

Inorganic–Organic Hybrid Materials: Synthesis and X-Ray Structure of *N,N'*-Dimethylimidazolium Salts [(Me₂Im)₂][Cd₂(SCN)₆] and *N,N'*-Dicyclohexylimidazolium [(Cy₂Im)₂][Cd₂(SCN)₆] · C₃H₆O

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Two novel *N,N'*-dialkylimidazolium thiocyanate–cadmium complexes [(R₂Im)₂][Cd₂(SCN)₆] for R = Me (**3**), and cyclohexyl (**4**) have been synthesized and characterized by single-crystal X-ray diffraction. Compound **3** crystallizes in the monoclinic unit cell dimensions of 17.468(3), 7.7273(12), 10.6750(16) Å, 104.833(2)°, and space group C2 with two [(Me₂Im)₂][Cd₂(SCN)₆] per unit cell. The two cadmium atoms in **3** are octahedrally coordinated in 4N2S and 2N4S coordination environment, and linking into one-dimensional zigzag chains. Compound **4** belongs to the monoclinic space group Cc with unit cell of dimensions 13.3049(12), 17.5550(16), 20.8012(19) Å, 101.494(2)°, and four [(Cy₂Im)₂][Cd₂(SCN)₆] · C₃H₆O per unit cell. The cadmium atoms in **4** are all 3N3S hexa-coordinated with six bridging SCN⁻ ions in an *fac* configuration and form infinite zigzag polymeric chains. The infinite chains in **3** form an approximate hexagonal array, making triangular channels which are occupied by *N,N'*-dimethylimidazolium ions, whereas the chains in **4** form layered structure, and the layers are stacked perpendicularly with respect to the orientation of the infinite anionic chains alternatively. *N,N'*-dicyclohexylimidazolium cations and solvent molecules fill in between layers. © 2002

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Key Words: imidazolium; cadmium; thiocyanate; X-ray structure.

INTRODUCTION

Construction of supramolecular compounds through coordination chemistry is currently of great interest in research. The use of transition metal centers and coordination chemistry for directing the formation of complex structures has evolved into one of the most widely used strategies for organizing molecular building blocks into

supramolecular arrays (1). The linear triatomic pseudohalide, SCN⁻, is an ambidentate ligand with two donor atoms, which may coordinate through either S or N atom or both (2). It was reported that some one-dimensional (1-D) cadmium–thiocyanate coordination polymers, which are described as inorganic polymers with organic spacers, have been found to be nonlinear optical crystals with wide spectral range (2,3). These hybrid materials are expected to take the advantage of organic, inorganic and polymeric materials. Cadmium(II) and thiocyanate ions form various structures depending on the size, shape, and symmetry of the counter cations, and also the ratio of cadmium and SCN⁻ ions. A number of 1-D single chains such as [Cd(SCN)₃]⁻ (3–7), 1-D double chains such as [Cd₂(SCN)₅]⁻ (2), 2-D networks such as [Cd₂(SCN)₆]²⁻ and [Cd₃(SCN)₈]²⁻ (8), and 3-D structures (9) have been reported and reviewed (2).

N,N'-dialkylimidazolium salts are playing an increasing role in optimizing organic reactions (10). Heterocyclic carbenes, derived from imidazolium form complexes with many transition metals, which have been employed as catalysts for Heck and Suzuki coupling (11). Incorporation of *N,N'*-dialkylimidazolium ions into cadmium–thiocyanate coordination solids may lead to new organic–inorganic hybrid materials, and the size, shape, symmetry of imidazolium cations can be easily tuned by the variation of *N*-substituents. The substituents can be either linear or cyclic. The substituents can also contain various functional groups and chiral centers.

Indeed, two new cadmium–thiocyanate compounds using *N,N'*-dialkylimidazolium as spacers and controllers were obtained by one-pot reactions. In this paper, we report the synthesis, characterization, and single-crystal X-ray structures of the two salts, [(R₂Im)₂][Cd₂(SCN)₆] (R = methyl, **3**; R = cyclohexyl, **4**). Both **3** and **4** consist of 1-D infinite zigzag chains. It is interesting to note that the neighboring cadmium atoms in compound **3** exhibit

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different 4N2S and 2N4S coordination spheres rather than the typical 3N3S sphere, and compound **4** shows novel spatial arrangement of the anionic cadmium–thiocyanate chains, which has not been observed in the literature.

EXPERIMENTAL SECTION

All chemical reagents were used as received without further purification. In the NMR spectra (recorded on a Varian 300 MHz spectrometer), chemical shifts of ^1H are relative to tetramethylsilane. Analysis of C, H, and N were obtained with a Carlo Erba 1106 analyzer.

