Supplementary Material (ESI) for Chemical Communications

Concerted halogen and hydrogen bonding in $RuI_2(H_2dcbpy)(CO)_2]\cdots I_2\cdots(CH_3OH)\cdots I_2\cdots[RuI_2(H_2dcbpy)(CO)_2]$

Matti Tuikka[a], Mika Niskanen[a], Pipsa Hirva[a], Kari Rissanen[b], Arto Valkonen[b], and Matti Haukka[a]*

[a]Department of Chemistry, University of Eastern Finland, P.O. Box 111, FI-80101 Joensuu, Finland, Email: matti.haukka@uef.fi, [b]Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, FI-40014 University of Jyväskylä, Finland

SUPPORTING MATERIAL

Table S1: Properties of the electron density at the bond critical points of the Ru-I···I-I···I-I···I-Ru system. For numbering of the BCPs, see Figure 2.

BCP #	distance (Å)	$\rho(\mathbf{r}_c)$ (e/Å^3)	E_{int} kJ/mol	$\nabla^2\rho(\mathbf{r}_c)$ (e/Å^5)	λ1/λ3	G($\mathbf{r}_c$)*	V($\mathbf{r}_c$)*	H($\mathbf{r}_c$)*	V/G
1	3.24	0.183	-17.9	1.13	0.205	0.012686	-0.01367	-0.00098	1.08
2	2.74	0.476	-64.0	-0.34	0.578	0.022638	-0.04881	-0.02617	2.16
3	3.54	0.096	-8.2	0.83	0.149	0.007432	-0.00624	0.00119	0.84
4	2.77	0.453	-59.7	-0.13	0.539	0.022048	-0.04548	-0.02343	2.06
5	3.14	0.218	-22.7	1.14	0.240	0.014571	-0.01730	-0.00273	1.19
6	2.93	0.058	-4.9	0.56	0.176	0.004773	-0.00371	0.00106	0.78
7	3.09	0.044	-4.4	0.50	0.152	0.004275	-0.00335	0.00092	0.78

* Hartree/Bohr^3

Experimental and Computational Details

The metal complex *trans*(I)-[RuI_2(H2dcbpy)$(CO)_2$] was synthesized as reported earlier.[S1] The iodine compound was synthesized by dissolving the metal complex (10mg, 0.015mmol) and metallic iodine (21.4 mg, 0.084mmol) separately in methanol (1+1ml) and mixing the methanol solutions. The combined solution was left to evaporate in a small glass vial protected from light and after three days the product was obtained as brown single crystals suitable for X-ray analysis. Metallic iodine was obtained as a side product as well as some amorphous residue. All chemicals except the metal complex were obtained from commercial sources and used without further purification.

Calculations were done with the Gaussian03 program package[S2] using the PBE0 hybrid density functional[S3] (also known as PBE1PBE). The basis sets used were Lanl2TZ(f)[S4] ECP for ruthenium, Lanl2DZspdf[S5] ECP for iodine and standard all-electron 6-311++G** for other atoms.

Electron density was calculated using the experimental geometry and analyzed according to Bader's Quantum Theory of Atoms in Molecules (QTAIM)[S6] as implemented in AIM2000.[S7]

References

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X-ray Structure Determinations. The crystal of $C_{15}H_{12}I_2N_2O_6Ru{\cdot}2I_2{\cdot}CH_3OH$ **1** was immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data was collected on a Bruker AXS ApexII Duo diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The *APEX2*[1] program package was used for cell refinements and data reductions. The structure was solved by direct methods using the *SHELXS-97*[2] program with the *WinGX*[3] graphical user interface. A numerical absorption correction (*SADABS*)[4] was applied to the data. Structural refinement was carried out using *SHELXL-97*.[2] The OH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.5 U_{eq} (parent atom). Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C-H = 0.95-0.98 Å and U_{iso} = 1.2-1.5 U_{eq}(parent atom). The crystallographic details are summarized in **Table S1** and bond lengths and angles in **Table S2**.

Table S2. Crystal data and structure refinement for $C_{15}H_{12}I_2N_2O_6Ru{\cdot}2I_2{\cdot}CH_3OH$.

