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Syntheses and crystal structures of four metal–organic co-ordination networks constructed from cadmium(II) thiocyanate and nicotinic acid derivatives with hydrogen bonds

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Received 14th November 2000, Accepted 8th January 2001
First published as an Advance Article on the web 9th February 2001

Four novel non-interpenetrating metal–organic co-ordination networks of the Cd^{II}–L–NCS^- system have been prepared using potentially bridging nicotinic acid derivatives L [nicotinic acid (HL^1), nicotinamide (L^2), isonicotinamide (L^3), or isonicotinate (L^4)]. Their crystal structures were determined by X-ray diffraction. In $[Cd(SCN)_2(HL^1)_2]\cdot HL^1$ **1** each pair of cadmium(II) ions is bridged by two inversely related μ-NCS^--*N*,*S* ligands to form infinite chains with the remaining two *trans* positions of six-co-ordinated Cd atoms being occupied by two HL^1 ligands, which form head-to-head double hydrogen bonds using the unco-ordinated carboxyl groups between adjacent chains to form two-dimensional layers. Weak S···S interactions between the NCS^- ligands extend the layers into a three-dimensional framework with the channels enclosing HL^1 guest molecules, which are interlinked into chains through O–H···N hydrogen bonds. $[Cd(SCN)_2(L^2)_2]\cdot H_2O$ **2** and $[Cd(SCN)_2(L^3)_2]$ **3** are interesting in that they contain unprecedented 16-membered $[Cd_4(\mu\text{-}SCN\text{-}N,S)_4]$ rings in the two-dimensional sheets. Between the sheets N–H···O amide–amide hydrogen bonds extend the two-dimensional layers to three-dimensional structures. $[Cd(SCN)(L^4)(H_2O)]$ **4** exhibits two-dimensional wave-like networks with bridging NCS^- and L^4 ligands using both ends in co-ordination. The results demonstrate that the structures of the Cd^{II}–L–NCS system deeply depend on the nature of the nicotinic acid derivatives L.

Introduction

Metal–organic frameworks are widely regarded as promising materials for application in catalysis, separation and molecular recognition.[1] In construction of one- to three-dimensional frameworks multidentate ligands are usually used to bridge between metal centres to form polymeric structures. For instance, metal–organic co-ordination frameworks based on 4,4′-bipyridine or polycarboxylic acids have extensively been studied.[2,3] Besides covalent bonds, hydrogen bonds are frequently used as a powerful crystal engineering tool to form frameworks.[4]

As a part of our work towards rational design and preparation of functional co-ordination frameworks,[5] we recently carried out a study of cadmium thiocyanate adducts of organic ligands.[5e] Such complexes have extensively been studied by crystal structural analyses, where the monodentate organic ligands included methyl-substituted pyridines, benzylamine, dibenzylamine, tricyclohexyl-, triphenyl- or tri-*m*-tolyl-phosphine, 1*H*-1,2,4-triazole and imidazole.[6] All of these adducts exhibit chain structures, where each pair of adjacent cadmium(II) atoms is bridged by two inversely related μ-SCN^--*N*,*S* ligands and the remaining co-ordination sites are occupied by monodentate organic ligands. Nicotinic derivatives, *e.g.* nicotinic acid (HL^1), nicotinamide (L^2), isonicotinamide (L^3) and isonicotinic acid (HL^4), can act as good monodentate ligands,[7] and deprotonated nicotinic acid or isonicotinic acid as chelate[8] and bridging[9] ligands through their pyridine and/or carboxylate ends. Moreover a few metal complexes with nicotinic acids in their acid forms have also been reported.[4b,10] Hence we believe that it is possible to extend Cd–SCN co-ordination chains or layers into higher dimensional architectures by replacement of the organic ligands with nicotinic acids as bridging ligands through covalent or hydrogen bonds since the carboxylic groups may form head-to-head O–H···O hydrogen bonds [$R_2^2(8)$]. This expectation may also be achieved with L^2 and L^3, which may also show N–H···O hydrogen bonds in their metal complexes.[11,12] Thus, the above four nicotinic derivatives can be used to bridge metal ions through either covalent or hydrogen bonds (Scheme 1).

We report herewith the syntheses and crystal structures of four new metal–organic co-ordination frameworks, namely $[Cd(SCN)_2(HL^1)_2]\cdot HL^1$ **1**, $[Cd(SCN)_2(L^2)_2]\cdot H_2O$ **2**, $[Cd(SCN)_2(L^3)_2]$ **3** and $[Cd(SCN)(L^4)(H_2O)]$ **4**.

