

## 2,2'-Dipyridylketone (dpk) as Ancillary Acceptor and Reporter Ligand in Complexes [(dpk)(Cl)Ru( $\mu$ -tppz)Ru(Cl)(dpk)]<sup>n+</sup> where tppz = 2,3,5,6-Tetrakis(2-pyridyl)pyrazine

Sandeep Ghumaan,<sup>†</sup> Biprajit Sarkar,<sup>‡</sup> Nripen Chanda,<sup>†</sup> Monika Sieger,<sup>‡</sup> Jan Fiedler,<sup>§</sup> Wolfgang Kaim,<sup>\*,‡</sup> and Goutam Kumar Lahiri<sup>\*,†</sup>

Department of Chemistry, Indian Institute of Technology—Bombay, Powai, Mumbai - 400076, India, Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany, and J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic

Received May 22, 2006

The tppz-bridged diruthenium(II) complex [(dpk)(Cl)Ru<sup>II</sup>( $\mu$ -tppz)Ru<sup>II</sup>(Cl)(dpk)](ClO<sub>4</sub>)<sub>2</sub>, [2](ClO<sub>4</sub>)<sub>2</sub>, and mononuclear [(dpk)(Cl)Ru<sup>II</sup>(tppz)](ClO<sub>4</sub>), [1](ClO<sub>4</sub>) [tppz = 2,3,5,6-tetrakis(2-pyridyl)pyrazine, dpk = 2,2'-dipyridylketone], have been synthesized. The 260 mV separation between successive one-electron oxidation couples in [2]<sup>2+</sup> translates to a relatively small comproportionation constant,  $K_c$ , of  $2.5 \times 10^4$  for the intermediate. It is shown how electrochemical data ( $E_{ox}$ ,  $E_{red}$ ,  $K_c$ ) reflect the donor/acceptor effects of ancillary ligands L in a series of systems [(L)ClRu( $\mu$ -tppz)-RuCl(L)]<sup>n</sup>, particularly the competition between L and tppz for electron density from the metal. According to EPR ( $g_1 = 2.470$ ,  $g_2 = 2.195$ , and  $g_3 = 1.873$  at 4 K) the intermediate [2]<sup>3+</sup> is a mixed-valent Ru<sup>II</sup>Ru<sup>III</sup> species which shows a rather narrow intervalence charge transfer (IVCT) band at 1800 nm ( $\epsilon = 1500 \text{ M}^{-1} \text{ cm}^{-1}$ ). The width at half-height ( $\Delta\nu_{1/2}$ ) of 700 cm<sup>-1</sup> of the IVCT band is much smaller than the calculated value of 3584 cm<sup>-1</sup>, obtained by using the Hush formula  $\Delta\nu_{1/2} = (2310E_{op})^{1/2}$  ( $E_{op} = 5556 \text{ cm}^{-1}$ , energy of the IVCT transition) which would be applicable to localized (Class II) mixed-valent Ru<sup>II</sup>Ru<sup>III</sup> systems. Valence delocalization in [2]<sup>3+</sup> is supported by the uniform shift of the  $\nu_{C=O}$  band of the N,N'-coordinated dpk ligands from 1676 cm<sup>-1</sup> in the Ru<sup>II</sup>Ru<sup>II</sup> precursor to 1690 cm<sup>-1</sup> in the Ru<sup>2.5</sup>Ru<sup>2.5</sup> form, illustrating the use of the dpk acceptor to act as reporter ligand via the free but  $\pi$ -conjugated organic carbonyl group. The apparent contradiction between the moderate value of  $K_c$  and the narrow IVCT band is being discussed considering "borderline" or "hybrid" "Class II–III" concepts of mixed-valency, as well as coordination aspects, i.e., the bis-tridentate nature of the  $\pi$ -acceptor bridging ligand. Altogether, the complex ions [1]<sup>+</sup> and [2]<sup>2+</sup> display four and five successive reduction processes, respectively, involving both tppz- and dpk-based unoccupied  $\pi^*$  orbitals. The one-electron reduced form [2]<sup>+</sup> has been assigned as a tppz<sup>-</sup> radical-anion-containing species which exhibits a free-radical-type EPR signal at 4K ( $g_{||} = 2.002$ ,  $g_{\perp} = 1.994$ ) and one moderately intense ligand-based low-energy band at 965 nm ( $\epsilon = 1100 \text{ M}^{-1} \text{ cm}^{-1}$ ).

### Introduction

The bridging ligand-induced intermetallic electronic coupling in mixed-valent polyruthenium systems has been the focus of continuous scrutiny<sup>1</sup> since the discovery of pyrazine-mediated strong electronic coupling between the Ru<sup>II</sup>–Ru<sup>III</sup> centers in the Creutz–Taube ion, [(NH<sub>3</sub>)<sub>5</sub>Ru( $\mu$ -pyrazine)-

Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>.<sup>2</sup> This interest is partially due to the fact that such studies extend the basis towards the design of molecular electronic devices such as molecular wires and switches<sup>3</sup> besides their potential relevance for bioinorganic chemistry<sup>4</sup> and for theoretical aspects of electron-transfer mechanisms.<sup>5</sup> Mixed-valent species are frequently categorized into classes, based on criteria put forward by Robin and Day:<sup>6a</sup> Class II denotes a situation where the valence configurations of the metal ions are in localized, e.g., Ru<sup>n+</sup>(L)Ru<sup>(n+1)+</sup>, states. Frequently, such systems exhibit moderate comproportionation constants ( $K_c$  values, calculated using the equation  $RT$

\* To whom correspondence should be addressed. E-mail: lahiri@chem.iitb.ac.in (G.K.L.); kaim@iac.uni-stuttgart.de (W.K.).

<sup>†</sup> Indian Institute of Technology—Bombay.

<sup>‡</sup> Universität Stuttgart.

<sup>§</sup> Academy of Sciences of the Czech Republic.

In  $K_c = nF(\Delta E)^{12}$ . Class II systems typically exhibit relatively broad and solvent-dependent intervalence charge transfer (IVCT) transitions, often in the near-IR region. On the other hand, completely valence-delocalized Class III systems such as  $\text{Ru}^{n+0.5}(\text{L})\text{Ru}^{n+0.5}$  show often higher  $K_c$  values and typically solvent-independent narrow IVCT transitions in the NIR region. Mixed-valent species with narrow IVCT bands as typical for Class III systems despite relatively low  $K_c$  ( $<10^5$ ) values have been designated in

