

First Structurally Characterised Mono- and Dinuclear Ruthenium Complexes Derived from Zwitterionic Quinonoid Ligands†‡

Hari Sankar Das,^a Atanu Kumar Das,^a Roberto Pattacini,^b Ralph Hübner,^a Biprajit Sarkar^{a,*} and Pierre Braunstein^{b,*}

^aInstitut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550, Stuttgart, Germany. Fax: (+)4971168564165; Tel: (+)4971168564235; E-mail: sarkar@iac.uni-stuttgart.de

^bLaboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal, F-67070, Strasbourg Cédex, France. Fax: (+)33390241322; Tel: (+)33390241308; E-mail: braunstein@chimie.u-strasbg.fr

Experimental Section

Materials and physical methods

cis-Ru(bpy)₂Cl₂ was obtained from ABCR and AgClO₄ from STREM. The quinonoid ligand **L** was synthesised according to the published procedure^[S-1] from 4,6-Diaminoresorcinol dihydrochloride which was obtained from Acros. All the reagents were used as supplied. The solvents used for metal complex synthesis were dried and distilled by standard techniques.

The ¹H NMR spectra were recorded on a Bruker AC 250 spectrometer. Electronic absorption studies were recorded on J&M TIDAS and Shimadzu UV 3101 PC spectrophotometers. EPR spectra in the X-band were recorded with a Bruker System EMX. Cyclic voltammetry was carried out in 0.1M Bu₄NPF₆ solutions using a three-electrode configuration (glassy-carbon working electrode, Pt counter electrode, Ag wire as pseudo reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc⁺) couple served as internal reference. Spectroelectrochemistry was performed using an optically transparent thin-layer electrode (OTTLE) cell. Elemental analyses were performed by the Perkin-Elmer Analyzer 240.

Synthesis of [Ru(bpy)₂L_H](ClO₄), **1**(ClO₄).

To solid KO^tBu (0.0135 g, 0.12 mmol) in a Schlenk flask was added **L** (0.0266 g, 0.12 mmol) and 15 ml THF under argon atmosphere resulting immediate color change from purple to orange. The reaction mixture was stirred overnight at room temperature. The solvent was then removed under reduced pressure. In an another Schlenk flask [Ru(bpy)₂Cl₂] (0.0581 g, 0.12 mmol), AgClO₄ (0.0622 g, 0.3 mmol) and 25 ml ethanol was added and refluxed for 3 h

under argon atmosphere. It was then filtered under argon to the previous deprotonated ligand residue through G4 crucible containing a celite bed. The resulting mixture was refluxed for 6 h and color changed from red to pink. It was then reduced to 7-8 ml and an excess saturated aqueous solution of NaClO₄ was added to it. The solid precipitate thus obtained was filtered off and dried in vacuum. It was then purified on an alumina (neutral) column. The pink product was eluted with CH₂Cl₂/CH₃CN (2:1). Evaporation of the solvent under reduced pressure afforded the pure complex. Yield: 0.022 g (25%). C₃₂H₃₃N₆O₆RuCl·1/2(CH₂Cl₂) (776.65): calcd. C 50.26, H 4.40, N 10.82%; found C 50.35, H 4.58, N 10.94%. ¹H NMR (250 MHz, CD₃CN) δ/ppm: 0.29 (3H, d, ³J = 6.5 Hz, CH₃-CH-NH), 0.86 (3H, d, ³J = 6.4 Hz, CH₃-CH-NH), 1.22 (3H, d, ³J = 6.4 Hz, CH₃-CH-N), 1.26 (3H, d, ³J = 6.7 Hz, CH₃-CH-N), 3.72 (1H, m, CH₃-CH-NH), 4.45 (1H, m, CH₃-CH-N), 5.46 (1H, s, N-C-CH), 5.72 (1H, s, O-C-CH), 6.13 (1H, d, br, ³J = 8.3 Hz, NH), 7.09-7.22 (2H, m, bpy), 7.27-7.34 (1H, m, bpy), 7.60-7.72 (2H, m, bpy), 7.74-7.89 (3H, m, bpy), 8.03-8.16 (2H, m, bpy), 8.31-8.42 (2H, m, bpy), 8.43-8.55 (3H, m, bpy), 8.60-8.68 (1H, m, bpy). ES-MS (m/z): 635 [M - ClO₄]⁺.

