Supporting Information

New Structural Motifs Resulting from Internal Constraints in Chelating bis(NHC) Ligands: A Dinuclear Ruthenium(II) Complex Featuring an η^2-Arene Binding Mode, and a Remarkable New Tetrameric Silver(I) Halide Form

Peter V. Simpson,[†,‡] David H. Brown,[†,‡,*] Brian W. Skelton,[†,#] Allan H. White,[†,] and Murray V. Baker,[†,*]

[†] School of Chemistry and Biochemistry, M310, The University of Western Australia, Crawley, WA 6009, Australia.

[‡] Nanochemistry Research Institute, Department of Chemistry, Curtin University of Technology, GPO Box U1987, Perth WA 6845, Australia.

[#] Current Address: Centre for Microscopy, Characterisation and Analysis, M310, The University of Western Australia, Crawley, WA 6009, Australia.

Contents **Page**

Table S1. Molecular core geometries for **7**·MeCN

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Ag(0)-Br(1)	2.9080(10)	Ag(2)-C(62)	2.143(7)
Ag(0)-Br(2)	2.7755(11)	Ag(2)-Br(1)	2.8820(10)
Ag(0)-Br(3)	2.6484(10)	Ag(2)-Br(2)	2.5842(10)
Ag(0)-Br(4)	2.5962(11)	Ag(2)...C(65^{i})	3.389(7)
Ag(1)-C(22)	2.092(8)	Ag(2)...C(66^{i})	3.178(8)
Ag(1)-C(42)	2.120(7)	Ag(3)-C(82)	2.122(7)
Ag(1)-Br(4)	2.9386(9)	Ag(3)-Br(1)	2.5666(10)
Ag(0)...Ag(1)	2.9802(7)	(Ag(3)-Br(2)	3.4005(8))
Ag(0)...Ag(2)	3.3951(8)	Ag(3)-Br(3)	2.8929(9)
Ag(0)...Ag(3)	3.1805(8)	Ag(2)...Ag(3)	3.0933(8)
Angles (degrees)			
Br(1)-Ag(0)-Br(2)	98.24(2)	Br(4)-Ag(1)-C(22)	106.7(2)
Br(1)-Ag(0)-Br(3)	90.58(2)	Br(4)-Ag(1)-C(42)	103.9(2)
Br(1)-Ag(0)-Br(4)	104.79(3)	C(22)-Ag(1)-C(42)	149.5(3)
Br(2)-Ag(0)-Br(3)	99.68(3)	C(62)-Ag(2)-Br(1)	111.9(2)
Br(2)-Ag(0)-Br(4)	109.63(3)	C(62)-Ag(2)-Br(2)	143.8(2)
Br(3)-Ag(0)-Br(4)	144.13(4)	Br(1)-Ag(2)-Br(2)	103.57(3)
C(82)-Ag(3)-Br(1)	160.1(2)	Ag(0)-Br(1)-Ag(2)	71.80(2)
C(82)-Ag(2)-Br(3)	107.0(2)	Ag(0)-Br(1)-Ag(3)	70.73(2)
Br(1)-Ag(3)-Br(3)	92.57(3)	Ag(2)-Br(1)-Ag(3)	68.90(3)
Ag(0)-Br(2)-Ag(2)	78.52(3)	Ag(0)-Br(4)-Ag(1)	64.82(2)
Ag(0)-Br(3)-Ag(3)	69.90(2)		

Transformation i is (1–*x*, 1–*y*, 1–*z*)

Table S2. Selected cation geometries for $(\mathbf{5}^{+})(AgCl_2^{-})\cdot 3C_6H_6$

