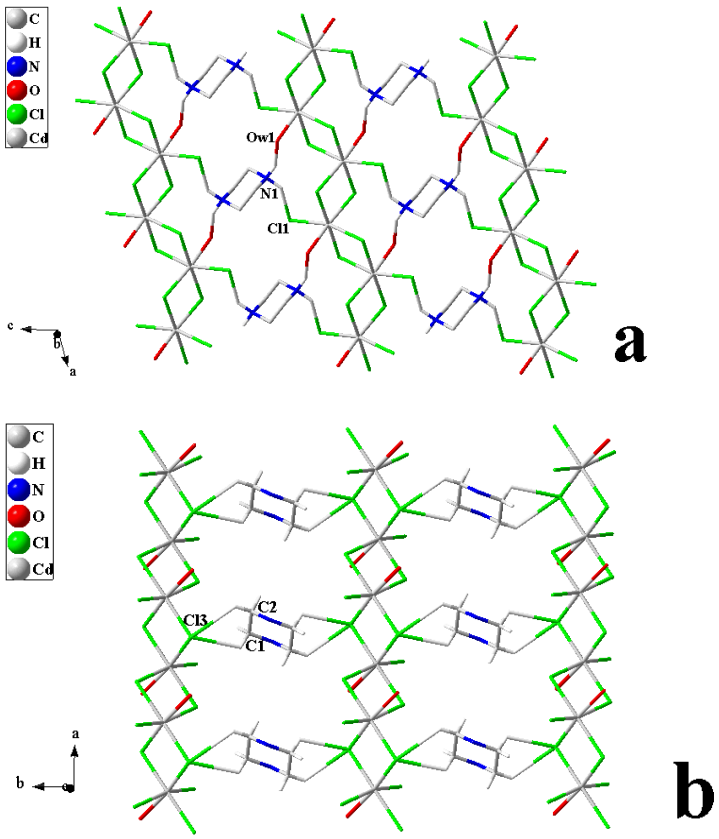

Fig. S1 The 2-D hydrogen-bonded layers in *ac* plane self-assembled by N-H···Cl and N-H···Ow hydrogen bonds (a) and in *ab* plane self-assembled by C-H···Cl hydrogen bonds (b) in compound **1**.

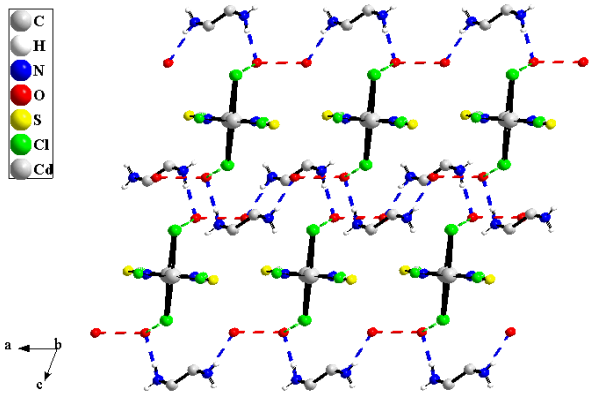

Fig. S2 The 3-D supramolecuar network in (010) direction in compound **3**.

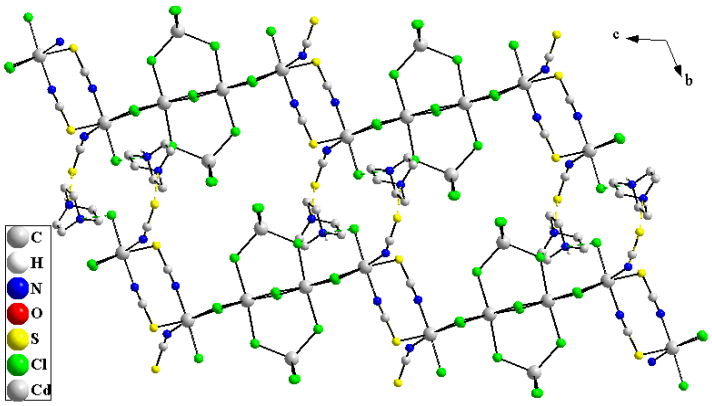

Fig. S3 The 2-D supramolecular network of compound **4** (the dabco molecules used to provide the charge balence are omitted for clarity).

Table S1 A summary of bond distance variations (Å)