- (1) (a) Kaim, W.; Klein, A.; Glöckle, M. *Acc. Chem. Res.* **2000**, *33*, 755. (b) McCleverty, J. A.; Ward, M. D. *Acc. Chem. Res.* **1998**, *31*, 842. (c) Astruc, D. *Acc. Chem. Res.* **1997**, *30*, 383. (d) Ward, M. D. *Chem. Soc. Rev.* **1995**, *24*, 121. (e) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273. (f) Giuffrida, G.; Campagna, S. *Coord. Chem. Rev.* **1994**, *135–136*, 517. (g) Kaim, W. *Coord. Chem. Rev.* **2002**, *230*, 126. (h) Brunshwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, *31*, 168. (i) Crutchley, R. J. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Amsterdam, 2004; Vol. 2, p 235. (j) Hupp, J. T. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Amsterdam, 2004; Vol. 2, p 709. (k) Breedlove, B. K.; Yamaguchi, T.; Ito, T.; Londergan, C. H.; Kubiak, C. P. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Amsterdam, 2004; Vol. 2, p 717. (l) Sarkar, B.; Laye, R. H.; Mondal, B.; Chakraborty, S.; Paul, R. L.; Jeffery, J. C.; Puranik, V. G.; Ward, M. D.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **2002**, 2097. (m) Chakraborty, S.; Laye, R. H.; Munshi, P.; Paul, R. L.; Ward, M. D.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **2002**, 2348. (n) Patra, S.; Sarkar, B.; Ghumaan, S.; Fiedler, J.; Kaim, W.; Lahiri, G. K. *Inorg. Chem.* **2004**, *43*, 6108. (o) Ghumaan, S.; Sarkar, B.; Patra, S.; Parimal, K.; van Slageren, J.; Fiedler, J.; Kaim, W.; Lahiri, G. K. *Dalton Trans.* **2005**, 706. (p) Kar, S.; Miller, T. A.; Chakraborty, S.; Sarkar, B.; Pradhan, B.; Sinha, R. K.; Kundu, T.; Ward, M. D.; Lahiri, G. K. *Dalton Trans.* **2003**, 2591. (q) Patra, S.; Miller, T. A.; Sarkar, B.; Niemeyer, M.; Ward, M. D.; Lahiri, G. K. *Inorg. Chem.* **2003**, *42*, 4707. (r) Patra, S.; Sarkar, B.; Ghumaan, S.; Fiedler, J.; Zalis, S.; Kaim, W.; Lahiri, G. K. *Dalton Trans.* **2004**, 750. (s) Kar, S.; Sarkar, B.; Ghumaan, S.; Roy, D.; Urbanos, F. A.; Fiedler, J.; Sunoj, R. B.; Jimenez-Aparicio, R.; Kaim, W.; Lahiri, G. K. *Inorg. Chem.* **2005**, *44*, 8715. (t) Browne, W. R.; O'Boyle, N. M.; Henry, W.; Guckian, A. L.; Horn, S.; Fett, T.; O'Connor, C. M.; Duati, M.; De Cola, L.; Coates, C. G.; Ronayne, K. L.; McGarvey, J. J.; Vos, J. G. *J. Am. Chem. Soc.* **2005**, *127*, 1229. (u) Laye, R. H.; Couchman, S. M.; Ward, M. D. *Inorg. Chem.* **2001**, *40*, 4089. (v) Meyer, W. E.; Amoroso, A. J.; Horn, C. R.; Jaeger, M.; Gladysz, J. A. *Organometallics* **2001**, *20*, 1115. (w) Ritchie, J. E.; Murray, R. W. *J. Am. Chem. Soc.* **2000**, *122*, 2964. (x) Weyland, T.; Coustas, K.; Toupet, L.; Halet, J. F.; Lapinte, C. *Organometallics* **2000**, *19*, 4228. (y) Baitalik, S.; Florke, U.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1999**, 719.
- (2) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988. (b) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086. (c) Fuerholz, U.; Joss, S.; Buerger, H. B.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 943.
- (3) (a) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178–180*, 431. (b) Ward, M. D. *Chem. Ind.* **1996**, 568. (c) Ward, M. D. *Chem. Ind.* **1997**, 640. (d) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines: A Journey into the Nanoworld*; Wiley-VCH: Weinheim, Germany, 2003. (e) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001. (f) Kahn, O.; Launay, J.-P. *Chemtronics* **1988**, *3*, 140. (g) Frayssse, S.; Coudret, C.; Launay, J.-P. *J. Am. Chem. Soc.* **2003**, *125*, 5880. (h) Frayssse, S.; Coudret, C.; Launay, J.-P. *Eur. J. Inorg. Chem.* **2000**, *7*, 1581. (i) Ward, M. D. *J. Chem. Educ.* **2001**, *78*, 321. (j) Joulié, L. F.; Schatz, E.; Ward, M. D.; Weber, F.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1994**, 799.
- (4) Solomon, E. I.; Brunold, T. C.; Davis, M. I.; Kemsley, J. N.; Lee, S. K.; Lehnert, N.; Neese, F.; Skulan, A. J.; Yang, Y. S.; Zhou, J. *Chem. Rev.* **2000**, *100*, 235.
- (5) (a) Brunshwig, B. S.; Sutin, N. *Coord. Chem. Rev.* **1999**, *187*, 233. (b) Bencini, A.; Ciofini, I.; Daul, C. A.; Ferretti, A. *J. Am. Chem. Soc.* **1999**, *121*, 11418.
- (6) (a) Robin, M. B.; Day, P. *Adv. Inorg. Radiochem.* **1967**, *10*, 247. (b) Al-Noaimi, M.; Yap, G. P. A.; Crutchley, R. J. *Inorg. Chem.* **2004**, *43*, 1770. (c) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655.
- (7) (a) Poppe, J.; Moscherosch, M.; Kaim, W. *Inorg. Chem.* **1993**, *32*, 2640. (b) Patra, S.; Sarkar, B.; Ghumaan, S.; Fiedler, J.; Kaim, W.; Lahiri, G. K. *Dalton Trans.* **2004**, 754. (c) Chellamma, S.; Lieberman, M. *Inorg. Chem.* **2001**, *40*, 3177.

**Table 1.** Variation in Oxidation Potentials<sup>a</sup> and Corresponding  $K_c$  Values Depending on L in Complexes  $[(\text{L})\text{Ru}(\mu\text{-tpz})\text{Ru}(\text{L})]^{n+}$

ancillary ligands (L)	$E^\circ(\text{ox1})/\text{V}$	$E^\circ(\text{ox2})/\text{V}$	$\Delta E/\text{mV}$	$K_c$	ref
$(\text{NH}_3)_3^b$	0.81	1.31	500	$3.0 \times 10^8$	9a
dpa, $\text{Cl}^-$	0.68	1.06	380	$2.7 \times 10^6$	9b
V-tpy	1.36	1.72	360	$1.3 \times 10^6$	9c
trpy	1.40	1.71	310	$1.7 \times 10^5$	9c
trtpy	1.40	1.70	300	$1.2 \times 10^5$	9d
bpy, $\text{Cl}^-$	0.96	1.25	290	$8.2 \times 10^4$	9e
$\text{L}^2$ , $\text{Cl}^-$	0.95	1.23	280	$5.6 \times 10^4$	9g
$\text{L}^1$ , $\text{Cl}^-$	0.92	1.19	270	$3.8 \times 10^4$	9g
$\text{L}^4$ , $\text{Cl}^-$	0.78	1.04	260	$2.6 \times 10^4$	9g
$\text{L}^3$ , $\text{Cl}^-$	0.43	0.69	260	$2.6 \times 10^4$	9g
dpk, $\text{Cl}^-$	1.04	1.30	260	$2.5 \times 10^4$	present work
pap, $\text{Cl}^-$	1.28	1.51	230	$7.9 \times 10^3$	9f

<sup>a</sup> In  $\text{CH}_3\text{CN}$  unless noted otherwise. <sup>b</sup> In DMF.

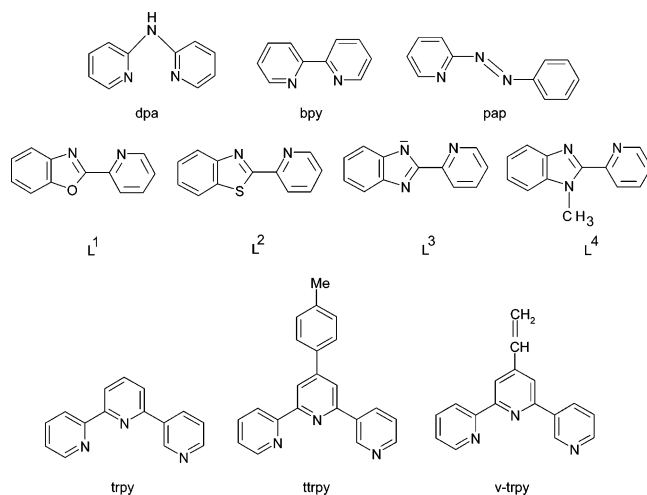
recent years as “borderline” or “hybrid Class II–III”;<sup>6b,c</sup> the opposite, i.e., very high  $K_c$  values for species with only very weak IVCT bands, has also been observed.<sup>1n,7</sup> This report will point to the structural and electronic requirements for such seemingly “deviant” behavior.

