Dreyfus Foundation, Inc., which he gratefully acknowledges. J.C.H. thanks the Marshall H. Wrubel Computing Center for a generous gift of computing time.

Supplementary Material Available: Listings of final positional and thermal parameters, bond distances and angles, and NMR data for the compounds shown in Scheme II (7 pages); structure factor table for **2** (4 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Charge Distribution of Bis(4-*tert*-butylpyridine)bis(3,5-di-*tert*-butylquinone)ruthenium

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Metal–ligand electron transfer occurs as a fundamental step in redox processes of complexed metal ions, but only in rare cases has it been studied directly. Intramolecular charge separation induced photochemically contributes to the activity of photocatalysts where oxidative and reductive centers result from transfer of charge between localized metal and ligand electronic levels. Ruthenium bipyridine and diimine complexes have been of particular interest in this context[5] and recent studies on *o*-quinone complexes indicate even more facile electron-transfer properties.[6] Quinone ligands[7] chelated to metal ions as either semiquinone or catecholate form complexes with quinone π^* electronic levels and metal d-orbitals close in energy yet discrete in the molecular orbital structure of the complex.[8] This has permitted studies on parameters which direct charge distribution within the metal–quinone chelate ring.[9]

Air oxidation of $Ru(bpy)_2(DBCat)$ yields the $Ru^{II}(bpy)_2(DBSq)^+$ cation with oxidation occuring at the catecholate ligand.[10] This charge distribution has been determined from the structural features of the cation[11] and from electronic spectroscopic considerations.[10] Complexes containing two quinone ligands bonded to ruthenium were prepared by treating $Ru_2(OAc)_4Cl$ with DBCat. Addition of excess 4-*tert*-butylpyridine gave $Ru(t\text{-}Bupy)_2(DBQ)_2$.[12] The results of a crystallographic molecular structure determination on the complex show the quinone ligands are bonded strongly to the metal in the trans structure of the molecule (Figure 1).[13] Ruthenium–oxygen bond lengths in this structure are 0.05 Å shorter than values found[11] for $Ru(bpy)_2(DBSq)^+$ but are 0.02 Å longer than the 1.974 (4) Å length reported for *trans*-dichlorobis(triazene 1-oxidato)ruthenium(IV).[14] Quinone C–O lengths of the structure are intermediate between values expected for a semiquinone ligand, 1.29 Å, and a catecholate, 1.34 Å. The equivalence of the two quinone ligands and the absence of anisotropy in the oxygen thermal ellipsoids provide evidence that the two quinone ligands are of the same charge, i.e., $(DBCat)^2$ or $(DBSq)_2$, and not of mixed charge, (DBCat)(DBSq). Moreover, such mixed valence systems commonly show very broad, relatively weak, near-infrared absorptions,[6a,15] not evident here.

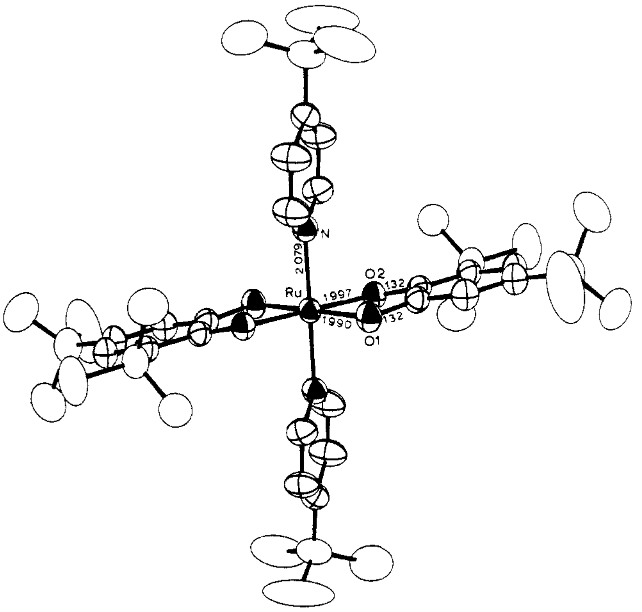

Figure 1. ORTEP plot of the centrosymmetric $Ru(t\text{-}Bupy)_2(DBQ)_2$ molecule. Standard deviations on Ru–O and Ru–N bond lengths are 0.003 and 0.005 Å on C–O lengths.

