

AD-A172 653

OFFICE OF NAVAL RESEARCH

Contract N00014-84-G-0201

Task No. 0051-865

Technical Report #8

DTIC
SELECTED
OCT 07 1988
S D

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

By

Masa-aki Haga, Elaine S. Dodsworth, A.B.P. Lever
Steven R. Boone, and Cortlandt G. Pierpont

in the

Journal of the American Chemical Society

York University
Department of Chemistry, 4700 Keele St., North York
Ontario, Canada M3J 1P3

DTIC FILE COPY

Reproduction in whole, or in part, is permitted for any purpose of the
United States Government

*This document has been approved for public release and sale; its
distribution is unlimited

*This statement should also appear in Item 10 of the Document Control
Data-DD form 1473. Copies of the form available from cognizant contract
administrator

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER #8	2. GOVT ACCESSION NO. AD-A172 653	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Synthesis, Characterization, and Charge Distribution of Bis(4-t-butylpyridine)bis(3,5-di-t-butylquinone)ruthenium		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Masa-aki Haga, Elaine S. Dodsworth, A.B.P. Lever Steven R. Boone, and Cortlandt G. Pierpont		8. CONTRACT OR GRANT NUMBER(s) N00014-84-G-0201
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, York University, 4700 Keele St., North York, Ontario M3J 1P3		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Arlington, VA 22217		12. REPORT DATE July, 1986
		13. NUMBER OF PAGES 14
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for publication in the Journal of the American Chemical Society		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) X-Ray, Ruthenium, Quinone, Semi-Quinone, Electrochemistry		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The synthesis and characterization of bis(4-t-butyl-pyridine)bis(3,5-di-t-butylquinone)ruthenium is reported. A crystallographic molecular structure determination carried out on the complex has shown that it exists as the <u>trans</u> isomer and that ligand C-O lengths are relatively long for a semi-quinone complex being at the bottom end of the range observed for catecholate complexes. Both quinone ligands appear structurally and electronically equivalent. The complex is diamagnetic and shows a well-resolved spectrum. Electrochemically, the complex undergoes four redox processes, all of which		

20. Abstract cont'd

most likely involve both metal and quinone ligands. There are charge-transfer bands in the visible region, and an exceptionally intense and structured band in the near infrared region. The ground state is viewed as a mixture of bis(4-t-butylpyridine)bis(3,5-di-t-butylsemiquinone)ruthenium(II) and bis(4-t-butylpyridine)bis(3,5-di-t-butylcatecholato)ruthenium(IV), with the former dominant.



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

**Masa-aki Haga,^{1,3} Elaine S. Dodsworth,^{2,3} A. B. P. Lever,^{3*}
Steven R. Boone,⁴ and Cortlandt G. Pierpont^{4*}**

**Contribution from the
Department of Chemistry
York University
North York, Ontario
Canada M3J 1P3**

**and the
Department of Chemistry and Biochemistry
University of Colorado
Boulder, Colorado 80309**



Accession For		
NTIS	CRA&I	<input checked="" type="checkbox"/>
DTIC	TAB	<input type="checkbox"/>
Unannounced		<input type="checkbox"/>
Justification		
By		
Distribution/		
Availability Codes		
Dist	Avail and/or Special	
A-1		

Abstract

The synthesis and characterization of bis(4-*t*-butylpyridine)bis(3,5-di-*t*-butylquinone)ruthenium is reported. A crystallographic molecular structure determination carried out on the complex has shown that it exists as the trans isomer and that ligand C-O lengths are relatively long for a semiquinone complex being at the bottom end of the range observed for catecholato complexes. Both quinone ligands appear structurally and electronically equivalent. The complex is diamagnetic and shows a well-resolved NMR spectrum. Electrochemically, the complex undergoes four redox processes, all of which most likely involve both metal and quinone ligands. There are charge-transfer bands in the visible region, and an exceptionally intense and structured band in the near infrared region. The ground state is viewed as a mixture of bis(4-*t*-butylpyridine)bis(3,5-di-*t*-butylsemiquinone)ruthenium(II) and bis(4-*t*-butylpyridine)bis(3,5-di-*t*-butylcatecholato)ruthenium(IV), with the former dominant.

