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Synthesis and crystal structure of selenocyanato bridged two dimensional supramolecular coordination compounds of cadmium(II) †

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Two novel 2D polymers of cadmium(II), $[Cd(medien)(SeCN)_2]_n$ (**1**) (medien = N''-methyldiethylenetriamine) and $[Cd_2(iprdien)(SeCN)_4]_n$ (**2**) (iprdien = N'-isopropyldiethylenetriamine) have been synthesized and their molecular structure determined by X-ray crystallography. In complex **1** each octahedral cadmium(II) unit of a 1D coordination chain contains one pendant SeCN, binding through Se. These pendant SeCN form mutual relationships with other 1D chains through non-covalent interactions (H-bonding) giving rise to a 2D infinite sheet like structure. The molecular structure of **2** reveals a 2D infinite coordination polymer possessing alternating N-bonded octahedral and Se-bonded tetrahedral cadmium(II) centres exhibiting symbiotic phenomena. Both complexes undergo melting but complex **1** remains as a supercooled liquid in the temperature region 78–131 °C.

Introduction

Supramolecular architectures[1–10] are of considerable contemporary interest by virtue of their potential applications in various fields *e.g.*, nonlinear optics,[11] molecular recognition,[12] catalysis,[13] design of porous solids with novel inclusions,[14] electrical conductivity,[15] magnetism,[16] *etc.* Two types of interactions have been exploited in the construction of such supramolecular materials: 1) coordinate covalent bonds connecting metal centres and appropriate ligand types and 2) non-covalent interactions (hydrogen bonds). In the specific case of coordination polymers, the expectation is that the geometry of the metal will be propagated through the bridging ligand. The approach to the design of such coordination polymers has been to exploit neutral organic ligands or to incorporate an anion as an essential element of the coordination polyhedra for imposing a specific uncharged architecture.[17–19] Following this approach our laboratory reported a number of interesting 3D uncharged polymeric compounds of cadmium(II) fully using the bridging potential of the hard and soft coordination centres of the ambidentate thiocyanate ligand.[20–22] Like the thiocyanate anion examples of the versatility of selenocyanate as an effective building block are rare;[23] it should allow a controlled synthesis as the softer Se centre is expected to coordinate more preferably to cadmium(II). So when SeCN acts as a monodentate ligand this will be ligated through Se leaving the more electronegative N uncoordinated and able to provide strong H-bonding interactions. This three-centre four-electron interaction depends upon the nature of the acceptors and donors and/or polarity of the group. On the other hand, according to the Jørgenson symbiotic theory,[24] hard species will tend to increase the hardness of the atom to which they are bound and thus increase its tendency to attract more hard species, *i.e.*, the hard N centre of the SeCN ligand will bind more preferably to that cadmium centre to which it is ligated through N of an amine ligand, and conversely the presence of some soft ligands enhance the ability of the central atom to accept other soft ligands *i.e.*, the Se centre of the SeCN ligand.

Our current work is based on the controlled assembly of donor and acceptor building blocks to generate an entirely supramolecular polymer. In this paper we report the synthesis, characterization and single crystal structures of two novel supramolecular polymers of cadmium(II), $[Cd(medien)(SeCN)_2]_n$ (**1**) and $[Cd_2(iprdien)(SeCN)_4]_n$ (**2**) (medien = N''-methyldiethylenetriamine and iprdien = N'-isopropyldiethylenetriamine) using SeCN as a bridging ligand.

Experimental

Materials

High purity (98%) N''-methyldiethylenetriamine (medien), N'-isopropyldiethylenetriamine (iprdien) and potassium selenocyanate were purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals used were AR grade.

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyser and cadmium(II) content was estimated gravimetrically.[25] Infrared spectra (4000–400 cm^{-1}) were taken using a Nicolet Magna-IR 750 spectrometer series-II where KBr was used as medium. The thermal analyses (TG-DTA-DSC) were carried out on a Shimadzu DT-30 thermal analyser in a dynamic atmosphere of dinitrogen (flow rate: 30 cm^3 min^{-1}) and a Perkin-Elmer DSC-7 differential scanning calorimeter respectively. The sample particle size was within 150–200 mesh. The enthalpy changes of the phase transitions were calculated using indium metal as calibrant.