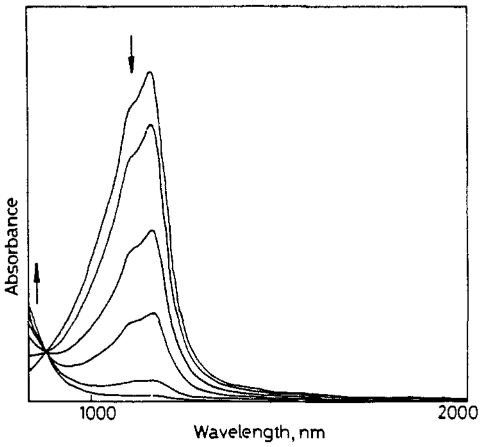

Figure 2. Near-infrared spectrum of $Ru(t\text{-}Bupy)_2(DBQ)_2$ showing absorptions in the 1100-nm region and disappearance of these absorptions upon coulometric oxidation of the complex.

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(5) (a) Sutin, N. *J. Photochem.* **1979**, *10*, 19–40. (b) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391–4393. (c) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275–282. (d) Meyer, T. *Prog. Inorg. Chem.* **1983**, *30*, 389–440. (e) Hager, M-A.; Dodsworth, E. S.; Eryavec, G.; Seymour, P.; Lever, A. B. P. *Inorg. Chem.* **1985**, *24*, 1901–1906.

(6) (a) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951–4957. (b) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041–2049.

(7) The abbreviations DBCat and DBSq are used to refer to the catecholate and semiquinone forms of 3,5-di-*tert*-butyl-1,2-benzoquinone. The term quinone is used as a general reference to the ligand without specification of charge.

(8) (a) Gordon, D. J.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2907–2915. (b) Buchanan, R. M.; Claflin, J.; Pierpont, C. G. *Inorg. Chem.* **1983**, *22*, 2552–2556.

(9) (a) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45–87. (b) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1981**, *103*, 3961–3963.

(10) Haga, M-A.; Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1985**, *24*, 447–453.

(11) Boone, S. R.; Pierpont, C. G.; manuscript in preparation.

(12) Liu, W.; Nevin, W. A.; Haga, M.-A.; Dodsworth, E. S.; Melnik, M.; Lever, A. B. P. to be submitted to *Inorg. Chem.*

(13) Triclinic, $P\bar{1}$, $a = 9.072$ (2) Å, $b = 11.068$ (2) Å, $c = 11.554$ (2) Å, $\alpha = 90.25$ (2)°, $\beta = 99.51$ (2)°, $\gamma = 95.96$ (2)°, $V = 1137.7$ (3) Å^3 at 297 K, $D_{calcd} = 1.185$ g cm^{-3}, $D_{exptl} = 1.17$ (2) g cm^{-3}, $Z = 1$, $R = 0.048$, $R_w = 0.059$ for 3918 observed reflections ($F > 6\sigma(F)$).

(14) Bhattacharya, S.; Chakravorty, A.; Cotton, F. A.; Mukherjee, R.; Schwotzer, W. *Inorg. Chem.* **1984**, *23*, 1709–1713.

(15) Lynch, M. W.; Valentine, M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1982**, *104*, 6982–6989.

0002-7863/86/1508-7413$01.50/0

Ru(t-Bupy)$_2$(DBQ)$_2$ is diamagnetic and has a proton NMR spectrum consistent with the trans structure.[16] Cyclic voltammetry, in 1,2-dichloroethane (100 mV/s), shows four couples at +0.62, −0.19, −1.12, and −2.00 (vs. Fc$^+$/Fc), the most negative being irreversible. Assignments will be discussed elsewhere.[12]

The optical absorption spectrum consists of bands at 280 nm (13 000 M^{-1} cm^{-1}), 325 (4060), 400 (3780), and 580 (1100) in the UV and visible regions. The most interesting feature is a remarkably intense, structured band centered at 1160 nm (35 300) in the near-IR (Figure 2). It is surely significant that the species Ru^{II}(bpy)$_2$(DBSq)$^+$ and Ru^{II}py$_4$(DBSq)$^+$ show similar, structured, intense bands at comparable energies[10] and assigned as Ru(II) → DBSq metal to ligand charge-transfer (MLCT) transitions.[17]

The photoelectron spectrum[18] shows a ruthenium 3d$_{3/2}$ signal at a bonding energy of 280.8 eV, being the same as that found for [Ru^{II}(bpy)$_2$(DBSq)]PF$_6$.[10]

There are two limiting electronic structures for the title species, Ru^{II}(t-Bupy)$_2$(DBSq)$_2$ and Ru^{IV}(t-Bupy)$_2$(DBCat)$_2$. We favor the ruthenium(II) formulation as the dominant (but not exclusive) contribution to the structure for the following reasons: (a) the near-IR absorption appears to be a MLCT feature, and its presence therefore favors Ru(II); (b) the PES bonding energy is appropriate for Ru(II), rather than Ru(III) (ca. 281.5–282 eV)[19a] or Ru(IV) (ca. 282 eV).[19b,20]

In its Ru(II) form, this would be the first structurally characterized example of a complex in which two equivalent semiquinone ligands lie in the same plane. The diamagnetism observed in this case must result from strong ligand–ligand coupling through the ruthenium center.

