Supporting Information for:

Capturing the Missing $[AgF_2]^-$ Anion Within an Ru_2(III/III) Dimeric Dumbbell Complex

Amanda R. Corcos and John F. Berry*

Department of Chemistry, University of Wisconsin–Madison, 1101 University Ave. Madison, WI 53706

Email: berry@chem.wisc.edu

Experimental Section.

General Procedures. All syntheses were conducted under a dry N_2 atmosphere in an MBraun glovebox; product workup and isolation were achieved under ambient conditions. CH_2Cl_2 was dried with CaH_2 and distilled before use. Tetrahydrofuran (THF) and hexanes were obtained from a Vacuum Atmospheres Solvent System and degassed prior to use. All materials were commercially available and used as received, unless otherwise noted. The compound $Ru_2(ap)_4Cl$ was prepared according to a literature procedure,[1] and the Hap ligand was purified by sublimation prior to use.

Synthesis. {$[Ru_2(ap)_4]_2[AgF_2]\}[BF_4]_3$ ({**2**}$[BF_4]_3$). $Ru_2(ap)_4Cl$ (150 mg, 0.164 mmol, 1.00 eq.) and $AgBF_4$ (82.5 mg, 0.423 mmol, 2.58 eq.) were dissolved in 12 mL of freshly distilled CH_2Cl_2 and 4 mL THF. The solution changed color from forest green to scarlet red and formation of a gray precipitate (presumably Ag/AgCl) was observed almost instantly. The reaction mixture was allowed to stir overnight at RT under N_2. The reaction mixture was then filtered through a fine frit. After concentrating the CH_2Cl_2/THF solution, the filtrate was layered with hexanes and allowed to crystallize by slow diffusion at RT. Yield: 146.4 mg, 82.5%. MW: 2164.18 g mol^{-1}. MALDI-TOF (m/z): 898 $[M - Ag(Ru_2(ap)_4F)(BF_4)_3]^+$. IR (ATR) ν/$cm^{-1}$: 1598 (s), 1482 (s), 1462 (s), 1425 (s), 1340 (m), 1287 (m), 1259 (m), 1208 (s), 1164 (m), 1057 (s), 1023 (m), 963 (m), 923 (m), 868 (s), 837 (w), 764 (s), 729 (s), 699 (s), 653 (w). UV-Vis in CH_2Cl_2 λ = 390 nm (sh), 489 nm, 925 nm. Anal. for $[C_{88}H_{72}AgB_3F_{14}N_{16}Ru_4]\bullet CH_2Cl_2$: calcd. C 47.53, H 3.32, N 9.96; found C 47.73, H 3.77, N 9.51.

Physical Measurements. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry data were obtained using an anthracene matrix on a Bruker ULTRAFLEX® III mass spectrometer equipped with a SmartBeam® laser in positive ion detection mode. UV-Vis spectra were obtained using a StellarNet Miniature BLUE-wave UV-Vis dip probe with a Tungsten-Krypton light source and a 10 mm path length tip. IR spectra were taken on a Bruker Tensor 27 spectrometer using an ATR adapter (no matrix). Cyclic voltammograms were taken on a BASi Potentiostat using Epsilon software in CH_2Cl_2 solutions with 0.1 M NBu_4BF_4 and 1.0 mM substrate. The electrodes were as follows: glassy carbon (working), Pt wire (auxiliary) and Ag/Ag^+ in CH_3CN (reference). The potentials were referenced versus the ferrocene/ferrocenium redox couple, by externally added ferrocene. Elemental analysis was performed at Midwest Microlab, LLC in Indianapolis, IN, USA.

X-ray Crystallography. Crystallographic data were measured at the Molecular Structure Laboratory of the Chemistry Department of the University of Wisconsin–Madison. Suitable crystals of {**2**}$[BF_4]_3$•$3CH_2Cl_2$ were selected under oil and ambient conditions. For {**2**}$[BF_4]_3$•$3CH_2Cl_2$, a red plate shaped crystal with dimensions 0.219 x 0.079 x 0.068 mm was selected. The crystal was attached to the tip of a MiTeGen MicroMount©, mounted in a stream of cold nitrogen at 100(1) K, and centered in the X-ray beam using a video monitoring system. The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEX-II diffractometer with Mo-Kα (λ = 0.71073 Å) radiation. The data were collected using a routine to survey the reciprocal and were indexed by the SMART program.[2] The structures were solved via direct methods and refined by iterative cycles of least-squares refinement on F^2 followed by difference Fourier synthesis.[3, 4] All hydrogen atoms were included in the final structure factor

calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Absorption corrections were based on a fitted function to the empirical transmission surface as sampled by multiple equivalent measurements.[5] The space group $P\bar{1}$ was chosen for refinement of the structure of {**2**}$[BF_4]_3$•$3CH_2Cl_2$ on the basis of intensity statistics indicating a centrosymmetric structure, and this choice yields a chemically reasonable and computationally stable refinement.[6]

