Electronic Supplementary Information (ESI) for

$Cd(NH_2SO_3)_2 \cdot xH_2O$ (x = 0, 2): new sulfamates with unique coordination environment and reversible phase transitions

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Table of contents

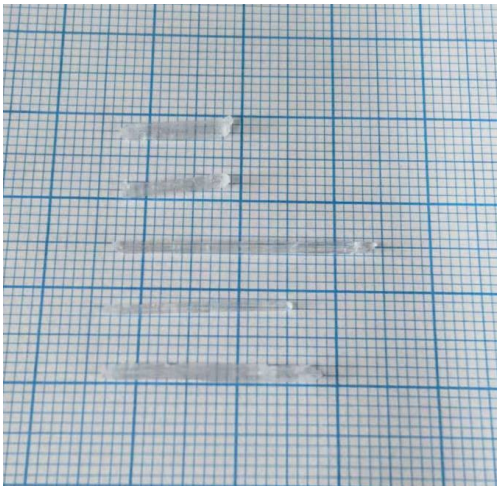
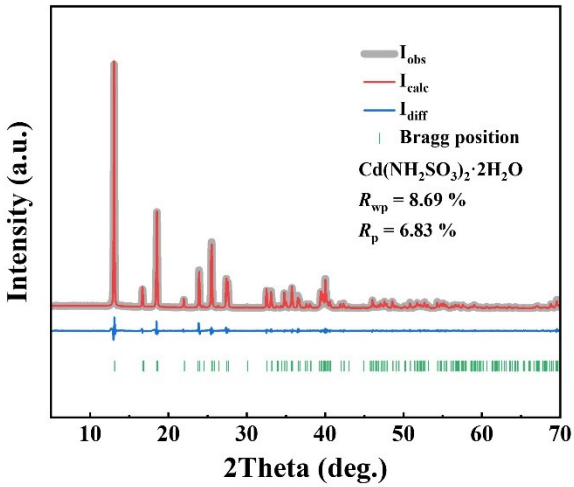


Figure S1. As-grown single crystals of $Cd(SO_3NH_2)_2 \cdot 2H_2O$ with the sizes up to 0.15 × 0.15 × 2.7 cm^3.



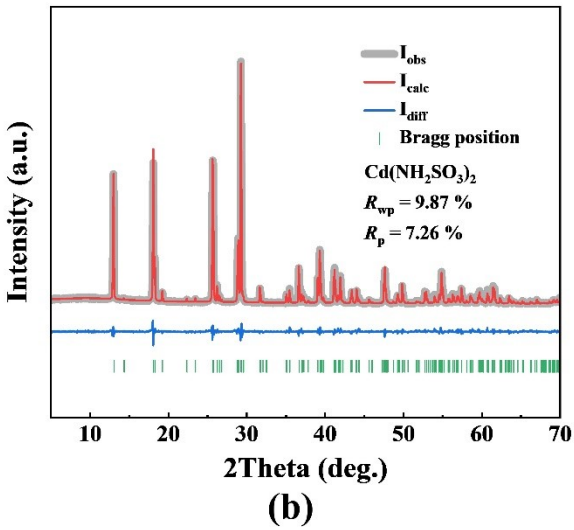


Figure S2. Rietveld refinements results for (a) $Cd(SO_3NH_2)_2 \cdot 2H_2O$ and (b) $Cd(SO_3NH_2)_2$.