Preparation of $[Cd(medien)(SeCN)_2]_n$ (1)

An aqueous solution (5 cm^3) of potassium selenocyanate

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† Electronic supplementary information (ESI) available: Corey–Pauling–Koltun diagram of **2**. See http://www.rsc.org/suppdata/dt/b1/b101064f/

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(0.288 g, 2 mmol) was added to an aqueous solution (10 cm^3) of cadmium perchlorate hexahydrate (0.419 g, 1 mmol) with constant stirring. After 10 min medien (0.117 g, 1 mmol) was added very slowly to the reaction mixture and stirred for 30 min. Then it was filtered and the filtrate was kept in a $CaCl_2$ desiccator. After a few days shiny, colourless crystals suitable for single crystal structure determination were obtained. Yield: 80%. Analytical data: Found (%) C, 19.09; H, 3.42; N,15.93; Cd, 25.62. Calc. for $C_7H_{15}N_5Se_2Cd$ (%): C, 19.12; H, 3.41; N, 15.93; Cd, 25.58.

Preparation of [Cd_2(iprdien)(SeCN)$_4$]$_n$ (2)

An aqueous solution (5 cm^3) of potassium selenocyanate (0.288 g, 2 mmol) was added to an aqueous solution (15 cm^3) of cadmium perchlorate hexahydrate (0.419 g, 1 mmol) with constant stirring. After a while iprdien (0.142 g, 1 mmol) was added very slowly to the reaction mixture and immediately a sticky oily compound separated out at the bottom of the beaker. After filtration the clear solution was kept in a $CaCl_2$ desiccator. After a few days shiny, colourless crystals suitable for single crystal structure determination were obtained. Yield: 60%. Analytical data: Found (%) C, 16.79; H, 2.44; N, 12.42; Cd, 28.61. Calc. for $C_{11}H_{19}N_7Se_4Cd_2$ (%): C, 16.77; H, 2.41; N, 12.45; Cd, 28.58.

The composition of the complex **2** shows that the cadmium to iprdien ratio is 2 : 1. We tried to synthesize it following this metal to ligand ratio, but our repeated attempts were not successful.

Crystallographic data collection and refinement

Suitable single crystals of complexes **1** and **2** were mounted on a Siemens CCD diffractometer equipped with graphite monochromated Mo-K$_\alpha$ (λ = 0.71073 Å) radiation. The unit cell parameters and crystal-orientation matrices were determined for both complexes by least squares refinements of 25 accurately centred reflections. In both cases the crystal and instrument stabilities were monitored with a set of three standard reflections measured at regular intervals; in all cases no significant variations were found. The intensity data were corrected for Lorentz and polarization effects[26] and an empirical absorption correction based on ψ scans was also employed for **1** and **2**. Both structures were solved by Patterson syntheses and followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on F^2 were carried out using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon or nitrogen atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of their parent atom. Since complex **2** crystallized in a non-centrosymmetric space group, the absolute configuration was determined [Flack x parameter = −0.01(1)].[27] Complex neutral atom scattering factors[28] were used throughout. All calculations were carried out using the SHELXS 86,[29] SHELXL 97,[30] PLATON 99[31] and ORTEP-3[32] programs. All crystallographic data for complexes **1** and **2** are summarized in Table 1.

CCDC reference numbers 157823 and 157824.

See http://www.rsc.org/suppdata/dt/b1/b101064f/ for crystallographic data in CIF or other electronic format.

Results and discussion

IR spectroscopy

The complexes **1** and **2** show several strong bands in the range 3248–3360 cm^{-1}, which can be assigned to the ν(NH) stretching frequency of the corresponding triamine ligands. Several bands in the range 2800–3000 cm^{-1} are assigned to the aliphatic ν(CH) stretching vibrations. The most intense split ν(CN) bands are observed at 2094, 2103 cm^{-1} and at 2113, 2119, 2137 cm^{-1} for complexes **1** and **2** respectively. The higher frequency is consistent with the bridging selenocyanato group whereas the lower frequency could be assigned to a terminally bound SeCN group.[33] All other bands appear at their usual positions.