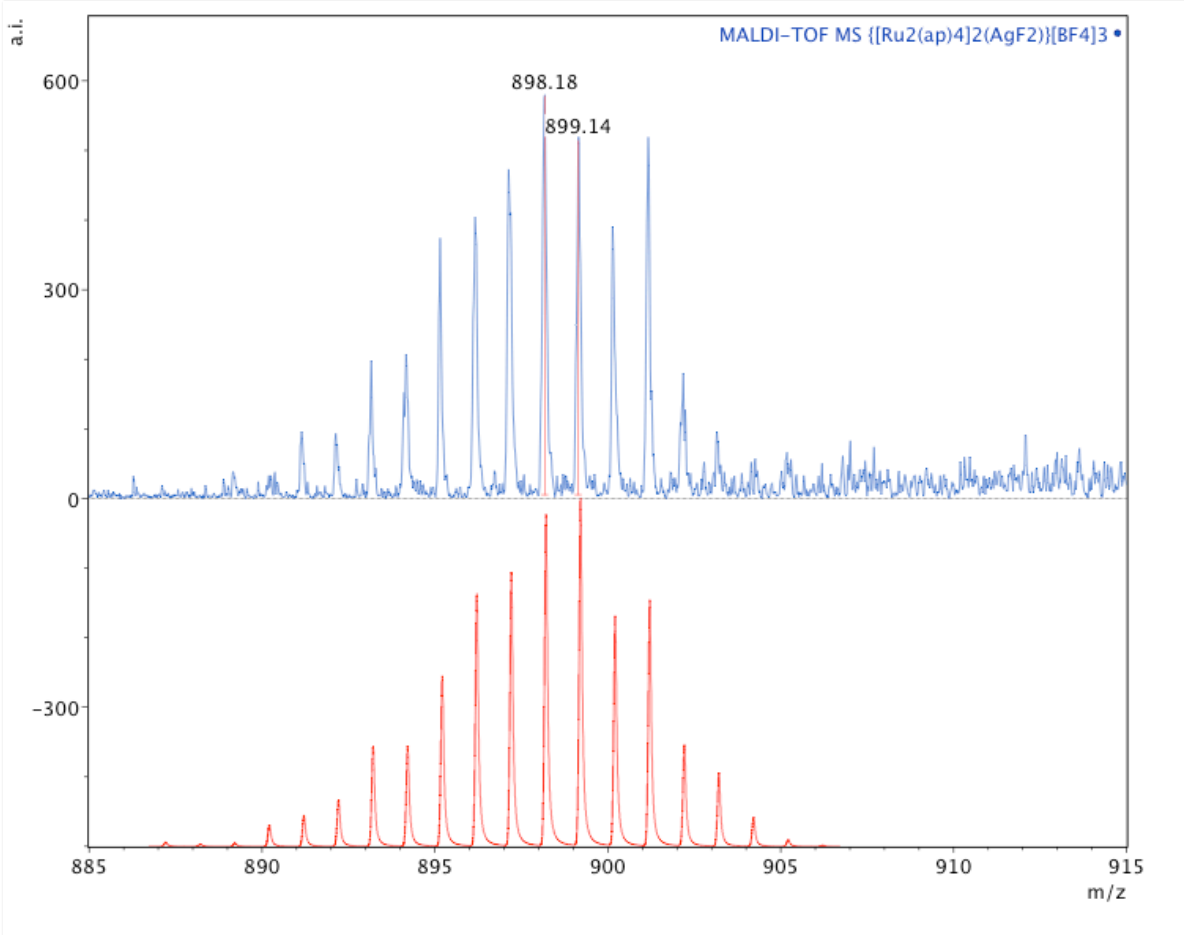

Figure S1. Mass spectrum for {**2**}$[BF_4]_3$. This data (top, simulation below) indicates the complex flies as $[Ru_2(ap)_4F]^+$.