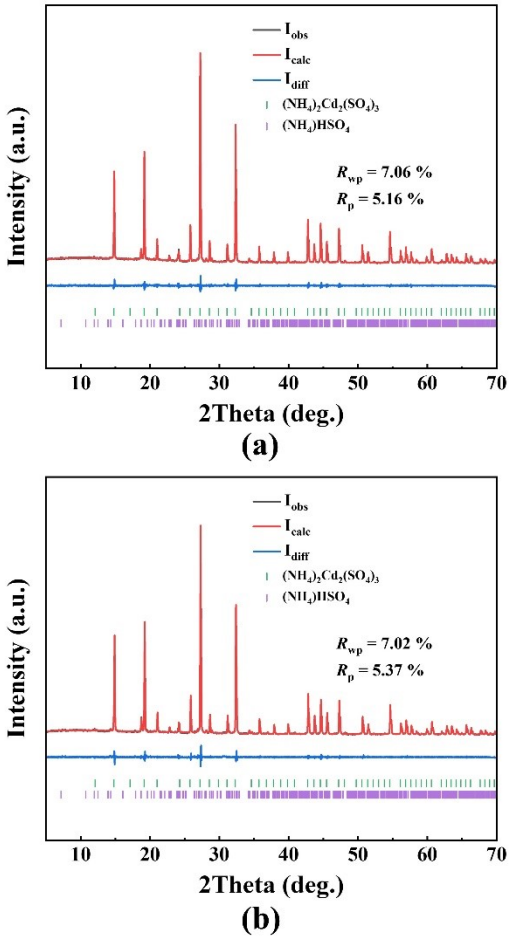


Figure S3. Pawley phase fitting for the annealed (a) $Cd(SO_3NH_2)_2{\cdot}2H_2O$ and (b) $Cd(SO_3NH_2)_2$ samples at 250 °C for 12 h.

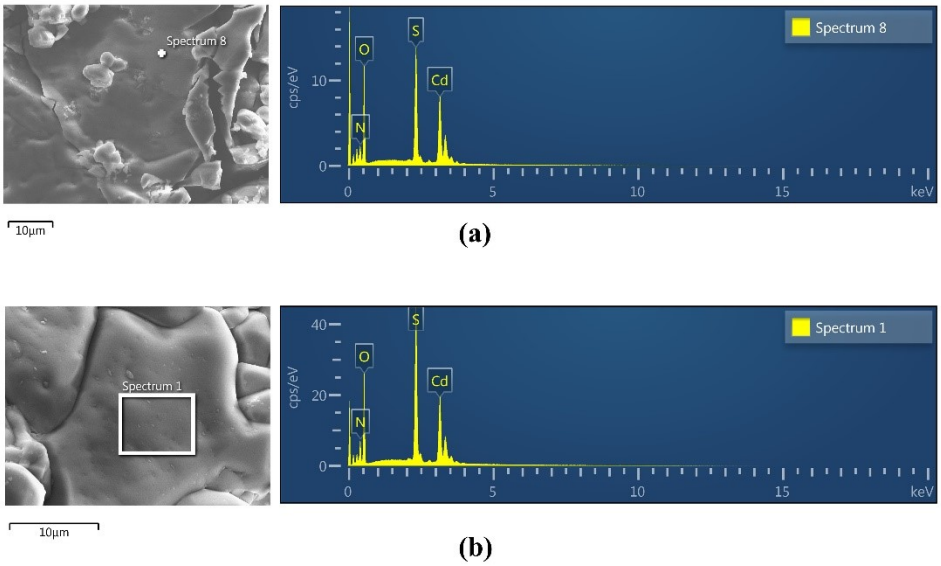


Figure S4. SEM-EDX for (a) $Cd(SO_3NH_2)_2{\cdot}2H_2O$ and (b) $Cd(SO_3NH_2)_2$.