Empirical formula	$C_{15}H_{12}I_6\ N_2O_7Ru$	
Formula weight	1194.74	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 7.5481(2) Å	α= 96.7880(10)°
	b = 11.2104(3) Å	β= 103.1250(10)°
	c = 16.1242(4) Å	γ = 90.9920(10)°
Volume	1318.05(6) $Å^3$	
Z	2	
Density (calculated)	3.010 Mg/m^3	
Absorption coefficient	7.658 mm^3	
F(000)	1068	
Crystal size	0.24 x 0.11 x 0.08 mm^3	
Theta range for data collection	1.83 to 32.50°.	
Index ranges	-11<=h<=11, -16<=k<=16, -24<=l<=24	
Reflections collected	83823	
Independent reflections	9551 [R(int) = 0.0299]	
Completeness to theta = 32.50°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.5794 and 0.2587	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9551 / 0 / 281	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0187, wR2 = 0.0401	
R indices (all data)	R1 = 0.0238, wR2 = 0.0416	
Largest diff. peak and hole	1.448 and -1.024 $e.Å^{-3}$	

Table S3. Selected bond lengths, I···I contacts [Å] ,and angles [°] for $C_{15}H_{12}I_2N_2O_6Ru{\cdot}2I_2{\cdot}CH_3OH$.

I(1)-Ru(1)	2.7028(2)	O(5)-C(12)	1.325(3)
I(1)-I(3)	3.2376(2)	O(6)-C(12)	1.206(3)
I(2)-Ru(1)	2.6987(2)		
I(2)-I(6)#1	3.1442(2)	Ru(1)-I(1)-I(3)	104.045(6)
I(3)-I(4)	2.7401(2)	Ru(1)-I(2)-I(6)#1	95.257(6)
I(4)-I(5)	3.5371(2)	I(4)-I(3)-I(1)	172.802(7)
I(5)-I(6)	2.7672(2)	I(3)-I(4)-I(5)	177.370(7)
I(6)-I(2)#2	3.1442(2)	I(6)-I(5)-I(4)	137.789(7)
Ru(1)-C(1)	1.895(2)	I(5)-I(6)-I(2)#2	176.214(8)
Ru(1)-C(2)	1.897(2)	C(1)-Ru(1)-C(2)	89.16(9)
Ru(1)-N(2)	2.1082(18)	N(2)-Ru(1)-N(1)	77.12(7)
Ru(1)-N(1)	2.1155(17)	I(2)-Ru(1)-I(1)	174.226(8)
O(3)-C(6)	1.313(3)	O(4)-C(6)-O(3)	124.2(2)
O(4)-C(6)	1.217(3)	O(6)-C(12)-C(11)	122.89(19)

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z-1 #2 x+1,y,z+1

Table S4. Hydrogen bonds for $C_{15}H_{12}I_2N_2O_6Ru{\cdot}2I_2{\cdot}CH_3OH$ [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(3)-H(3O)...O(7)#3	0.82	1.83	2.634(2)	167.5
O(5)-H(5O)...O(4)#4	0.86	1.82	2.664(2)	166.3
O(7)-H(7O)...I(5)	0.9	2.93	3.7983(17)	162.8
O(7)-H(7O)...I(4)	0.9	3.09	3.6609(17)	123.8

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z-1 #2 x+1,y,z+1 #3 x-1,y,z #4 -x+2,-y+2,-z+2

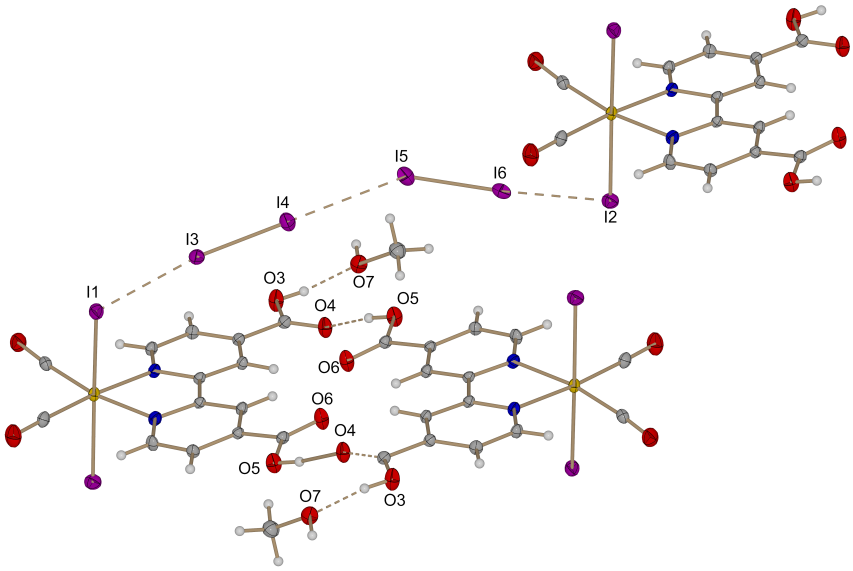

Figure S1. Intermolecular interactions in $C_{15}H_{12}I_2N_2O_6Ru{\cdot}2I_2{\cdot}CH_3OH$.