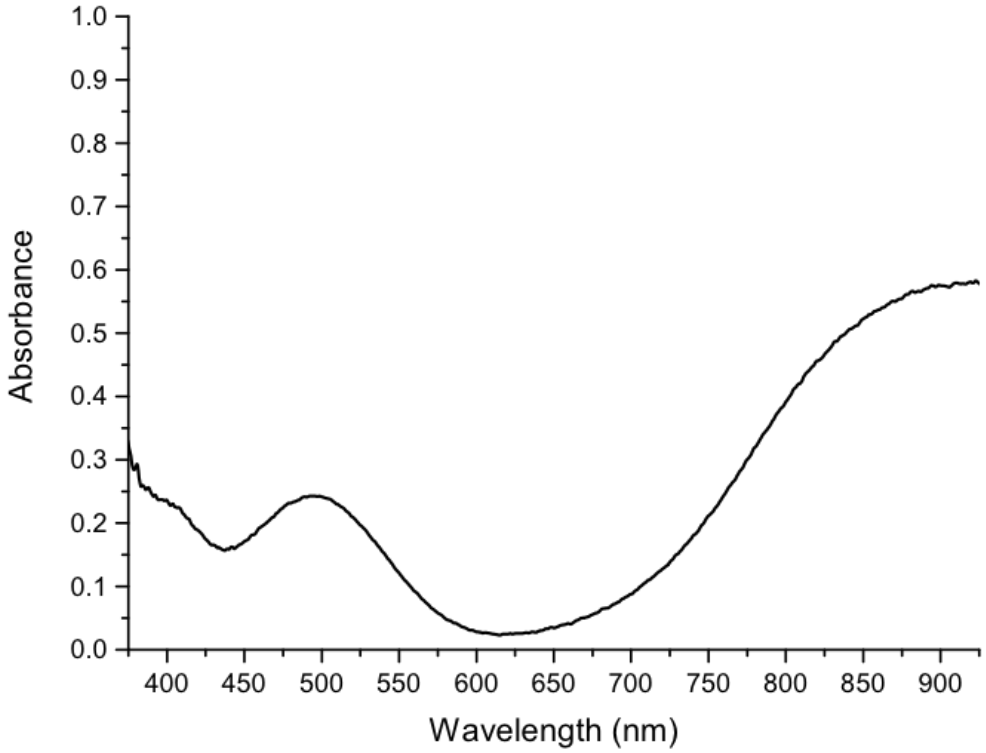

Figure S2. Electronic absorption spectrum for {**2**}$[BF_4]_3$ in CH_2Cl_2.

Table S1. Summary of X-ray crystallographic data for {**2**}$[BF_4]_3$•$3CH_2Cl_2$

Compound	{**2**}$[BF_4]_3$•$3CH_2Cl_2$
Formula	$C_{91}H_{78}Ag_1B_3Cl_6F_{14}N_{16}Ru_4$
Formula Weight g/mol	2418.97
Temperature (K)	100(1)
Crystal system	Triclinic
Space Group	$P\bar{1}$
a, Å	9.9382(4)
b, Å	12.7219(5)
c, Å	18.5759(8)
α °	87.507(2)
β °	88.869(2)
γ °	82.265(2)
V, Å ^{3}	2324.8(2)
Z	1
Density (calculated)	1.728 g/cm^3
Crystal size	0.219 x 0.079 x 0.068 mm^3
Data / restraints / parameters	13265 / 296 / 662
Goodness-of-fit on F^2	1.094
$R1^a$, w$R2^b$ (I<2σ(I))	0.0330, 0.0786
$R1^a$, w$R2^b$ (all data)	0.0411, 0.0823

$^aR1=\Sigma||F_o|-|Fc||/\Sigma|F_o|$. $^bwR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table S2. Crystallographic bond distances and for {**2**}$[BF_4]_3$•$3CH_2Cl_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ag1	F1	2.274(1)	C19	C20	1.374(5)
Ag1	F1[a]	2.274(1)	C20	C21	1.379(5)
Ru1	Ru2	2.2835(3)	C21	C22	1.387(4)
Ru1	F1	2.054(1)	C23	C24	1.376(4)
Ru1	N1	2.068(2)	C24	C25	1.398(5)
Ru1	N3	2.056(2)	C25	C26	1.363(5)
Ru1	N5	2.064(2)	C26	C27	1.417(4)
Ru1	N7	2.059(2)	C28	C29	1.379(7)
Ru2	N2	2.020(2)	C28	C33	1.396(7)
Ru2	N4	2.019(2)	C28A	C33A	1.3900
Ru2	N6	2.007(2)	C28A	C29A	1.3900
Ru2	N8	2.016(2)	C33A	C32A	1.3900
N1	C1	1.359(3)	C32A	C31A	1.3900
N1	C5	1.361(3)	C31A	C30A	1.3900
N2	C5	1.365(3)	C30A	C29A	1.3900
N2	C6	1.417(3)	C29	C30	1.401(7)
N3	C12	1.353(3)	C30	C31	1.383(8)
N3	C16	1.362(3)	C31	C32	1.372(8)
N4	C16	1.358(3)	C32	C33	1.395(7)
N4	C17	1.429(3)	C34	C35	1.369(3)
N5	C23	1.356(3)	C35	C36	1.394(4)
N5	C27	1.362(3)	C36	C37	1.370(4)
N6	C27	1.359(3)	C37	C38	1.414(3)
N6	C28	1.451(5)	C39	C40	1.391(4)
N6	C28A	1.377(8)	C39	C44	1.395(3)
N7	C34	1.354(3)	C40	C41	1.392(4)
N7	C38	1.367(3)	C41	C42	1.384(4)
N8	C38	1.356(3)	C42	C43	1.383(4)
N8	C39	1.430(3)	C43	C44	1.392(4)
C1	C2	1.371(3)	Cl3	C46	1.7601
C2	C3	1.397(4)	Cl4	C46	1.7605
C3	C4	1.370(3)	Cl3A	C46A	1.7598

