Electronic Supplementary Information (ESI)

Designing a Novel Perovskite-Type $KCd(NH_2SO_3)_3$ with Deep-Ultraviolet Transparency and Strong Second-harmonic Generation Response

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Table S1. Crystal Data and Structure Refinement of $KCd(NH_2SO_3)_3$

Formula	$KCd(NH_2SO_3)_3$
Formula weight	204.07
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
space group	$P6_3$
a (Å)	8.559(4)
b (Å)	8.559(4)
c (Å)	7.949(4)
α (deg.)	90
β (deg.)	90
γ (deg.)	120
V ($Å^3$)	504.3(5)
Z	4
Calculated density (mg/m^3)	2.688
Absorption coefficient (mm^{-1})	5.394
F(000)	375
Theta range (deg.)	2.748 to 27.483
Limiting indices	-11<=h<=11
	-11<=k<=11
	-10<=l<=8
Reflections collected / unique	3022 / 253
R(int)	0.0432
Completeness to θ = 25.242 (%)	100.0
Goodness-of-fit on F^2	1.052
R/wR (I>2σ(I))	R1 = 0.0168
	wR2 = 0.0389
R/wR (all data)	R1 = 0.0174,
	wR2 = 0.0390
Absolute structure parameter	0.03(3)
$^{a}R_1 = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	
$^{b}{}_{w}R_2(F_o^2) = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$	

Table S2. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $KCd(NH_2SO_3)_3$.

Atom	x	y	z	U(eq)	BVS
Cd(01)	6667	3333	7380(1)	13(1)	2.023
S(002)	3645(1)	3124(1)	4140(1)	14(1)	5.938
K(003)	0	0	6686(2)	24(1)	1.091
O(004)	1747(4)	2533(4)	4200(5)	22(1)	1.925
O(005)	4236(4)	2596(4)	5650(4)	25(1)	1.933
O(006)	4211(4)	2653(5)	2607(5)	31(1)	1.731
N(007)	4665(5)	5393(4)	4111(5)	21(1)	4.217

Table S3. Bond lengths [A] and angles [deg] for $KCd(NH_2SO_3)_3$.

Cd(01)-O(005)#1	2.303(3)	O(005)#2-Cd(01)-N(007)#3	84.05(14)
Cd(01)-O(005)#2	2.303(3)	O(005)-Cd(01)-N(007)#3	169.00(12)
Cd(01)-O(005)	2.303(3)	O(005)-Cd(01)-N(007)#5	99.27(11)
Cd(01)-N(007)#3	2.371(4)	N(007)#3-Cd(01)-N(007)#4	89.73(15)
Cd(01)-N(007)#4	2.371(4)	N(007)#3-Cd(01)-N(007)#5	89.73(15)
Cd(01)-N(007)#5	2.371(4)	N(007)#5-Cd(01)-N(007)#4	89.73(15)
S(002)-K(003)	3.5548(19)	K(003)#6-S(002)-K(003)	68.42(4)
S(002)-K(003)#6	3.5135(19)	O(004)-S(002)-K(003)	46.00(13)
S(002)-O(004)	1.440(3)	O(004)-S(002)-K(003)#6	48.30(15)
S(002)-O(005)	1.459(3)	O(004)-S(002)-O(005)	111.6(2)
S(002)-O(006)	1.441(4)	O(004)-S(002)-O(006)	114.0(2)
S(002)-N(007)	1.684(3)	O(004)-S(002)-N(007)	104.44(16)
K(003)-O(004)#5	2.773(4)	O(005)-S(002)-K(003)	66.97(13)
K(003)-O(004)#7	2.773(4)	O(005)-S(002)-K(003)#6	122.30(13)
K(003)-O(004)#8	2.773(4)	O(005)-S(002)-N(007)	107.95(18)
K(003)-O(004)#9	2.757(4)	O(006)-S(002)-K(003)#6	67.20(15)
K(003)-O(004)	2.757(4)	O(006)-S(002)-K(003)	124.20(16)
K(003)-O(004)#10	2.757(4)	O(006)-S(002)-O(005)	113.03(19)
K(003)-O(005)#10	3.272(3)	O(006)-S(002)-N(007)	104.9(2)
K(003)-O(005)	3.272(3)	N(007)-S(002)-K(003)#6	128.38(14)
K(003)-O(005)#9	3.272(3)	N(007)-S(002)-K(003)	129.00(15)
K(003)-O(006)#8	3.240(4)	O(004)#10-K(003)-O(004)#7	105.96(7)
K(003)-O(006)#5	3.240(4)	O(004)-K(003)-O(004)#8	105.96(7)
K(003)-O(006)#7	3.240(4)	O(004)#5-K(003)-O(004)#7	73.79(11)
N(007)-H(00A)	0.89	O(004)#10-K(003)-O(004)	74.29(12)
N(007)-H(00B)	0.89	O(004)-K(003)-O(004)#5	105.96(7)
O(005)#1-Cd(01)-O(005)#2	88.00(12)	O(004)#9-K(003)-O(004)	74.29(12)
O(005)#1-Cd(01)-O(005)	88.00(12)	O(004)#9-K(003)-O(004)#8	179.68(12)
O(005)#2-Cd(01)-O(005)	88.00(12)	O(004)#10-K(003)-O(004)#5	179.68(12)
O(005)#1-Cd(01)-N(007)#5	84.05(13)	O(004)#8-K(003)-O(004)#7	73.79(11)
O(005)-Cd(01)-N(007)#4	84.05(13)	O(004)#9-K(003)-O(004)#7	105.96(7)
O(005)#1-Cd(01)-N(007)#4	169.00(12)	O(004)-K(003)-O(004)#7	179.68(12)
O(005)#2-Cd(01)-N(007)#5	169.00(12)	O(004)#9-K(003)-O(004)#5	105.96(7)
O(005)#1-Cd(01)-N(007)#3	99.27(11)	O(004)#10-K(003)-O(004)#8	105.96(7)
O(005)#2-Cd(01)-N(007)#4	99.27(11)	O(004)#10-K(003)-O(004)#9	74.29(12)
O(004)#7-K(003)-O(005)	133.93(9)	O(004)#7-K(003)-O(006)#5	74.37(10)