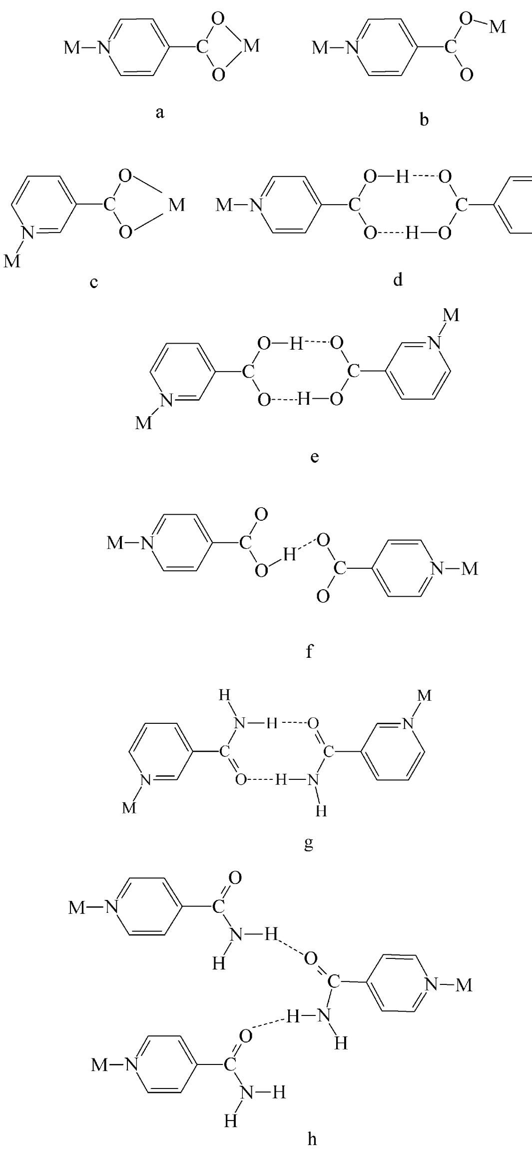
Experimental

All reagents were commercially available and used as received. The C, H, N and S microanalyses were carried out with an Elementar Vario EL elemental analyser. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX FT-IR spectrometer. Thermogravimetric data were collected on a Siemens NETZSCH TG209 analyser in flowing dinitrogen at a heating rate of 10 °C min^{-1}.

Syntheses

$[Cd(SCN)_2(HL^1)_2]\cdot HL^1$ 1. An aqueous solution of $Cd(NO_3)_2\cdot 4H_2O$ (0.308 g, 1 mmol) and NH_4SCN (0.152 g, 2 mmol) was added to a hot aqueous solution (20 cm^3, 70 °C) of HL^1 (0.246 g, 2 mmol) with stirring. After filtration, the final clear solution was left to stand in a desiccator for several days. Colourless prismatic crystals suitable for X-ray work were formed. Yield: 70% (based on nicotinic acid). Calc. for $C_{20}H_{15}CdN_5O_6S_2$: C 40.2, H 2.5, N 11.7, S 10.7. Found: C 40.2, H 2.7, N 11.9, S 10.8%. IR data (cm^{-1}): 3534s, 3479m, 3430s, 3355w, 3298w, 3172s,br, 3078w, 2108vs, 1685vs, 1610s, 1575m, 1429m, 1392s, 1335w, 1203m, 1150w, 1110m, 1029m, 936w, 910w, 839m, 773s, 722w, 691s, 646m, 489s, 460m and 429w.

DOI: 10.1039/b009129o



Scheme 1 The bridging modes of nicotinic acids [L^1 (c); HL^1 (e); L^4 (a), (b); HL^4 (d), (f)] and nicotinamides [L^2 (g); L^3 (h)].

[Cd(SCN)$_2$(L^2)$_2$]·H$_2$O 2. An aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.308 g, 1 mmol) and NH_4SCN (0.152 g, 2 mmol) was added to a hot aqueous solution (20 cm^3) of L^2 (0.244 g, 2 mmol) with stirring. A white precipitation was formed immediately. The mixture was slowly heated to nearly boiling, during which time the precipitation dissolved. After cooling to room temperature, the clear solution was allowed to stand for several hours to give colourless crystals. Yield: 80%. Calc. for $C_{14}H_{14}CdN_6O_3S_2$: C 34.3, H 2.9, N 17.1, S 13.1. Found: C 34.4, H 2.9, N 17.4, S 13.0%. IR data (cm^{-1}): 3473m, 3424s, 3402s, 3360s, 3194s, 3071w, 2090vs, 1996w, 1667vs, 1604s, 1574w, 1404s, 1202m, 1143w, 1115w, 1047w, 793w, 753w, 693m, 646m, 549m, 514w, 487w and 459w.

[Cd(SCN)$_2$(L^3)$_2$] 3. This complex was prepared as for **2** using L^3 instead of L^2. Colorless crystals suitable for X-ray analysis were obtained in 80% yield. Calc. for $C_{14}H_{12}CdN_6O_2S_2$: C 35.6, H 2.6, N 17.8, S 13.6. Found: C 35.6, H 3.3, N 17.8, S 13.7%. IR data (cm^{-1}): 3424s, 3314m, 3264w, 3197w, 3071w, 2098vs, 1707w, 1672vs, 1629w, 1606s, 1556s, 1418w, 1397s, 1229m, 1148w, 1084w, 1062m, 1018m, 860m, 762s, 741m, 623s, 546s and 450w.