Though a large number of pyrazine- or substituted pyrazine-bridged diruthenium(II)/(III) complexes under the categories of Class II or III have been studied,<sup>8</sup> only a limited number of diruthenium complexes  $[(\text{L})\text{Ru}(\mu\text{-tpz})\text{Ru}(\text{L})]^{n+}$  of the bis-tridentate nonplanar bridging ligand 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tpyz) have been reported so far<sup>9</sup> (Tables 1 and 2). The mixed-valent  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  states of  $[(\text{L})\text{Ru}(\mu\text{-tpyz})\text{Ru}(\text{L})]^{n+}$  with  $\text{L} = \text{NH}_3$ ,<sup>9a</sup> dpa<sup>9b</sup> (2,2'-dipyridylamine), V-tpy<sup>9c</sup> (4'-vinyl-2,2':6',2''-terpyridine), and trtpy<sup>9d</sup> (4'-tolyl-2,2':6',2''-terpyridine) have been defined as delo-

- (8) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Sommovigo, M.; Denti, G.; Serroni, S.; Campagna, S.; Mingazzini, C.; Mariotti, C.; Juris, A. *Inorg. Chem.* **2001**, *40*, 3318. (c) Campagna, S.; Denti, G.; Rosa, G. D.; Sabatino, L.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1989**, *28*, 2565. (d) Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 4750. (e) Ceroni, P.; Paolucci, F.; Paradisi, C.; Juris, A.; Roffia, S.; Serroni, S.; Campagna, S.; Bard, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 5480. (f) Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064. (g) Hage, R.; Lempers, H. E. B.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1997**, *36*, 3139. (h) Brady, I.; Leane, D.; Hughes, H. P.; Foster, R. J.; Keyes, T. E. *Dalton Trans.* **2004**, 334.
- (9) (a) Ruminski, R.; Kiplinger, J.; Cockroft, T.; Chase, C. *Inorg. Chem.* **1989**, *28*, 370. (b) Chanda, N.; Sarkar, B.; Fiedler, J.; Kaim, W.; Lahiri, G. K. *Dalton Trans.* **2003**, 3550. (c) Arana, C. R.; Abruna, H. D. *Inorg. Chem.* **1993**, *32*, 194. (d) Collin, J. P.; Laine, P.; Launay, J.-P.; Sauvage, J. P.; Sour, A. *J. Chem. Soc., Chem. Commun.* **1993**, 434. (e) Hartshorn, V.; Daire, N.; Tondreau, V.; Loeb, B.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1999**, *38*, 3200. (f) Chanda, N.; Laye, R. H.; Chakraborty, S.; Paul, R. L.; Jeffery, J. C.; Ward, M. D.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **2002**, 3496. (g) Chanda, N.; Sarkar, B.; Kar, S.; Fiedler, J.; Kaim, W.; Lahiri, G. K. *Inorg. Chem.* **2004**, *43*, 5128. (h) Thummel, R. P.; Chirayil, S. *Inorg. Chim. Acta* **1988**, *154*, 77. (i) Vogler, L. M.; Scott, B.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 898. (j) Lee, J.-D.; Vrana, L. M.; Bullock, E. R.; Brewer, K. J. *Inorg. Chem.* **1998**, *37*, 3575. (k) Akasheh, T. S.; Marji, D.; Al Ahmed, Z. M. *Inorg. Chim. Acta* **1988**, *141*, 125. (l) Vogler, L. M.; Brewer, K. J. *Inorg. Chem.* **1996**, *35*, 818. (m) Dattelbaum, D. M.; Hartshorn, C. M.; Meyer, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 4938.
- (10) Sarkar, S.; Sarkar, B.; Chanda, N.; Kar, S.; Mobin, S. M.; Fiedler, J.; Kaim, W.; Lahiri, G. K. *Inorg. Chem.* **2005**, *44*, 6092.
- (11) (a) Sarkar, B.; Patra, S.; Fiedler, J.; Sunoj, R. B.; Janardanan, D.; Mobin, S. M.; Niemeyer, M.; Lahiri, G. K.; Kaim, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 5655. (b) Zampese, J. A.; Keene, F. R.; Steel, P. J. *Dalton Trans.* **2004**, 4124.
- (12) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135.

**Table 2.** Variation in Potentials Corresponding to the First Two One-Electron Reductions and Corresponding  $K_c$  Values Depending on L in  $[(L)Ru(\mu\text{-tppz})Ru(L)]^{n+}$  <sup>a</sup>

ancillary ligands (L)	$E^\circ(\text{red1})/V$	$E^\circ(\text{red2})/V$	$\Delta E/mV$	$K_c$	ref
$L^3, Cl^-$	-0.84	-1.37	530	$9.6 \times 10^8$	9g
dpa, $Cl^-$	-0.76	-1.27	510	$4.4 \times 10^8$	9b
$L^2, Cl^-$	-0.59	-1.10	510	$4.4 \times 10^8$	9g
ttrpy	-0.35	-0.85	500	$2.9 \times 10^8$	9d
bpy, $Cl^-$	-0.60	-1.10	500	$2.9 \times 10^8$	9e
V-trpy	-0.41	-0.90	490	$2.0 \times 10^8$	9c
$L^4, Cl^-$	-0.71	-0.19	480	$1.4 \times 10^8$	9g
trpy	-0.39	-0.86	470	$9.2 \times 10^7$	9c
$L^1, Cl^-$	-0.63	-1.10	470	$9.2 \times 10^7$	9g
dpk, $Cl^-$	-0.62	-1.01	390	$4.1 \times 10^6$	present work
pap, $Cl^-$	-0.44	-0.81	370	$1.9 \times 10^6$	9f

<sup>a</sup> In acetonitrile solution.

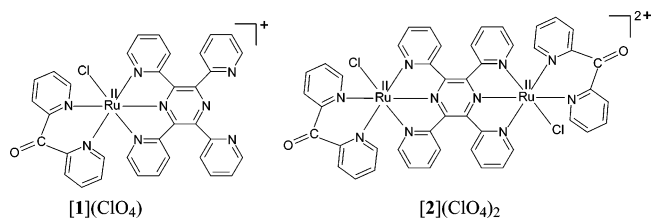
calized Class III systems, primarily based on their rather high  $K_c$  values ( $\geq 10^6$ ) along with narrow and intense IVCT bands. The complexes with  $L = \text{bpy}^{9c}$  (2,2'-bipyridine),  $\text{pap}^{9f}$  (2-phenylazopyridine), and pyridyl/azoles<sup>9g</sup> which, despite their moderate  $K_c$  values ( $10^3\text{--}10^4$ ), exhibit narrow IVCT bands were associated with a Class II–III borderline situation.

The above observations of the influence of the electronic nature of ancillary ligands (L) on the mixed-valence characteristics of tppz-bridged diruthenium complexes initiated the present study of dealing with the complex  $[(L)Ru(\mu\text{-tppz})Ru(L)]^{n+}$  where  $L = 2,2'$ -dipyridylketone = dpk. This ligand is a good  $\pi$  acceptor involving potentially  $\pi$ -conjugated pyridine and spectroscopically valuable  $C=O$  functions; its chelating ability to form not necessarily planar six-membered rings is, however, less advantageous for metal/ligand interaction.

