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Supporting information

Nonlinear optical effects in two mercury cyanamide/guanidinium chlorides $Hg_3(NCN)_2Cl_2$ and $Hg_2(C(NH_2)_3)Cl_5$

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Table S1 Crystallographic data and fractional coordinates (all atoms on 4*a*) for $Hg_3(NCN)_2Cl_2$ with standard deviations given in parentheses. The thermal displacement parameters of Cl, C and N were constrained to be equal.

Atom	*x*	*y*	*z*	U_{iso} (Å^2)
Hg1	0.7088(5)	0.0841(3)	0.9481(7)	0.0174(11)
Hg2	0.9896(6)	0.44473(31)	–0.0024(7)	0.0211(11)
Hg3	0.2302(6)	0.2061(4)	0.6382(9)	0.0198(12)
Cl1	0.0797(28)	0.1998(24)	0.8868(22)	0.056(6)
Cl2	0.652(3)	0.2870(24)	0.0694(25)	"
N1	0.206(10)	0.031(6)	0.607(5)	"
C1	0.143(6)	0.962(7)	0.698(7)	"
N2	0.068(8)	0.909(7)	0.776(6)	"
N3	0.195(9)	0.386(5)	0.142(5)	"
C2	0.155(10)	0.450(5)	0.236(6)	"
N4	0.129(9)	0.521(5)	0.323(7)	"

Orthorhombic, *Pca*2_1 (No. 29), $Z = 4$, $a = 7.0102(4)$ Å, $b = 10.7779(7)$ Å, $c = 10.4973(7)$ Å; $R_{wp} = 1.797$ %, $R_p = 1.206$ %.

Table S2 Selected bond lengths and angles in $Hg_3(NCN)_2Cl_2$ with standard deviations given in parentheses. Note that C–N bond and N–C–N angle restraints were introduced to stabilize the refinement based on the prior (superior) single-crystal data.

Bond length (Å)		Bond angle (°)	
Hg1–Cl2	2.256(24)	Cl2–Hg1–N2	109.3(21)
Hg1–N1	2.16(6)	N1–Hg3–N3	166.9(26)
Hg1–N2	2.06(7)	N1–C1–N2	172.7(7)
Hg2–N3	2.19(6)	N3–C2–N4	173.3(7)
Hg2–N4	2.05(6)		
Hg3–Cl1	2.815(26)		
Hg3–Cl2	2.909(24)		
Hg3–N1	1.93(6)		
Hg3–N3	2.00 (5)		
N1–C1	1.277(7)		
C1–N2	1.134(7)		
N3–C2	1.232(7)		
N4–C2	1.205(7)		

Table S3 Crystallographic data and fractional coordinates for $Hg_2(C(NH_2)_3)Cl_5$ with standard deviations given in parentheses. The thermal displacement parameters of C, N and H were constrained to be equal. The thermal displacement parameters of H were fixed as 0.1 $Å^2$.

Atom	Wyckoff site	*x*	*y*	*z*	U_{iso} ($Å^2$)
Hg	8*c*	0.3702(6)	0.36957(16)	–0.03790(11)	0.0429(6)
Cl1	4*a*	0.8605(31)	½	0	0.021(4)
Cl2	8*c*	0.3679(30)	0.3120(6)	0.0794(5)	0.034(3)
Cl3	8*c*	0.3823(30)	0.3900(7)	–0.1601(4)	0.030(3)
C	4*b*	0	0.3796(17)	¼	0.016(8)
N1	8*c*	0.910(6)	0.4279(12)	0.1956(8)	"
N2	4*b*	0	0.2927(17)	¼	"
H1	8c	0.823(12)	0.3988(28)	0.1510(16)	0.1
H2	8c	0.900(12)	0.4944(15)	0.2015(28)	"
H3	8c	0.224(6)	0.2594(24)	0.240(6)	"

Orthorhombic, $C222_1$ (No. 20), Z = 4, a = 4.03993(8) Å, b = 14.9618(4) Å, c = 18.4060(4) Å; R_{wp} = 2.765 %, R_p = 1.744 %.

Table S4 Selected bond lengths and angles in $Hg_2(C(NH_2)_3)Cl_5$ with standard deviations given in parentheses. Note that C–N bond and N–C–N angle restraints were introduced to stabilize the refinement based on the better single-crystal X-ray diffraction data. The N–H bond length restraints were introduced according to the single-crystal neutron-diffraction study on guanidine.

Bond length (Å)		Bond angle (°)	
Hg1–Cl1	2.921(9)	Cl2–Hg1–Cl3	165.9(4)
Hg1–Cl1	2.867(9)	N1–C1–N1	111.6(20)
Hg1–Cl2	2.325(9)	N1–C1–N2	124.2(10)
Hg1–Cl3	2.270(7)	C1–N1–H1	119.7(23)
C1–N1	1.287(8)	C1–N1–H2	119.1(24)
C1–N2	1.300(9)	C1–N2–H3	118.3(16)
N1–H1	0.994(13)	H1–N1–H2	120.7(23)
N1–H2	1.001(13)	H3–N2–H3	123(3)
N2–H3	1.050(9)		