The species Ru^{II}(bpy)$_2$(DBSq)$^+$ has a structure[10,11] distorted toward the electronic isomer Ru^{III}(bpy)$_2$(DBCat)$^+$. We have previously proposed[10] that the existence of the low-lying, near-infrared MLCT state is responsible, through mixing into the ground state, for this distortion. The relatively long C–O bonds observed in the title compound probably reflect similar mixing and indicate that the complex has Ru(IV) character. Note that the analogous complex Mn^{IV}(py)$_2$(DBCat)$_2$ has C–O bond lengths (1.35 Å) significantly longer than observed here, but that this manganese(IV) complex electronically isomerized to Mn^{II}(py)$_2$(DBSq)$_2$ when cooled below about 250 K.[6b] The title ruthenium(II) complex does not show similar temperature dependence.

In summary, the title compound, as a consequence of intramolecular electron transfer, shows properties of being both a Ru(II) and a Ru(IV) species, but with the former dominant.

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Supplementary Material Available: Table of atomic positional and thermal parameters for Ru(t-Bupy)$_2$(DBQ)$_2$ (1 page); table of observed and calculated structure factors for Ru(t-Bupy)$_2$(DBQ)$_2$ (17 pages). Ordering information is given on any current masthead page.

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(16) ^{1}H NMR (CDCl$_3$) δ 1.03 (s, 18 H), 1.42 (s, 18 H), 1.64 (s, 18 H), 5.85 (d, 2 H, ^4J = 5 Hz), 6.43 (2 d, 4 H, ^3J = 13, ^5J = 3 Hz), 7.07 (2 d, 4 H, ^3J = 13, ^5J = Hz), 7.73 (d, 2 H, ^4J = 5 Hz).

(17) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd Ed.; Elsevier Science Publishers: Amsterdam, The Netherlands, 1984.

(18) Photoelectron spectra were obtained courtesy of the "Surface Science Western" laboratory at the University of Western Ontario.

(19) (a) Battistoni, G.; Furlani, G.; Mattogno, G.; Tom, G.; *Inorg. Chim. Acta* **1977**, *21*, L25–L26. (b) Geselowitz, D. A.; Kutner, W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2015–2023. (c) Folkesson, B. *Acta Chem. Scand.* **1973**, *27*, 287–302.

(20) A bis(catecholato)ruthenium(IV) electronic isomer might have a binding energy depressed by the electron-donating catechol from the Ru(IV) into the Ru(II) binding energy region. Based on previous experience[21] it is very unlikely that such a dramatic shift would be observed; however, the possibility is being investigated.

(21) Bancroft, G. M.; Chan, T.; Puddephatt, R. J.; Brown, M. P. *Inorg. Chim. Acta* **1981**, *53*, L119–L120.

Chiral Probe for A-Form Helices of DNA and RNA: Tris(tetramethylphenanthroline)ruthenium(II)

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There has been considerable interest in exploring local variations in the structure of DNA along the strand and in developing small molecular probes which, like DNA-binding proteins, may be targeted to particular sites or sequences.[1] We have focused on the use of chiral metal complexes in designing spectroscopic probes and photoactivated DNA cleaving agents for DNA.[2] In particular, a chiral tris(diphenylphenanthroline)cobalt(III) complex has been useful in targetting specific sites in a left-handed conformation in supercoiled plasmids and viral DNA.[3] We report here the design of a probe that is specific for the A conformation.[4] Tris(3,4,7,8-tetramethylphenanthroline)ruthenium(II), Ru(TMP)$_3^{2+}$, binds preferentially to A-form helices, displays enantiomeric discrimination in its binding, and upon irradiation with visible light cleaves A-form helices preferentially.