Preparation of $[(\text{Me}_2\text{Im})\text{I}]\text{I}$, **1**

A solution of CH_3I (3.0 g, 21 mmol) in 10 mL of toluene was slowly added to a solution of *N*-methylimidazolium (1.64 g, 20 mmol) in 30 mL of toluene with vigorous stirring. After 1 h, the mixture was condensed to ca 10 mL, a pale-yellow solid was afforded by adding 50 mL of diethyl ether, which was collected by filtration and washed with diethyl ether. Yield: 88.0%. Anal. calcd for $\text{C}_5\text{H}_9\text{IN}_2$: C, 26.80; H, 4.05; N, 12.50. Found: C, 26.26; H, 4.40; N, 11.83. ^1H NMR (D_2O): 9.51 (s, NCHN, 1H), 7.82 (unresolved AB, CHCH, 2H), 4.08 (s, CH_3 , 6H).

Preparation of $[(\text{Cy}_2\text{Im})\text{PF}_6]$, **2**

To a solution of $[(\text{Cy}_2\text{Im})\text{Cl}]$ (2.69 g, 10 mmol), which was prepared according to the published procedure (12), in 10 mL of water was added NH_4PF_6 (1.42 g, 10 mmol). A white solid was immediately produced. It was collected by filtration and successfully washed with water, EtOH, and Et_2O . Yield: 94%. Elemental analysis calcd for $\text{C}_{15}\text{H}_{25}\text{F}_6\text{N}_2\text{P}$: C, 47.62; H, 6.60; N, 7.40. Found: C, 47.38; H, 6.72; N, 7.25. ^1H NMR (acetone- d_6): 9.01 (s, NCHN, 1H), 7.81 (unresolved AB, CHCH, 2H), 4.41 (tt, $J_{\text{HH}} = 11.6$ Hz, $J_{\text{HH}} = 5.4$ Hz, NCH(cyclohexyl), 2H), 2.23–1.18 (m, other cyclohexyl H, 20H).

Preparation of $[(\text{Me}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6]$, **3**

To a mixture of 1 mL of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (1 mol/L) and 1 mL of NH_4SCN (3 mol/L) in water was added $[(\text{Me}_2\text{Im})\text{I}]$ (22.4 mg, 1.0 mmol). A white precipitate was immediately formed. Acetone was added to the resulted mixture till all the precipitate dissolved again. Slow evaporation of the pale-yellow solution afforded colorless prisms. Yield: 86%. Elemental analysis calcd for $\text{C}_8\text{H}_9\text{N}_5\text{S}_3\text{Cd}$: C, 25.04; H, 2.36; N, 18.25. Found: C, 24.86; H, 2.52; N, 18.09. ^1H NMR (acetone- d_6): δ 9.02 (s, NCHN, 1H), 7.73 (s, CHCH, 2H), 4.10 (s, CH_3 , 6H).

Preparation of $[(\text{Cy}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6] \cdot \text{C}_3\text{H}_6\text{O}$, **4**

Compound **4** was prepared in the same way as for **3**. Yield: 92%. Elemental analysis calcd for $\text{C}_{18}\text{H}_{25}\text{N}_5\text{S}_3\text{Cd} \cdot 0.5\text{C}_3\text{H}_6\text{O}$: C, 42.66; H, 5.14; N, 12.75. Found: 42.43; H, 5.20; N, 12.47. ^1H NMR (acetone- d_6): 9.15 (s, NCHN, 1H), 7.88 (s, CHCH, 2H), 4.46 (unresolved t, NCH(cyclohexyl), 2H), 2.29–1.31 (m, C_6H_{11} , 20H). Suitable crystals for X-ray crystallographic study were obtained by slow evaporation of the acetone/water solution.

X-Ray Crystallography

Table 1 summarizes the crystal data collection and refinement parameters. Data collection was performed on a Bruker Smart-CCD diffractometer using monochromatized $\text{MoK}\alpha$ radiation, $\lambda = 0.71073$ Å at room temperature. Data reduction was performed using SAINT+ Version 6.02 software (13). The data were corrected for absorption using the program SADABS within the SAINTPLUS package. The structures were solved by direct method. This solution yielded cadmium atoms, S, N, and some C atoms. Subsequent Fourier synthesis gave the remaining C-atom positions. The hydrogen atoms were geometrically fixed and allowed to ride on their attached atoms, and refined within the XSELL software (14). The final refinement included anisotropic thermal parameters on all of the non-hydrogen atoms and converged to the R1 and wR2 values

