

From achiral tetrazolate-based tectons to chiral coordination networks: Effects of substituents on the structures and NLO properties

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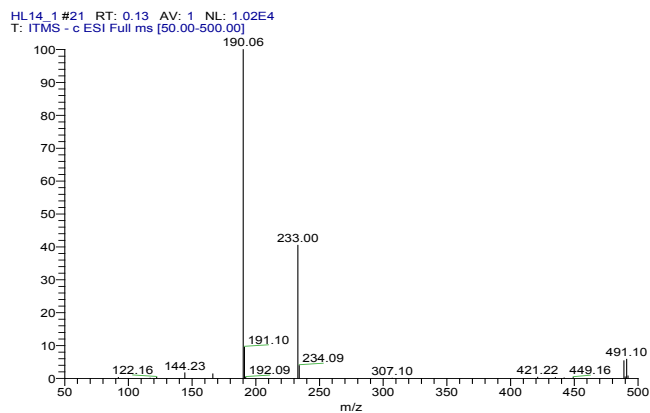


Figure S1. The MS of the H-NTBAN

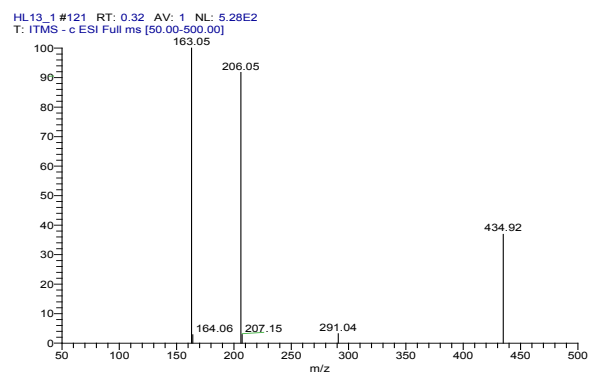


Figure S2. The MS of the H-NTBAF

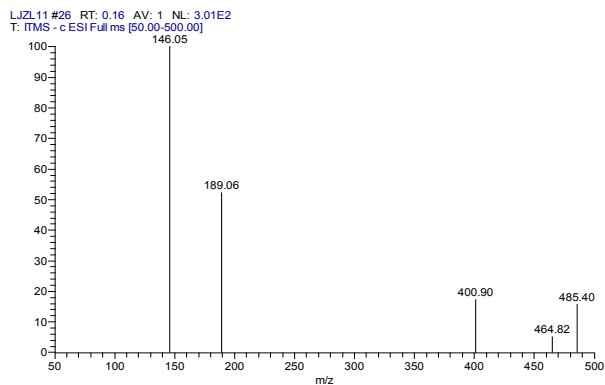


Figure S3. The MS of the H-NTINA

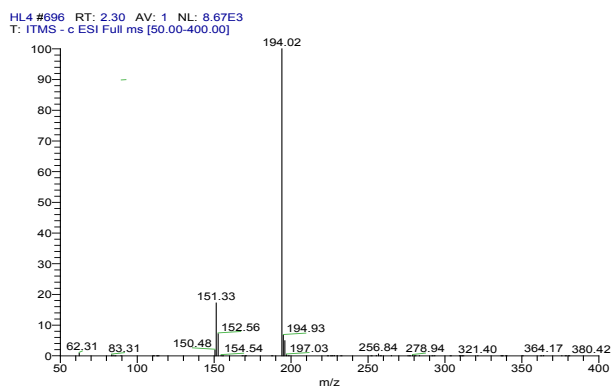


Figure S4. The MS of the H-NTTCA

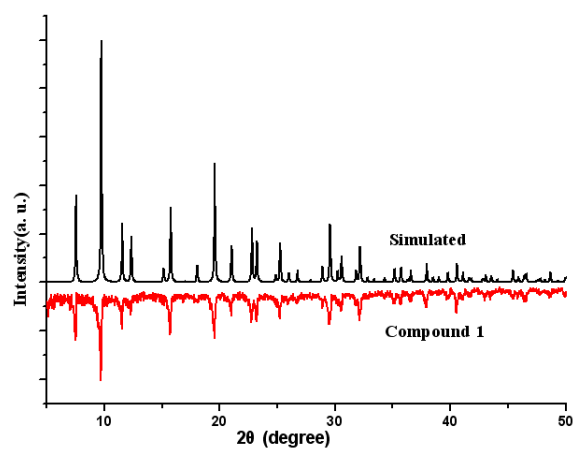


Figure S5. XRD patterns of **1** and the simulated pattern based on the single crystal **1**.