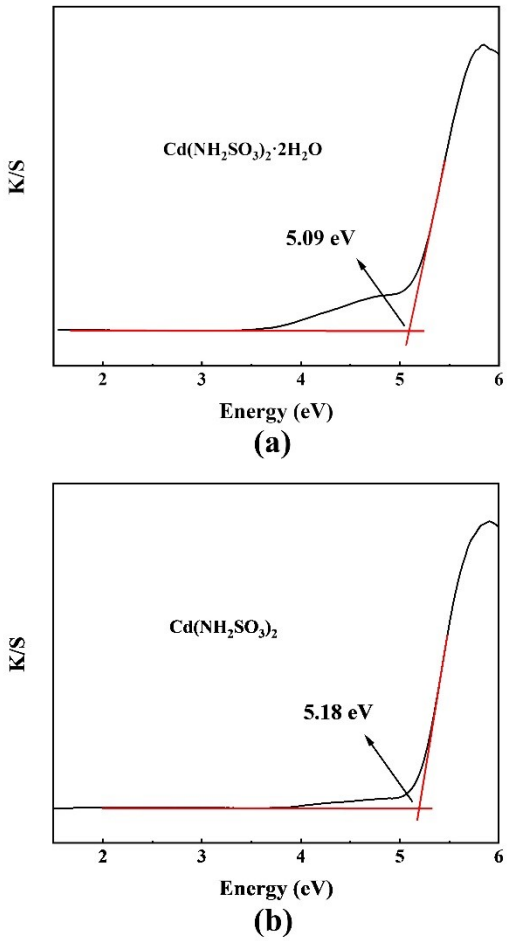


Figure S5. Experimental band gap obtained from the converted UV-vis spectra by using Kubelka-Munk function for (a) $Cd(SO_3NH_2)_2 \cdot 2H_2O$ and (b) $Cd(SO_3NH_2)_2$.

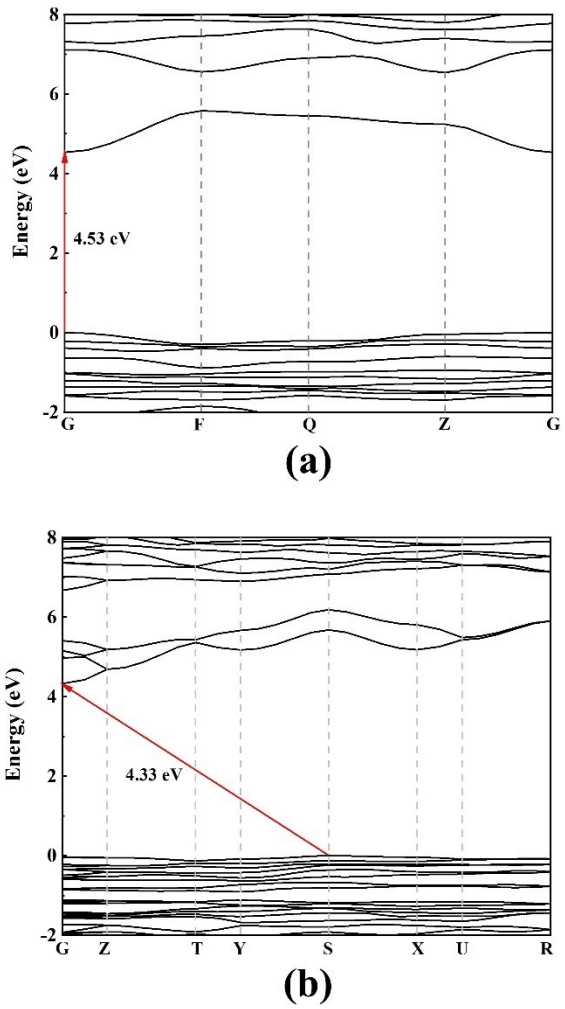


Figure S6. Electronic band structures for (a) $Cd(SO_3NH_2)_2 \cdot 2H_2O$ and (b) $Cd(SO_3NH_2)_2$.