[Cd(SCN)(L^4)(H$_2$O)] 4. An aqueous acetonitrile solution (10 cm^3) of $Cd(NO_3)_2 \cdot 4H_2O$ (0.308 g, 1 mmol) and NH_4SCN (0.152 g, 2 mmol) was added to a hot aqueous solution (20 cm^3) of HL^4 (0.244 g, 2 mmol). The resulting solution was allowed to stand in a desiccator for two to three weeks to yield a small amount of pale yellow prismatic crystals of complex **4** and unchanged HL^4. The crystals of **4** were carefully separated by hand, yield *ca.* 10%. Calc. for $C_7H_4CdN_2O_3S$: C 27.1, H 2.0, N 9.0, S 10.3. Found: C 27.2, H 2.1, N 9.0, S 10.2%. IR data (cm^{-1}): 3386s, 3259m,sh, 2115vs, 1647m, 1607w, 1580s, 1542s, 1508w, 1413vs, 1226m, 1058m, 1018m, 866m, 773s, 701s, 572w, 531w and 461w.

X-Ray crystallography

Diffraction intensities for the four complexes were collected at 21 °C on a Siemens R3m diffractometer employing graphite-monochromated Mo-Kα radiation (λ 0.71073 Å) with ω-scan mode. Empirical absorption corrections based on ψ scans were applied.[13] The structures were solved with the Patterson methods of SHELXS 97 and refined by full-matrix least-squares technique using SHELXL 97.[14,15] Non-hydrogen atoms were refined anistropically. The hydrogen atoms of the organic ligands were generated geometrically (C–H 0.96 Å) and those of the water molecules located from difference maps. The crystallographic data for complexes **1**–**4** are listed in Table 1, selected bond lengths and angles in Table 2.

CCDC reference numbers 152859–152862.

See http://www.rsc.org/suppdata/dt/b0/b009129o/ for crystallographic data in CIF or other electronic format.

Results and discussion

Syntheses and characterisation

All of the complexes were prepared straightforwardly by mixing $Cd(NO_3)_2 \cdot 4H_2O$ and NH_4SCN with L in different molar ratios. For **1**, we found that the product was independent of the $Cd^{2+}:SCN^-:HL^1$ molar ratio in the range 1:2:1 to 1:2:4. For **2** and **3**, the products were independent of the Cd^{2+}: SCN^-:L^2(or L^3) molar ratio ranging from 1:2:2 to 1:2:1. Complex **4** was obtained in rather low yield. Its crystals are usually blended with unchanged HL^4. We attempted to increase the yield by increasing the pH of the reaction mixture to 5, taking into consideration the existence of L^4 in **4**; to our surprise, the product obtained was $[Cd(L^4)_2(H_2O)_4]$, a known mononuclear complex.[7d] It is also worthy of mention that when other metal ions, such as Mn^{II}, Co^{II} and Ni^{II} were used, the resulting structures were drastically different.

The IR spectra show the C≡N stretching vibrations of thiocyanate at 2108 and 2115 cm^{-1} for **1** and **4**, respectively, suggesting a bridging mode.[16] Two absorption peaks at lower wavenumbers (2090 and 2098 cm^{-1}) were observed for ν(C≡N) of the thiocyanate groups in **2** and **3**, respectively, implying a different binding mode in accord with the X-ray analyses in that both **2** and **3** exhibit two-dimensional networks featuring [Cd$_4$(μ-SCN-*S*,*N*)$_4$] subunits, a novel cadmium–thiocyanate skeleton different from that found in **1**. The IR spectrum of **1** has a strong absorption band for the C=O stretching at 1685 cm^{-1}, which indicates clearly the presence of the hydrogen bonded dimer of nicotinic acid. On the other hand, the absence of a strong peak in the 1700–1680 cm^{-1} region and the presence of strong peaks at 1542 and 1413 cm^{-1} in the IR spectrum of **4** indicates deprotonation of HL^4. The separation (Δ) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ is 129 cm^{-1}, which is consistent with chelation of the carboxylate group in **4**.

Thermogravimetric analysis (TGA) was performed for complexes **1** and **2** on polycrystalline samples in a nitrogen atomosphere. The TGA curve of **1** showed a large weight loss in the 190–300 °C range, corresponding to loss of HL^1 molecules (observed, 60.1%; calculated, 61.8%). Subsequent weight loss in the range 300–450 °C may correspond to decomposition of the thiocyanate groups. The final product at 600 °C should, at least