The present contribution thus covers the synthesis and characterization of mononuclear  $[(L)(Cl)Ru^{II}(tppz)]^+ [1]^+$  and dinuclear  $[(L)(Cl)Ru^{II}(\mu\text{-tppz})Ru^{II}(Cl)(L)]^{2+} [2]^{2+}$  complexes. The mixed-valence characteristics of  $[2]^{3+}$  have been investigated via spectroelectrochemistry and EPR studies.

## Results and Discussion

**Synthesis and Characterization.** The mononuclear  $[(L)(Cl)Ru^{II}(tppz)](ClO_4)$ ,  $[1](ClO_4)$ , and the dinuclear  $[(L)(Cl)Ru^{II}(\mu\text{-tppz})Ru^{II}(Cl)(L)](ClO_4)_2$ ,  $[2](ClO_4)_2$ , have been synthesized via the reaction of ethanolic solutions of the



precursor complex  $[(Cl)_3Ru^{III}(\mu\text{-tppz})Ru^{III}(Cl)_3]$  with 2,2'-dipyridylketone (L) in a molar ratio of 1:2 in the presence of excess LiCl under a dinitrogen atmosphere, followed by conversion to the perchlorate salt and by chromatographic separation using a neutral alumina column. Apparently, partial dissociation on the column or incomplete conversion have produced the mononuclear compound.

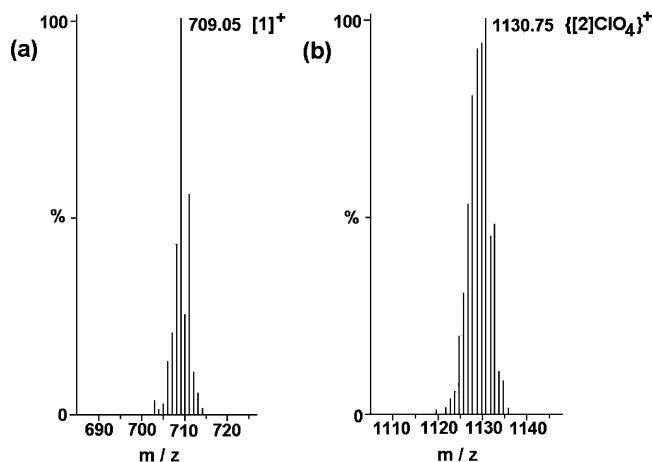
The microanalytical data of  $[1](ClO_4)$  and  $[2](ClO_4)_2$  agree well with the calculated values, and the diamagnetic complexes  $[1](ClO_4)$  and  $[2](ClO_4)_2$  exhibit 1:1 and 1:2 conductivities in  $CH_3CN$ , respectively (see the Experimental Section). The formation of  $[1](ClO_4)$  and  $[2](ClO_4)_2$  has been authenticated by their electrospray mass spectral data (Figure 1);  $[1](ClO_4)$  and  $[2](ClO_4)_2$  exhibit molecular ion peaks at 709.05 and 1130.75, corresponding to  $\{[1](ClO_4) - ClO_4\}^+$  (calculated mass = 709.08) and  $\{[2](ClO_4)_2 - ClO_4\}^+$  (calculated mass = 1128.96), respectively.

The  $\nu(C=O)$  stretching frequency of free 2,2'-dipyridylketone ligand appears at  $1683\text{ cm}^{-1}$  in a KBr disk which is shifted to lower values at  $1666\text{ cm}^{-1}$  on complexation in  $[1](ClO_4)$  and to even lower energy at  $1630\text{ cm}^{-1}$  on second metalation in  $[2](ClO_4)_2$ . The presence of only one  $\nu(C=O)$  band in  $[2](ClO_4)_2$  in corroboration with a single Ru–Cl vibration band at  $335\text{ cm}^{-1}$  signifies a single isomer, most probably the trans compound, with respect to the position of two chloride groups. The preferential formation of the trans geometry has also been reported in the analogous complexes with  $L = 2,2'$ -bipyridine,<sup>9e</sup> 2-phenylazopyridine,<sup>9f</sup> 2,2'-dipyridylamine,<sup>9b</sup> and 2-(2-pyridyl)azoles.<sup>9g</sup> The perchlorate vibrations appear at  $1090/622$  and  $1088/626\text{ cm}^{-1}$  for  $[1](ClO_4)$  and  $[2](ClO_4)_2$ , respectively.

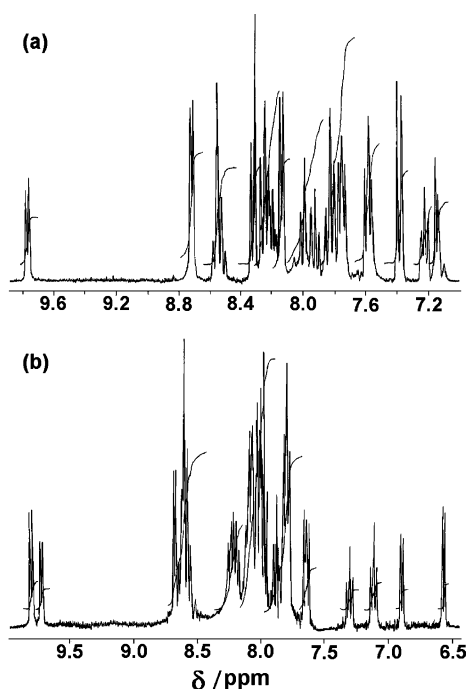
The  $^1H$  NMR spectrum of  $[1]^+$  in  $(CD_3)_2SO$  shows the partial overlapping expected for 24 signals in the “aromatic” region (Figure 2a, see the Experimental Section). The appearance of 32 such severely overlapping signals from  $[2]^{2+}$  (Figure 2b, see the Experimental Section) illustrates either a lack of symmetry due to the nonplanarity<sup>9f</sup> of tppz, as well as dpk ligands,<sup>10</sup> or the presence of a mixture of two diastereoisomeric forms in solution.<sup>11</sup>

**Electrochemistry, Spectroelectrochemistry (UV–Vis–NIR, IR), and EPR.** The quasi-reversible  $Ru^{III}\text{--}Ru^{II}$  couple for  $[1]^+$  in  $CH_3CN$  appears at 0.88 V vs SCE (couple I, Figure 3a) which is about 100 mV more positive than that of the corresponding mononuclear derivative having  $L = 2,2'$ -dipyridylamine.<sup>9b</sup> Thus, the  $Ru^{III}$  state is destabilized substantially on switching from  $L = 2,2'$ -dipyridylamine to 2,2'-dipyridylketone in  $[1]^+$  due to the effect of the  $\pi$ -electron-withdrawing conjugated  $C=O$  group in the framework of 2,2'-dipyridylketone as opposed to the  $\pi$ -donating amine group in 2,2'-dipyridylamine. Two successive reversible



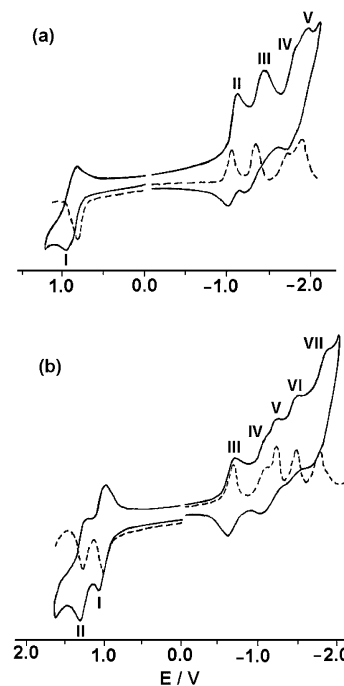


**Figure 1.** Electrospray mass spectra of (a) [(dpk)(Cl)Ru<sup>II</sup>(tppz)](ClO<sub>4</sub>), [1](ClO<sub>4</sub>), and (b) [(dpk)(Cl)Ru<sup>II</sup>(μ-tppz)Ru<sup>II</sup>(Cl)(dpk)](ClO<sub>4</sub>)<sub>2</sub>, [2](ClO<sub>4</sub>)<sub>2</sub>, in CH<sub>3</sub>CN.



