Verdazyl radicals as redox-active, non-innocent, ligands. Contrasting electronic structures as a function of electron-poor and electron-rich ruthenium bis(β-diketonate) co-ligands

Stephen D.J. McKinnon, Brian O. Patrick, A. B. P. Lever, and Robin G. Hicks

Supporting Information

General Experimental

Solvents, reagents…EPR, UV-vis, IR, CV. Pyvd and Ru(LL)$_2$(MeCN)$_2$ were made according to literature methods.

All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques unless stated otherwise. Solvents were dried and distilled under argon prior to use. All reagents were purchased from Aldrich and used as received. Verdazyl **1a**[1] and Ru(LL)$_2$(MeCN)$_2$ (LL = acac[2], hfac[3]) were prepared via literature methods. Infrared spectra were recorded as KBr pellets using a Perkin Elmer Spectrum One instrument. UV-Vis spectra were recorded using a Cary 50 Scan instrument. EPR spectra were recorded on a Bruker EMX EPR instrument equipped with an X-band microwave bridge. Cyclic voltammetry experiments were performed with a Bioanalytical Systems CV50 voltammetric analyzer. Typical electrochemical cells consisted of a three-electrode setup including a glassy carbon working electrode, platinum counter electrode, and silver reference. Experiments were run at a scan rate of 100 mV/s. Acetonitrile solutions of analyte (~1 mM) and electrolyte (0.1 M $Bu_4N^+BF_4^-$) were referenced against an internal standard (~1 mM Fc). Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, BC.

[1] (a) J. B. Gilroy, B. D. Koivisto, R. McDonald, M. J. Ferguson, and R. G. Hicks, *J. Mater. Chem.* 2006, **16**, 2618.(b) E. C. Pare, D. J. R. Brook, A. Brieger, M. Badik, and M. Schinke, *Org. Biomol. Chem.* 2005, **3**, 4258.
[2] T. Kobayashi, Y. Nishina, K. Shimizu and G. P. Satô , *Chem. Lett.*, **1988**, *17*, 1137-1140.
[3] I. R. Baird, S. J. Rettig, B. R. James, and K. A. Skov, *Can. J. Chem.* **1999,** *77*, 1821–1833

X-ray crystallography: All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. Data were collected and integrated using the Bruker SAINT[1] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 6.44 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS)[2].

1H: The structures were solved by direct methods[3]. The material crystallizes with two independent molecules in the asymmetric unit. While the assigned space group is *Pna*2$_1$, there appears to be a local pseudo-inversion center between the two independent molecules found at x = 1/8, y = 0. All non-hydrogen atoms were refined anisotropically. Some pairs of atoms, specifically some of those related by the pseudo-inversion center, were refined with equivalent anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement[4] on F^2 was based on 12183 reflections and 540 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.142$$

$$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2)/ \Sigma w(Fo^2)^2]^{1/2} = 0.180$$

The standard deviation of an observation of unit weight[5] was 0.98. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.63 and –0.61 $e^-/Å^3$, respectively.

2F: The structure was solved by direct methods[3]. The material crystallizes with two independent molecules in the asymmetric unit. One molecule, containing Ru11, has a number of disordered fragments. First, the position of the Ru atom is disordered in two positions. This disorder influences the orientation of the verdazyl ligand, leading to disorder. Finally, three of its four CF_3 groups have disordered fluorine atoms, each was modeled in two orientations. All non-hydrogen atoms except C41, C41B, C65, C65B and N22B were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement[4] on F^2 was based on 13302 reflections and 1009 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.073$$

$$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2)/ \Sigma w(Fo^2)^2]^{1/2} = 0.123$$

The standard deviation of an observation of unit weight[5] was 1.10. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.68 and –0.71 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[6]. Anomalous dispersion effects were included in Fcalc[7]; the values for Δf' and Δf" were those of Creagh and McAuley[8]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[9]. All refinements were performed using the SHELXTL[10] crystallographic software package of Bruker-AXS.

References

(1) SAINT. Version 7.03A. Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2003).
(2) SADABS. Bruker Nonius area detector scaling and absorption correction - V2.10, Bruker AXS Inc., Madison, Wisconsin, USA (2003).
(3) SIR97 - Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C. , Guagliardi A., Moliterni A.G.G., Polidori G.,Spagna R. (1999) J. Appl. Cryst. 32, 115-119.
(4) Least Squares function minimized:

$$\Sigma w(F_o^2-F_c^2)^2$$

(5) Standard deviation of an observation of unit weight:

$[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$

where: N_O = number of observations; N_V = number of variables

(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).
(8) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
(9) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
(10) SHELXTL Version 5.1. Bruker AXS Inc., Madision, Wisconsin, USA. (1997).