Table 1 Crystal data and structure refinement for complexes **1** and **2**

Formula	$C_7H_{15}CdN_5Se_2$	$C_{11}H_{19}Cd_2N_7Se_4$
Formula weight	439.56	789.99
Space group	*Pbca*	*Pc* (no. 7)
a/Å	11.357(2)	8.2970(10)
b/Å	12.311(2)	7.9377(9)
c/Å	19.422(3)	17.184(2)
Crystal system	Orthorhombic	Monoclinic
β/°	90	92.396(2)
T/K	293(2)	297(2)
Z	8	2
V/Å^3	2715.3(8)	1130.7(2)
λ(Mo-K$_\alpha$)/Å	0.71073	0.71073
D_{calc}/g cm^{-3}	2.151	2.320
μ(Mo-K$_\alpha$)/mm^{-1}	6.9	8.3
Total data	3096	6965
Unique data (R_{int})	2076, 0.077	4630, 0.070
Observed data [$I > 2\sigma(I)$]	2076	3854
R	0.0392	0.0432
wR	0.0934	0.1080

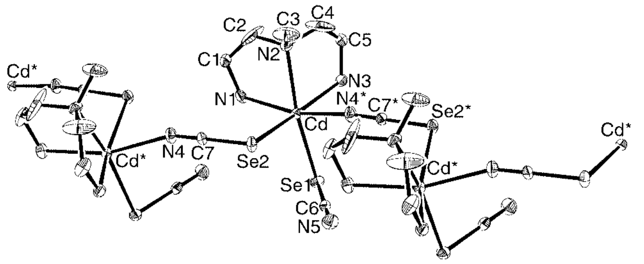

Fig. 1 ORTEP plot of the 1D coordination chain of [Cd(medien)(SeCN)$_2$]$_n$, **1** with atom numbering scheme. Ellipsoids are drawn at 50% probability.

Description of the structure 1

The structure determination reveals that the cadmium atoms are bridged by end-to-end selenocyanato ligands with the occurrence of a 1D coordination polymeric chain along the a-axis. An ORTEP drawing of the chain with atom labelling scheme is shown in Fig. 1. Each cadmium atom is linked with two neighbouring symmetry related counterparts by a bridging selenocyanate ligand and the other SeCN group remains pendant. The geometry around each cadmium atom is best described as a distorted octahedron with a CdN_4Se_2 chromophore. The two nitrogen atoms (N1, N3) of the triamine, and one selenium atom (Se2) of the bridging SeCN group and the symmetry related nitrogen atom (N4*) define the equatorial plane around each cadmium atom. The apical positions of the octahedron are occupied by a selenium atom (Se1) of the terminal SeCN and the tertiary nitrogen atom (N2) of the medien ligand. Deviation of the cadmium atom from the mean plane formed by the four equatorial atoms is about 0.306(7) Å and the maximum deviation of any equatorial atom (N4*) from the mean plane is 0.071(6) Å. In the coordination network Cd–N bond distances (Table 2) are in the range 2.333(5)–2.449(6) Å and the Cd–Se1, Cd–Se2 bond distances are 2.723(1), 2.858(1) Å respectively. The bridging Cd–N4*–C7*, Cd–Se2–C7 and the terminal Cd–Se1–C6 angles are 160.2(5), 101.0(2) and 93.0(2)° respectively. It is interesting to note that due to the soft–soft interaction between the Cd and Se atoms, the pendant SeCN binds through Se leaving the more electronegative nitrogen centre free. In accordance with our expectations the N atom of the pendant SeCN is engaged in two distinct, strong inter- as well as intra-molecular H-bonding

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Cd–Se1	2.723(1)	Cd–Se2	2.858(1)
Cd–N1	2.333(5)	Cd–N2	2.421(6)
Cd–N3	2.353(5)	Cd–N4*	2.449(6)
Se1–Cd–Se2	97.5(1)	Se1–Cd–N1	104.2(1)
Se1–Cd–N2	166.5(2)	Se1–Cd–N3	92.0(1)
Se1–Cd–N4*	93.8(1)	Se2–Cd–N1	92.0(2)
Se2–Cd–N2	96.1(2)	Se2–Cd–N3	163.4(1)
Se2–Cd–N4*	82.1(1)	N3–Cd–N4*	83.7(1)
N1–Cd–N3	98.9(2)	N1–Cd–N4*	161.7(1)

Symmetry code: * $-1/2 + x, 1/2 - y, z$.

Table 3 Hydrogen bonds (Å, °) for complex **1**

D–H···A	D–H	H···A	D···A	D–H···A
N1–H11···N5^{I}	0.90	2.194	3.046(9)	157.8
N1–H12···N5^{II}	0.90	2.432	3.194(9)	142.6
N3–H31···Se1^{III}	0.90	2.842	3.681(6)	155.7

Symmetry code: I $1/2 - x, 1/2 + y, 1 - z$; II $1/2 + x, 1/2 - y, z$; III $-x, 1 - y, 1 - z$.