O(004)#8-K(003)-O(005)	107.48(9)	O(004)-K(003)-O(006)#7	133.56(10)
O(004)#10-K(003)-O(005)	117.03(11)	O(004)#8-K(003)-O(006)#7	74.37(10)
O(004)#9-K(003)-O(005)#9	45.91(8)	O(004)#5-K(003)-O(006)#7	117.90(11)
O(004)#8-K(003)-O(005)#10	63.27(9)	O(005)#9-K(003)-O(005)#10	113.89(5)
O(004)-K(003)-O(005)#9	117.03(11)	O(005)#10-K(003)-O(005)	113.89(5)
O(004)-K(003)-O(005)	45.91(8)	O(005)#9-K(003)-O(005)	113.89(5)
O(004)#5-K(003)-O(005)#9	107.48(8)	O(006)#8-K(003)-O(005)#10	64.51(9)
O(004)#5-K(003)-O(005)#10	133.93(9)	O(006)#5-K(003)-O(005)	64.51(9)
O(004)#8-K(003)-O(005)#9	133.93(9)	O(006)#7-K(003)-O(005)#10	66.52(9)
O(004)#7-K(003)-O(005)#10	107.48(9)	O(006)#5-K(003)-O(005)#9	66.52(9)
O(004)#7-K(003)-O(005)#9	63.27(9)	O(006)#7-K(003)-O(005)#9	64.51(9)
O(004)#9-K(003)-O(005)	72.54(9)	O(006)#8-K(003)-O(005)#9	178.13(11)
O(004)#10-K(003)-O(005)#10	45.91(8)	O(006)#5-K(003)-O(005)#10	178.13(11)
O(004)#5-K(003)-O(005)	63.27(9)	O(006)#7-K(003)-O(005)	178.13(11)
O(004)#9-K(003)-O(005)#10	117.03(11)	O(006)#8-K(003)-O(005)	66.52(9)
O(004)-K(003)-O(005)#10	72.54(9)	O(006)#8-K(003)-O(006)#5	115.05(5)
O(004)#10-K(003)-O(005)#9	72.54(9)	O(006)#7-K(003)-O(006)#5	115.05(5)
O(004)#9-K(003)-O(006)#8	133.56(10)	O(006)#8-K(003)-O(006)#7	115.05(5)
O(004)#10-K(003)-O(006)#8	105.62(10)	S(002)-O(004)-K(003)#6	108.88(18)
O(004)-K(003)-O(006)#5	105.62(10)	S(002)-O(004)-K(003)	111.92(17)
O(004)-K(003)-O(006)#8	61.80(10)	K(003)-O(004)-K(003)#6	91.91(10)
O(004)#10-K(003)-O(006)#5	133.56(10)	Cd(01)-O(005)-K(003)	125.32(13)
O(004)#5-K(003)-O(006)#8	74.37(10)	S(002)-O(005)-Cd(01)	144.29(19)
O(004)#8-K(003)-O(006)#5	117.90(11)	S(002)-O(005)-K(003)	88.80(14)
O(004)#8-K(003)-O(006)#8	46.61(9)	S(002)-O(006)-K(003)#6	88.59(15)
O(004)#7-K(003)-O(006)#7	46.61(9)	Cd(01)#11-N(007)-H(00A)	108.2
O(004)#7-K(003)-O(006)#8	117.90(11)	Cd(01)#11-N(007)-H(00B)	108.2
O(004)#9-K(003)-O(006)#5	61.80(10)	S(002)-N(007)-Cd(01)#11	116.54(18)
O(004)#10-K(003)-O(006)#7	61.80(10)	S(002)-N(007)-H(00A)	108.2
O(004)#5-K(003)-O(006)#5	46.61(9)	S(002)-N(007)-H(00B)	108.2
O(004)#9-K(003)-O(006)#7	105.62(10)	H(00A)-N(007)-H(00B)	107.3