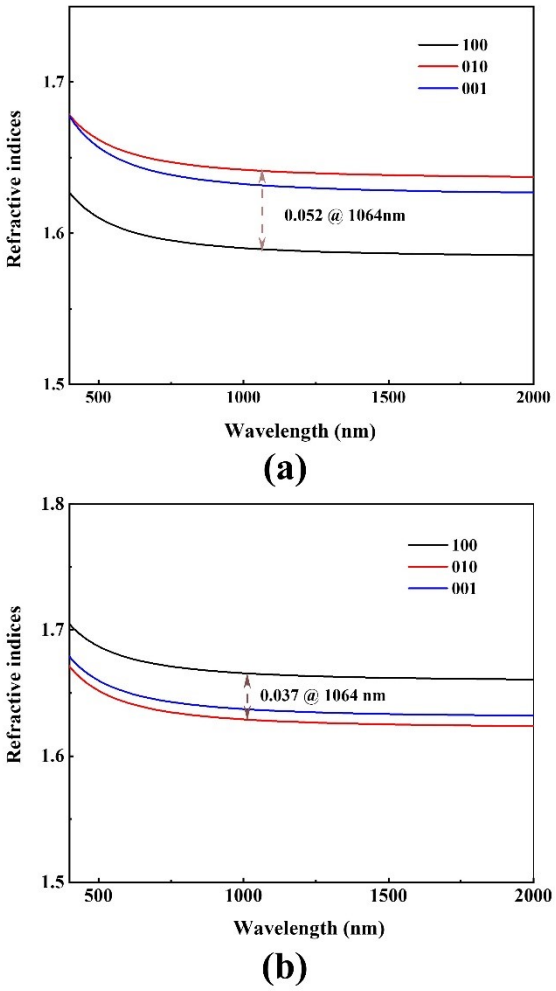


Figure S7. Calculated birefringence for (a) $Cd(SO_3NH_2)_2 \cdot 2H_2O$ and (b) $Cd(SO_3NH_2)_2$.

Table S1. Crystallographic data of $Cd(SO_3NH_2)_2·2H_2O$ and $Cd(SO_3NH_2)_2$.

	$Cd(SO_3NH_2)_2·2H_2O$	**$Cd(SO_3NH_2)_2$**
Formula weight	340.60	304.57
Temp/K	298.0	298.0
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
a/Å	5.4674(5)	6.9140(4)
b/Å	5.4729(5)	6.9380(4)
c/Å	7.1520(6)	13.5784(7)
α/°	102.547(3)	90
β/°	103.452(3)	90
γ/°	94.970(4)	90
V/Å^3	201.03(3)	651.35(6)
Z	1	4
ρ_{calc} g/cm^3	2.813	3.106
μ/mm^{-1}	3.257	3.980
F(000)	166.0	584.0
Crystal size/mm^3	0.112 × 0.101 × 0.046	0.114 × 0.078 × 0.038
2 theta range/°	6.042 to 56.688	6 to 59.172
Index ranges	$-7 \le h \le 7$, $-7 \le k \le 7$, $-9 \le l \le 9$	$-9 \le h \le 9$, $-9 \le k \le 9$, $-18 \le l \le 18$
Reflns collected	9157	23643
Independent reflns	1013 (R_{int} = 0.0730)	1838 (R_{int} = 0.1146)
Data/restraints/param	1013/1/72	1838/4/117
Goof on F^2	1.134	1.110
R_1[a]/wR_2[b] [I≥2σ (I)]	0.0349/0.0536	0.0399/0.0757
R_1[a]/wR_2[b] [all data]	0.0439/0.0558	0.0462/0.0778
Largest diff peak/hole / e Å^{-3}	0.79/-0.68	1.00/-1.07
Flack parameter	N/A	0.08(4)

[a]$R_1 = \Sigma||F_o| - |F_o||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$

Table S2. Fractional atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence sum (BVS) for the non-H atoms in $Cd(SO_3NH_2)_2 \cdot 2H_2O$ and $Cd(SO_3NH_2)_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)	BVS
$Cd(SO_3NH_2)_2 \cdot 2H_2O$					
Cd1	10000	10000	5000	13.66(13)	2.08
S1	3918.5(17)	6870.5(17)	2396.2(13)	13.9(2)	6.04
O1	4046(5)	9022(5)	1561(4)	23.1(6)	1.67
O2	2980(5)	7302(5)	4183(4)	19.6(6)	1.54
O3	2658(5)	4529(5)	988(4)	22.9(6)	1.61
O4	10695(5)	8523(6)	7752(4)	25.2(7)	0.39
N1	6980(6)	6499(7)	3237(5)	16.2(7)	1.59
$Cd(SO_3NH_2)_2$					
Cd1	7617.4(7)	-208.8(7)	1946.5(4)	11.50(16)	2.09
S1	7039(2)	79(3)	4455.4(12)	11.3(4)	6.05
S2	7528(2)	4979(2)	2316.6(12)	11.7(3)	6.14
O1	5400(9)	-1012(10)	4795(4)	22.3(14)	1.65
O2	7947(8)	-799(8)	3583(4)	18.2(12)	1.87
O3	6719(10)	2123(9)	4346(5)	22.1(14)	1.63
O4	5590(8)	5271(11)	2691(4)	23.4(13)	1.96
O5	7845(9)	3118(8)	1882(4)	19.0(13)	1.99
O6	8176(9)	6556(9)	1694(4)	17.2(14)	1.93
N1	8664(9)	-94(10)	5366(5)	13.8(13)	1.63
N2	9009(9)	5056(11)	3289(4)	13.1(13)	1.61