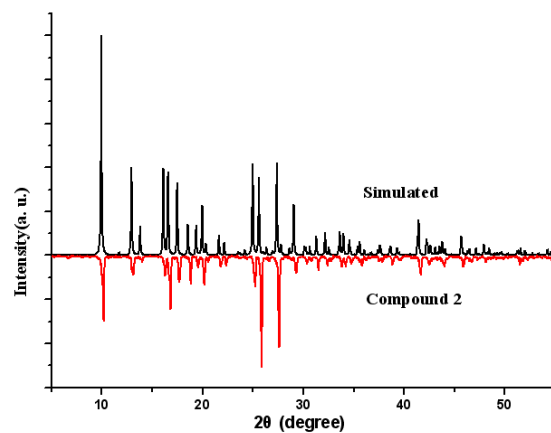


Figure S6. XRD patterns of **2** and the simulated pattern based on the single crystal **2**.

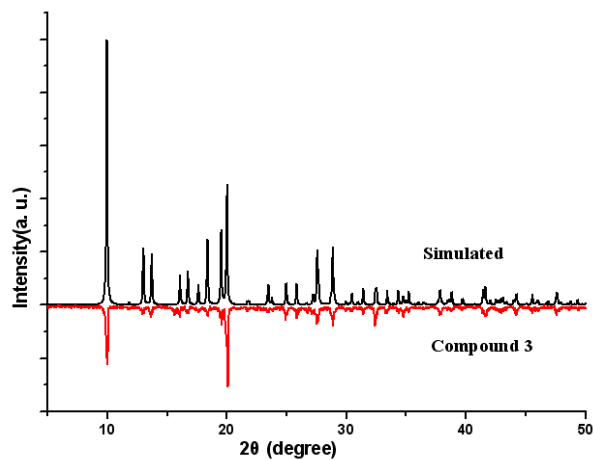


Figure S7. XRD patterns of **3** and the simulated pattern based on the single crystal **3**.

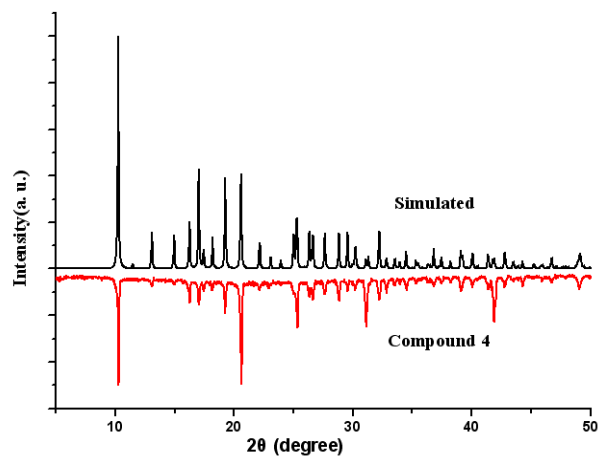


Figure S8. XRD patterns of **4** and the simulated pattern based on the single crystal **4**.

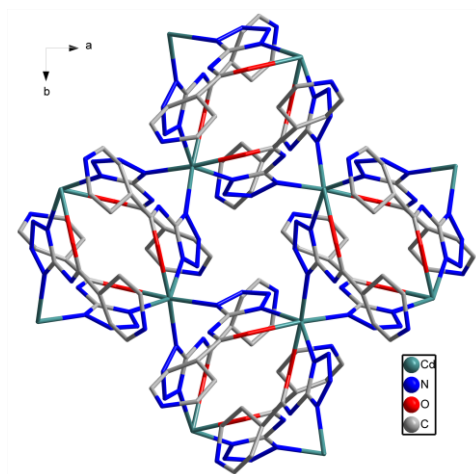


Figure S9. View of the 3D network structure of **3** (All H atoms are also omitted for clarity).