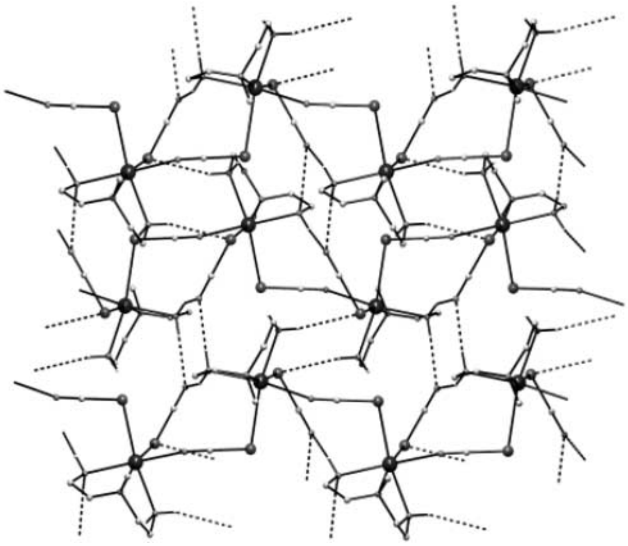

Fig. 2 Infinite 2D supramolecular view of complex **1** showing H-bonding motifs in the *ab*-plane.

interactions and the Se atom is involved in intermolecular H-bonding interactions (Table 3) forming a 2D supramolecular polymeric network (Fig. 2); these H-bonding interactions are responsible for the conformation and stability of the supramolecular polymeric network. This network lies in the *ab*-plane and stacks orthogonal to the *c*-axis. The shortest distance between two Cd(II) centres lying in two adjacent sheets is 9.224 Å.

Description of the structure 2

The single crystal structure determination reveals that the coordination compound **2** contains an infinite 2D alternating octahedral and tetrahedral cadmium(II) network bridging through selenocyanate lying in the *ac*-plane. Fig. 3 shows a 2D layer with atom numbering scheme. To the best of our knowledge this is the first ever observation of an alternating tetrahedral and octahedral array in a cadmium(II) system. It is also interesting to note that every octahedral cadmium atom, Cd2, is surrounded by six nitrogen atoms and every tetrahedral cadmium atom, Cd1, is surrounded by four selenium atoms. Thus the geometry around Cd2 is distorted octahedral with a CdN_6 chromophore and around Cd1 is distorted tetrahedral with a $CdSe_4$ chromophore. Leaving one SeCN arm pendant, there are three branches emanating from the Cd1 centre. In each branch Cd1 is linked to Cd2 *via* SeCN bridges. Every such Cd2, in turn, produces two other branches that are connected to two other Cd1 by means of SeCN bridges to form a 2D coordination polymeric sheet which stacks perpendicular to the *b*-axis. A side view (Fig. 4) of the 2D layers shows that the backbone of the Cd–NCSe–Cd linkages adopts a corrugated sheet like structure. The Cd–NCSe–Cd entities of one sheet protrude into the grooves of the neighbouring sheets.

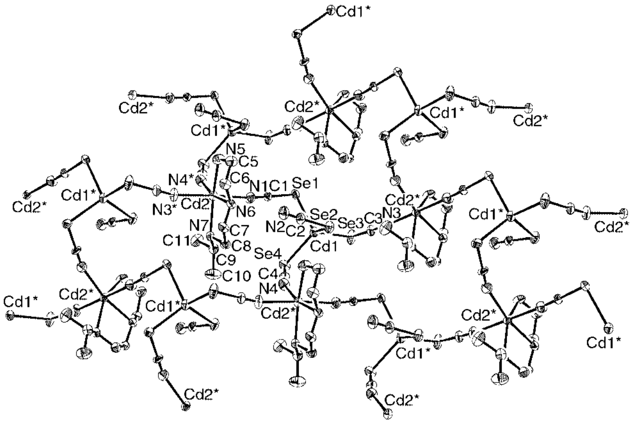

Fig. 3 ORTEP plot of the 2D polymeric sheet, with an alternating octahedral and tetrahedral arrangement, of $[Cd_2(iprdien)(SeCN)_4]_n$, **2** along the *ac*-plane with atom numbering scheme. Ellipsoids are drawn at 50% probability.