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,x-y,z #2 -x+y+1,-x+1,z #3 x-y+1,x,z+1/2 #4 -x+1,-y+1,z+1/2 #5 y,-x+y,z+1/2

#6 -x,-y,z-1/2 #7 -x,-y,z+1/2 #8 x-y,x,z+1/2 #9 -x+y,-x,z #10 -y,x-y,z #11 -x+1,-y+1,z-1/2

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $KCd(NH_2SO_3)_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd(01)	15(1)	15(1)	15(1)	0	0	7(1)
S(002)	16(1)	13(1)	16(1)	-1(1)	-3(1)	7(1)
K(003)	28(1)	28(1)	15(1)	0	0	14(1)
O(004)	13(1)	20(2)	32(2)	2(2)	-2(2)	6(1)
O(005)	26(2)	22(2)	26(2)	6(2)	-11(2)	11(2)
O(006)	39(2)	36(2)	24(2)	-4(2)	5(2)	24(2)
N(007)	22(2)	13(2)	27(2)	0(2)	-7(2)	7(2)

Table S5. The degree of distortion, dipole moment, and hyperpolarizability of the [CdN_3O_3] octahedral unit with different N-Cd-O bond angles.

[CdN_3O_3] Unit	Bond angle(°)	Distortion	Dipole moment (D)	Hyperpolarizability
1	169.007	0.2174	7.5713	512.71
2	180.000	0.0482	6.9678	667.01

Table S6. Cd-based UV/DUV NLO Crystal ($\lambda_{cut\text{-}off}$ < 300nm).

Cmpound	SHG(×KDP)	$\lambda_{cut\text{-}off}$(nm)	Crystal Size(mm^3)
$LiCd(IO_3)_3$[1]	12	297	\
$Cd_2(IO_3)(PO_4)$[2]	4	243	\
$KCdCO_3F$[3]	2.84	235	\
$RbCdCO_3F$[3]	4.58	233	\
$Cd_{1.62}Mg_{0.38}(IO_3)(PO_4)$[2]	3.5	231	\
$Cd(NH_2SO_3)_2{\cdot}2H_2O$[4]	0.15	210	1.5×1.5×2.7
$K_7CdGd_2B_{15}O_{30}$[5]	1.7	206	\
$K_7CdSc_2B_{15}O_{30}$[5]	1.5	200	\
$K_7CdY_2B_{15}O_{30}$[5]	1.6	200	
$Cd(NH_4)_2(PO_3F)_2{\cdot}2H_2O$[6]	0.78	<200	0.3 × 5 × 0.1
$CsLiCdP_2O_7$[7]	1.5	<200	0.11×0.09 ×0.08
$K_7CdLu_2B_{15}O_{30}$[5]	1.9	192	\
$RbCdP_3O_9$[8]	0.1	<190	\
$KCd(NH_2SO_3)_3$*	1.1	<190	20×17×5

* This work.