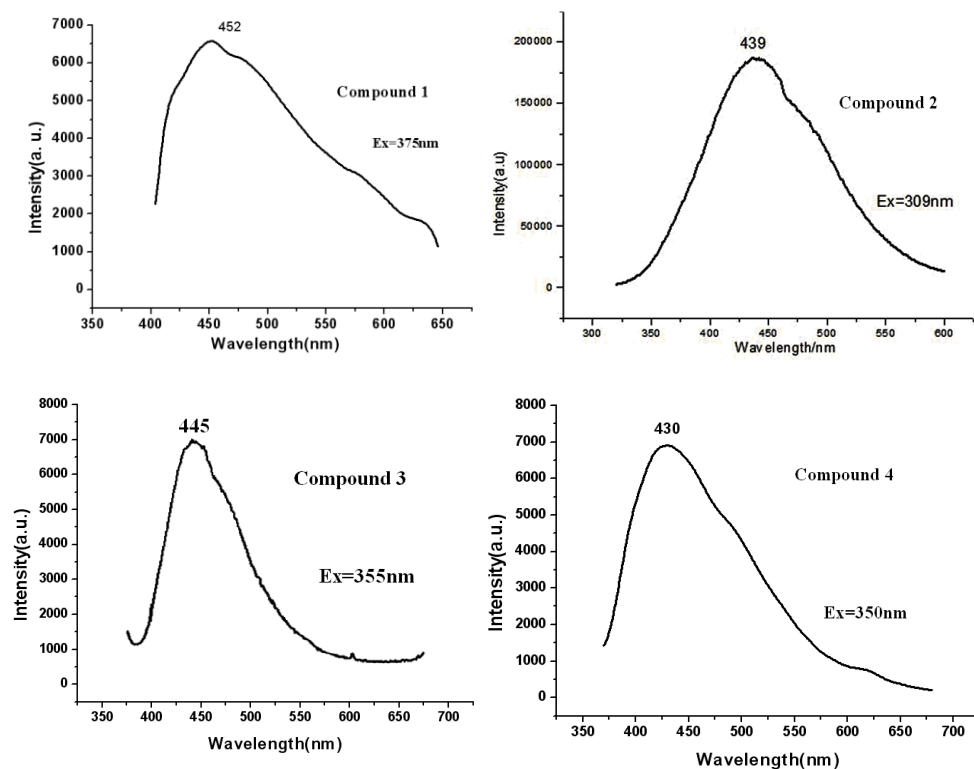


Figure S10. Luminescent spectra of compounds 1-4.

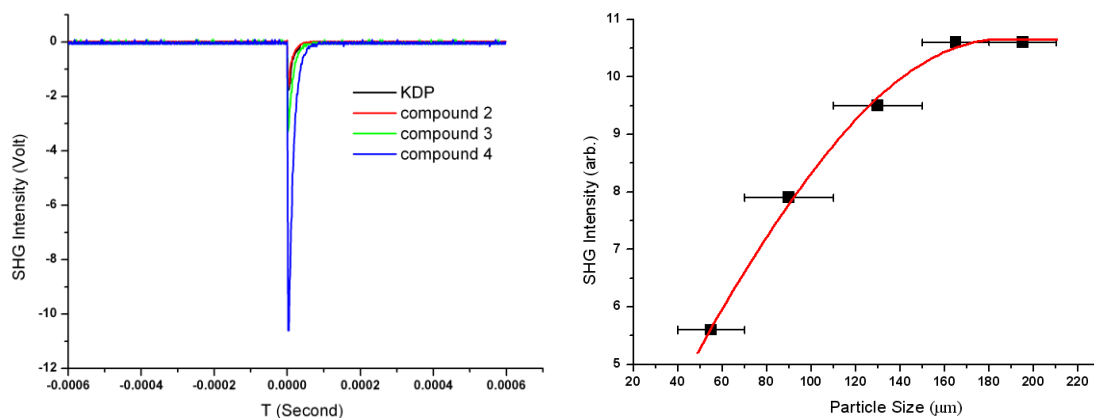


Figure S11. Oscilloscope traces of the SHG signals of KDP and compounds 2~4 at the same particle size of 150–180 μm (left) and the phase-matching curve for compound 4 (The curve drawn is to guide the eye and not a fit to the data) (right).