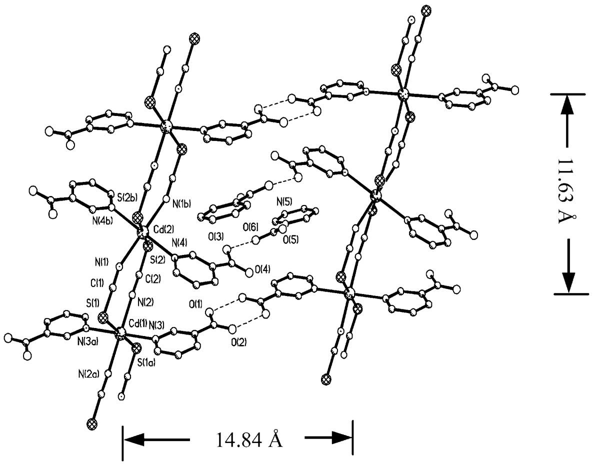


Fig. 1 Perspective view of a structural unit in complex **1** with atomic numbering. The dashed lines represent hydrogen bonds.

mainly, be CdS according to the residual weight (observed, 26.1%; calculated, 24.2%). The TGA curve of **2** showed a slight weight loss in the 40–120 °C range, indicating the existence of lattice water molecules in the solid state. In the range 160–320 °C, **2** experienced a weight loss of 57.9%, suggesting that loss of L^2 and decomposition of thiocyanate groups occurred almost simultaneously.

Crystal structures

X-Ray single-crystal structural determination reveals that two kinds of structurally different cadmium(II) atoms exist in **1** and both are located on inversion centres. Each is co-ordinated by two pyridyl nitrogen atoms of two HL^1 ligands, two thiocyanate nitrogen atoms and two sulfur atoms of another two thiocyanate ligands in a *trans* octahedral geometry. The Cd–N(SCN) (2.294(3)–2.381(3) Å) and Cd–S bond lengths (2.709(2) and 2.738(2) Å) are close to those for reported complexes containing eight-membered [Cd$_2$(SCN)$_2$] rings.[6]

Each pair of adjacent metal atoms is bridged by two inversely related μ-SCN-*S*,*N* ligands, resulting in a chain structure comprising eight-membered (N–C–S–Cd)$_2$ rings, which have been well documented in Cd^{II}–L–NCS systems.[6] The remaining two *trans* positions around the six-co-ordinated Cd are occupied by two *N*-co-ordinated HL^1 ligands. On the other hand, it is interesting that one crystallographically independent HL^1 ligand is co-ordinated to the Cd(1) atom, forming head-to-head double hydrogen bonds [O(1) ⋯ O(2^i) 2.686(3) Å, symmetry code (i) $1 - x$, $1 - y$, $2 - z$] with an inversely related HL^1 ligand from an adjacent chain (R$_2^2$(8), Scheme 1e), leading to large parallelogram cavities (size 11.63 × 14.84 Å). Meanwhile, another crystallographically independent HL^1 ligand co-ordinated to the Cd(2) atom is located in the cavity as shown in Fig. 1, reducing the size of the cavity. Even so, the smaller cavity is still large enough to hold two guest HL^1 molecules. Two guest HL^1 molecules are anchored to the cavity, each by a strong, head-to-head single hydrogen bond (O(3) ⋯ O(6) 2.508(3) Å) between the carboxylic groups of the unco-ordinated and *N*-co-ordinated HL^1 ligands.

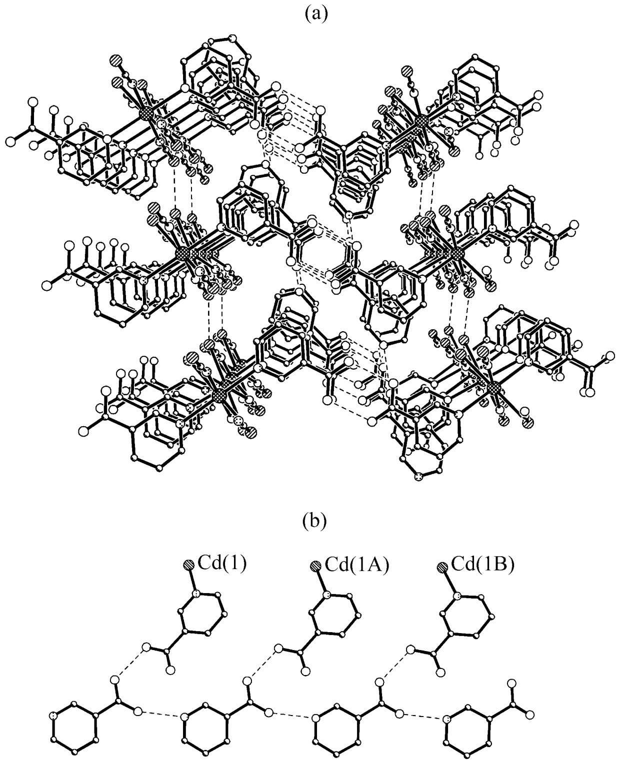


Fig. 2 Perspective views of molecular packing of complex **1** showing the channel formed by the S ⋯ S interactions and hydrogen bonds (dashed lines) (a) and the hydrogen bonded chain in the channel (b).