**Figure 2.** <sup>1</sup>H NMR spectra of (a) [(dpk)(Cl)Ru<sup>II</sup>(tppz)](ClO<sub>4</sub>), [1](ClO<sub>4</sub>), and (b) [(dpk)(Cl)Ru<sup>II</sup>(μ-tppz)Ru<sup>II</sup>(Cl)(dpk)](ClO<sub>4</sub>)<sub>2</sub>, [2](ClO<sub>4</sub>)<sub>2</sub>, in (CD<sub>3</sub>)<sub>2</sub>-SO.

couples were observed for the dinuclear complex [2]<sup>2+</sup> (Table 1, Figure 3b). The presence of the second metal ion in [2]<sup>2+</sup> increases the stability of the Ru<sup>II</sup> center by 160 mV, and the stability of the ruthenium(III) state varies, depending on both the charge and on the electronic donor/acceptor nature of the ancillary ligands L (Table 1). The 260 mV separation in potential ( $\Delta E$ ) between the successive oxidation couples translates to a comproportionation constant of  $K_c = 2.5 \times 10^4$  ( $RT \ln K_c = nF(\Delta E)^{12}$ ) at 298 K. Thus, an appreciable decrease in electrochemical coupling has taken place on changing the ancillary ligand from the  $\pi$ -donor-containing 2,2'-dipyridylamine to the corresponding  $\pi$ -acceptor ketone dpk (Table 1). The  $\pi$ -electron-withdrawing effect of 2,2'-dipyridylketone in [2]<sup>2+</sup> in essence reduces the capacity of the  $\pi$ -accepting tppz bridge to mediate electron-transfer-type valence exchange processes.<sup>1</sup> A stronger ancillary ligand

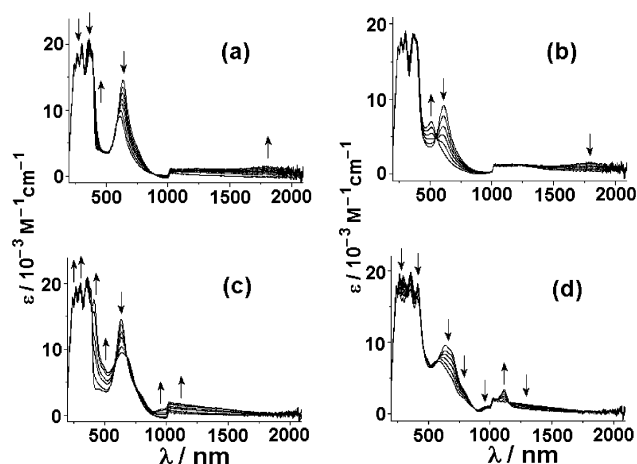


**Figure 3.** Cyclic voltammograms (—) and differential pulse voltammograms (---) of (a) [(dpk)(Cl)Ru<sup>II</sup>(tppz)](ClO<sub>4</sub>), [1](ClO<sub>4</sub>), and (b) [(dpk)(Cl)Ru<sup>II</sup>(μ-tppz)Ru<sup>II</sup>(Cl)(dpk)](ClO<sub>4</sub>)<sub>2</sub>, [2](ClO<sub>4</sub>)<sub>2</sub>, in CH<sub>3</sub>CN/0.1M Et<sub>4</sub>-NClO<sub>4</sub>.

effect has only been observed for the analogous complex with L = 2-phenylazopyridine (pap),<sup>9f</sup> comparable behavior to dpk was found for pyridyl/azole-containing ancillary ligands (Table 1).<sup>9g</sup>

In principle, tppz<sup>9</sup> and dpk<sup>10</sup> can accept two electrons each in the electrochemically accessible region by populating the LUMO; thus, reductions by four and six electron equivalents can be expected for the mononuclear ([1]<sup>+</sup>) and dinuclear ([2]<sup>2+</sup>) complex ions, respectively. Four and five successive one-electron reduction waves are indeed observed for [1]<sup>+</sup> and [2]<sup>2+</sup> within the experimental potential limit of -2.0 V vs SCE (Figure 3, Table 2). Considering the strong  $\pi$ -acceptor characteristics of tppz, the first two reduction steps are associated with the tppz ligand, i.e.,  $[tppz] \rightleftharpoons [tppz]^{-}$  and  $[tppz]^{-} \rightleftharpoons [tppz]^{2-}$ . The subsequent reduction processes probably involve the dpk ligand(s).<sup>10</sup> The less negative potential of the reduction of [2]<sup>2+</sup> as compared to [1]<sup>+</sup> arises from the difference in overall charge, +2 vs +1. This confers additional stability to the  $\pi^*(tppz)$  orbitals in [2]<sup>2+</sup>. The difference in electronic nature and charge of the ancillary ligands is also reflected by the shifts of the reduction potentials (Table 2). The potential difference between the first two tppz-centered reduction waves and the corresponding  $K_c$  values diminish on increasing the  $\pi$ -acceptor character of the ancillary ligand L, reflecting once more the competition between L and tppz<sup>9</sup> for the metal electron density.

A moderately intense Ru<sup>II</sup>-to- $\pi^*(tppz)$  MLCT transition has been observed for [1]<sup>+</sup> at 569 nm in CH<sub>3</sub>CN in addition to multiple strong intraligand transitions in the UV region<sup>9b</sup> (see the Experimental Section). The spectral features of the dinuclear complex [2]<sup>2+</sup> in different accessible oxidation states ( $n = 0, +, 2+, 3+, 4+$ ) have been studied in the UV—



**Figure 4.** UV-vis-NIR spectroelectrochemistry of the conversions (a)  $[2]^{2+} \rightarrow [2]^{3+}$ , (b)  $[2]^{3+} \rightarrow [2]^{4+}$ , (c)  $[2]^{2+} \rightarrow [2]^+$ , and (d)  $[2]^+ \rightarrow [2]$  in  $\text{CH}_3\text{CN}/0.1\text{M Bu}_4\text{NPF}_6$ .

vis-NIR region using an OTTLE cell.<sup>21</sup> Spectra are shown in Figure 4, and the data are listed in Table 3. The complex ion  $[2]^{2+}$  exhibits an intense  $\text{Ru}^{\text{II}}\text{-to-}\pi^*(\text{tppz})$  MLCT transition at 636 nm in  $\text{CH}_3\text{CN}$  (Figure 4a), bathochromically shifted in comparison to  $[1]^+$ . On oxidation to the mixed-valent  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  state in  $[2]^{3+}$ , the intensity of the  $\text{Ru}^{\text{II}}\text{ to } \pi^*(\text{tppz})$  MLCT transition decreases from 14500 to 9100  $\text{M}^{-1}\text{cm}^{-1}$  due to the reduction in number of  $\text{Ru}^{\text{II}}$  donor centers. Moreover, a moderately intense  $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$  intervalence charge transfer (IVCT) band is observed in the near-IR region at 1800 nm ( $\epsilon = 1500\text{ M}^{-1}\text{cm}^{-1}$ ).<sup>9b,f,g</sup> (Figure 4a). On further one-electron oxidation to the isoivalent  $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$  congener in  $[2]^{4+}$  the IVCT band disappears completely and the  $\text{Ru}^{\text{II}}$ -