C4	C5	1.417(3)	Cl3B	C46B	1.8528
C6	C7	1.391(3)	Cl4A	C46A	1.7601
C6	C11	1.396(3)	Cl4B	C46B	1.6289
C7	C8	1.390(4)	F6	B2	1.3832
C8	C9	1.380(4)	F7	B2	1.3885
C9	C10	1.386(4)	F8	B2	1.4054
C10	C11	1.391(4)	F9	B2	1.3930
C12	C13	1.371(3)	F2	B1	1.3926
C13	C14	1.395(4)	F3	B1	1.3836
C14	C15	1.371(4)	F4	B1	1.4049
C15	C16	1.416(3)	F5	B1	1.3681
C17	C18	1.388(4)	Cl1	C45	1.7657
C17	C22	1.393(3)	Cl2	C45	1.7721
C18	C19	1.394(4)			

[a] From symmetry operation; Ag1 lies on a crystallographic inversion center.

Table S3. Crystallographic bond angles and for {**2**}$[BF_4]_3$•$3CH_2Cl_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
F1	Ag1	F1[a]	180.00(7)	C12	C13	C14	118.7(3)
F1	Ru1	Ru2	179.15(4)	C15	C14	C13	119.8(2)
F1	Ru1	N1	90.76(7)	C14	C15	C16	119.7(2)
F1	Ru1	N3	90.14(7)	N3	C16	C15	119.7(2)
F1	Ru1	N5	91.47(7)	N4	C16	N3	116.5(2)
F1	Ru1	N7	90.08(7)	N4	C16	C15	123.9(2)
N1	Ru1	Ru2	88.45(6)	C18	C17	N4	121.1(2)
N3	Ru1	Ru2	90.13(6)	C18	C17	C22	119.9(2)
N3	Ru1	N1	87.38(8)	C22	C17	N4	119.0(2)
N3	Ru1	N5	90.07(8)	C17	C18	C19	119.1(3)
N3	Ru1	N7	179.24(8)	C20	C19	C18	120.9(3)
N5	Ru1	Ru2	89.34(6)	C19	C20	C21	119.9(3)
N5	Ru1	N1	176.62(8)	C20	C21	C22	120.1(3)
N7	Ru1	Ru2	89.66(6)	C21	C22	C17	120.0(3)
N7	Ru1	N1	93.34(8)	N5	C23	C24	122.0(3)
N7	Ru1	N5	89.20(8)	C23	C24	C25	118.5(3)
N2	Ru2	Ru1	90.84(6)	C26	C25	C24	120.4(3)
N4	Ru2	Ru1	89.45(6)	C25	C26	C27	119.3(3)
N4	Ru2	N2	89.11(8)	N5	C27	C26	119.9(2)
N6	Ru2	Ru1	90.14(6)	N6	C27	N5	116.1(2)
N6	Ru2	N2	178.62(8)	N6	C27	C26	124.1(3)
N6	Ru2	N4	89.93(8)	C29	C28	N6	119.4(5)
N6	Ru2	N8	90.69(8)	C29	C28	C33	120.1(4)
N8	Ru2	Ru1	90.25(6)	C33	C28	N6	120.5(4)
N8	Ru2	N2	90.27(8)	N6	C28A	C33A	115.8(7)
N8	Ru2	N4	179.31(8)	N6	C28A	C29A	123.6(7)
Ru1	F1	Ag1	175.79(8)	C33A	C28A	C29A	120.0
C1	N1	Ru1	119.6(2)	C28A	C33A	C32A	120.0
C1	N1	C5	119.6(2)	C31A	C32A	C33A	120.0
C5	N1	Ru1	120.7(2)	C32A	C31A	C30A	120.0
C5	N2	Ru2	120.0(2)	C31A	C30A	C29A	120.0
C5	N2	C6	119.8(2)	C30A	C29A	C28A	120.0
C6	N2	Ru2	120.2(2)	C28	C29	C30	120.0(5)
C12	N3	Ru1	120.6(2)	C31	C30	C29	119.6(5)

