O,N-coordinated metal centers.

Upon oxidation to the 3+ forms, the MLCT transitions to π^*(bpy) are shifted hypsochromically by about 3000 cm^{-1}, the donor-substituted species exhibiting the smallest such shifts. Regardless of the site of electron removal, oxidation should stabilize the 4d orbitals of ruthenium and thus increase the MLCT transition to the less affected 2,2′-bipyridine ancillary ligands. The most striking absorption feature of the 3+ ions are intense and slightly structured bands in the near-infrared region (Figures 7 and 8). For mixed-valent species such bands are expected and are assigned to intervalence transitions (IT) between metal ions of different valencies (localized situation) or different combinations of metal-centered MOs (delocalized situation).[2,20] However, radical ions and their complexes may also exhibit long-wavelength bands due to low-lying transitions originating from or directed to the singly occupied molecular orbital (SOMO).[8,23a,25,37,38] A recent study of the mixed-valent complex **5** with a similar bis(chelate) coordination arrangement as in complexes **3** showed a very weak ($\epsilon \approx 500$ M^{-1} cm^{-1}) "MMCT" band in the near-IR region;[13] in contrast, typical molar extinction coefficients ϵ around 10^4 M^{-1} cm^{-1} and bandwidths of about 2000 cm^{-1} at half-height illustrate the unusually high intensity of the near-IR transitions in the present case. The near-IR band intensities of the 3+ ions are thus larger than that of the Creutz–Taube system **1** (Table 5); smaller values for ϵ were also reported for dinuclear bis(2,2′-bipyridine)ruthenium complexes of the dianionic bridging ligands **8**–**10** and related systems.[24]

There is a slight bathochromic shift of the absorption maximum of this broad near-IR band upon increasing the

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Table 5. Electrochemical and Absorption Characteristics of Ligand-Bridged Ru(III)/Ru(II) Mixed-Valent Complexes

complex	K_c[a]	near-infrared band ν_{max} (cm^{-1})	 ϵ_{max} (M^{-1} cm^{-1})	 $\Delta\nu_{1/2}$ (cm^{-1})[b]	solvent
1	4×10^6	6400	5000	$\approx$1250	D_2O/D_2SO_4[c]
6	1×10^{15}	6880	500	$\approx$1600	D_2O/DCl[d]
$\{[\mu\text{-L})[Ru(bpy)_2]_2\}^{3+}$					
L = **10**	8×10^4	5130	3400	2300	CH_3CN[e]
L = (adc-OC_2H_5)	4×10^8	6990	9550	2410	ClH_2CCH_2Cl
L = (adc-CH_3)	6×10^8	6450	9330	1620	ClH_2CCH_2Cl
L = (adc-C_6H_5)	5×10^9	6240	11750	1670	ClH_2CCH_2Cl
L = (adc-C_6H_4COOH)	1×10^8	5790	6920	1620	ClH_2CCH_2Cl

[a] According to ref 18. [b] Bandwidth at half-height. [c] From refs 2c–e, 3. [d] From ref 13. [e] From refs 24c,e.

acceptor effect of the substituent R, indicating decreasing metal–metal coupling via stabilized ligand π orbitals; the shapes of the bands are different and reveal the overlap of two or more components. The solvatochromism of these bands is very small (Table 4), which suggests a delocalized ($Ru^{2.5}/Ru^{2.5}$) situation in the mixed-valent formulation.[2c]

Only the most electron-rich complexes in the series **3** could be oxidized chemically to the green tetracations. The band at about 375 nm (Figure 7) can be assigned to a further hypsochromically shifted charge transfer transition from the metal centers or the (adc-R)$^{2-}$ ligand to π^*(bpy). The spectra of the 4+ ions are dominated, however, by a very strong (ϵ 2.5 × 10^4 M^{-1} cm^{-1}) absorption around 900 nm which can be attributed either to an MLCT (d(Ru^{II}) $\rightarrow$ π^*(adc-R)) or LMCT transition (π[(adc-R)$^{2-}$] $\rightarrow$ d(Ru^{III})), depending on the formulation of that state (see Scheme 2). The rather small width of that band ($\Delta\nu_{1/2} \approx$ 1900 cm^{-1}) and little solvent dependence suggest an intermediate situation with considerable electron delocalization between the metal sites and the bridging ligand.

The radical ion complex **5** does not exhibit a detectable band in the near-IR region, in agreement with spectroelectrochemical results on other substituted and metal-coordinated 1,2,4,5-tetrazine anion radicals.[39] The long-wavelength absorption maximum at 480 nm can thus be attributed to an MLCT transition d(Ru) $\rightarrow$ π^*(bpy). In the 4+ state of this complex, generated by oxidation of **5** with $AgPF_6$ in DCE, the bpy-centered MLCT band moves to 405 nm while two new MLCT transitions to low-lying unoccupied tetrazine-based MOs occur, as expected,[23b] at 520 (sh) and 677 nm.

Conclusions. By using various physical methods, we could for the first time illustrate the continuity which links true ligand-bridged Ru(III)/Ru(II) mixed-valent systems such as **1**, **2**, or **6** with similarly constructed Ru(II)/Ru(II) complexes of radical anion bridging ligands like **4** or **5**. In contrast to dinuclear semiquinone complexes of the $Ru(bpy)_2$ complex fragment,[23a] the (adc-R)-bridged complexes are more on the mixed-valent side than in the radical anion region (Scheme 2); however, the strong substituent dependence of the particularly useful EPR and XPS spectra suggest a pronounced susceptibility to perturbation. The three-center model (Chart 2) can straightforwardly explain this result, especially when the unusually high degree of metal/ligand/metal interaction at the four heteroatom π centers and the high-lying π donor orbital of (adc-R)$^{2-}$ are being considered. The latter factors can also explain the unusually intense near-infrared features of these complexes **3**; however, they also illustrate that great care has to be exercised in correlating electrochemical stability results with optical absorption data.

As Table 5 clearly indicates by example of several systems with comparable absorption energies in the near-IR region, such correlations can only make sense when complexes with comparable charges, coordination arrangements, and thus metal/ligand orbital overlap situations are contrasted. While the bis(chelate)-bridged diruthenium(III,II) and related d^5/d^6 systems[28] with neutral acceptor ligands such as **6** are distinguished by large K_c and small ϵ values, the donor-bridged 3+ ions as presented here show comparatively small K_c but large ϵ parameters. The correlation between comproportionation stability and near-IR band intensity is different again for the classical nonchelate ligand-bridged species of the kind of the Creutz–Taube ion;[2,3,40] recently reported Ru(III)/Ru(II) dimers with the metals bridged by bis(tris-chelate)[41a–c] or π middle deck ligands[41d] exhibit yet other correlations of K_c vs ϵ(MMCT).

The (adc-R) ligand is thus an effectively metal–metal-bridging redox system which does not "waste" π centers, as do most other ligands such as **8**–**10**: Four of the six π centers are metal binding and the remaining two serve for efficient tuning by substituent effects. Particularly in the dianionic form, the small, polarizable, molecular bridging system (adc-R) thus resembles somewhat the atomic bridge O^{2-} with its noted capability of mediating metal–metal interactions in extended lattice structures.[42]

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