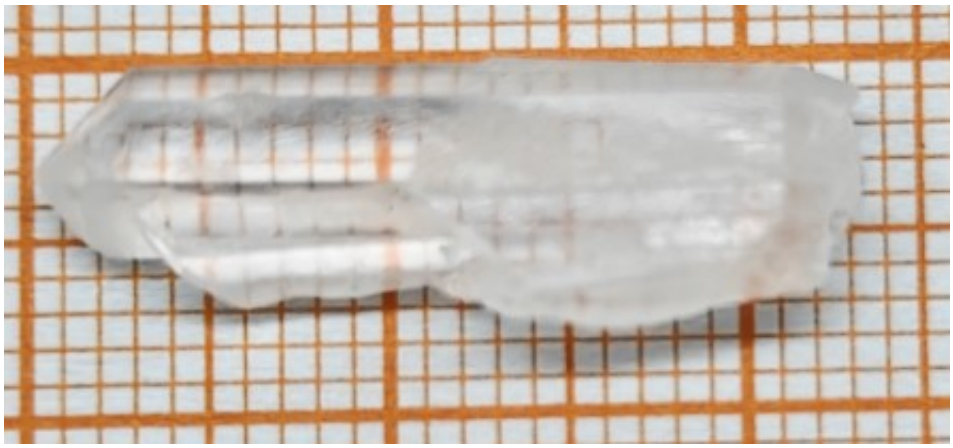

Figure S1. Photograph of $KCd(NH_2SO_3)_3$ crystal.

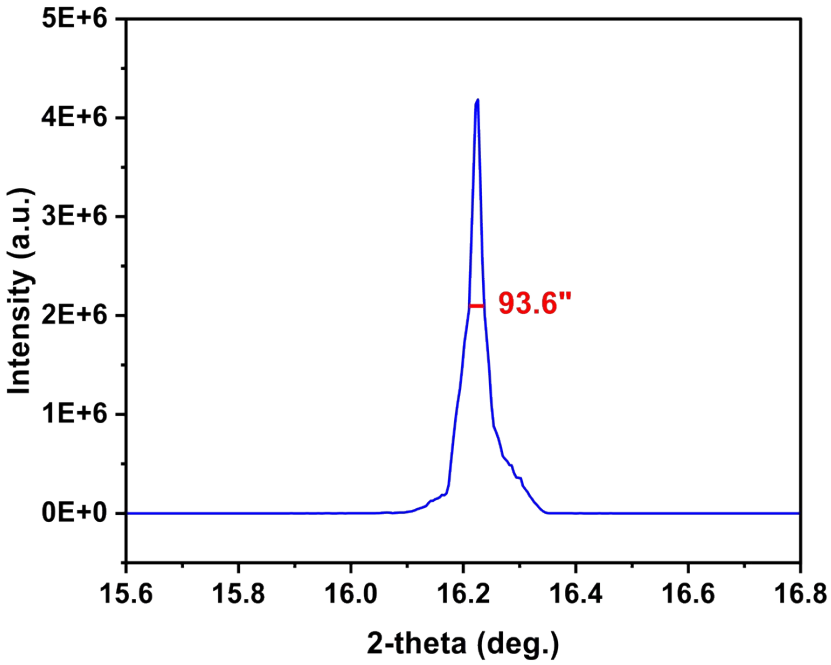

Figure S2. The rocking curve of $KCd(NH_2SO_3)_3$ single crystal

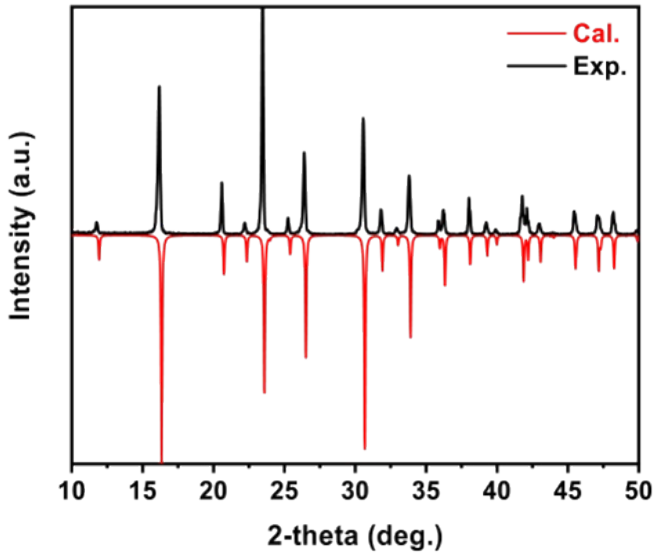

Figure S3. Calculated and experimental powder X-ray diffraction patterns of $KCd(NH_2SO_3)_3$. No obvious impurity peaks were found, confirming the phase purity.