Table S3. Selected bond lengths (Å) and angles (°) for $Cd(SO_3NH_2)_2 \cdot 2H_2O$.

Cd1-O2[1]	2.380(3)	O4-Cd1-O4[3]	180.0
Cd1-O2[2]	2.380(3)	O4[3]-Cd1-N1	88.40(12)
Cd1-O4	2.252(3)	O4-Cd1-N1[3]	88.40(12)
Cd1-O4[3]	2.252(3)	O4[3]-Cd1-N1[3]	91.60(12)
Cd1-N1[3]	2.329(3)	O4-Cd1-N1	91.60(12)
Cd1-N1	2.329(3)	N1-Cd1-O2[2]	84.40(10)
S1-O1	1.435(3)	N1[3]-Cd1-O2[1]	84.40(10)
S1-O2	1.465(3)	N1[3]-Cd1-O2[2]	95.60(10)
S1-O3	1.447(3)	N1-Cd1-O2[1]	95.60(10)
S1-N1	1.688(3)	N1[3]-Cd1-N1	180.0
		O1-S1-O2	114.10(17)
O2[2]-Cd1-O2[1]	180.00(12)	O1-S1-O3	114.61(17)
O4-Cd1-O2[2]	82.92(10)	O1-S1-N1	104.58(18)
O4-Cd1-O2[1]	97.08(10)	O2-S1-N1	103.60(17)
O4[3]-Cd1-O2[1]	82.92(10)	O3-S1-O2	111.78(16)
O4[3]-Cd1-O2[2]	97.08(10)	O3-S1-N1	106.99(17)

[1]1-*x*, 2-*y*, 1-*z*; [2]1+*x*, +*y*, +*z*; [3]2-*x*, 2-*y*, 1-*z*; [4]-1+*x*, +*y*, +*z*

Table S4. Selected bond lengths (Å) and angles (°) for $Cd(SO_3NH_2)_2$.

Cd1-O6[1]	2.303(6)	O4[4]-Cd1- N1[3]	79.5(2)
Cd1-O4[4]	2.296(5)	O2-Cd1-O6[1]	87.3(2)
Cd1-O2	2.271(5)	O2-Cd1-O4[4]	85.0(2)
Cd1-O5	2.315(6)	O2-Cd1-O5	102.1(2)
Cd1-N2[2]	2.362(6)	O2-Cd1-N2[2]	92.7(2)
Cd1-N1[3]	2.330(6)	O2-Cd1-N1[3]	162.8(2)
S2-O6	1.453(6)	O5-Cd1-N2[2]	81.4(2)
S2-O4	1.447(6)	O5-Cd1-N1[3]	84.3(2)
S2-O5	1.437(6)	N1[3]-Cd1-N2[2]	104.1(2)
S2-N2	1.672(6)	O6-S2-N2	104.3(4)
S1-O2	1.472(5)	O4-S2-O6	112.6(4)
S1-O3	1.443(6)	O4-S2-N2	106.6(3)
S1-O1	1.439(6)	O5-S2-O6	113.0(4)
S1-N1	1.675(6)	O5-S2-O4	114.3(4)
		O5-S2-N2	105.0(4)
O6[1]-Cd1-O5	162.7(2)	O2-S1-N1	106.2(3)
O6[1]-Cd1-N2[2]	83.7(3)	O3-S1-O2	112.9(3)
O6[1]-Cd1-N1[3]	90.8(2)	O3-S1-N1	104.4(4)
O4[4]-Cd1-O6[1]	109.6(2)	O1-S1-O2	112.1(4)
O4[4]-Cd1-O5	85.9(2)	O1-S1-O3	115.4(4)
O4[4]-Cd1- N2[2]	166.4(2)	O1-S1-N1	104.7(4)