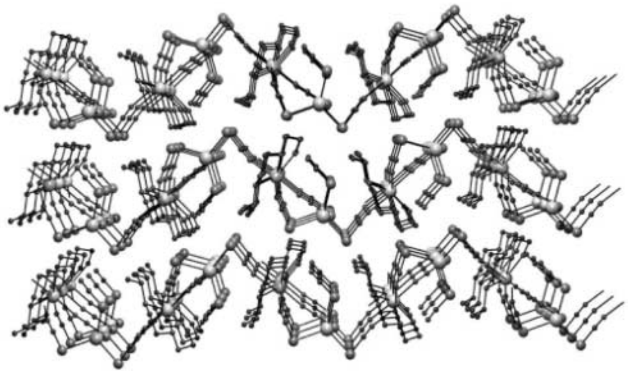

Fig. 4 A perspective view of the 2D polymeric sheet of complex **2**.

The three nitrogen atoms (N5, N6, N7) of the triamine and the symmetry related nitrogen atom (N4*) of the bridging selenocyanate ligand define the equatorial plane around Cd2 atom. The apical positions of the octahedron are occupied by N1 and the symmetry related N3* atom from two bridging selenocyanate ligands. The deviation of Cd2 from the mean plane formed by the four equatorial nitrogen atoms is about 0.019(5) Å and the maximum deviation of N6 above the mean plane of all the equatorial nitrogen atoms is 0.173(6) Å. It is noted that each Cd2 atom coordinated by the nitrogen atoms of the iprdien ligand is invariably linked with the hard atom nitrogen of the selenocyanate ligand. In other words the nitrogen atoms of the iprdien ligand "harden" Cd2, so that the selenocyanate ligands bind to it preferentially through the N atoms. Conversely the soft end of the selenocyanate ligands (Se atom) is coordinated to tetrahedral Cd1 making it "soft". Thus all of the Se atoms of selenocyanate ligands are arranged together around Cd1. The Cd–N and Cd–Se bond distances (Table 4) are in the range 2.279(10)–2.428(10) Å and 2.620(1)–2.672(1) Å respectively and are somewhat shorter than the corresponding values of **1**. The bridging Cd2–N–C [range 158.6(9)–172.8(9)°], Cd1–Se–C [range 94.5(3)–97.9(3)°] and the terminal Cd1–Se2–C2 [95.9(3)°] are more or less comparable to those of complex **1**. The selenocyanate ligands are quasi-linear [175.6(11)–179.4(9)°]. The other bond distances and angles of the complex

Table 4 Selected bond lengths (Å) and angles (°) for complex **2**

Cd1–Se1	2.672(1)	Cd1–Se2	2.620(1)
Cd1–Se3	2.634(2)	Cd1–Se4	2.652(1)
Cd2–N1	2.389(10)	Cd2–N5	2.333(9)
Cd2–N6	2.337(8)	Cd2–N7	2.356(8)
Cd2–N4*	2.279(10)	Cd2–N3*	2.428(10)
Se1–Cd1–Se2	113.3(1)	Se1–Cd1–Se3	103.6(1)
Se1–Cd1–Se4	106.5(1)	Se3–Cd1–Se4	112.1(1)
Se2–Cd1–Se4	115.8(1)	N1–Cd2–N6	87.6(3)
N1–Cd2–N5	96.1(3)	N1–Cd2–N4*	86.8(3)
N1–Cd2–N7	92.2(3)	N4*–Cd2–N5	94.2(3)
N1–Cd2–N3*	176.7(3)	N4*–Cd2–N7	115.5(3)
N5–Cd2–N7	149.6(3)	N3*–Cd2–N6	94.3(3)
N3*–Cd2–N5	86.9(3)	N3*–Cd2–N7	85.7(3)
N4*–Cd2–N6	167.3(3)		

Symmetry code: N4(*) $-1 + x, y, z$; N3(*) $-1 + x, -y, -1/2 + z$.

Table 5 Hydrogen bonds (Å, °) for complex **2**

D–H···A	D–H	H···A	D···A	D–H···A
N5–H5···Se2^{I}	0.90	2.928	3.810(10)	167.1
N6–H6···N2	0.91	2.218	3.064(14)	154.3

Symmetry code: I $-1 + x, y, z$.