**Table 3.** UV-vis-NIR Data of  $2^n$  [ $n = 0, 1, 2, 3, 4$ ] from Spectroelectrochemistry<sup>a</sup>

complex	$\lambda_{\text{max}}$ (nm) ( $\epsilon$ ( $\text{M}^{-1}\text{cm}^{-1}$ ))
$[2]$	1115 (3300), 783 <sup>b</sup> , 690 <sup>b</sup> , 586 (7400), 408 (16 400), 356 (17 400), 372 <sup>b</sup> , 291 <sup>b</sup> , 266 (17 000), 244 (17 100)
$[2]^+$	1200 <sup>b</sup> , 965 (1100), 785 <sup>b</sup> , 698 <sup>b</sup> , 635 (9600), 490 <sup>b</sup> , 415 (17 600), 357 (19 700), 302 (18 900), 267 (19 600), 241 (17 700)
$[2]^{2+}$	636 (14 500), 453 <sup>b</sup> , 388 <sup>b</sup> , 359 (21 000), 304 (20 000), 267 (18 900), 242 (17 100)
$[2]^{3+}$	1800 (1500), 613 (9100), 420 <sup>b</sup> , 367 (18 600), 304 (18 800), 267 (17 900), 243 (16 600)
$[2]^{4+}$	606 (3300), 514 (7000), 397 <sup>b</sup> , 371 (18 300), 302 (18 200), 268 (17 800), 243 (16 700)

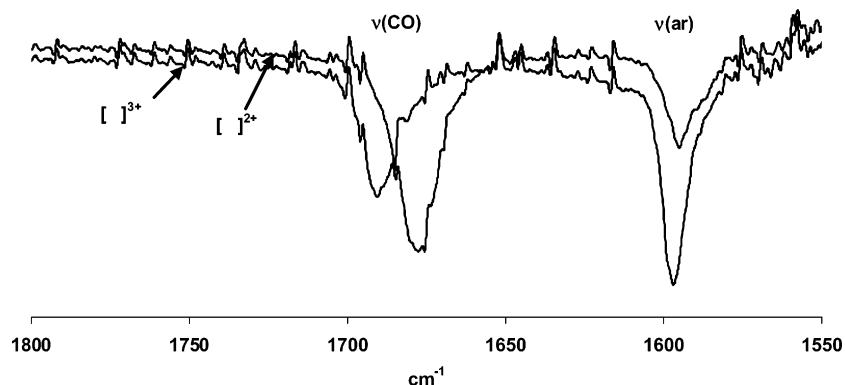
<sup>a</sup> Measurements in  $\text{CH}_3\text{CN}/0.1\text{M Bu}_4\text{NPF}_6$  (OTTLE spectroelectrochemistry). <sup>b</sup> Shoulder.

based MLCT band is replaced by a  $\text{Ru}^{\text{III}}$ -based LMCT transition at 514 nm (Figure 4b).<sup>13</sup> The width at half-height ( $\Delta\nu_{1/2}$ ) of the IVCT band at about 700  $\text{cm}^{-1}$  is much narrower than the calculated value of 3584  $\text{cm}^{-1}$  obtained by using the Hush formula  $\Delta\nu_{1/2} = (2310E_{\text{op}})^{1/2}$ ,<sup>12a,14</sup> ( $E_{\text{op}} = 5556\text{ cm}^{-1}$ , energy of the IVCT band), which is applicable to localized Class II mixed-valent  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  systems. For a weakly coupled valence-localized Class II system, the experimental  $\Delta\nu_{1/2}$  of the IVCT band is expected to match the calculated value from the Hush approach. However, for a strongly coupled delocalized (Class III) system, the experimentally derived  $\Delta\nu_{1/2}$  is known to be much smaller than the calculated value. Thus, on the basis of the IVCT band, the mixed-valent  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  state in  $[2]^{3+}$  can be considered as delocalized (Class III,  $\text{Ru}^{2.5}\text{Ru}^{2.5}$ ) despite the small electrochemical parameter  $K_c$  of  $2.5 \times 10^4$ .

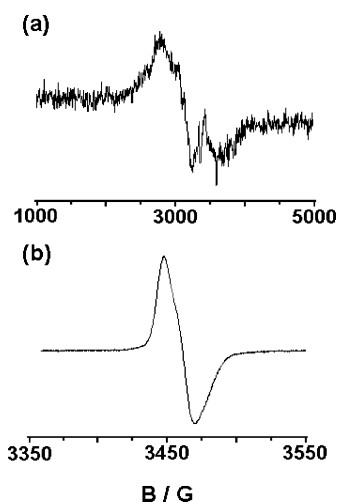
Valence delocalization on the rather short time scale of vibrational spectroscopy<sup>15</sup> is further supported by the shift of the single  $\nu_{\text{C=O}}$  band of the  $\text{N,N}'$ -coordinated dpk ligands from 1676  $\text{cm}^{-1}$  in  $[2]^{2+}$  to 1690  $\text{cm}^{-1}$  in  $[2]^{3+}$  ( $\text{CH}_3\text{CN}/0.1\text{M Bu}_4\text{NPF}_6$ ); the aryl-based band at about 1595  $\text{cm}^{-1}$  shows no discernible shift (Figure 5). Whereas shifts of metal carbonyl bands have been widely used to study the charge and (de)localization situation in mixed-valent complexes,<sup>15b,c,e</sup> the example of  $[2]^{3+}$  shows that uncoordinated carbonyl groups of organic ligands such as the chelating ketone dpk may also be used to monitor apparent valence averaging. The  $\pi$  conjugation of the  $\text{C=O}$  function with the coordinating pyridyl groups in dpk helps to increase the necessary sensitivity.

Discrepancies between the small charge-related electrochemical interaction parameter  $K_c$  and the significant, orbital overlap-controlled electronic coupling have been observed in other tppz-bridged diruthenium systems  $[(\text{L})(\text{Cl})\text{Ru}(\mu\text{-tppz})\text{Ru}(\text{Cl})(\text{L})]^{n+}$ .<sup>9e,f,g</sup> The mixed-valent  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  state in those instances was defined as “hybrid Class II–III”, i.e., the rate of intramolecular electron transfer may be on the order of the relaxation time of the solvent.<sup>6b,c</sup> On the other hand, the analogue with  $\text{L} = \text{dpa}$  is a clear Class III case. Small  $K_c$  values in conjunction with intense narrow IVCT bands have been reported previously for  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  complexes with *bis-tridentate* acceptor bridges<sup>9d,16</sup> other than tppz;<sup>9</sup> the opposite response, i.e., weak IVCT features for  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$