Synthesis of [{Ru(bpy)₂}]₂(μ-L_{2H})(ClO₄)₂, 2(ClO₄)₂

In an Schlenk flask [Ru(bpy)₂Cl₂] (0.068 g, 0.14 mmol), AgClO₄ (0.0725 g, 0.35 mmol) and 25 ml ethanol was added under argon atmosphere and refluxed for 3 h. It was then filtered under argon to the another Schlenk flask through G4 crucible containing a celite bed. Then L (0.0155 g 0.07 mmol) and 0.2 ml NaOMe was added to the reaction mixture and refluxed overnight under argon atmosphere resulting colour change to blue. It was then reduced to 7-8 ml and an excess saturated aqueous solution of NaClO₄ was added to it. The solid precipitate thus obtained was filtered off and dried in vacuum. It was then purified on an alumina (neutral) column. The deep blue product was eluted with CH₂Cl₂/CH₃CN (2:1). Evaporation of the solvent under reduced pressure afforded the pure complex. Yield: 0.020 g (22%). C₅₂H₄₈N₁₀O₁₀Ru₂Cl₂·(CH₂Cl₂) (1331): calcd. C 47.83, H 3.79, N 10.52%; found C 47.71, H 4.09, N 10.32%. ¹H NMR (250 MHz, CD₃CN) δ: 0.24 (6H, d, ³J = 6.4 Hz, CH₃-CH-N), 0.78 (6H, d, ³J = 6.7 Hz, CH₃-CH-N), 4.08 (2H, m, CH₃-CH-N), 5.68 (1H, s, N-C-CH), 5.72 (1H, s, O-C-CH), 7.07-7.19 (4H, m, bpy), 7.27-7.35 (2H, m, bpy), 7.55-7.72 (4H, m, bpy), 7.74-7.88 (6H, m, bpy), 8.01-8.16 (4H, m, bpy), 8.27-8.42 (6H, m, bpy), 8.43-8.53 (4H, m, bpy), 8.68-8.78 (2H, m, bpy). ES-MS (m/z): 524 [M-2ClO₄]²⁺.

Crystallographic details

X-ray data collection, structure solution and refinement for all compounds

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. The intensity data were collected on a Kappa CCD diffractometer^[S-ii] (graphite monochromated MoK α radiation, $\lambda = 0.71073 \text{ \AA}$) at 173(2) K for *meso*-**2(ClO₄)·2CH₂Cl₂** and at 100(2) K for **1(ClO₄)·CH₂Cl₂**. Crystallographic and experimental details for the structures are summarized in Table S1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2 , SHELXL-97)^[S-iii] with anisotropic thermal parameters for all the non-hydrogen atoms. For **2(ClO₄)·2CH₂Cl₂**, one of the dichloromethane molecules was found disordered in three positions with unequal occupancy factors, having the carbon atom in common. The chlorine atoms having the highest occupancy factors were refined anisotropically. In **1(ClO₄)·CH₂Cl₂** the dichloromethane molecule was found disordered in two very close positions having equal occupancy factors. The atoms were refined with restrained anisotropic parameters. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms with the exception of H1N in **1(ClO₄)·CH₂Cl₂**. CCDC 727537 & 727536 (**1(ClO₄)·CH₂Cl₂** and **2(ClO₄)·2CH₂Cl₂**, respectively) contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S-1

	2(ClO₄)·2CH₂Cl₂	1(ClO₄)·CH₂Cl₂
Chemical formula	C ₅₂ H ₄₈ N ₁₀ O ₂ Ru ₂ ·2CH ₂ Cl ₂ ·2ClO ₄	C ₃₂ H ₃₃ N ₆ O ₂ Ru·CH ₂ Cl ₂ ·ClO ₄
M_r	1415.90	819.09
Cell setting, space group	Triclinic, <i>P</i> -1	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature(K)	173(2)	100(2)
$a, b, c(\text{\AA})$	12.8148(5), 13.9252(3), 17.7605(6)	9.8944(2), 18.0252(2), 19.8545(3)
$\alpha, \beta, \gamma(^{\circ})$	68.649(2), 86.397(2), 88.834(2)	90.00, 99.260(1), 90.00
$V(\text{\AA}^3)$	2945.97(16)	3494.9(1)
Z	2	4
$D_x(\text{Mg m}^{-3})$	1.596	1.557
Radiation type	Mo $K\alpha$	Mo $K\alpha$
$\mu(\text{mm}^{-1})$	0.85	0.73
Crystal size(mm)	0.12 × 0.12 × 0.10	0.22 × 0.15 × 0.15

Absorption correction	None	None
Meas., indep. and obsvd refl.	18481, 12203, 8157	15946, 8319, 6724
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.151, 1.02	0.037, 0.127, 1.17
No. of parameters	754	479
R_{int}	0.034	0.029
$\theta_{\text{max}}(^{\circ})$	26.5	27.9
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}(\text{e } \text{\AA}^{-3})$	1.35, -0.88	1.09, -1.43

Table S-2: Comparison of selected bond lengths in **1(ClO₄).CH₂Cl₂**, **2(ClO₄).2CH₂Cl₂** and **L**.