TABLE 1
Crystal Data and Structure Refinement for $[(\text{Me}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6]$ (**3**) and $[(\text{Cy}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6] \cdot \text{C}_3\text{H}_6\text{O}$ (**4**)

Compound	$[(\text{Me}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6]$	$[(\text{Cy}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6] \cdot \text{C}_3\text{H}_6\text{O}$
Formula	$\text{C}_{16}\text{H}_{18}\text{Cd}_2\text{N}_{10}\text{S}_6$	$\text{C}_{39}\text{H}_{56}\text{Cd}_2\text{N}_{10}\text{OS}_6$
Fw	767.56	1098.10
Crystal system	Monoclinic	Monoclinic
Space group	C2	Cc
<i>a</i> Å	17.468(3)	13.3049(12)
<i>b</i> Å	7.7273(12)	17.5550(16)
<i>c</i> Å	10.6750(16)	20.8012(19)
β deg	104.833(2)	101.494(2)
<i>V</i> Å ³	1392.9(4)	4761.0(7)
<i>Z</i>	2	4
<i>D</i> _{calc} , mg/m ³	1.830	1.532
<i>T</i> (K)	293.2	293.2
λ Å	0.71073	0.71073
<i>F</i> (000)	752	2240
Abs. coefficient (mm ⁻¹)	2.002	1.198
Reflections collected	4134	12807
Reflections unique (<i>R</i> _{int})	2929 (0.0386)	8158 (0.0963)
Goodness-of-fit	1.047	1.031
Absolute structure parameter	0	-0.06(4)
<i>R</i> 1, w <i>R</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0322, 0.0869	0.0775, 0.1916
<i>R</i> 1, w <i>R</i> 2 (all data)	0.0325, 0.0873	0.0787, 0.1944

listed in Table 1. The atomic coordinates are given in Tables 2 and 3.

RESULTS AND DISCUSSION

Synthesis and Characterization

N,N'-dimethylimidazolium iodide, **1** can be easily prepared from *N*-methylimidazole and methyl iodide at room temperature in high yield. Compound **1** was isolated as a pale-yellow hygroscopic solid. Compound **2** was prepared by metathesis reaction of *N,N'*-dicyclohexylimidazolium chloride with ammonium hexafluorophosphate in water and obtained as a white solid. Both **1** and **2** were characterized by ¹H NMR spectra and elemental analysis. The structure of **2** has been recently described (16). The obtained carbon and nitrogen percentage of **1** is lower than that required due to its hygroscopic property. The compounds [(Me₂Im)₂][Cd₂(SCN)₆] (**3**) and [(Cy₂Im)₂][Cd₂(SCN)₆]·C₃H₆O (**4**) were synthesized by mixing the corresponding *N,N'*-dialkylimidazolium salts, cadmium nitrate, and ammonium thiocyanate (1:1:3) in a water–acetone solvent. The freshly prepared compounds **3** and **4** are soluble in acetone and ethanol.

X-Ray Molecular Structure of [(Me₂Im)₂][Cd₂(SCN)₆] (**3**)

The structure of compound **3** is shown in Fig. 1, and selected bond distances and angles are collected in Table 4.

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for [(Me₂Im)₂][Cd₂(SCN)₆]

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Compound 3				
C(1)	9403(2)	4585(5)	7077(4)	39(1)
C(2)	9386(3)	192(6)	7493(4)	44(1)
C(3)	11,201(2)	2464(6)	8059(4)	43(1)
C(4)	7659(3)	7817(8)	1912(7)	67(1)
C(5)	8754(3)	6747(9)	3115(8)	74(2)
C(6)	8890(3)	7259(9)	1999(8)	81(2)
C(7)	8085(5)	8668(11)	−29(8)	87(2)
C(8)	7592(5)	6746(14)	4084(9)	101(3)
Cd(1)	10,000	2858(1)	10000	43(1)
Cd(2)	10,000	1932(1)	5000	42(1)
N(1)	9554(3)	4028(5)	6166(3)	48(1)
N(2)	9411(4)	771(6)	8489(4)	71(1)
N(3)	11,027(3)	2839(8)	8997(4)	62(1)
N(4)	8194(2)	7927(6)	1253(5)	64(1)
N(5)	7981(2)	7094(6)	3060(6)	66(1)
S(1)	9207(1)	5383(2)	8388(1)	47(1)
S(2)	9333(1)	−647(2)	6070(1)	48(1)
S(3)	11,475(1)	1937(2)	6763(1)	52(1)

^a *U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

TABLE 3
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for [(Cy₂Im)₂][Cd₂(SCN)₆]·C₃H₆O