[1]+*x*, -1+*y*, +*z*; [2]2-*x*, -1/2+*y*, 1/2-*z*; [3]3/2-*x*, -*y*, -1/2+*z*; [4]1-*x*, -1/2+*y*, 1/2-*z*; [5]+*x*, 1+*y*, +*z*; [6]1-*x*, 1/2+*y*, 1/2-*z*; [7]2-*x*, 1/2+*y*, 1/2-*z*; [8]3/2-*x*, -*y*, 1/2+*z*

Table S5. Hydrogen Bonds for $Cd(SO_3NH_2)_2 \cdot 2H_2O$.

D-H…A	d_{D-H} (Å)	d_{H-A} (Å)	d_{D-A} (Å)
O4-H1…O3[2]	0.85	1.99	2.803(4)
O4-H2…O1[1]	0.85	2.07	2.849(4)
O4-H2…O1[3]	0.85	2.40	2.950(4)
N1-H3…O3[4]	0.85(5)	2.22(5)	3.008(4)
N1-H4…O2[1]	0.82(6)	2.25(6)	3.064(5)

[1]1-*x*, 2-*y*, 1-*z*; [2]1+*x*, +*y*, +*z*; [3]2-*x*, 2-*y*, 1-*z*; [4]-1+*x*, +*y*, +*z*

Table S6. Hydrogen Bonds for $Cd(SO_3NH_2)_2$.

D-H…A	d_{D-H} (Å)	d_{H-A} (Å)	d_{D-A} (Å)
N1-H1A…O3[1]	0.85(3)	2.19(5)	2.977(9)
N2-H2A…O3	0.85(3)	2.16(5)	2.951(9)
N1-H1B…O1[2]	0.85(3)	2.13(3)	2.965(9)
N2-H2B…O5[3]	0.85(3)	2.37(13)	3.049(9)

[1]1/2+*x*, 1/2-*y*, 1-*z*; [2]1/2+*x*, -1/2-*y*, 1-*z*; [3]2-*x*, 1/2+*y*, 1/2-*z*

Table S7. The direction and magnitude of the dipole moments in the [CdO_6] for $Cd(SO_3NH_2)_2{\cdot}2H_2O$ and $Cd(SO_3NH_2)_2$

					magnitude	
Compound	**species**	**x (a)**	**y (b)**	**z (c)**	**debye**	**10^{-4}esu·cm/Å^3**
$Cd(SO_3NH_2)_2{\cdot}2H_2O$	$Cd1O_4N_2$	0	0	0	0	0
$Cd(SO_3NH_2)_2$	$Cd1O_4N_2$	-0.3495	0.9054	-0.1302	0.9792	60

Table S8. Calculated and experimental residual weight for $Cd(SO_3NH_2)_2{\cdot}2H_2O$ and $Cd(SO_3NH_2)_2$ in TGA.

		$Cd(SO_3NH_2)_2{\cdot}2H_2O$		**$Cd(SO_3NH_2)_2$**	
Temperature (°C)	**Product**	**Cal. (%)**	**Exp. (%)**	**Cal. (%)**	**Exp. (%)**
135	$Cd(SO_3NH_2)_2$	89.42	90.68	100	100
650	$CdSO_4$	61.20	60.04	68.44	67.83

Table S9. Weight and atomic ratios for (a) $Cd(SO_3NH_2)_2{\cdot}2H_2O$ and (b) $Cd(SO_3NH_2)_2$ obtained from SEM-EDX.