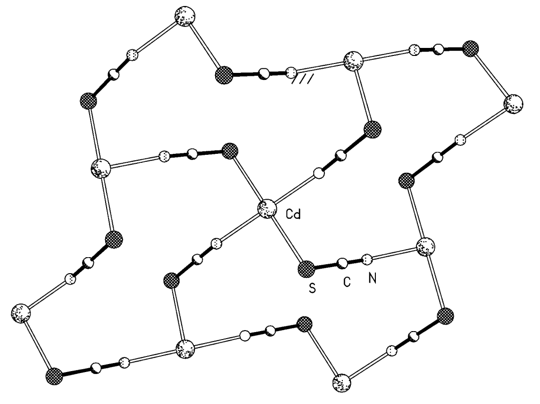


Fig. 3 Perspective view of a sheet in complex **2** or **3**. The nicotinamide ligands are omitted for clarity.

As shown in Fig. 2(a), the layers are further packed into a three-dimensional framework through interlayer weak S ⋯ S interactions of the NCS$^-$ ligands (3.52 Å), generating channels along the *a* axis. It is noteworthy that the guest HL^1 molecules are not only anchored to co-ordinated HL^1 ligands of the channel by hydrogen bonds, but also interlinked into a chain in the channel through carboxyl–pyridyl O–H ⋯ N hydrogen bonds [O(5) ⋯ N(5^{ii}) 2.645(4) Å, symmetry code (ii) $1 + x$, y, z] between adjacent guest molecules (Fig. 2(b)). Significant π–π stacking interaction is evident by the dihedral angle (13.2°) and separation (3.51 Å) between the pyridyl rings of the guest HL^1 molecule and adjacent HL^1 ligands ligating Cd(1) atoms, which may also contribute to the formation of such a host–guest complex. Presumably, the presence of these guest molecules as well as and the weak supramolecular interactions such as hydrogen bonds, π–π stacking and weak S ⋯ S interaction play a vital role in the formation of the channel structure.

The structure of complex **2** consists of two-dimensional cadmium–thiocyanate sheets. Each Cd^{II} is placed in a centrosymmetrical octahedral environment, being co-ordinated by two *trans*-related L^2 and four NCS$^-$ ligands with Cd–N and Cd–S bond lengths of 2.328(3) and 2.349(3) and 2.764(1) Å, respectively. The co-ordination environment is very similar to that in **1**, however the NCS$^-$ ligands and Cd atoms are interconnected to form two-dimensional sheets in **2**, featuring hourglass-shaped, 16-membered [Cd$_4$(μ-SCN-*N*,*S*)$_4$] macrocycles as subunits, as shown in Fig. 3. The intralayer Cd ⋯ Cd distance in **2** is 6.231(1) Å, slightly longer than the intrachain one in **1** [5.812(1) Å]. This may be ascribed to the fact that only one μ-NCS-*S*,*N* ligand bridges each pair of Cd atoms in **2**. To our knowledge, such a [Cd$_4$(μ-SCN-*N*,*S*)$_4$] arrangement of the

Table 1 Crystal data and structure refinement for complexes **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_{20}H_{15}CdN_5O_6S_2$	$C_{14}H_{14}CdN_6O_3S_2$	$C_{14}H_{12}CdN_6O_2S_2$	$C_7H_6CdN_2O_3S$
M	597.89	490.83	472.82	310.60
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/n$
a/Å	7.305(5)	24.290(12)	11.786(10)	6.052(2)
b/Å	11.625(5)	9.863(4)	9.667(4)	14.763(8)
c/Å	14.837(5)	7.617(3)	8.112(4)	11.423(5)
α/°	109.05(5)			
β/°	102.49(5)	92.67(2)	107.62(2)	94.26(2)
γ/°	94.14(5)			
V/Å^3	1148.8(10)	1822.8(14)	880.9(9)	1017.8(8)
Z	2	4	2	4
μ(Mo-Kα)/mm^{-1}	1.180	1.455	1.497	2.332
No. unique data	6147	1981	1193	2972
No. data with $I > 2\sigma(I)$	4473	1582	1041	2398
$R1$, $wR2$	0.0362, 0.0757	0.0341, 0.0797	0.0296, 0.0750	0.0392, 0.1057