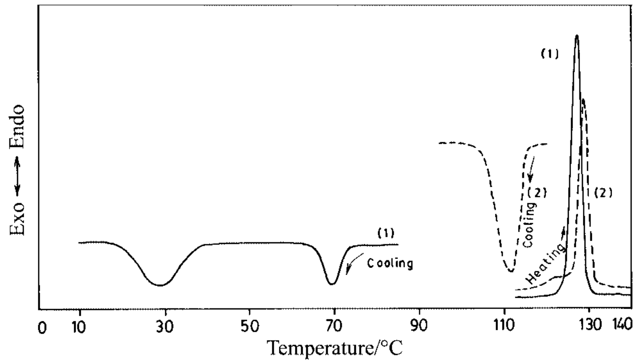

Fig. 5 DSC curves of $[Cd(medien)(SeCN)_2]_n$, **1** (—) (sample mass, 4.59 mg) and $[Cd_2(iprdien)(SeCN)_4]_n$ **2** (---) (sample mass, 6.00 mg).

are close to the expected values. The only pendant SeCN ligand (Se2–C2–N2), attached to tetrahedral Cd1, is engaged in two distinct, strong intramolecular H-bonding interactions (Table 5); these interactions are also responsible for the conformation and stability of the supramolecular polymeric network. The shortest Cd···Cd intra-chain separation is 6.667 Å and inter-chain is 6.823 Å.

Thermal properties

The melting phenomenon of complex **1** is very interesting. DSC measurement shows (Fig. 5) a sharp endothermic peak for melting (temperature range 122–131 °C; peak temperature 127 °C) with $\Delta H = 66.34$ J g^{-1}. Upon cooling the molten sample to 0 °C two exothermic peaks (first, temperature range 68–78 °C, peak temperature 74 °C, $\Delta H = -6.49$ J g^{-1}; second, temperature range 15–39 °C, peak temperature 28 °C, $\Delta H = -16.47$ J g^{-1}) are observed. The sum of the ΔH values (22.96 J g^{-1}) of the two exothermic peaks is much less than that of the endotherm for melting. However on re-heating the sample melts with a heat of fusion identical to that of the virgin sample. The above mentioned facts reveal that the molten compound remains supercooled over a long temperature range, 78–131 °C. Complex **2** also melts upon heating (temperature range 112–135 °C, peak temperature 129 °C, $\Delta H = 27.82$ J g^{-1}) and on cooling to 0 °C solidifies showing only one exotherm (temperature range 98–118 °C, peak temperature 110 °C, $\Delta H = -11.10$ J g^{-1}) (Fig. 5). However on re-heating the sample after 1 h it melts with an identical heat of fusion to that of the virgin sample. Such difference in thermal behaviour as exhibited by these 2D supramolecular complexes is probably due to their structural variation (see Figs. 2 and 3), *i.e.*, complex **1** is formed by non-covalent (H-bonding) interactions whereas complex **2** is formed by covalent interactions.

Concluding remarks

The synthetic procedure adopted for the preparation of complexes **1** and **2** is identical but their structural features are different from each other. In structure $[Cd(medien)(SeCN)_2]_n$ **1**, each cadmium atom is coordinated by both N and Se atoms of the bridging SeCN ligand and one pendant SeCN, binding through Se. The pendant arms form a mutual relationship with another 1D chain through non-covalent interactions giving rise to a 2D infinite sheet like structure. But in $[Cd_2(iprdien)(SeCN)_4]_n$ **2**, there are two types of Cd environment, one involving only nitrogen donors (octahedral, Cd2) and the other only Se donors (tetrahedral, Cd1), which is rather unique. It is worth mentioning that we have reported 3D cadmium complexes[21,22] where the octahedral cadmium centres are linked to each other *via* NCS bridges in such a way that two types of Cd environment (one involving only N donor atoms and the other only S donor atoms) are produced showing symbiosis. The formation of a 2D sheet having alternating tetrahedral and octahedral cadmium centres in complex **2** may be due to the bulkiness of iprdien in comparison to medien, as a tetrahedral geometry occupies less space than the octahedral environment. On the other hand as tetrahedral Cd1 is sp^3 hybridized and the octahedral Cd2 is sp^{3}d^2 hybridized, the Cd1 centre is more electronegative than Cd2. As a result Cd1 binds with the less electronegative and larger Se atom, *i.e*, the soft centre, and Cd2 binds with the more electronegative hard N-centre of the SeCN ligand following Jørgenson's principle of symbiosis.[24] Thus the soft–soft interaction between Cd and Se and the non-covalent (H-bonding) and covalent interactions play a significant role in the formation of such supramolecular networks as found in complexes **1** and **2**. The potential of the systems clearly relies on the d^{10} configuration as it permits a wide variety of geometries and coordination numbers.

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