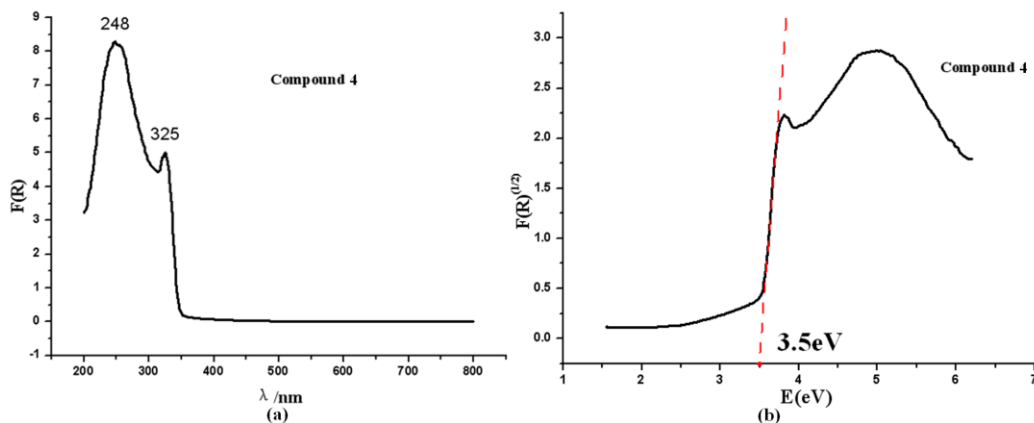


Figure S12. UV absorption spectra (a) and optical diffuse reflectance spectra (b) for compound 4.

Theoretical Calculations

Computational Descriptions. Single crystal structural data of our three compounds were used for the theoretical calculations. The momentum matrix elements and energy eigenvalues were calculated with density functional theory (DFT) using Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation performed by CASTEP code.^{1S,2S} The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential.^{3S} The following orbital electrons were treated as valence electrons: Cd, $4d^{10}5s^2$; C, $2s^22p^2$; N, $2s^22p^3$; O, $2s^22p^4$; S, $3s^23p^4$ and H, $1s^1$. The numbers of plane waves included in the basis sets were determined by cutoff energy of 800eV for all three compounds and the numerical integration of the Brillouin zone was performed using a Monkhorst-Pack k-point sampling of $2 \times 2 \times 2$. The parameters and convergent criteria were the default values of CASTEP code.

To evaluate the second harmonic generation (SHG) coefficients, we have adapted the formalism proposed by Rashkeev^{4S} and later improved by Lin.^{5S} This sum-over-states type formalism is explicitly expressed with terms having momentum matrix elements in numerator and energy eigenvalue difference in denominator. The entire SHG coefficient of a molecule or a crystal are divided into contribution from virtual hole (VH), virtual electron (VE), and two-band processes. The contribution from two-band process is extremely small and can be neglected. Furthermore, because DFT-GGA fails to correctly predict the CB energies, so the CB energy should be corrected by adding a scissor operator, and meanwhile, the momentum matrix elements were also renormalized in the present work.^{6S} (Seeing in Table 1S, Table 2S and Table 3S).