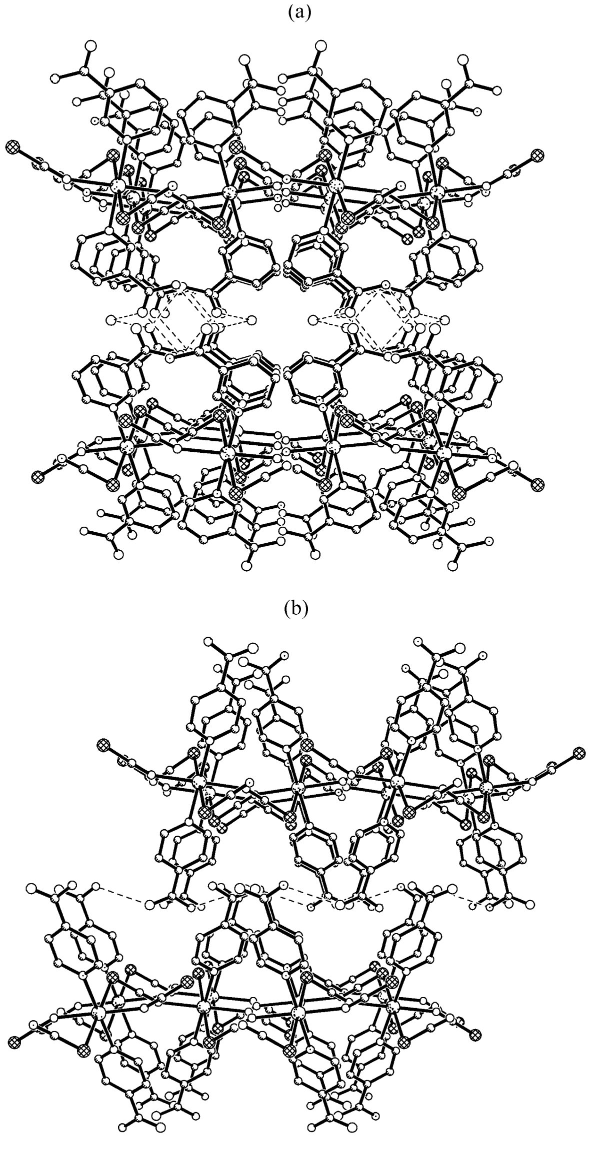


Fig. 4 Molecular packing plots of compex **2** (a) and **3** (b) viewed along the *c* axis.

subunit is unprecedented in cadmium–thiocyanate system,[17] and only two similar structures have been reported for two transition metal complexes, namely [Mn(EtOH)$_2$(NCS)$_2$] and [Mn(4-acpy)$_2$(N$_3$)$_2$] (4-acpy = 4-acetylpyridine), which contain [Mn$_4$(SCN)$_4$] and [Mn$_4$(N$_3$)$_4$] subunits, respectively.[18,19]

As shown in Fig. 4(a) and Scheme 1g, the two-dimensional [Cd$_4$(SCN)$_4$] layers are further linked by centrosymmetrical amide–amide double hydrogen bonds [$R_2^2(8)$] between the lateral L^2 ligands into a three-dimensional structure [N(3)···O(1^i) 2.960(4) Å, symmetry code (i) $-x$, $1 - y$, $1 - z$]. Similar hydrogen bonds between the amide groups have been observed in a Cr^{III}–L^2 complex. In the latter case, however, the two amide–amide hydrogen bonds are crystallographically independent.[11] The lattice water molecules also contribute, to some extent, to the formation of three-dimensional structure through water–amide O–H···O hydrogen bonds (O···O 2.766(6) Å).

Complex **3** exhibits a similar two-dimensional structural pattern to that of **2**, featuring hourglass-shaped, 16-membered [Cd$_4$(μ-SCN-*N*,*S*)$_4$] macrocycles as subunits. The Cd atom, located on an inversion centre, is co-ordinated by two *trans*-related L^3 and four NCS$^-$ ligands in an N$_4$S$_2$ octahedral geometry, the bond distances and bond angles being comparable with those of **2** (Table 2). The intralayer Cd···Cd separation through a μ-SCN-*S*,*N* ligand is 6.310(1) Å. The main difference between the structures of **2** and **3** lies in the hydrogen bonds which link the layers into three-dimensional structures. The amide–amide hydrogen bonds between a pair of the L^3 ligands from two adjacent layers display catemer-type interactions in **3** with an N–H···O distance of 2.989(4) Å (see Fig. 4b and Scheme 1h), in contrast with the head-to-head double hydrogen bonds for the L^2 ligands in **2**. It has been established that amide–amide interaction typically involves "head-to-head" or catemer hydrogen bonds in metal complexes of L^3.[4b,c,12]

Complexes **2** and **3** exhibit different structural patterns from that of **1**, which may arise by replacement of the amide group for the carboxylic group on the pyridyl ring. Therefore, the different arrangements of Cd–NCS skeletons in **1**, **2** and **3** are plausibly triggered off by the subtle dissimilarity of hydrogen bonds these substitution groups form and/or the co-ordination ability of the ligands.

X-Ray analysis reveals two-dimensional wave-like polymeric networks for complex **4**, in which each Cd atom is six-co-ordinated by one aqua, two bridging μ-NCS-*S*,*N* and two bridging L^4 ligands in a distorted octahedral O$_3$N$_2$S geometry, as shown in Fig. 5. The two-dimensional sheet is constructed by interconnection of the Cd–NCS–Cd chains to neighbouring chains with L^4 ligands functioning in a μ-*N*,*O*,*O*′ bridging mode (Scheme 1a).[9f] The adjacent Cd···Cd separations in the parallelogram structural unit are 6.052(1) (through NCS$^-$) and 9.376(1) Å (through L^4). The dihedral angle is 78.4° between the adjacent two parallelograms sharing the longer sides. Thus, the two-dimensional sheets are folded in a highly wavy way, shown in Fig. 6.