[1,5-diisopropyl-3-(2-pyridyl)-6-oxoverdazyl]bis(acetylacetonato)ruthenium (2H). $Ru(acac)_2(CH_3CN)_2$ (0.353 g, 0.927 mmol) and **1**(0.254 g, 0.977 mmol) were combined in ethanol (25 mL). The mixture was sparged with Ar for 30 min before being refluxed for approximately 1 hr., during which time the solution turned from a red-brown to a dark green. Once the reaction was complete by TLC, it was allowed to cool to room temperature and the solvent was removed *in vacuo*. Chromatography of the dark green solid (neutral alumina, ethyl acetate) gave 465 mg (89.8 %) of **2H**. Crystals suitable for X-ray crystallography were grown from a mixture of CH_3CN/water. FT-IR (KBr), cm^{-1}: 3065 (vw), 2969 (w), 2927 (w), 1664 (s), 1568 (m), 1515 (s), 1386 (m), 1292 (w), 1268 (w), 1212 (w), 1056 (w), 1026 (w), 935 (w), 776 (w), 638 (w). UV/Vis (CH_2Cl_2), λ_{max} nm(ε, , $M^{-1}cm^{-1}$): 366(7000), 692(3900), 884(4400). Anal. Calcd. for $C_{23}H_{32}N_5O_5Ru$: C, 49.36; H, 5.76; N, 12.51. Found: C, 50.35; H, 5.99; N, 12.45. EPR: g = 2.0390

[1,5-diisopropyl-3-(2-pyridyl)-6-oxoverdazyl] bis(hexafluoroacetylacetonato)ruthenium (2F). To a solution of $Ru(hfac)_2(CH_3CN)_2$ (0.242 g, 0.405 mmol) in toluene (2 ml) was added **1**(0.104 g, 0.400 mmol). The reaction mixture was refluxed for 1 hr., during which time the solution turned from a red-brown to an intense green. After cooling to room temperature, the solvent was removed *in vacuo*, yielding a deep green solid. Chromatography of the solid (neutral alumina, CH_2Cl_2) gave 204 mg (65.8 %) of **2F**. Crystals suitable for X-ray crystallography were grown by slow evaporation of a hexanes solution. FT-IR (KBr), cm^{-1}: 2983 (w), 2938 (w), 1675 (m), 1546 (w), 1468 (m), 1338 (w), 1262 (m), 1197 (m), 1150 (s), 1095 (w), 1055 (w), 943 (w), 798 (w), 692 (w), 599 (w). UV/Vis (CH_2Cl_2), l_{max} nm(e, , $M^{-1}cm^{-1}$): 340(4200), 448(9900), 594(5200), 718(4600). Anal. Calcd. for $C_{23}H_{20}F_{12}N_5O_5Ru$: C, 35.62; H, 2.60; N, 9.03. Found: C, 36.08; H, 2.75; N, 8.98. EPR (CH_2Cl_2): g = 2.009, $a(^{15}N)$ = 6.5, 4.5, 4.4, 4.9G; $a(^{1}H)$ = 1.2, 0.8G; $a(^{99/101}Ru)$ = 8.0G.

Computational Details

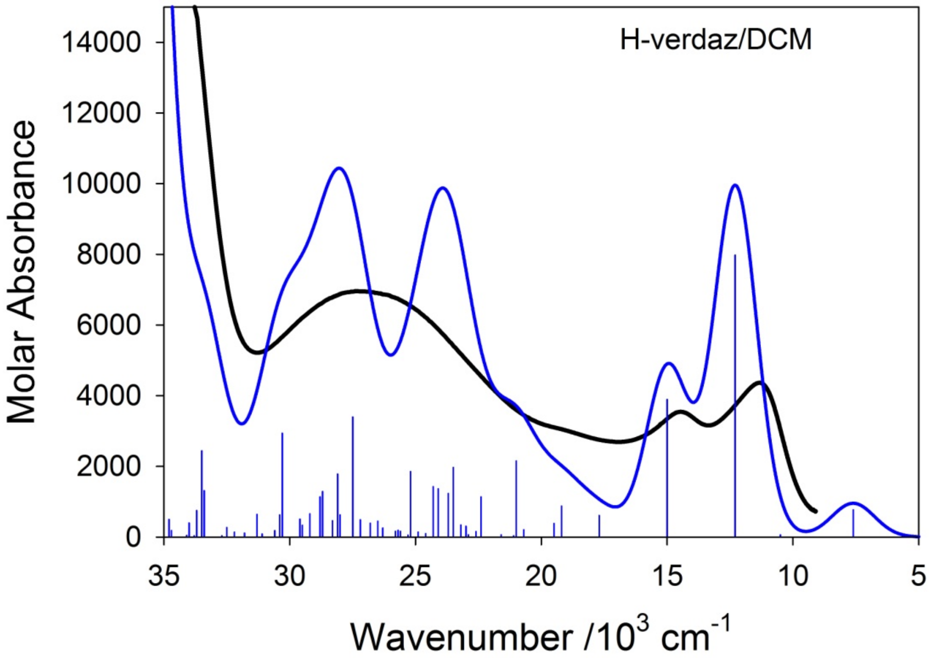
Density functional theory (DFT) calculations utilized the *Gaussian 03* (Revision C.01) program .[1] Optimized geometries were calculated using the B3LYP exchange-correlation functional[2] with the LANL2DZ basis set[3-6] or all elements. Tight SCF convergence criteria (10^{-8} a.u.) were used for all calculations. Vibrational frequency calculations were performed to ensure that the stationary points were minima. Wavefunctions were checked for stability.

