Published in "Zeitschrift für anorganische und allgemeine Chemie
637(14-15): 2089–2092, 2011" which should be cited to refer to this work.

Supplementary materials:

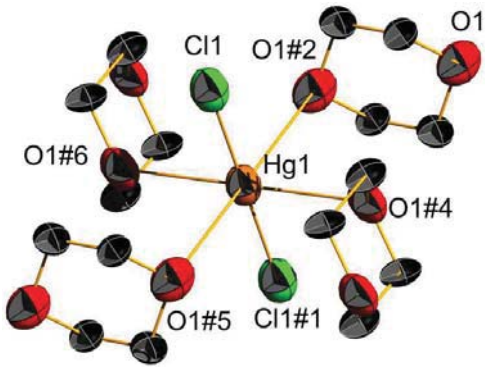

Figure 1: Molecular view of **1**, H atoms are omitted for clarity, #1 = -x, -y, -z; #2 = 1-x, -y, z; #3 = x, y, -z; #4 = y, 1-x, z; #5 = x-1, y, z; (left) 50% of probability, (right) with polyhedron.

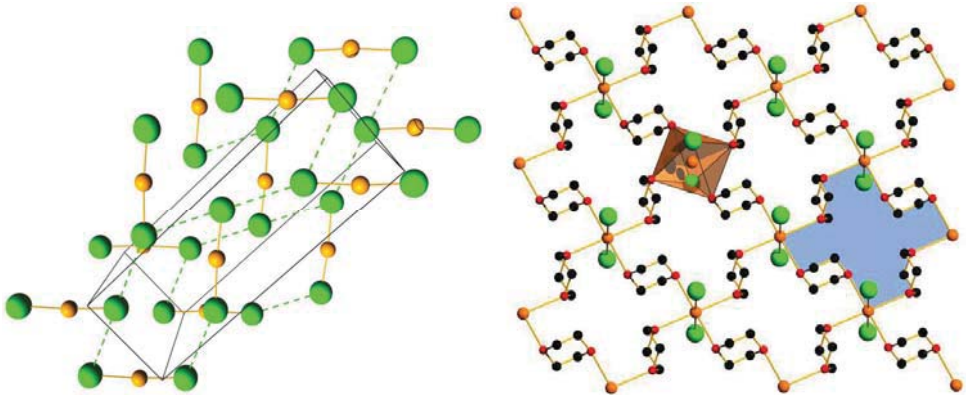

Figure 2: Molecular packing of $HgCl_2$ (left) with Cl–Cl short contact in dash grey and molecular packing of **1** (right), Hg of the above and below plane are located in the centre of the shaded regions; H atoms are omitted for clarity.

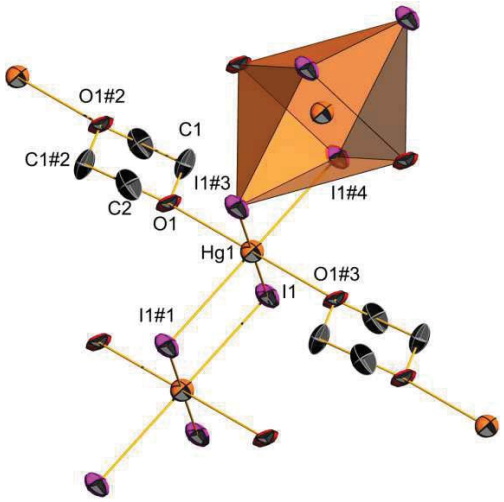

Figure 3: Molecular view of **2**, H atoms are omitted for clarity, #1 = 1-x, 1-y, -z; #2 = -x, -y, 1-z; #3 = -x, 1-y, -z; #4 = x-1, y, z; 80% of