Figure 1 shows the result of an equilibrium dialysis experiment[5] using racemic Ru(TMP)$_3^{2+}$ and dialysis of poly(rI)·poly(rC) and poly(rG)·poly(dC), two A-form polymers, or poly[d(GC)] and calf thymus DNA, ostensibly in the B form, against the ruthenium complex.[6,7] As is evident in the plot of the ratio of bound metal per nucleotide (r_b) vs. the formal added ratio (r_f) of metal per nucleotide, the highest degree of binding is found with the double-stranded RNA. DNA–RNA hybrids show also cooperative binding by the ruthenium complex. In comparison, no binding to poly[d(GC)] is detectable and for a native, heterogeneous calf thymus DNA, at most a small level of binding is observed. Hence Ru(TMP)$_3^{2+}$ is seen to bind cooperatively to the A-form polymer under conditions where little binding to B DNA is detected.

Besides electrostatic considerations, the binding of the complex to the polynucleotide may involve hydrophobic interactions of ligands bound against the shallow groove of the A helix. We earlier found that Ru(phen)$_3^{2+}$ binds to B DNA via two modes, one intercalative, one surface bound.[7] Intercalative binding through the major groove was characterized by an increase in luminescence lifetime of the complex and the preferential binding to the right-handed helix of the Δ-isomer. The hydrophobic surface-bound mode showed no enhancement in luminescence and a small preference in binding of the Λ-isomer. It occurred to us

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(1) (a) Barton, J. K. *Science (Washington, D.C.)* **1986**, *233*, 727. (b) Dervan, P. B. *Science (Washington, D.C.)* **1986**, *232*, 464. (c) Spassky, A.; Sigman, D. S. *Biochemistry* **1985**, *24*, 8050. (d) Lilley, D. M. J.; Gough, G. W.; Hallem, L. R.; Sullivan, K. M. *Biochimie* **1985**, *67*, 697.

(2) (a) Barton, J. K.; Danishefsky, A. T.; Goldberg, J. M. *J. Am. Chem. Soc.* **1984**, *67*, 2172. (b) Barton, J. K.; Basile, L. A.; Danishefsky, A. T.; Alexandrescu, A. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 1961. (c) Kumar, C. V.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5518. (d) Barton, J. K.; Raphael, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 2466.

(3) (a) Barton, J. K.; Raphael, A. L. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6460. (b) Muller, B. M.; Raphael, A. L.; Barton, J. K., submitted for publication.

(4) DNA–RNA hybrids, double-stranded RNA, and perhaps as well local DNA sequences adopt various right-handed A-helical conformations. See, for example: (a) Chamberlin, M. J.; Patterson, D. L. *J. Mol. Biol.* **1965**, *12*, 410. (b) O'Brien, E. J.; MacEwan, A. W. *J. Mol. Biol.* **1970**, *48*, 243. (c) Arnott, S.; Hukins, D. W. L.; Dover, S. D. *Biochem. Biophys. Res. Commun.* **1972**, *48*, 1392. (d) Fuller, W.; Wilkins, M. H. F.; Hamilton, H. R.; Arnott, S. *J. Mol. Biol.* **1965**, *12*, 60. (e) Shakked, Z.; Rabinovich, D.; Cruse, W. B. T.; Egert, E.; Kennard, O.; Sala, G.; Salisbury, S. A.; Viswamitra, M. A. *Proc. R. Soc. London, B* **1981**, *231*, 479. (f) Conner, B. N.; Takano, T.; Tanaka, S.; Itakura, K.; Dickerson, R. E. *Nature (London)* **1982**, *295*, 294.

(5) Dialyses in 5 mM Tris, pH 7.3, and 50 mM NaCl were performed at 25 °C for at least 48 h to achieve equilibration. Each sample consisted of 3.2 mL of dialysate containing *rac*-Ru(TMP)$_3^{2+}$ (42–250 μM) and, inside, 1 mL of 1 mM nucleotides. Free ruthenium concentrations were determined spectrophotometrically ($\epsilon_{438} = 2.45 \times 10^4$ M cm^{-1}).[6] Bound concentrations in the presence of nucleic acid were determined spectrophotometrically after dilution into buffer or ethanol ($\epsilon_{438} = 2.60 \times 10^4$ M^{-1} cm^{-1} in 75% ethanol).

(6) [Ru(TMP)$_3$]Cl$_2$ was synthesized as described by: Lin, C. T.; Bottcher, W.; Creutz, C.; Sutin, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 6536.

(7) Barton, J. K.; Goldberg, J. M.; Kumar, C. V.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 2081.

0002-7863/86/1508-7414$01.50/0