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
C(1)	9843(8)	3051(5)	4688(4)	35(2)
C(2)	7969(7)	2194(5)	3501(5)	32(2)
C(3)	9540(6)	3468(4)	3077(4)	26(2)
C(4)	5976(6)	5115(4)	4477(4)	27(2)
C(5)	12928(6)	1003(4)	3971(5)	30(2)
C(6)	6039(7)	5223(5)	2811(4)	34(2)
C(7)	2904(6)	8834(5)	1664(4)	28(2)
C(8)	2886(8)	8827(6)	598(5)	39(2)
C(9)	3213(8)	9531(5)	842(5)	36(2)
C(10)	2294(9)	7619(5)	1062(6)	43(2)
C(11)	3035(17)	7089(7)	787(7)	80(6)
C(12)	2570(20)	6271(8)	724(7)	102(8)
C(13)	2457(15)	5977(6)	1386(7)	69(5)
C(14)	1716(13)	6515(8)	1650(9)	71(4)
C(15)	2134(9)	7330(6)	1726(6)	46(2)
C(16)	3488(6)	10152(4)	1981(4)	27(2)
C(17)	4657(7)	10235(5)	2180(5)	33(2)
C(18)	4873(8)	10861(5)	2710(6)	42(2)
C(19)	4383(8)	11622(6)	2459(7)	51(3)
C(20)	3224(9)	11520(6)	2220(6)	46(2)
C(21)	2982(8)	10900(5)	1703(5)	36(2)
C(22)	7239(8)	636(5)	4266(5)	41(2)
C(23)	5875(9)	47(6)	4392(6)	49(2)
C(24)	6356(8)	−411(5)	4043(5)	40(2)
C(25)	6250(20)	1319(8)	4962(7)	101(9)
C(26)	6360(30)	1013(14)	5688(8)	147(15)
C(27)	6456(14)	1895(13)	6126(9)	93(6)
C(28)	5448(17)	2234(13)	5884(11)	91(5)
C(29)	5310(19)	2460(10)	5163(12)	96(6)
C(30)	5349(12)	1741(8)	4751(9)	69(4)
C(31)	7990(7)	−287(5)	3591(5)	32(2)
C(32)	8449(8)	−1052(6)	3857(6)	42(2)
C(33)	9204(9)	−1373(6)	3465(6)	46(2)
C(34)	8738(9)	−1426(5)	2734(6)	45(2)
C(35)	8306(8)	−654(6)	2464(5)	41(2)
C(36)	7524(7)	−348(6)	2850(5)	38(2)
C(37)	9464(9)	700(11)	5773(7)	69(4)
C(38)	10314(15)	218(19)	6078(10)	130(12)
C(39)	9610(20)	1491(17)	5893(19)	150(13)
Cd(1)	7689(1)	4084(1)	3862(1)	27(1)
Cd(2)	10492(1)	1777(1)	3663(1)	28(1)
N(1)	10409(7)	2676(5)	4490(4)	39(2)
N(2)	8690(6)	1838(4)	3513(5)	36(2)
N(3)	8945(5)	3834(4)	3279(4)	30(1)
N(5)	8180(6)	5368(5)	4031(5)	39(2)
N(6)	6335(6)	4401(5)	2753(5)	42(3)
N(7)	2693(6)	8411(4)	1125(4)	32(1)
N(8)	3219(6)	9516(4)	1504(4)	30(1)
N(9)	6421(9)	686(5)	4534(5)	48(2)
N(10)	7212(6)	−24(4)	3949(4)	35(2)
O(1)	8682(9)	439(7)	5458(7)	88(4)
S(1)	9014(2)	3594(2)	4988(1)	42(1)
S(2)	6887(2)	2678(1)	3471(2)	45(1)
S(3)	10390(2)	2955(1)	2785(1)	34(1)
S(4)	6442(2)	4270(1)	4717(1)	33(1)
S(5)	12602(2)	1915(1)	3918(1)	31(1)
S(6)	10429(3)	979(2)	2551(2)	60(1)