C12	N3	C16	119.7(2)	C32	C31	C30	120.6(4)
C16	N3	Ru1	119.2(2)	C31	C32	C33	120.2(5)
C16	N4	Ru2	122.0(2)	C32	C33	C28	119.5(5)
C16	N4	C17	118.0(2)	N7	C34	C35	122.8(2)
C17	N4	Ru2	119.2(2)	C34	C35	C36	118.8(2)
C23	N5	Ru1	120.3(2)	C37	C36	C35	119.7(2)
C23	N5	C27	119.9(2)	C36	C37	C38	119.7(2)
C27	N5	Ru1	119.6(2)	N7	C38	C37	119.9(2)
C27	N6	Ru2	121.9(2)	N8	C38	N7	116.5(2)
C27	N6	C28	119.8(3)	N8	C38	C37	123.6(2)
C27	N6	C28A	121.6(6)	C40	C39	N8	121.4(2)
C28	N6	Ru2	116.7(3)	C40	C39	C44	120.0(2)
C28A	N6	Ru2	116.5(6)	C44	C39	N8	118.6(2)
C34	N7	Ru1	120.6(2)	C39	C40	C41	119.2(2)
C34	N7	C38	119.1(2)	C42	C41	C40	121.0(3)
C38	N7	Ru1	119.7(2)	C43	C42	C41	119.8(3)
C38	N8	Ru2	121.7(2)	C42	C43	C44	119.9(2)
C38	N8	C39	117.0(2)	C43	C44	C39	120.1(3)
C39	N8	Ru2	120.4(2)	Cl3	C46	Cl4	112.9
N1	C1	C2	122.6(2)	Cl3A	C46A	Cl4A	112.9
C1	C2	C3	118.3(2)	Cl4B	C46B	Cl3B	108.5
C4	C3	C2	120.2(2)	F6	B2	F7	114.3
C3	C4	C5	119.5(2)	F6	B2	F8	102.6
N1	C5	N2	116.2(2)	F6	B2	F9	109.4
N1	C5	C4	119.7(2)	F7	B2	F8	107.7
N2	C5	C4	124.0(2)	F7	B2	F9	113.0
C7	C6	N2	120.0(2)	F9	B2	F8	109.2
C7	C6	C11	119.3(2)	F2	B1	F4	107.1
C11	C6	N2	120.6(2)	F3	B1	F2	109.6
C8	C7	C6	120.3(2)	F3	B1	F4	110.1
C9	C8	C7	120.3(3)	F5	B1	F2	109.7
C8	C9	C10	119.9(3)	F5	B1	F3	110.2
C9	C10	C11	120.3(3)	F5	B1	F4	110.1
C10	C11	C6	119.9(2)	Cl1	C45	Cl2	111.1
N3	C12	C13	122.4(2)				

[a] From symmetry operation; Ag1 lies on a crystallographic inversion center.

Table S4. Number of known complexes containing the free $[X–M–X]^-$ anion, where X is a halogen and M is a coinage metal (Cu, Ag, or Au).[7]

	F	Cl	Br	I
Cu	0	153	41	6
Ag	0	13	7	6
Au	0	63	38	40

Table S5. Number of known ligated M'–[X–M–X]–M' complexes, where X is a halogen, M is a coinage metal (Cu, Ag, or Au), and M' is another metal.[7]

	F	Cl	Br	I
Cu	0	13	6	0
Ag	0	2	0	2
Au	0	0	0	0

References.

[1] A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *Inorg. Chem.* **1985**, *24*, 172.
[2] SMART, Bruker-AXS, Madison, WI, **2009**.
[3] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
[4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Psuchmann, *J. Appl. Cryst.* **2009**, *42*, 339.
[5] SADABS, Bruker-AXS, Madison, WI, **2012**.
[6] G. M. Sheldrick, *CELL_NOW*, University of Gottingen, Germany, **2008**.
[7] Based on a search of the Cambridge Structural Database.