	1(ClO₄).CH₂Cl₂	2(ClO₄).2CH₂Cl₂	L^[S-i]
C1-C2	1.385(4)	1.386(6)	1.390(4)
C2-C3	1.412(4)	1.378(6)	1.391(4)
C3-C4	1.503(4)	1.500(6)	1.526(5)
C5-C6	1.429(4)	1.408(6)	1.387(4)
C4-C5	1.376(4)	1.394(6)	1.391(4)
C6-C1	1.492(4)	1.495(6)	1.529(4)
O1-C1	1.291(3)	1.287(5)	1.253(4)
C3-O2	1.254(3)	1.286(5)	1.252(4)
N1-C6	1.314(3)	1.336(6)	1.316(4)
N2-C4	1.348(4)	1.337(6)	1.316(4)

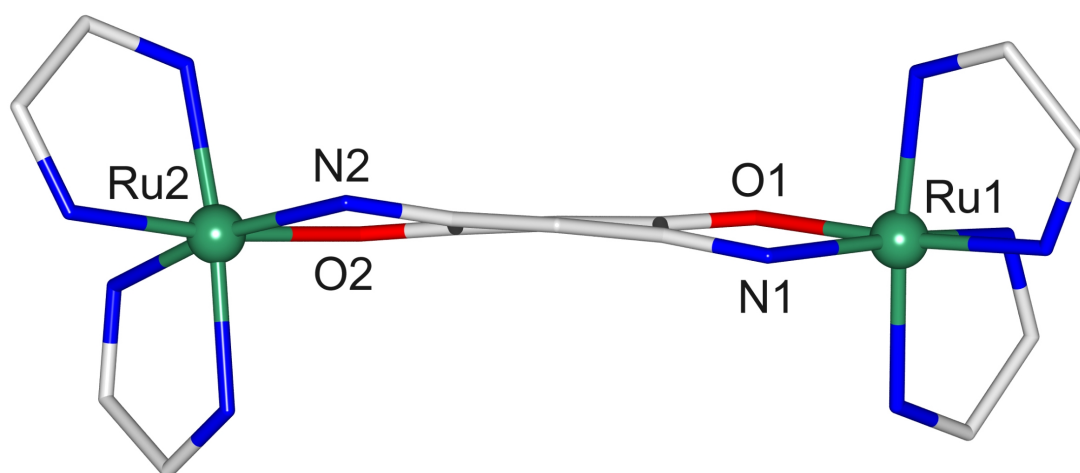


Figure S1: Structural diagram of the cation in *meso*-2(ClO₄)·2CH₂Cl₂, emphasizing the twisting of the quinonoid ligand. Only the chelation rings are depicted for the pyridine ligands, hydrogen atoms and isopropyl groups are omitted for clarity. The O1, C1, C2, C3 and O2 atoms are almost coplanar (maximum deviation from the mean plane: 0.027(4) Å for C3) as well as the N1, C6, C5, C4 and N2 (maximum deviation from the mean plane: 0.059(4) Å for C6). The two planes form an angle of 9.0(1)°.

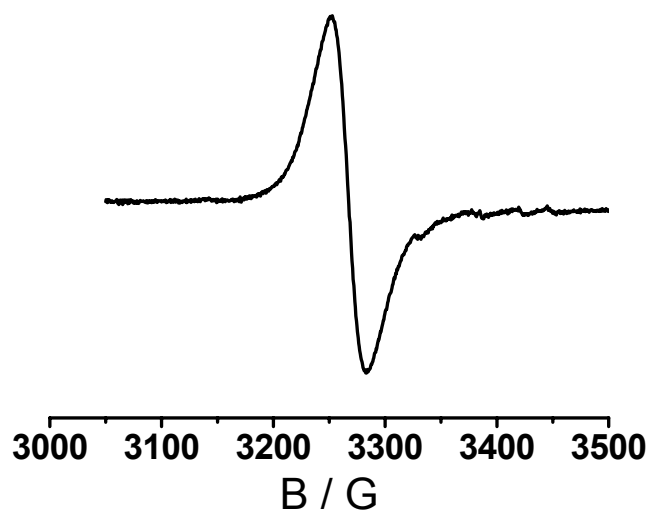


Figure S2: EPR spectrum of the electrogenerated [2]³⁺ in CH₃CN / 0.1 M Bu₄NPF₆ at 110K.

[S-ⁱ] P. Braunstein, D. Bubrin and B. Sarkar, *Inorg. Chem.* 2009, **48**, 2534.

[S-ⁱⁱ] Bruker-Nonius, *Kappa CCD Reference Manual*, Nonius BV, The Netherlands, **1998**.

[S-ⁱⁱⁱ] Sheldrick, M; *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Germany, **1997**.