Table S1 Optics of compound **2**

ABC	VE(pm/V)	VH(pm/V)	X ⁽²⁾ (pm/V)	d _{xy}	SHG(10 ⁻⁹ esu)
111	-0.0476	0.00132	-0.0463	11	-0.0553
122	0.046	2.78E-4	0.0463	12	0.0553
133	-0.00177	5.48E-5	-0.00172	13	-0.00205
123	-0.062	-0.00637	-0.0683	14	-0.0816
113	-0.0227	-0.00108	-0.0238	15	-0.0284
112	-0.0407	-3.1E-4	-0.041	16	-0.0489
211	-0.0407	-3.1E-4	-0.041	21	-0.0489
222	0.0441	-0.00108	0.0431	22	0.0514
233	0.0562	0.00609	0.0623	23	0.0744
223	0.0209	0.00114	0.022	24	0.0263
213	-0.062	-0.00637	-0.0683	25	-0.0816
212	0.046	2.78E-4	0.0463	26	0.0553
311	-0.0227	-0.00108	-0.0238	31	-0.0284
322	0.0209	0.00114	0.022	32	0.0263
333	-8.47E-5	-8.33E-4	-9.18E-4	33	-0.0011
323	0.0562	0.00609	0.0623	34	0.0744
313	-0.00177	5.48E-5	-0.00172	35	-0.00205
312	-0.062	-0.00637	-0.0683	36	-0.0816

Table S2 Optics of compound **3**

ABC	VE(pm/V)	VH(pm/V)	X ⁽²⁾ (pm/V)	d _{xy}	SHG(10 ⁻⁹ esu)
111	-2.53E-03	-2.03E-04	-2.73E-03	11	-3.26E-03
122	1.80E-02	5.54E-04	1.86E-02	12	2.22E-02
133	-1.71E-02	1.46E-03	-1.56E-02	13	-1.87E-02
123	9.65E-05	-1.57E-04	-6.00E-05	14	-2.58E-02
113	-1.34E-02	-3.41E-03	-1.68E-02	15	-2.01E-02
112	-2.09E-02	-7.66E-04	-2.16E-02	16	-7.16E-05

211	-2.09E-02	-7.66E-04	-2.16E-02	21	-7.16E-05
222	3.32E-03	3.97E-04	3.72E-03	22	4.44E-03
233	1.54E-02	-2.08E-03	1.33E-02	23	1.58E-02
223	1.18E-02	3.51E-03	1.53E-02	24	1.83E-02
213	9.65E-05	-1.57E-04	-6.00E-05	25	-2.58E-02
212	1.80E-02	5.54E-04	1.86E-02	26	2.22E-02
311	-1.34E-02	-3.41E-03	-1.68E-02	31	-2.01E-02
322	1.18E-02	3.51E-03	1.53E-02	32	1.83E-02
333	2.22E-03	-5.11E-04	1.71E-03	33	2.04E-03
323	1.54E-02	-2.08E-03	1.33E-02	34	1.58E-02
313	-1.71E-02	1.46E-03	-1.56E-02	35	-1.87E-02
312	9.65E-05	-1.57E-04	-6.00E-05	36	-2.58E-02

Table S3 Optics of compound **4**

ABC	VE(pm/V)	VH(pm/V)	X ⁽²⁾ (pm/V)	d _{xy}	SHG(10 ⁻⁹ esu)
111	0.04862	0.0022	0.05081	11	0.06065
122	-0.05327	-0.00285	-0.05612	12	-0.06699
133	-0.00212	1.553E-4	-0.00196	13	-0.00234
123	-4.53	-2.717	-7.247	14	-8.65
113	-0.02116	1.525E-4	-0.02101	15	-0.02508
112	-0.01005	-0.00212	-0.01217	16	-0.01453
211	-0.01005	-0.00212	-0.01217	21	-0.01453
222	0.04394	-0.0025	0.04145	22	0.04947
233	-0.0372	-3.38E-4	-0.03754	23	-0.0448
223	0.01825	0.00466	0.02292	24	0.02735
213	-4.53	-2.717	-7.247	25	-8.65
212	-0.05327	-0.00285	-0.05612	26	-0.06699
311	-0.02116	1.525E-4	-0.02101	31	-0.02508
322	0.01825	0.00466	0.02292	32	0.02735
333	0.05056	-0.00233	0.04823	33	0.05757
323	-0.0372	-3.38E-4	-0.03754	34	-0.0448

313	-0.00212	1.553E-4	-0.00196	35	-0.00234
312	-4.53	-2.717	-7.247	36	-8.65

Table S4. Selected bond lengths (Å) and angles (°) for compounds **1-4**.[#]