^a *U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

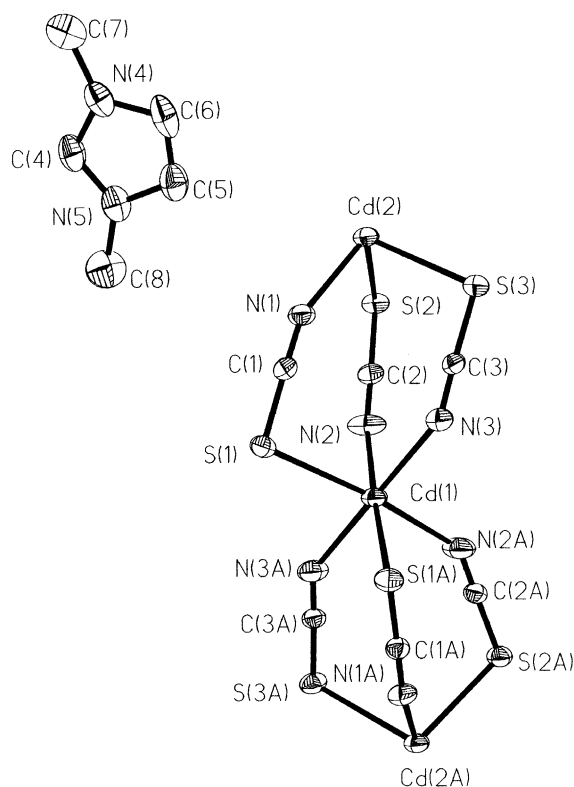


FIG. 1. A view of the asymmetric unit of **3** with atomic numbering scheme. Thermal ellipsoids of 30% probability are presented. Hydrogen atoms were omitted for clarity.

Overall, the structure consists of the expected 1-D cadmium–thiocyanate chains. Compound **3** crystallizes in the monoclinic unit cell of dimensions $a = 17.468(3) \text{ \AA}$, $b = 7.7273(12) \text{ \AA}$, $c = 10.6750(16) \text{ \AA}$, $\beta = 104.833(2)^\circ$, and space group $C2$ with two $[(\text{Me}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6]$ per unit cell. The cadmium atoms and thiocyanate ions form 1-D chain. The two independent Cd atoms are octahedrally coordinated in a $4N2S$ and $2N4S$ coordination environment, respectively. This is quite different from other known 1-D cadmium–thiocyanate complexes, in which the cadmium atoms are typically coordinated by three N atoms and three S atoms in a *fac* configuration, and all the nitrogen atoms are *trans* to the sulfur atoms around cadmium center, dictated by *trans* effect (2, 3). The average Cd–S and Cd–N lengths are 2.737 \AA and 2.312 \AA , and the average Cd–S–C and Cd–N–C angles are 97.90° and 147.91° , respectively. These values are consistent with those found in triply bridged (3–9) and doubly bridged (16) cadmium–thiocyanate compounds. The N–C–S bridging ligands are almost linear with an average angle of 178.7° , and the average C–S and C–N bond distances are 1.634 \AA and 1.151 \AA .

For the alignment of Cd atoms, each cadmium atom is triply bridged by six SCN^- ions, thus forming on infinite zigzag chains. The neighboring Cd...Cd separation is

5.385 \AA , and the Cd...Cd...Cd angle is 164.72° . The adjacent chains are parallel each other, as shown in Fig. 2(a). The infinite chains form an approximate hexagonal array, as viewed along the crystallographic c -axis. Three neighboring chains consist of triangular channels, which are occupied by imidazolium cations (Fig. 2(b)). The imidazolium cations interact with the anionic cadmium–thiocyanate chains through very weak hydrogen bonds, C(4)–H(4)···S(1) (2.893 \AA) and electronic interactions. The hexagonal arrangement is also adopted by the anionic $[\text{Cd}(\text{SCN})_3]^-$ chains in $[(12\text{-C-4})_2\text{Na}][\text{Cd}(\text{SCN})_3]$ (**3c**), $[\text{Et}_4\text{N}][\text{Cd}(\text{SCN})_3]$ (**3b**, **4a**), and $[\text{Me}_4\text{N}][\text{Cd}(\text{SCN})_3]$ (**3b**, **4b**).

X-Ray Molecular Structure of $[(\text{C}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6]$ (**4**)

Compound **4** crystallizes in the monoclinic unit cell of dimensions $a = 13.3049(12) \text{ \AA}$, $b = 17.5550(16) \text{ \AA}$, $c = 20.8012(19) \text{ \AA}$, $\beta = 101.494(2)^\circ$, and space group Cc , with four $[(\text{C}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6] \cdot \text{C}_3\text{H}_6\text{O}$ per unit cell. A view of the molecular structure with atomic numbering scheme is shown in Fig. 3. Selected bond distances and angles are given in Table 5.