	Compound **1**	Compound **2**	Compound **3**	Compound **4**
Cd-N			Cd-N3=2.291(4)	Cd-N5=2.435(4) Cd-N6=2.270(4)
Cd-S			Cd-S=2.7460(12)	Cd-S#1=2.7952(16)
Cd-Ow	Cd-Ow=2.453(3)			
Cd_o-Cl(t)	Cd-Cl1=2.5438(13)	Cd1-Cl1=2.5087(7) Cd2-Cl6=2.4920(9)	Cd-Cl1=2.5949(12) Cd-Cl2=2.6024(12)	Cd1-Cl1=2.5404(13)
Cd_o-Cl(μ_2)	Cd-Cl3#1=2.5894(11) Cd-Cl3=2.6199(12) Cd-Cl2#2=2.6468(12) Cd-Cl2=2.6646(12)	Cd1-Cl2=2.6193(9) Cd1-Cl4=2.6644(8) Cd2-Cl2#2=2.5869(8) Cd2-Cl4=2.6263(7)	Cd-Cl3=2.7038(10) Cd-Cl3#1=2.7157(10)	Cd1-Cl2=2.6728(16) Cd1-Cl3=2.7017(14) Cd2-Cl3=2.5875(15) Cd2-Cl5=2.6998(17) Cd2-Cl5#2=2.6212(15) Cd2-Cl2=2.6278(13)
Cd_o-Cl(μ_3)		Cd1-Cl3#1=2.6100(7) Cd1-Cl3=2.6244(7) Cd1-Cl5=2.9152(9) Cd2-Cl5#3=2.6173(8) Cd2-Cl5=2.6331(8) Cd2-Cl3=3.117		Cd2-Cl4=2.7482(14) Cd2-Cl6#2=2.7545(14)
Cd_t-Cl				Cd3-Cl7=2.4306(14) Cd3-Cl8=2.4611(14) Cd3-Cl6=2.4804(17) Cd3-Cl4=2.4860(12)

Symmetry transformations used to generate equivalent atoms: #1 -*x*, -*y*+1, -*z* #2 -*x*+1, -*y*+1, -*z* for **1**; #1 –*x*+1, -*y*+1, -*z* #2 *x*+1, *y*, *z* #3 –*x*+2, -*y*+1, -*z* for **2;** #1 -*x*+1, -*y*+2, -*z*+1 for **3**; #1 -*x*-1, -*y*+1, -*z*+1 #2 -*x*-1,-*y*+1,-*z* for **4**;

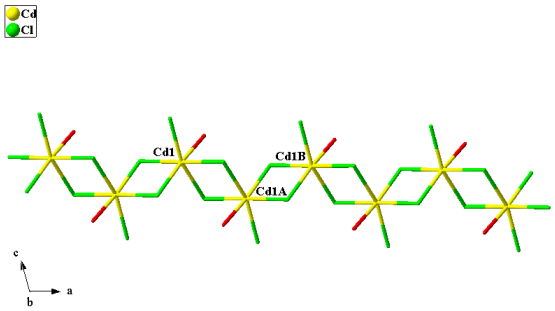

Fig. S4 The 1-D $[Cd_2Cl_6(H_2O)_2]^{2-}$ chain in compound **1** extending in the *a*-direction.

As shown in Figure S4, Cd1A is obtained from Cd1 by an inversion center, and Cd1B is obtained by the translation of Cd1 along *a* direction.

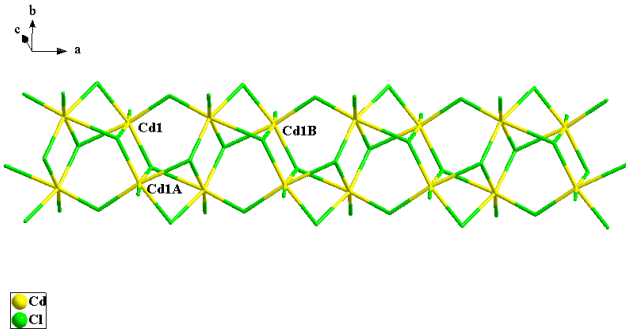

Fig. S5 The 1-D $[Cd_2Cl_6]^{2-}$ chain in compound **2** extending in the *a*-direction.

As shown in Figure S5, Cd1A is obtained from Cd1 by an inversion center, and Cd1B is obtained by the translation of Cd1 along *a* direction.

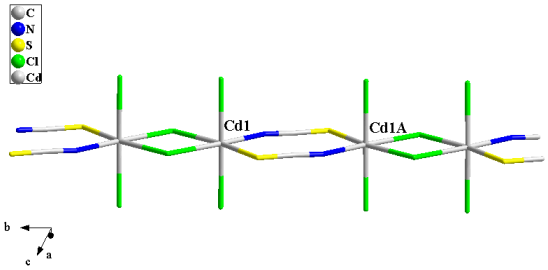

Fig. S6 The 1-D $[CdCl_3(SCN^-)]^{2-}$ chain in compound **3** extending in the *b*-direction.

As shown in Figure S6, Cd1A is obtained from Cd1 by an inversion center along *b* direction.

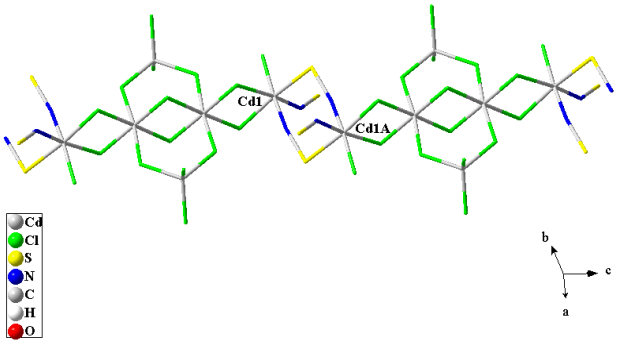

Fig. S7 The 1-D $[Cd_3Cl_8(SCN^-)_2]^{4-}$ chain in compound **4** extending in the *c*-direction.

As shown in Figure S7, Cd1A is obtained from Cd1 by an inversion center along *c* direction.