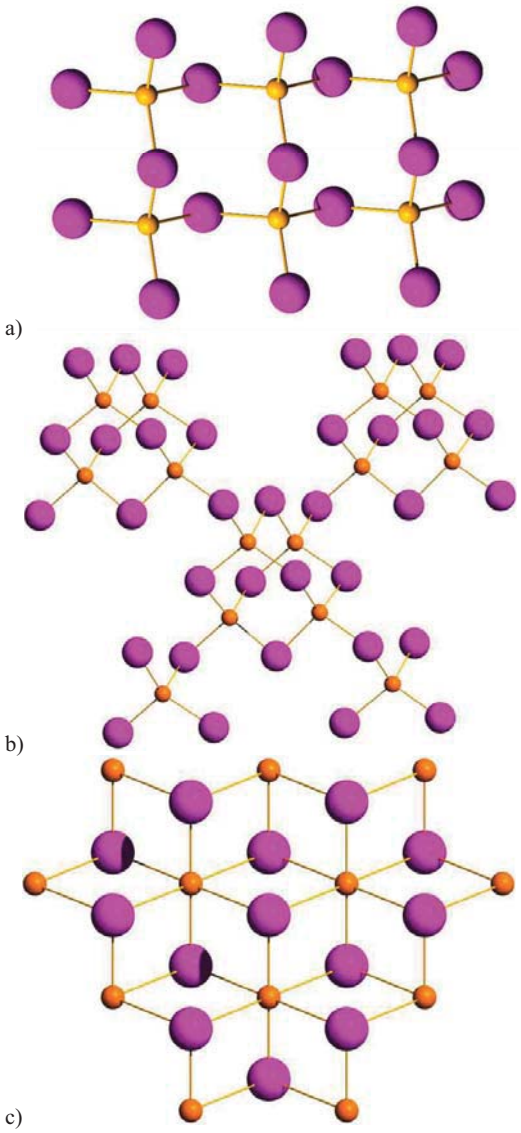

Figure 4: Molecular packing of a) α-HgI_2(red), b) γ-HgI_2 (orange), c) (right) β-HgI_2 (yellow).

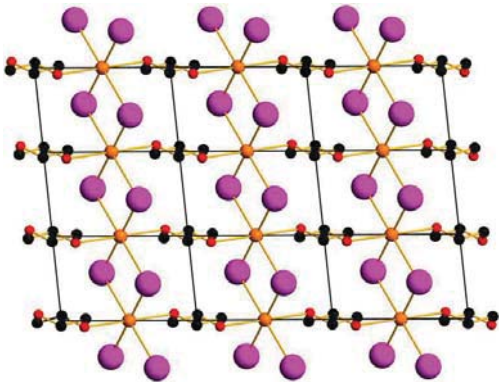

Figure S1: molecular packing of **2** H atoms are omitted for clarity view along *c* axis (right).