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Ru(1)-Cl(2)	2.4235(15)	Ru(2)-Cl(1)	2.4215(14)
Ru(1)-Cl(1)	2.5069(14)	Ru(2)-Cl(2)	2.5307(15)
Ru(1)-Cl(3)	2.5289(14)	Ru(2)-Cl(3)	2.5278(14)
Ru(1)-C(22)	2.004(6)	Ru(2)-C(62)	1.997(6)
Ru(1)-C(42)	1.967(6)	Ru(2)-C(82)	1.994(6)
Ru(1)-C(31)	2.331(6)	Ru(2)-C(71)	2.321(6)
Ru(1)-C(32)	2.299(6)	Ru(2)-C(72)	2.327(6)
Ru(1)-C(30)	2.21_8	Ru(2)-C(70)	2.21_7
C(31)-C(32)	1.405(9)	C(71)-C(72)	1.407(9)
C(31)-C(36)	1.453(9)	C(71)-C(76)	1.461(9)
C(32)-C(33)	1.435(9)	C(72)-C(73)	1.440(9)
C(33)-C(34)	1.333(10)	C(73)-C(74)	1.356(10)
C(35)-C(36)	1.348(10)	C(75)-C(76)	1.343(10)
C(34)-C(35)	1.404(11)	C(74)-C(75)	1.412(11)
Ru(1)...Ru(2)	3.3518(8)	Cl(1)...Cl(2)	3.060(3)
Cl(1)...Cl(3)	3.253(2)	Cl(2)...Cl(3)	3.255(2)
Ag(1)...Cl(11)	2.313(7)	Ag(1)...Cl(12)	2.315(2)
Ag(1)...C(33)	3.360(9)	Ag(1)...C(34)	3.345(10)
Angle (degrees)			
Cl(2)-Ru(1)-Cl(1)	76.70(5)	Cl(1)-Ru(2)-Cl(2)	76.29(5)
Cl(2)-Ru(1)-Cl(3)	82.14(5))	Cl(1)-Ru(2)-Cl(3)	82.15(5)
Cl(1)-Ru(1)-Cl(3)	80.47(5)	Cl(2)-Ru(2)-Cl(3)	80.09(5)
C(30)-Ru(1)-Cl(2)	171.3_6	C(70)-Ru(2)-Cl(3)	171.3_8
C(30)-Ru(1)-Cl(1)	96.9_2	C(70)-Ru(2)-Cl(2)	96.9_6
C(30)-Ru(1)-Cl(3)	102.7_4	C(70)-Ru(2)-Cl(3)	102.1_9
C(30)-Ru(1)-C(22)	90.0_0	C(70)-Ru(2)-C(62)	$90._7$
C(30)-Ru(1)-C(42)	$82._2$	C(70)-Ru(2)-C(82)	$83._2$
C(22)-Ru(1)-C(42)	88.7(2)	C(62)-Ru(2)-C(82)	87.9(2)
C(22)-Ru(1)-Cl(2)	96.1(2)	C(62)-Ru(2)-Cl(1)	96.3(2)

C(42)-Ru(1)-Cl(2)	91.9(2)	C(82)-Ru(2)-Cl(1)	92.0(2)
Cl(1)-Ru(1)-C(22)	172.6(2)	Cl(2)-Ru(2)-C(62)	172.0(2)
Cl(1)-Ru(1)-C(42)	89.8(2)	Cl(2)-Ru(2)-C(82)	95.2(2)
Cl(3)-Ru(1)-C(22)	100.5(2)	Cl(3)-Ru(2)-C(62)	96.2(2)
Cl(3)-Ru(1)-C(42)	169.5(2)	Cl(3)-Ru(2)-C(82)	173.2(2)
Ru(1)-Cl(1)-Ru(2)	85.68(5)	Ru(1)-Cl(2)-Ru(2)	85.12(5)
Ru(1)-Cl(3)-Ru(2)	83.03(4)	Cl(11)-Ag(2)-Cl(12)	170.24(13)

In the anion, Ag-Cl (1,2) are 2.313(3), 2.315(2) Å; Cl(1)-Ag-Cl(2) is 170.24(13)°.

Structure determination of 3·2HCl·H_2O

The structure of **3**·2HCl·H_2O is the same as that of its bromide counterpart[1] but with some significant improvement in quality, albeit due to the small size and poor quality of the crystals, data for the structure were collected using Cu Kα radiation (λ = 1.5417$_8$ Å). The crystal and refinement data for **3**·2HCl·H_2O are summarized in Table S3 with the structure of the cation depicted in Figures S1, where ellipsoids have been drawn at the 30% probability level. Hydrogen bonding details are listed on Table S4. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer. Following multiscan absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97.[2] One of the benzimidazolin-2-ylidene moieties was modelled as being disordered over two sets of sites, occupancies refining to 0.722(4) and complement. Two atoms of another n-BuO group were also modelled as being disordered with similar occupancies. Non-hydrogen atoms of the minor components of the disordered atoms were refined with isotropic displacement parameters after anisotropic refinement resulted in unacceptable ellipsoids even with reasonable restraints. Geometries and some displacement parameters of the minor components were restrained to reasonable values. Water molecule H-atoms were also refined but with restrained geometries. The remaining H-atoms were added at calculated positions and refined by using a riding model with isotropic displacement parameters based on those of the parent atom.