The coordination geometry around Cd(II) center is also octahedral. Each SCN^- bridges two adjacent Cd atoms, and each Cd atom is coordinated by three N and three S atoms in a *fac* configuration. All the three S atoms surrounding Cd atom are at the *trans* position of three N

TABLE 4
Selected Bond Lengths (\AA) and Angles (deg) for $[(\text{Me}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6]$

Cd(1)–S(1)	2.7326(12)	Cd(1)–N(2)	2.327(5)
Cd(1)–N(3)	2.313(4)	Cd(2)–N(1)	2.297(4)
Cd(2)–S(2)	2.7036(12)	Cd(2)–S(3)	2.7739(12)
C(1)–N(1)	1.154(6)	C(1)–S(1)	1.644(4)
C(2)–N(2)	1.144(6)	C(2)–S(2)	1.633(4)
C(3)–N(3)	1.154(6)	C(3)–S(3)	1.627(4)
N(1)–C(1)–S(1)	178.9(4)	N(2)–C(2)–S(2)	179.0(5)
N(3)–C(3)–S(3)	178.2(4)	N(3)#1–Cd(1)–N(3)	179.2(3)
N(3)#1–Cd(1)–N(2)	93.38(19)	N(3)–Cd(1)–N(2)	86.10(19)
N(2)–Cd(1)–N(2)#1	92.2(3)	N(3)–Cd(1)–S(1)	92.38(12)
N(3)–Cd(1)–S(1)#1	88.16(13)	N(2)–Cd(1)–S(1)#1	174.03(12)
N(2)–Cd(1)–S(1)	89.74(14)	S(1)#1–Cd(1)–S(1)	88.87(5)
N(1)#2–Cd(2)–N(1)	90.3(2)	N(1)#2–Cd(2)–S(2)	172.30(10)
N(1)–Cd(2)–S(2)	92.76(11)	S(2)–Cd(2)–S(2)#2	85.06(5)
N(1)#2–Cd(2)–S(3)	88.95(10)	N(1)–Cd(2)–S(3)	90.94(10)
S(2)–Cd(2)–S(3)	98.04(4)	S(2)#2–Cd(2)–S(3)	82.07(4)
S(3)–Cd(2)–S(3)#2	179.85(6)	C(1)–N(1)–Cd(2)	154.4(3)
C(2)–N(2)–Cd(1)	145.2(4)	C(3)–N(3)–Cd(1)	144.1(4)
C(1)–S(1)–Cd(1)	94.90(14)	C(2)–S(2)–Cd(2)	99.97(15)
C(3)–S(3)–Cd(2)	98.82(14)		

Note. Symmetry transformations used to generate equivalent atoms. #1: $-x + 2, y, -z + 2$; #2: $-x + 2, y, -z + 1$.