Compound 1			
Cd1—N4 ⁱ	2.330 (3)	Cd2—N3	2.299 (3)
Cd1—N4 ⁱⁱ	2.330 (3)	Cd2—N3 ^{iv}	2.299 (3)
Cd1—N4 ⁱⁱⁱ	2.330 (3)	Cd2—N3 ⁱⁱ	2.299 (3)
Cd1—N4	2.330 (3)	Cd2—O1 ⁱⁱ	2.305 (2)
Cd1—N4 ^{iv}	2.330 (3)	Cd2—O1 ^{iv}	2.305 (2)
Cd1—N4 ^v	2.330 (3)	Cd2—O1	2.305 (2)
N4 ⁱ —Cd1—N4 ⁱⁱ	180.00 (10)	N4 ⁱⁱⁱ —Cd1—N4 ^{iv}	180.00 (10)
N4 ⁱ —Cd1—N4 ⁱⁱⁱ	87.20 (10)	N4—Cd1—N4 ^{iv}	87.20 (10)
N4 ⁱⁱ —Cd1—N4 ⁱⁱⁱ	92.80 (10)	N4 ⁱ —Cd1—N4 ^v	87.20 (10)
N4 ⁱ —Cd1—N4	92.80 (10)	N4 ⁱⁱ —Cd1—N4 ^v	92.80 (10)
N4 ⁱⁱ —Cd1—N4	87.20 (10)	N4 ⁱⁱⁱ —Cd1—N4 ^v	87.20 (10)
N4 ⁱⁱⁱ —Cd1—N4	92.80 (10)	N4—Cd1—N4 ^v	180.00 (12)
N4 ⁱ —Cd1—N4 ^{iv}	92.80 (10)	N4 ^{iv} —Cd1—N4 ^v	92.80 (10)
N4 ⁱⁱ —Cd1—N4 ^{iv}	87.20 (10)	N3—Cd2—N3 ^{iv}	89.30 (9)
N3—Cd2—N3 ⁱⁱ	89.30 (9)	N3 ⁱⁱ —Cd2—O1 ^{iv}	135.80 (10)
N3 ^{iv} —Cd2—N3 ⁱⁱ	89.30 (9)	O1 ⁱⁱ —Cd2—O1 ^{iv}	84.15 (9)
N3—Cd2—O1 ⁱⁱ	135.80 (10)	N3—Cd2—O1	75.14 (9)
N3 ^{iv} —Cd2—O1 ⁱⁱ	130.56 (10)	N3 ^{iv} —Cd2—O1	135.80 (10)
N3 ⁱⁱ —Cd2—O1 ⁱⁱ	75.14 (9)	N3 ⁱⁱ —Cd2—O1	130.56 (10)
N3—Cd2—O1 ^{iv}	130.56 (10)	O1 ⁱⁱ —Cd2—O1	84.15 (9)
N3 ^{iv} —Cd2—O1 ^{iv}	75.14 (9)		
Compound 2			
Cd1—N4 ⁱ	2.288 (2)	Cd1—N1 ⁱⁱⁱ	2.314 (2)
Cd1—N4 ⁱⁱ	2.288 (2)	Cd1—O1 ⁱⁱ	2.364 (2)
Cd1—N1	2.314 (2)	Cd1—O1 ⁱ	2.364 (2)
N4 ⁱ —Cd1—N4 ⁱⁱ	141.65 (11)	N1—Cd1—O1 ⁱⁱ	172.16 (8)
N4 ⁱ —Cd1—N1	106.07 (8)	N1 ⁱⁱⁱ —Cd1—O1 ⁱⁱ	92.12 (9)
N4 ⁱⁱ —Cd1—N1	100.11 (8)	N4 ⁱ —Cd1—O1 ⁱ	72.73 (8)
N4 ⁱ —Cd1—N1 ⁱⁱⁱ	100.11 (8)	N4 ⁱⁱ —Cd1—O1 ⁱ	78.84 (8)
N4 ⁱⁱ —Cd1—N1 ⁱⁱⁱ	106.07 (8)	N1—Cd1—O1 ⁱ	92.12 (9)
N1—Cd1—N1 ⁱⁱⁱ	92.99 (12)	N1 ⁱⁱⁱ —Cd1—O1 ⁱ	172.16 (8)
N4 ⁱ —Cd1—O1 ⁱⁱ	78.84 (8)	O1 ⁱⁱ —Cd1—O1 ⁱ	83.44 (14)
N4 ⁱⁱ —Cd1—O1 ⁱⁱ	72.73 (8)		
Compound 3			