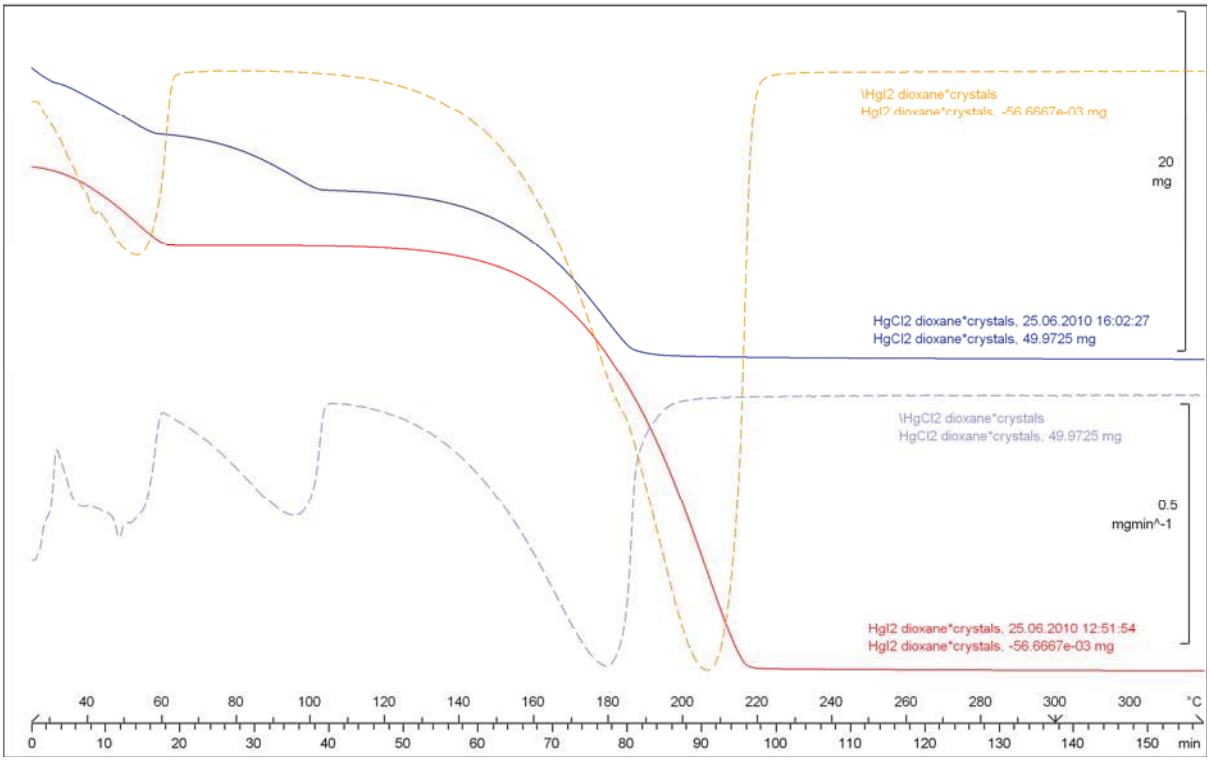

Figure S2: Comparison of TGA of **1** and **2** under air: 25-300 °C at 5 °C/min; Weight loss is drawn in plain lines and first derivatives in dashed lines; **1** measurement are in blue and purple; **2** are in red and orange.

Table S2 - Crystal Data and Structure refinement for **1**.

Empirical formula	$C_8 H_{16} Cl_2 Hg O_4$
Formula weight	447.70
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	*I* 4/m
Unit cell dimensions	*a* = 7.2471(2) Å
	c = 12.0237(5) Å
Volume	631.49(2) $Å^3$
Z	2
Density (calculated)	2.354 Mg/m^3
Absorption coefficient	12.601 mm^{-1}
F(000)	420
Crystal size	0.2 x 0.12 x 0.08 mm^3
Theta range for data collection	5.23 to 24.96°.
Index ranges	-8<=h<=8, -8<=k<=8, -14<=l<=14
Reflections collected	3357
Independent reflections	300 [*R*(int) = 0.0846]
Completeness to theta = 24.96°	99.0 %
Absorption correction	Empirical (SHELXA)
Max. and min. transmission	0.6219 and 0.1495
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	300 / 0 / 22
Goodness-of-fit on F^2	0.949
Final R indices [I>2sigma(I)]	*R1* = 0.0336, *wR2* = 0.0987
R indices (all data)	*R1* = 0.0336, *wR2* = 0.0987
Extinction coefficient	0.029(5)
Largest diff. peak and hole	2.841 and -1.942 $e.Å^{-3}$

Table S3 - Crystal Data and Structure refinement for **2**.

Empirical formula	$C_4 H_8 Hg I_2 O_2$	
Formula weight	542.49	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	*a* = 4.3431(4) Å	α = 64.083(7)°.
	b = 7.6214(8) Å	β = 84.466(8)°.
	c = 7.9252(8) Å	γ = 82.493(8)°.
Volume	233.70(4) $Å^3$	
Z	1	
Density (calculated)	3.855 Mg/m^3	
Absorption coefficient	23.011 mm^{-1}	
F(000)	234	
Crystal size	0.18 x 0.08 x 0.06 mm^3	
Theta range for data collection	4.74 to 25.00°.	
Index ranges	-5<=h<=5, -9<=k<=9, -9<=l<=9	
Reflections collected	5459	
Independent reflections	797 [*R*(int) = 0.1129]	
Completeness to theta = 25.00°	97.6 %	
Absorption correction	Empirical (SHELXA)	
Max. and min. transmission	0.6039 and 0.1330	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	797 / 0 / 38	
Goodness-of-fit on F^2	1.121	
Final R indices [I>2sigma(I)]	*R1* = 0.0745, *wR2* = 0.1693	
R indices (all data)	*R1* = 0.0778, *wR2* = 0.1710	
Extinction coefficient	0.038(6)	
Largest diff. peak and hole	3.016 and -7.083 $e.Å^{-3}$	