- (13) (a) Shirin, Z.; Mukherjee, K. *Polyhedron* **1992**, *11*, 2625. (b) Murray, K. S.; van der Bergen, A. M.; West, B. O. *Aust. J. Chem.* **1978**, *31*, 203. (c) Rodman, G. S.; Nagle, J. K. *Inorg. Chim. Acta* **1985**, *105*, 205.
- (14) (a) Chakraborty, S.; Laye, R. H.; Paul, R. L.; Gonnade, R. G.; Puranik, V. G.; Ward, M. D.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **2002**, 1172. (b) Sarkar, B.; Kaim, W.; Klein, A.; Schwederski, B.; Fiedler, J.; Duboc-Toia, C.; Lahiri, G. K. *Inorg. Chem.* **2003**, *42*, 6172.
- (15) (a) Lever, A. B. P. In *Comprehensive Coordination Chemistry*; McCleverty, J., Meyer, T. J., Eds.; Elsevier: Amsterdam, 2003; Vol. 2, p 435. (b) Salsman, J. C.; Kubiak, C. P.; Ito, T. *J. Am. Chem. Soc.* **2005**, *127*, 2382. (c) Cheah, M. H.; Borg, S. J.; Bondin, M. I.; Best, S. P. *Inorg. Chem.* **2004**, *43*, 5635. (d) Ashley, K.; Pons, S.; *Chem. Rev.* **1988**, *88*, 673. (e) Kaim, W.; Bruns, W.; Poppe, J.; Kasack, V. *J. Mol. Struct.* **1993**, *292*, 221.
- (16) (a) Beley, M.; Collin, J.-P.; Louis, R.; Metz, B.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8521. (b) Sutter, J.-P.; Grove, D. M.; Beley, M.; Collin, J.-P.; Veldman, N.; Spek, A. L.; Sauvage, J.-P.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1282. (c) Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1775.
- (17) (a) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187. (b) Remenyi, C.; Kaupp, M. *J. Am. Chem. Soc.* **2005**, *127*, 11399.
- (18) Patra, S.; Sarkar, B.; Mobin, S. M.; Kaim, W.; Lahiri, G. K. *Inorg. Chem.* **2003**, *42*, 6469.
- (19) (a) Scheiring, T.; Kaim, W.; Olabe, J. A.; Parise, A. R.; Fiedler, J. *Inorg. Chim. Acta* **2000**, *300–302*, 125. (b) Glöckle, M.; Kaim, W.; Klein, A.; Roduner, E.; Hübner, G.; Zalis, S.; van Slageren, J.; Renz, F.; Güttlich, P. *Inorg. Chem.* **2001**, *40*, 2256.
- (20) (a) Fletcher, N. C.; Robinson, T. C.; Behrendt, A.; Jeffery, J. C.; Reeves, Z. R.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1999**, 2999. (b) Ghosh, A. K.; Peng, S.-M.; Paul, R. L.; Ward, M. D.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **2001**, 336. (c) Auburn, P. R.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 2551. (d) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *Chem. Phys. Lett.* **1982**, *92*, 646.
- (21) Krejčík, M.; Danek, M.; Hartl, F. J. *Electroanal. Chem.* **1991**, *317*, 179.



**Figure 5.** IR spectroelectrochemistry of the conversion  $[2]^{2+} \rightarrow [2]^{3+}$  in  $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NPF}_6$ .



**Figure 6.** EPR spectra of electrogenerated (a)  $[(\text{dpk})(\text{Cl})\text{Ru}^{\text{II}}(\mu\text{-tppz})\text{Ru}^{\text{III}}(\text{Cl})(\text{dpk})]^{3+}$ ,  $[2]^{3+}$ , and (b)  $[(\text{dpk})(\text{Cl})\text{Ru}^{\text{II}}(\mu\text{-tppz}^{2-})\text{Ru}^{\text{II}}(\text{Cl})(\text{dpk})]^{+}$ ,  $[2]^{+}$ , in  $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NPF}_6$  at 4 K.

intermediates with very high comproportionation constants have been observed for systems with *bis*- or *tris*-bidentate bridges.<sup>7</sup> Obviously, the chelate coordination pattern can determine electronic and electrochemical metal–metal interaction in quite disparate ways, rendering simple correlations and criteria for the assignment of the Robin and Day “Classes” as less useful.

The in-situ-generated one-electron oxidized species  $[2]^{3+}$  displays a rhombic EPR spectrum at 4 K in  $\text{CH}_3\text{CN}$  with well-separated  $g$  components: ( $g_1 = 2.470$ ,  $g_2 = 2.195$ , and  $g_3 = 1.873$ , Figure 6a). The  $g$  anisotropy  $g_1 - g_3 = \Delta g = 0.597$  is lower than that of the Creutz–Taube ion ( $\Delta g = 1.457^a$ ) despite the built-in nonplanarity of the tppz bridging ligand in  $[2]^{3+}$ . The average  $g$  factor of  $\langle g \rangle = 2.193$  as derived from  $\langle g \rangle = [1/3(g_1^2 + g_2^2 + g_3^2)]^{1/2}$  confirms the metal-centered spin corresponding to the  $\text{Ru}^{2.5}\text{Ru}^{2.5}$  formulation.<sup>17</sup> The  $\Delta g$  and  $\langle g \rangle$  values for the dpa derivative are 1.693 and 2.53, respectively,<sup>9b</sup> reflecting a higher degree of participation of the heavy metal with its high spin–orbit coupling constant at the spin distribution. Thus, on changing L from dpa to dpk in  $[(\text{L})(\text{Cl})\text{Ru}^{\text{II}}(\mu\text{-tppz})\text{Ru}^{\text{III}}(\text{Cl})(\text{L})]^{3+}$ , the contribution from the metal ion at the singly occupied MO decreases and that of the ancillary ligands increases.<sup>17,18</sup> However, in the absence of hyperfine information, the extent

of localization of the unpaired spin,  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  or  $\text{Ru}^{2.5}\text{Ru}^{2.5}$ , cannot be specified with confidence.<sup>19</sup>

On one-electron reduction to  $[(\text{L})(\text{Cl})\text{Ru}^{\text{II}}(\mu\text{-tppz}^{\bullet-})\text{Ru}^{\text{II}}(\text{Cl})(\text{L})]^{+}$  ( $[2]^{+}$ ), the intensity of the MLCT transition at 635 nm decreases as a consequence of the new half-occupied  $\pi^*$ -acceptor orbital in  $\text{tppz}^{\bullet-}$  which was vacant in the  $\text{tppz}^0$  state. Moreover, one new weak low-energy band appears at 965 nm (Figure 4c). That band can be tentatively assigned as LLCT transition involving the  $\text{tppz}^{\bullet-}$  radical anion as donor and the vacant  $\pi^*$  level of dpk.<sup>20</sup> The doubly reduced species  $[(\text{L})(\text{Cl})\text{Ru}^{\text{II}}(\mu\text{-tppz}^{2-})\text{Ru}^{\text{II}}(\text{Cl})(\text{L})]$ ,  $[2]^{0}$ , also shows a low-energy band at 1115 nm which may then be assigned as the LLCT transition from  $\text{tppz}^{2-}$  to the  $\pi^*$  orbital of dpk (Figure 4d). The MLCT band of  $[2]^{0}$  is further blue-shifted to 586 nm with reduction in intensity. Similar LLCT features involving reduced tppz have been observed for analogous complexes with L = dpa, pap, and 2-pyridylazoles.<sup>9b,f,g</sup> The free radical-type EPR signal at  $g_{\parallel} = 2.002$  and  $g_{\perp} = 1.994$  for  $[2]^{+}$  (Figure 6b),  $\langle g \rangle = 1.997$ , confirms ligand-centered spin<sup>22</sup> on the  $\text{tppz}^{\bullet-}$  bridge.<sup>9b,f,g</sup>