Cd1—N1 ⁱ	2.265 (5)	Cd1—N4	2.312 (5)
Cd1—N1 ⁱⁱ	2.265 (5)	Cd1—O1 ⁱⁱ	2.404 (5)
Cd1—N4 ⁱⁱⁱ	2.312 (5)	Cd1—O1 ⁱ	2.404 (5)
N1 ⁱ —Cd1—N1 ⁱⁱ	141.1 (3)	N1 ⁱⁱ —Cd1—O1 ⁱⁱ	72.07 (17)
N1 ⁱ —Cd1—N4 ⁱⁱⁱ	104.89 (18)	N4 ⁱⁱⁱ —Cd1—O1 ⁱⁱ	169.82 (19)
N1 ⁱⁱ —Cd1—N4 ⁱⁱⁱ	100.68 (18)	N4—Cd1—O1 ⁱⁱ	92.2 (2)
N1 ⁱ —Cd1—N4	100.68 (18)	N1 ⁱ —Cd1—O1 ⁱ	72.07 (17)
N1 ⁱⁱ —Cd1—N4	104.89 (18)	N1 ⁱⁱ —Cd1—O1 ⁱ	78.24 (19)
N4 ⁱⁱⁱ —Cd1—N4	96.7 (3)	N4 ⁱⁱⁱ —Cd1—O1 ⁱ	92.2 (2)
N1 ⁱ —Cd1—O1 ⁱⁱ	78.24 (19)	N4—Cd1—O1 ⁱ	169.82 (19)
O1 ⁱⁱ —Cd1—O1 ⁱ	79.5 (3)		

Compound 4

Cd1—N1	2.213 (2)	Cd1—N4 ⁱⁱ	2.288 (2)
Cd1—N6 ⁱ	2.215 (2)	Cd1—O1	2.4278 (19)
Cd1—N9	2.287 (2)	Cd1—O2 ⁱ	2.600 (2)
N1—Cd1—N6 ⁱ	139.80 (9)	N9—Cd1—O1	76.60 (8)
N1—Cd1—N9	103.05 (9)	N4 ⁱⁱ —Cd1—O1	163.95 (8)
N6 ⁱ —Cd1—N9	111.04 (9)	N1—Cd1—O2 ⁱ	75.34 (8)
N1—Cd1—N4 ⁱⁱ	108.74 (8)	N6 ⁱ —Cd1—O2 ⁱ	71.76 (8)
N6 ⁱ —Cd1—N4 ⁱⁱ	93.80 (9)	N9—Cd1—O2 ⁱ	176.22 (8)
N9—Cd1—N4 ⁱⁱ	87.35 (9)	N4 ⁱⁱ —Cd1—O2 ⁱ	89.94 (9)
N1—Cd1—O1	75.34 (8)	O1—Cd1—O2 ⁱ	106.08 (8)
N6 ⁱ —Cd1—O1	92.15 (8)		

[#]Symmetry Code: **1**) (i) $y, -x+y, -z+1$; (ii) $-y, x-y, z$; (iii) $x-y, x, -z+1$; (iv) $-x+y, -x, z$; (v) $-x, -y, -z+1$. **2**) (i) $-y+3/2, x-1/2, z-1/4$; (ii) $x-1/2, -y+3/2, -z+1/4$; (iii) $y, x, -z$. **3**) (i) $-x-3/2, y+1/2, -z+1/4$; (ii) $y+1/2, -x-3/2, z-1/4$; (iii) $y, x, -z$. **4**) (i) $-x-1, y-1/2, -z-1/2$; (ii) $x-1/2, -y-1/2, -z$.

References

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