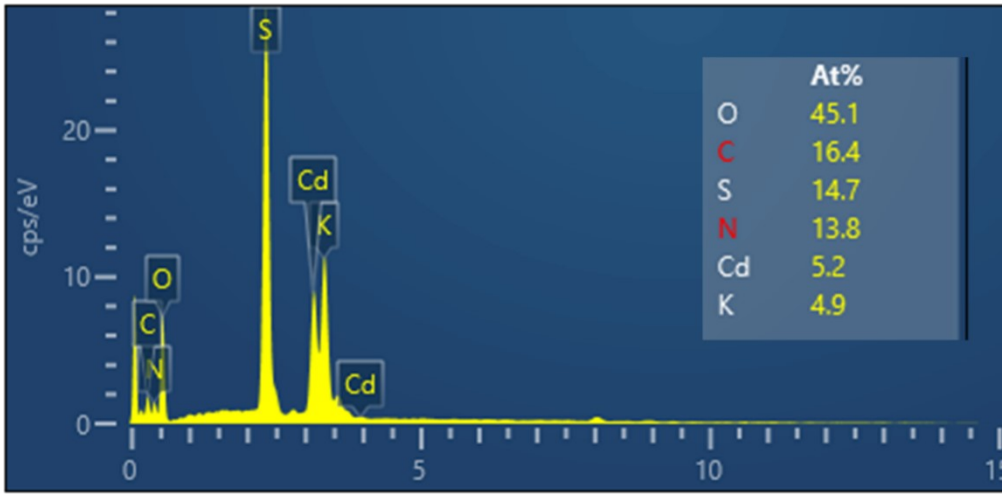

Figure S4. Energy dispersive X-ray spectroscopy analysis of $KCd(NH_2SO_3)_3$.

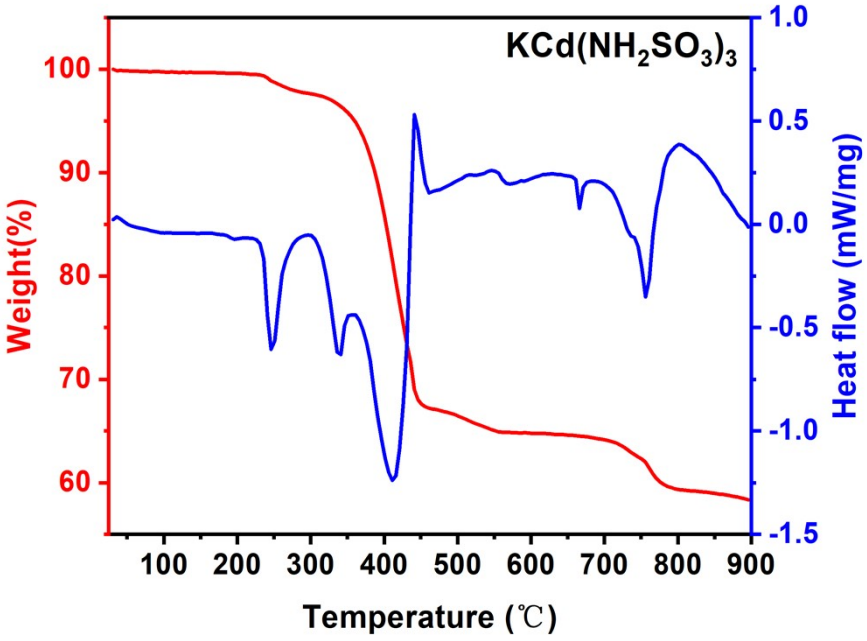

Figure S5. TG-DSC curves of $KCd(NH_2SO_3)_3$.