It should be pointed out that each sheet is non-centrosymmetrical, which probably originates from the highly

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**–**4**

Complex **1**			
Cd(1)–N(2)	2.294(3)	Cd(2)–N(1)	2.311(3)
Cd(1)–N(3)	2.381(3)	Cd(2)–N(4)	2.358(3)
Cd(1)–S(1)	2.709(2)	Cd(2)–S(2)	2.738(2)
N(2)–Cd(1)–N(3a)	92.7(1)	N(1b)–Cd(2)–N(4)	89.0(1)
N(2)–Cd(1)–N(3)	87.3(1)	N(1)–Cd(2)–N(4)	91.0(1)
N(2)–Cd(1)–S(1a)	85.1(1)	N(1)–Cd(2)–S(2b)	85.9(1)
N(3)–Cd(1)–S(1a)	90.1(1)	N(4)–Cd(2)–S(2b)	92.1(1)
N(2)–Cd(1)–S(1)	94.9(1)	N(1)–Cd(2)–S(2)	94.1(1)
N(3)–Cd(1)–S(1)	89.9(1)	N(4)–Cd(2)–S(2)	87.9(1)
C(1)–S(1)–Cd(1)	100.2(1)	C(2)–S(2)–Cd(2)	99.5(1)
C(2)–N(2)–Cd(1)	161.6(3)	C(1)–N(1)–Cd(2)	158.4(3)
N(1)–C(1)–S(1)	178.7(3)	N(2)–C(2)–S(2)	178.1(3)
Complex **2**			
Cd(1)–N(1a)	2.328(3)	Cd(1)–S(1)	2.764(1)
Cd(1)–N(2)	2.349(3)		
N(1a)–Cd(1)–N(2)	89.9(1)	C(1)–S(1)–Cd(1)	98.6(1)
N(1b)–Cd(1)–N(2)	90.1(1)	N(1)–C(1)–S(1)	178.5(4)
N(1a)–Cd(1)–S(1)	88.3(1)	C(1)–N(1)–Cd(1d)	156.7(3)
N(1b)–Cd(1)–S(1)	91.8(1)	C(2)–N(2)–Cd(1)	119.2(2)
N(2c)–Cd(1)–S(1)	88.2(1)	C(6)–N(2)–Cd(1)	122.9(3)
N(2)–Cd(1)–S(1)	91.8(1)		
Complex **3**			
Cd(1)–N(2)	2.334(4)	Cd(1)–S(1)	2.749(2)
Cd(1)–N(1b)	2.376(3)		
N(2a)–Cd(1)–N(1b)	89.8(1)	N(1c)–Cd(1)–S(1)	90.3(1)
N(2)–Cd(1)–N(1b)	90.2(1)	C(1)–S(1)–Cd(1)	100.1(1)
N(2a)–Cd(1)–S(1)	90.6(1)	C(1)–N(1)–Cd(1d)	155.8(3)
N(2)–Cd(1)–S(1)	89.4(1)	C(6)–N(2)–Cd(1)	121.3(2)
N(1b)–Cd(1)–S(1)	89.7(1)	C(2)–N(2)–Cd(1)	121.0(2)
N(1)–C(1)–S(1)	178.5(3)		
Complex **4**			
Cd(1)–O(1w)	2.288(3)	Cd(1)–O(1b)	2.381(3)
Cd(1)–N(1a)	2.289(4)	Cd(1)–O(2b)	2.448(3)
Cd(1)–N(2)	2.346(3)	Cd(1)–S(1)	2.588(1)
O(1w)–Cd(1)–N(1a)	84.4(1)	N(1a)–Cd(1)–S(1)	105.0(1)
O(1w)–Cd(1)–N(2)	162.1(1)	N(2)–Cd(1)–S(1)	100.9(1)
N(1a)–Cd(1)–N(2)	87.8(1)	O(1b)–Cd(1)–S(1)	100.8(1)
O(1w)–Cd(1)–O(1b)	87.5(1)	O(2b)–Cd(1)–S(1)	155.3(1)
N(1a)–Cd(1)–O(1b)	153.7(1)	C(1)–S(1)–Cd(1)	97.7(2)
N(2)–Cd(1)–O(1b)	92.5(1)	N(1)–C(1)–S(1)	177.5(4)
O(1w)–Cd(1)–O(2b)	84.8(1)	C(1)–N(1)–Cd(1c)	155.3(4)
N(1a)–Cd(1)–O(2b)	99.7(1)	C(6)–N(2)–Cd(1)	117.8(3)
N(2)–Cd(1)–O(2b)	80.6(1)	C(2)–N(2)–Cd(1)	123.5(3)
O(1b)–Cd(1)–O(2b)	54.6(1)	C(7)–O(1)–Cd(1d)	93.0(2)
O(1w)–Cd(1)–S(1)	96.8(1)	C(7)–O(2)–Cd(1d)	90.0(2)