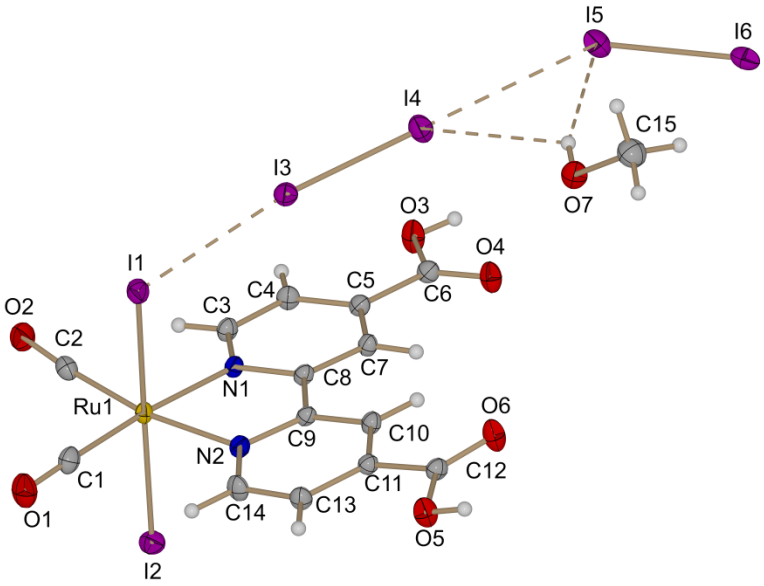

Figure S2. Thermal ellipsoid plot (at 60% probability level) of $C_{15}H_{12}I_2N_2O_6Ru{\cdot}2I_2{\cdot}CH_3OH$.

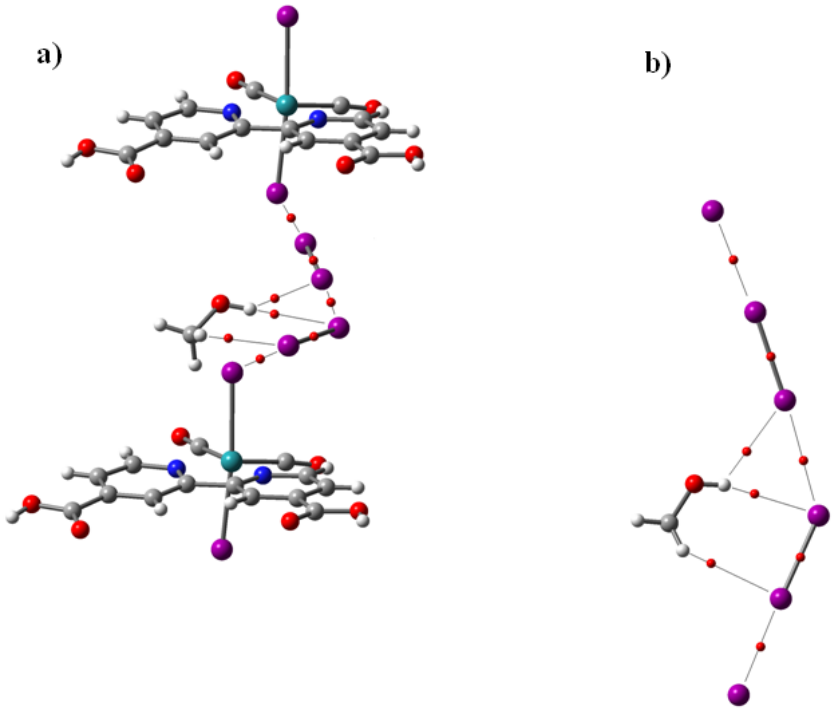

Figure S3. a) Bond critical points (BCPs) in the RuI···I-I···(MeOH) ···I-I…IRu system according to the charge density analysis; b) the metal complexes have been omitted for clarity.