Molecular orbital (MO) compositions and the overlap populations between molecular fragments were calculated using the *AOMix* program[7,8] using the Mulliken scheme.[9-12] Atomic charges were calculated using the Mulliken[9-12] and natural population analysis[13] methods (MPA and NPA, respectively) as implemented in *Gaussian 03.* The analysis of the MO compositions, and the charge decomposition analysis was performed using *AOMix-CDA.*(14) The PCM model[15,16] was used to model solvation assuming dichloromethane as solvent. Time dependent DFT[17-20] was used to predict the optical spectra and the output files were analyzed using the SWIZARD program of Gorelsky.[21]

Reference List

1. R.C.0. Gaussian 03. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004. (2004).
2. C. Lee, W. Yang, and R.G. Parr. Phys. Rev. 1988, B **37,** 785.
3. Jr.T.H. Dunning and P.J. Hay. Modern Theoretical Chemistry. Vol. 3. I.Ed. H.F. Schaefer. Plenum, New York. 1976. p. 1.
4. P.J. Hay and W.R. Wadt. J. Chem. Phys. 1985, **82** , 270.
5. P.J. Hay and W.R. Wadt. J. Chem.Phys. 1985, **82**, 299.
6. P.J. Hay and W.R. Wadt. J. Chem.Phys. 1985, **82**, 284.
7. S.I. Gorelsky and A.B.P. Lever. J. Organomet. Chem. 2001, **635**, 187.
8. S.I. Gorelsky. AOMix-CDA Program, Http://Www.Sg-Chem.Net/ (2005).
9. R.S. Mulliken, J. Chem. Phys. 1955, **23**, 2338.
10. R.S. Mulliken,J. Chem. Phys. 1955, **23**, 1833.
11. R.S. Mulliken, J. Chem. Phys. 1955, **23**, 2343.
12. R.S. Mulliken, J. Chem. Phys. 1955, **23**, 1841.
13. A.E. Reed, L.A. Curtiss, and F. Weinhold. Chem. Rev. 1988, **88**, 899.
14. S.I. Gorelsky, S. Ghosh, and E.I. Solomon. J. Am. Chem. Soc. 2006, **128**, 278.
15. L. Noodleman, T. Lovell, W.G. Han , T. Liu, and R.A. Torres. Comprehen. Coord.Chem. II. Elsevier, Oxford. 2004. pp. 491-510.
16. F.M. Bickelhaupt and E.J. Baerends. Reviews in Computational Chemistry. Vol. 15. K.B. Lipkowitz and D.R.E. Boyd. Wiley, New York. 2000. pp. 1-86.
17. R.E. Stratmann , G.E. Scuseria, and M.J. Frisch. J. Chem. Phys. 1998, **109**, 8218.
18. R. Bauernschmitt and R. Ahlrichs. Chem. Phys. Lett. 1996, **256**, 454.
19. M.E. Casida, C. Jamorski, K.C. Casida, and D.R. Salahub. J. Chem. Phys. **108**, 4439 (1998).
20. F. Neese. Coord. Chem. Rev. 2009, **253**, 526.
21. S.I. Gorelsky. SWIZARD [Web Page], 2008. Available at http://www.sg-chem.net/ CCRI, University of Ottawa, Ottawa, Canada, 2008.

Fig S1. Comparison of Experimental spectrum of **2H** in dichloromethane (black) with TD-DFT predicted spectrum (blue) assuming the PCM and dichloromethane solvent.


H-verdaz/DCM
Molar Absorbance
0
2000
4000
6000
8000
10000
12000
14000
35
30
25
20
15
10
5
Wavenumber /10^3 cm^{-1}