	$Cd(SO_3NH_2)_2{\cdot}2H_2O$		**$Cd(SO_3NH_2)_2$**	
Element	**Wt %**	**Atomic %**	**Wt %**	**Atomic %**
Cd	32.47	7.04	29.69	6.29
S	14.41	10.96	17.41	12.94
O	48.24	73.51	43.62	64.97
N	4.88	8.50	9.29	15.80
Total	100		100	

Table S10. Elemental analysis for $Cd(SO_3NH_2)_2{\cdot}2H_2O$ and $Cd(SO_3NH_2)_2$.

	$Cd(SO_3NH_2)_2{\cdot}2H_2O$		**$Cd(SO_3NH_2)_2$**	
Element	**Cal. (%)**	**Exp. (%)**	**Cal. (%)**	**Exp. (%)**
S	18.83	19.6074	21.06	21.5858
N	8.22	8.7123	9.20	9.5022
H	2.37	2.3893	1.32	1.3512

Table S11. Assigned vibration peaks for $Cd(SO_3NH_2)_2·2H_2O$ and $Cd(SO_3NH_2)_2$.

		$Cd(SO_3NH_2)_2·2H_2O$	$Cd(SO_3NH_2)_2$
Functional group	**Vibration type**	**Wavenumber (cm^{-1})**	
H_2O	stretching	3441, 3368	
NH_2	stretching	3210, 3175, 3053	3222, 3172, 3079
H_2O	bending	1622	
NH_2	bending	1532	1558, 1542
SO_3	Antisymmetric and symmetric stretching	1278, 1198, 1096, 1045	1300, 1265, 1235, 1194, 1079, 1050, 1027
NH_2	rocking and wagging	1149	1151
S-N		773	779
SO_3	Antisymmetric and symmetric deformation	651	645

Table S12. Investigation on the coordination of cations for sulfamates and the M-N (M = metal cations) bond lengths.

Compound	**MO_x polyhedra**	**M-N bond length (Å)**
$Li(NH_2SO_3)$[1]	$[LiO_4]$	
$Na(NH_2SO_3)$[2]	$[NaO_6]$	
$Cs(NH_2SO_3)$ (*Pnma*)[3]	$[CsO_7]$	
$Mg(NH_2SO_3)_2·4H_2O$[4]	$[MgO_6]$	
$Mg(NH_2SO_3)_2·3H_2O$[4]	$[MgO_6]$	
$Ca(NH_2SO_3)_2·4H_2O$[4]	$[CaO_8]$	
$Ca(NH_2SO_3)_2·H_2O$[4]	$[CaO_7]$	
$Sr(NH_2SO_3)_2·4H_2O$[4]	$[SrO_8]$	
$Sr(NH_2SO_3)_2·H_2O$[4]	$[SrO_9]$	
$Sr(NH_2SO_3)_2$ (*Pc*)[4, 5]	$[SrO_9]$	
$LiCs(NH_2SO_3)_2$[6]	$[LiO_4] + [CsO_8]$	
$K(NH_2SO_3)$[7]	$[KO_6N_2]$	K-N: 3.082
$LiK(NH_2SO_3)_2$[6]	$[LiO_4] + [KO_8N]$	K-N: 2.901
$KNO_3SO_3NH_3$[8]	$[KO_8N]$	K-N: 3.332
$Rb(NH_2SO_3)$[9]	$[RbO_7N_2]$	Rb-N: 3.172, 3.280
$LiRb(NH_2SO_3)_2$[6]	$[LiO_4] + [RbO_9] + [RbO_9N]$	Rb-N: 3.135
$Cs(NH_2SO_3)$ ($P2_1/c$)[3]	$[CsO_8N]$	Cs-N: 3.376
$Sr(NH_2SO_3)_2$ ($P2_1$)[4]	$[SrO_8N]$	Sr-N: 2.982
$Ba(NH_2SO_3)_2$[4, 5]	$[BaO_{10}N]$	Ba-N: 3.126 or 3.117
$Cd(NH_2SO_3)_2·2H_2O$[This work]	$[CdO_4N_2]$	Cd-N: 2.329
$Cd(NH_2SO_3)_2$[This work]	$[CdO_4N_2]$	Cd-N: 2.330, 2.362

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