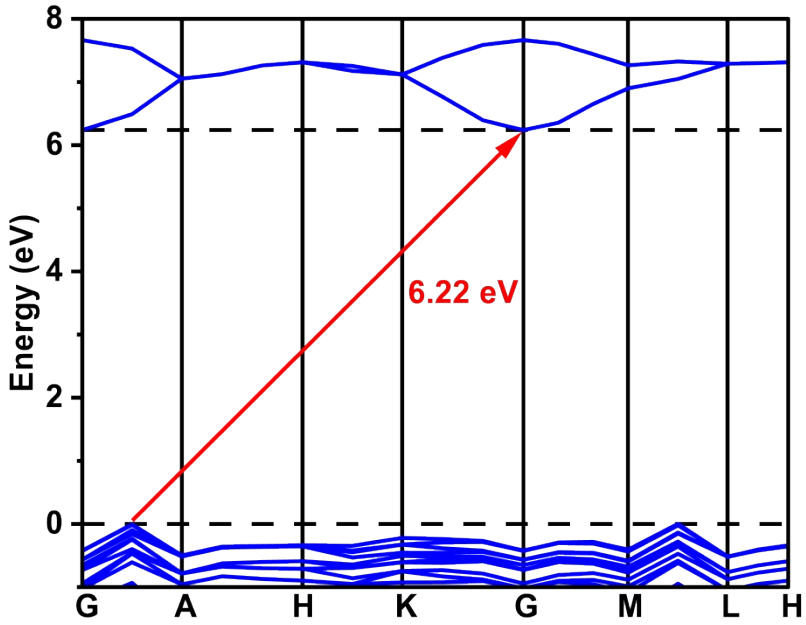

Figure S6. The calculated band structure of $KCd(NH_2SO_3)_3$.

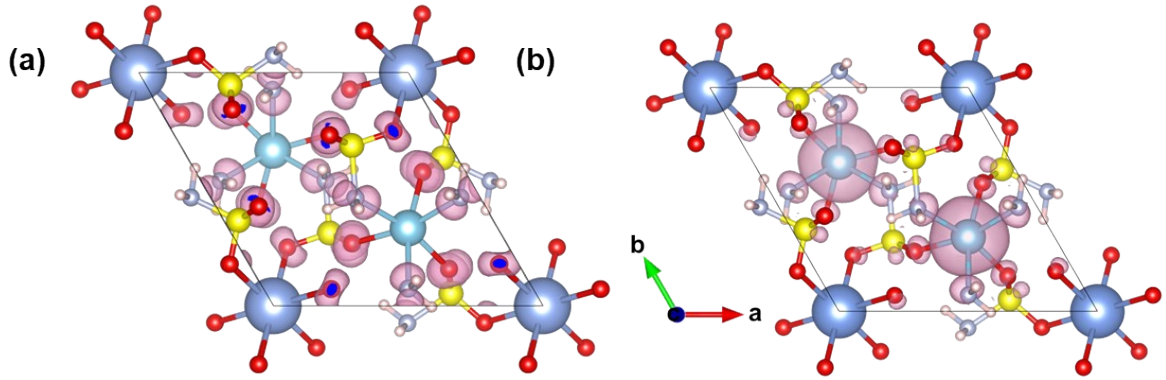

Figure S7. The SHG density of d_{33} in occupied state and unoccupied state for $KCd(NH_2SO_3)_3$.

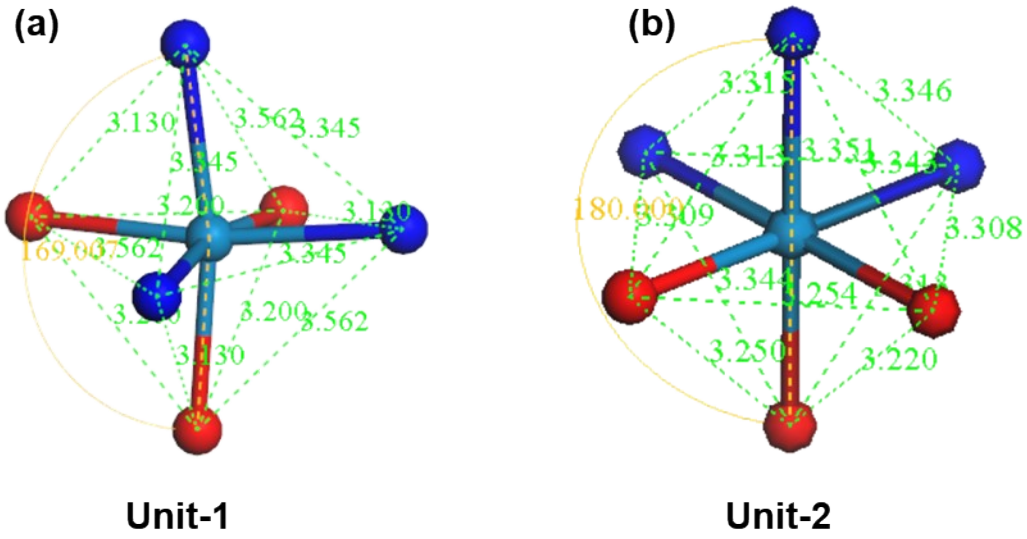

Figure S8. $KCd(NH_2SO_3)_3$ the $[CdN_3O_3]$ octahedral unit with different N-Cd-O bond angles and lengths of the octahedron.

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