Figure S1. Projection of the cation of **3**·2HCl·H_2O showing the major component only for the disordered groups.

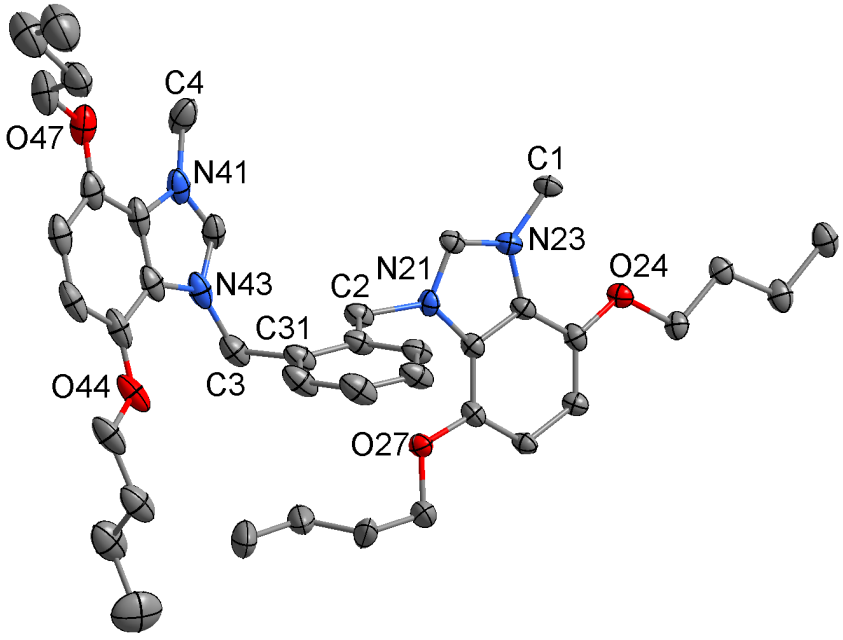

Table S3. Crystal data and structure refinement for **3**·2HCl·H_2O.

Empirical formula	$C_{40}H_{58}Cl_2N_4O_5$
Formula weight	745.80
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	*a* = 31.1544(15) Å
	b = 15.0002(8) Å
	c = 17.3313(8) Å
	β = 98.312(5)°
Volume	8014.2(7) $Å^3$
Z	8
Density (calculated)	1.236 Mg/m^3
μ	1.829 mm^{-1}
Crystal size	0.32 x 0.04 x 0.03 mm^3
θ range for data collection	2.87 to 67.23°.
Index ranges	-33<=h<=37, -17<=k<=17, -15<=l<=20
Reflections measured	23411
Independent reflections	7098 [*R*(int) = 0.0614]
Completeness to θ = 67.23°	98.7 %
Absorption correction	Semi-empirical from equivalents
Min/max transmission	0.80
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7098 / 116 / 568
Goodness-of-fit on F^2	0.970
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0610, *wR*2 = 0.1545
R indices (all data)	*R*1 = 0.1171, *wR*2 = 0.1821
Largest diff. peak and hole	0.424 and -0.269 e.$Å^{-3}$

Table S4. Hydrogen bonds for **3**·2HCl·H_2O [Å, °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(22)-H(22)...Cl(1)	0.95	2.51	3.365(8)	149.8
C(42)-H(42)...Cl(1)	0.95	2.61	3.396(4)	140.6
C(52)-H(52)...Cl(1)	0.95	2.51	3.364(18)	150.3
O(1)-H(1AO)...Cl(1)	0.83(3)	2.46(3)	3.273(4)	166(5)
O(1)-H(1BO)...Cl(2)	0.88(3)	2.28(3)	3.135(4)	166(6)

References

(1) Baker, M. V.; Brown, D. H.; Simpson, P. V.; Skelton, B. W.; White, A. H. *Dalton Trans*. 2009, 7294.

(2) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr*. 2008, *64*, 112.