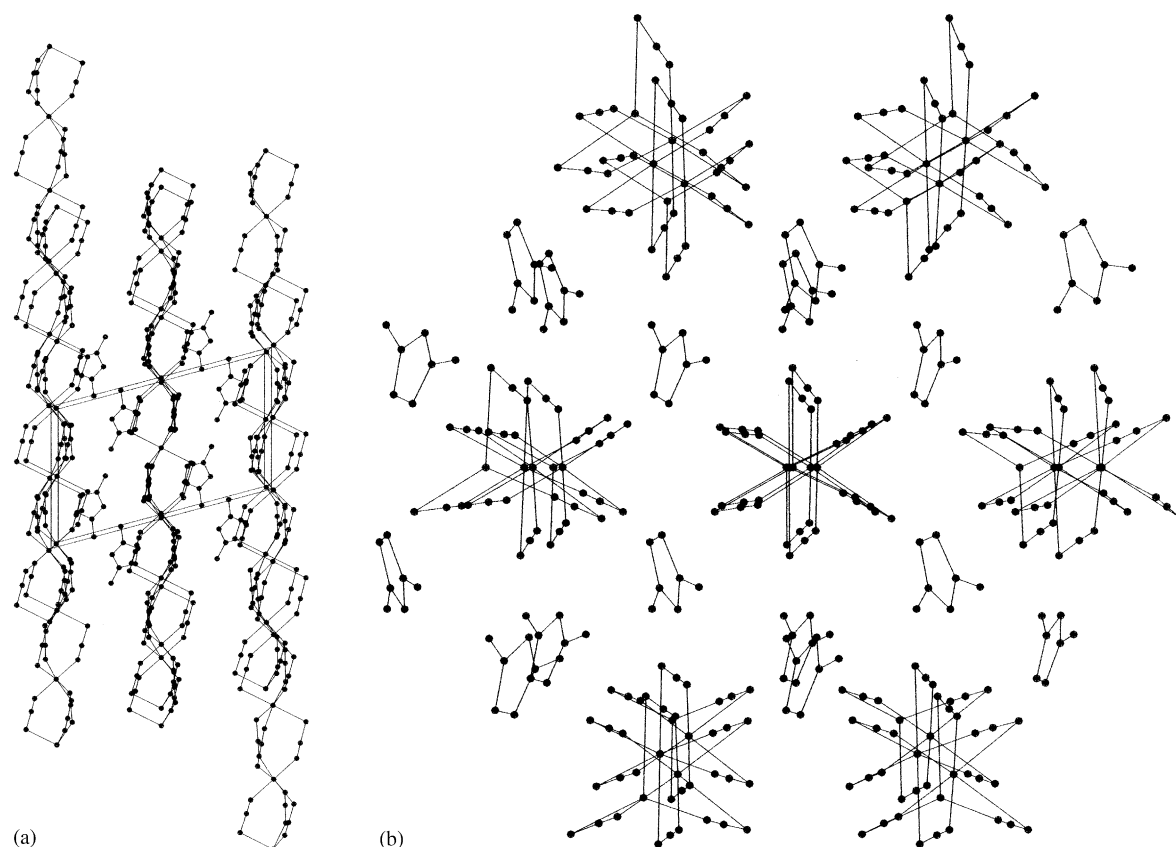


FIG. 2. Crystal packing of **3**. (a) Viewed along the crystallographic *a*-axis, the 1-D chains run in a parallel way. (b) Viewed along the crystallographic *c*-axis. Hexagonal arrangement of 1-D chains gives rise to triangular channels which are filled with cations.

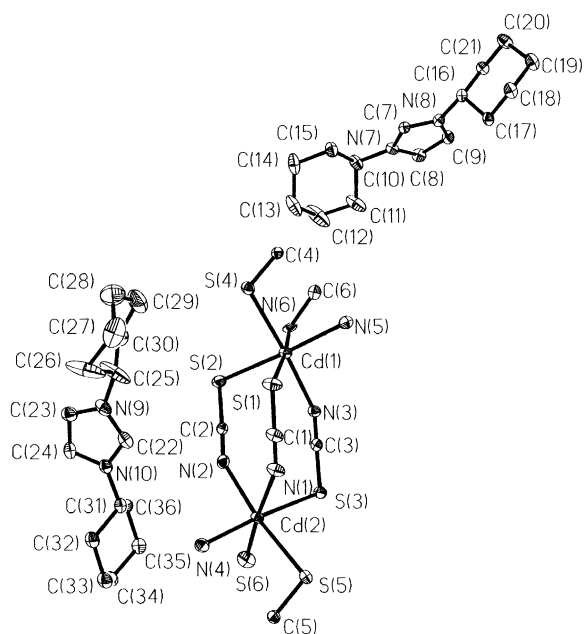


FIG. 3. A view of the asymmetric unit of **4** with atomic numbering scheme. Thermal ellipsoids of 30% are presented. Hydrogen atoms and acetone molecule were omitted for clarity.

atoms, respectively, dictated by *trans* effect. This kind of polymeric chain and coordination sphere of Cd atoms has been observed in a number of known cadmium–thiocyanate complexes (2). The average Cd–S bond lengths being 2.733 Å is not very different from the respective value of **3**. The Cd(1)–N(6) distance is much longer than the normal value, and the corresponding Cd(1)–N(6)–C(6) angle deviate much from the normal value due to disorder. The average Cd–N length is 2.331 Å, and the average Cd–S–C and Cd–N–C angles are 99.95° and 149.24° in the normal range.

It has been revealed that the arrangement and alignment of the infinite anionic $[\text{Cd}_2(\text{SCN})_6]^{2-}$ zigzag chains are dictated by the dimensions and symmetry of the cations to a large extent (2, 3). Indeed, when a bulkier cation *N,N'*-dicyclohexylimidazolium was used, a quite different spatial arrangement of the anionic chains was obtained. The anionic cadmium–thiocyanate chain in **4** is somewhat similar to that of **3**. The Cd...Cd distances are 5.577 and 5.530 Å, and the Cd...Cd...Cd angle is 165.15°, which are not very different from **3** and other related compounds (2). However, unlike its analog **3**, compound **4** shows quite

TABLE 5
Selected Bond Lengths (Å) and Angles (deg) for
 $[(\text{Cy}_2\text{Im})_2][\text{Cd}_2(\text{SCN})_6]\cdot\text{C}_3\text{H}_6\text{O}$