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 context⁵ and recent studies on o-quinone complexes indicate even more facile electron transfer properties.⁶ Quinone ligands⁷ 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 $\text{Ru}(\text{bpy})_2(\text{DBCat})$ yields the $\text{Ru}^{II}(\text{bpy})_2(\text{DBSq})^+$ cation with oxidation occurring at the catecholate ligand.¹⁰ This charge distribution has been determined from the structural features of the cation¹¹ and from electronic spectroscopic considerations.¹⁰ Complexes containing two quinone ligands bonded to ruthenium were prepared by treating $\text{Ru}_2(\text{OAc})_4\text{Cl}$ with DBCat. Addition of excess 4-t-butylpyridine gave $\text{Ru}(\text{t-Bupy})_2(\text{DBQ})_2$.¹² The results of a crystallographic molecular structure determination on the complex show that 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 0.05A shorter than values found¹¹ for $\text{Ru}(\text{bpy})_2(\text{DBSq})^+$ but are 0.02A longer than the 1.974(4)A 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, 1.29Å, and a catecholate, 1.34Å. The equivalence of the two quinone ligands, and the absence of anisotropy in the oxygen thermal ellipsoids provides 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 absorption,^{6a,15} not evident here. 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⁻¹cm⁻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}py₄(DBSq)⁺ show similar, structured, intense bands at comparable energies¹⁰ and assigned as Ru(II)→DBSq metal to ligand charge transfer (MLCT) transitions.¹⁷

The photoelectron spectrum¹⁸ 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)]PF₆.¹⁰

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 semi-quinone 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 $\text{Ru}^{2+}(\text{bpy})_2(\text{DBSq})^+$ has a structure^{10,11} distorted towards the electronic isomer $\text{Ru}^{2+}(\text{bpy})_2(\text{DBCat})^+$. We have previously proposed¹⁰ 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 $\text{Mn}^{2+}(\text{py})_2(\text{DBCat})_2$ has C-O bond lengths (1.35Å) significantly longer than observed here, but that this manganese(IV) complex electronically isomerized to $\text{Mn}^{2+}(\text{py})_2(\text{DBSq})_2$ 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.

Acknowledgment. Research at York University was supported by the Natural Science and Engineering Research Council (Ottawa) and the Office of Naval Research (Washington). Research at the University of Colorado was supported by the National Science Foundation under grants CHE 85-03222 and CHE 84-12182 (X-ray instrumentation).

Supplementary Material Available. Tables of atomic positional and thermal parameters and observed and calculated structure factors for bis(4-t-butylpyridine)bis(3,5-di-t-butylquinone)ruthenium (18 pages). Ordering information is given on any current masthead page.

References and Notes

1. Current address: Department of Chemistry, Mie University, 1515 Kamihama, Tsu 514, Mie, Japan.
2. Current address: Department of Chemistry, University College, Singleton Park, Great Britain SA2 8PP.
3. York University
4. University of Colorado
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) Haga, 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-t-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, P1, a = 9.072(2)Å, b = 11.068(2)Å, c = 11.554(2)Å,
 $\alpha = 90.25(2)^\circ$, $\beta = 99.51(2)^\circ$, $\gamma = 95.96(2)^\circ$,
 $V = 1137.7(3)\text{Å}^3$ at 297°K, $D_{\text{calc}} = 1.185 \text{ g cm}^{-3}$,
 $D_{\text{expt}} = 1.17(2) \text{ g cm}^{-3}$, $Z = 1$, $R = 0.048$, $R_w = 0.059$
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.
16. ^1H NMR (CDCl_3) δ 1.03(s, 18H), 1.42(s, 18H), 1.64(s, 18H),
5.85(d, 2H, $^4\text{J} = 5 \text{ Hz}$), 6.43(2d, 4H, $^3\text{J} = 13$ and $^5\text{J} = 3 \text{ Hz}$),
7.07(2d, 4H, $^3\text{J} = 13$ and $^5\text{J} = 3 \text{ Hz}$), and 7.73(d, 2H, $^4\text{J} = 5 \text{ Hz}$).
17. Lever, A. B. P., "Inorganic Electronic Spectroscopy", 1984,
2nd Ed., Elsevier Science Publishers, Amsterdam, The
Netherlands.
18. Photoelectron spectra were obtained courtesy of the "Surface
Science Western" laboratory at the University of Western
Ontario.
19. a) Battistoni, G.; Furlani, G.; Mattocono, G.; Tom, G.;

Inorg. Chim. Acta 1977, 21,

L25-L26.

b) Gesselowitz, 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 experience²¹ 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.

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

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