In summary, the tppz-bridged dinuclear complex  $[(\text{L})(\text{Cl})\text{Ru}^{\text{II}}(\mu\text{-tppz})\text{Ru}^{\text{II}}(\text{Cl})(\text{L})](\text{ClO}_4)_2$ ,  $[2](\text{ClO}_4)_2$ , and the corresponding mononuclear derivative  $[(\text{L})(\text{Cl})\text{Ru}^{\text{II}}(\text{tppz})](\text{ClO}_4)$ ,  $[1](\text{ClO}_4)$ , incorporating 2,2'-dipyridylketone as ancillary ligands (L) have been synthesized. The present work highlights the following salient features: (i) The change from L = 2,2'-dipyridylamine to stronger  $\pi$ -accepting L = 2,2'-dipyridylketone destabilizes the  $\text{Ru}^{\text{III}}$  state in  $[1]^{2+}$  and  $[2]^{3+}$  substantially. (ii) The coordination of the second metal complex fragment to tppz in  $[2]^{2+}$  stabilizes the  $\pi^*$  (tppz) orbital with respect to mononuclear  $[1]^{+}$ . (iii) Characteristic  $\text{Ru}^{\text{III}}$  or free radical-type EPR spectra of one-electron oxidized  $[2]^{3+}$  or reduced  $[2]^{+}$ , respectively, are evidence that the unpaired spin is preferentially localized on the metal in the former and on  $\text{tppz}^{\bullet-}$  in the latter. (iv) Both comproportionation constants  $K_c(+)$  and  $K_c(3+)$  for the  $[(\text{L})\text{Ru}(\mu\text{-tppz})\text{Ru}(\text{L})]$  core decrease on introduction of dpk, reflecting the competition of these ancillary ligands with the  $\text{tppz}^n$  bridge for  $\pi$ -electron density from the metal. The  $K_c$  for the first two metal-centered oxidation processes of tppz-bridged complexes decrease systematically with the increasing  $\pi$

(22) Kaim, W.; Ernst, S.; Kasack, V. *J. Am. Chem. Soc.* **1990**, *112*, 173.

acidity of the ancillary ligands (L). (v) The narrow Ru<sup>II</sup> → Ru<sup>III</sup> IVCT band in the intermediate [2]<sup>3+</sup> implies Class III behavior (valence averaging) despite the relatively small  $K_c$  value. (vi) Support for this interpretation comes from IR spectroelectrochemistry: Just like directly metal-bonded CO,<sup>15b,c,e</sup> the C=O function of organic carbonyl compounds as ancillary ligands can reflect the molecular symmetry and thus permit an estimate of the valence situation at the vibrational time scale.

## Experimental Section

The precursor complex [Cl<sub>3</sub>Ru<sup>III</sup>( $\mu$ -tppz)Ru<sup>III</sup>Cl<sub>3</sub>] was prepared following the reported procedure.<sup>9e</sup> 2,2'-Dipyridylketone was purchased from Aldrich. Other chemicals and solvents were reagent grade and used as received. For spectroscopic and electrochemical studies, HPLC grade solvents were used.

Solution electrical conductivity was checked using a Systronic conductivity bridge 305. Infrared spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. <sup>1</sup>H NMR spectra were recorded for (CD<sub>3</sub>)<sub>2</sub>SO solutions using a 300 MHz Varian FT spectrometer. UV–vis–NIR and IR spectroelectrochemical studies were performed in CH<sub>3</sub>CN/0.1 M Bu<sub>4</sub>NPF<sub>6</sub> at 298 K using an optically transparent thin layer electrode (OTTLE) cell mounted in the sample compartments of a J&M Tidas spectrophotometer and a Perkin-Elmer 1760X FTIR instrument, respectively.<sup>21</sup> Cyclic voltammetric and coulometric measurements were carried out using a PAR model 273A electrochemistry system. A platinum wire working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration. Tetraethylammonium perchlorate (TEAP) was the supporting electrolyte, and the solution concentration was ca. 10<sup>-3</sup> M; the scan rate used was 50 mV s<sup>-1</sup>. A platinum gauze working electrode was used in the coulometric experiments. All electrochemical experiments were carried out under dinitrogen atmosphere. The EPR measurements were made in a two-electrode capillary tube with a X-band Bruker system ESP300, equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter.<sup>22</sup> The elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Electrospray mass spectra were recorded on a Micromass Q-ToF mass spectrometer.

**CAUTION:** Perchlorate salts of metal complexes are generally explosive. Care should be taken while handling such complexes!

**Synthesis of [(L)ClRu<sup>II</sup>(tppz)](ClO<sub>4</sub>), [1](ClO<sub>4</sub>), and [(L)-ClRu<sup>II</sup>]<sub>2</sub>( $\mu$ -tppz)](ClO<sub>4</sub>)<sub>2</sub>, [2](ClO<sub>4</sub>)<sub>2</sub>.** The precursor complex [Cl<sub>3</sub>-Ru<sup>III</sup>( $\mu$ -tppz)Ru<sup>III</sup>Cl<sub>3</sub>] (100 mg, 0.124 mmol) and the free ligand L = dpk (50.45 mg, 0.274 mmol) were dissolved in ethanol (15 mL) and refluxed for 5 h under dinitrogen atmosphere in the presence of excess LiCl (54 mg, 1.3 mmol). The initial light-green solution gradually changed to greenish-blue. A saturated aqueous solution of NaClO<sub>4</sub> was then added to the concentrated acetonitrile solution of the product. The solid precipitate thus obtained was filtered and washed thoroughly by cold ethanol followed by ice-cold water. The dried product was then purified by using a neutral alumina column. The violet mononuclear complex [1](ClO<sub>4</sub>) and greenish-blue dinuclear complex [2](ClO<sub>4</sub>)<sub>2</sub> were eluted by 5:1 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN and 5:2 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN mixtures, respectively. Evaporation of solvent under reduced pressure yielded pure complexes [1](ClO<sub>4</sub>) and [2](ClO<sub>4</sub>)<sub>2</sub>, respectively. [1](ClO<sub>4</sub>): Yield: 10 mg (10%). Anal. Calcd (Found) for C<sub>35</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>5</sub>Ru: C, 51.98(51.44); H, 2.99-(2.88); N, 13.86(13.62). Molar conductivity [ $\Lambda_M$  ( $\Omega^{-1}$  cm<sup>2</sup> M<sup>-1</sup>)] in acetonitrile at 298 K: 116.  $\lambda_{\max}$ /nm ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>) in CH<sub>3</sub>CN at 298 K: 674 (711, shoulder), 569 (5339), 453 (1747, shoulder), 343 (21927), 284 (19702), 255 (17366, shoulder). <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>SO,  $\delta$ (J/Hz)]: 9.76(d, 5.4); 8.72(d, 4.8); 8.54(m); 8.32(d, 7.8); 8.22-(m); 8.13(d, 5.1); 7.99(d, 9.0); 7.92(t, 7.9, 7.5); 7.82(t, 8.7, 8.4); 7.75(t, 4.5, 6.3); 7.58(t, 5.7, 6.3); 7.38(d, 8.1); 7.22(t, 5.4, 5.7); 7.14(d, 5.4). [2](ClO<sub>4</sub>)<sub>2</sub>: Yield: 46 mg (30%). Anal. Calcd (Found) for C<sub>46</sub>H<sub>32</sub>Cl<sub>4</sub>N<sub>10</sub>O<sub>10</sub>Ru<sub>2</sub>: C, 44.95(44.71); H, 2.63(2.55); N, 11.40-(11.17). Molar conductivity: [ $\Lambda_M$  ( $\Omega^{-1}$  cm<sup>2</sup> M<sup>-1</sup>)] in acetonitrile at 298 K: 235. <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>SO,  $\delta$ (J/Hz)]: 9.79(d, 5.7); 9.71-(d, 6.0); 8.68(d, 4.8); 8.61(m); 8.21(m); 8.03(m); 7.87(t, 7.5, 6.0); 7.80(t, 6.3, 6.9); 7.64(t, 4.5, 7.5); 7.31(t, 7.2, 7.8); 7.12(t, 7.5, 7.5); 6.89(d, 6.0); 6.57(d, 5.4).

**Acknowledgment.** Financial support received from the Department of Science and Technology (DST) and Council of Scientific and Industrial Research (CSIR), New Delhi (India), the DAAD and the DFG (Germany) is gratefully acknowledged. Special acknowledgment is made to the Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology, Bombay, for providing the NMR facility.

IC060887L