Symmetry codes: **1** (a) $-x + 1, -y + 1, -z + 1$; (b) $-x + 1, -y, -z + 1$; **2** (a) $x, -y, z - \frac{1}{2}$; (b) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (c) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (d) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; **3** (a) $-x, -y, -z$; (b) $-x, y + \frac{1}{2}, -z - \frac{1}{2}$; (c) $x, -y - \frac{1}{2}, z + \frac{1}{2}$; (d) $-x, y - \frac{1}{2}, -z - \frac{1}{2}$; **4** (a) $x - 1, y, z$; (b) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (c) $x + 1, y, z$; (d) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

distorted co-ordination geometry around the Cd atoms. Each two adjacent sheets are actually a pair of enantiomers, interlinked *via* O–H · · · O hydrogen bonds [O(1w) · · · O(1^i) 2.842(4) Å, symmetry code (i) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$] in a centrosymmetrical way, resulting in a three-dimensional structure.

It is interesting that L^4, rather than isonicotinic acid, exists as the ligand in complex **4**. The pH (*ca.* 3) was not adjusted during the synthesis. When the pH was adjusted to 5 a mononuclear complex [Cd(L^4)$_2$(H$_2$O)$_4$] was obtained. Based on these results, we infer that there may be an equilibrium between **4** and [Cd(L^4)$_2$(H$_2$O)$_4$] in the reaction solution. **4** would become less stable when the concentration of L^4 increases at a higher pH value. It still remains to be unraveled why isonicotinic acid ligands cannot form hydrogen-bonded dimers [$R_2^2(8)$] in **4**. However, since the synthetic conditions are the same, we may conclude the dramatic structural difference between **1** and **4** may result from subtle changes in the site of the carboxyl group between nicotinic acid and isonicotinic acid. The auto-deprotonation of isonicotinic acid results in different co-ordination behaviour of the ligand, and consequently in the different network structure as compared to those of **1**–**3**.

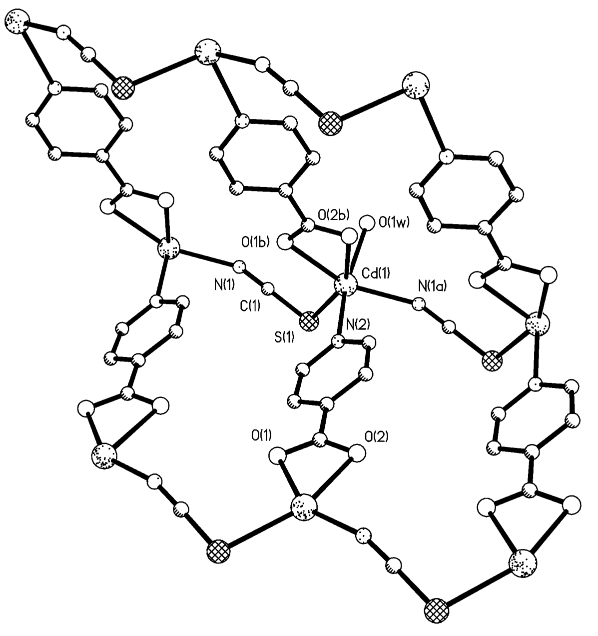


Fig. 5 Perspective view of a sheet in complex **4** with atomic numbering.

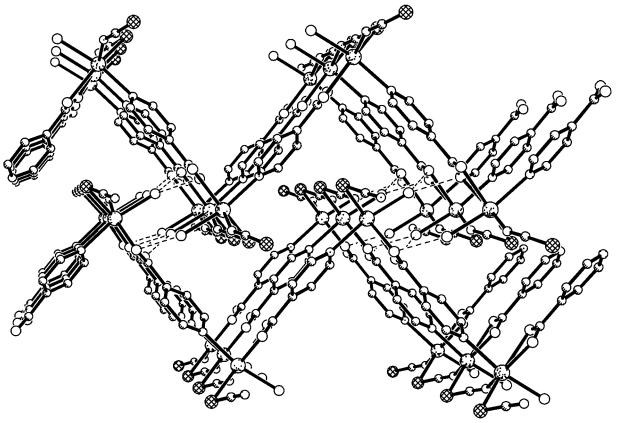


Fig. 6 Molecular packing of complex **4** viewed along the *a* axis.

Conclusion

By using bridging ligands instead of monodentate ligands, we successfully extended the one-dimensional chain structure into two-dimensional networks through covalent or hydrogen bonds in the Cd^{II}–L–SCN system. Our result shows that the structures of these complexes are sensitive to the nature of ligands L. Moreover, **4** represents a rare example in the Cd^{II}–L–SCN system with its negatively mono-charged bridging L^4 ligand.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grants No. 29971033 & 29625102) and the Ministry of Education of China.

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