Cd(1)–S(1)	2.772(2)	Cd(1)–S(2)	2.746(2)
Cd(1)–S(4)	2.682(2)	Cd(1)–N(3)	2.295(7)
Cd(1)–N(5)	2.355(8)	Cd(1)–N(6)	2.687(9)
Cd(2)–N(4)	2.296(8)	Cd(2)–N(1)	2.354(8)
Cd(2)–N(2)	2.358(8)	Cd(2)–S(3)	2.745(2)
Cd(2)–S(6)	2.691(4)	Cd(2)–S(5)	2.763(2)
C(1)–N(1)	1.137(13)	C(1)–S(1)	1.671(9)
C(2)–N(2)	1.140(12)	C(2)–S(2)	1.662(9)
C(3)–N(3)	1.162(11)	C(3)–S(3)	1.652(8)
C(4)–N(4)#1	1.161(12)	C(4)–S(4)	1.648(8)
C(5)–N(5)#2	1.163(12)	C(5)–S(5)	1.656(8)
C(6)–N(6)	1.506(12)	C(6)–S(6)#1	1.594(9)
<hr/>			
N(1)–C(1)–S(1)	179.2(9)	N(2)–C(2)–S(2)	177.5(9)
N(3)–C(3)–S(3)	179.3(8)	N(4)#1–C(4)–S(4)	178.9(9)
N(5)#2–C(5)–S(5)	177.4(9)	N(6)–C(6)–S(6)#1	153.5(8)
N(3)–Cd(1)–N(5)	93.0(3)	N(3)–Cd(1)–S(4)	170.2(2)
N(5)–Cd(1)–S(4)	88.5(2)	N(3)–Cd(1)–N(6)	91.1(2)
N(5)–Cd(1)–N(6)	92.8(3)	S(4)–Cd(1)–N(6)	98.46(16)
N(3)–Cd(1)–S(2)	87.29(19)	N(5)–Cd(1)–S(2)	169.9(2)
S(4)–Cd(1)–S(2)	92.91(7)	N(6)–Cd(1)–S(2)	77.1(2)
N(3)–Cd(1)–S(1)	88.8(2)	N(5)–Cd(1)–S(1)	93.4(2)
S(4)–Cd(1)–S(1)	81.43(7)	N(6)–Cd(1)–S(1)	173.8(2)
S(2)–Cd(1)–S(1)	96.63(9)	N(4)–Cd(2)–N(1)	97.1(3)
N(4)–Cd(2)–N(2)	94.7(3)	N(1)–Cd(2)–N(2)	82.6(3)
N(4)–Cd(2)–S(6)	94.0(3)	N(1)–Cd(2)–S(6)	168.4(2)
N(2)–Cd(2)–S(6)	93.1(2)	N(4)–Cd(2)–S(3)	173.9(2)
N(1)–Cd(2)–S(3)	88.7(2)	N(2)–Cd(2)–S(3)	87.9(2)
S(6)–Cd(2)–S(3)	80.30(9)	N(4)–Cd(2)–S(5)	89.5(2)
N(1)–Cd(2)–S(5)	89.7(2)	N(2)–Cd(2)–S(5)	171.6(2)
S(6)–Cd(2)–S(5)	93.82(9)	S(3)–Cd(2)–S(5)	88.56(7)
C(1)–N(1)–Cd(2)	141.5(8)	C(2)–N(2)–Cd(2)	148.9(7)
C(3)–N(3)–Cd(1)	156.5(6)	C(4)#2–N(4)–Cd(2)	152.6(8)
C(5)#1–N(5)–Cd(1)	146.7(7)	C(6)–N(6)–Cd(1)	105.7(6)
C(1)–S(1)–Cd(1)	102.6(3)	C(2)–S(2)–Cd(1)	99.6(3)
C(3)–S(3)–Cd(2)	96.4(3)	C(4)–S(4)–Cd(1)	98.8(3)
C(5)–S(5)–Cd(2)	99.8(3)	C(6)#2–S(6)–Cd(2)	102.5(4)

Note. Symmetry transformations used to generate equivalent atoms.
 #1: $x - \frac{1}{2}, y + \frac{1}{2}, z$; 2: $x + \frac{1}{2}, y - \frac{1}{2}, z$.

different stacking of the anionic zigzag chains. For the former, all the polymeric chains are arranged in a parallel way and form hexagonal array with triangular channels (Fig. 2(b)). Whereas in **4**, the alignment of cadmium–thiocyanate chains forms a layered structure, in which one-half arranges along approximately the crystallographic *a*-axis, and another half arranges along approximately the *c*-axis. Thus, this arrangement results in AB layer structure, and the adjacent layers are stacked perpendicularly with respect to the orientation of the anionic chains in an alternative fashion, as shown in Fig. 4. Within the layers, the alignment of chains is similar to its analog in a parallel manner. This kind of arrangement of the anionic chains represents a rare example of cadmium–thiocyanate complexes. To the best of our knowledge, this has never been observed in the known 1-D cadmium–thiocyanate compounds.

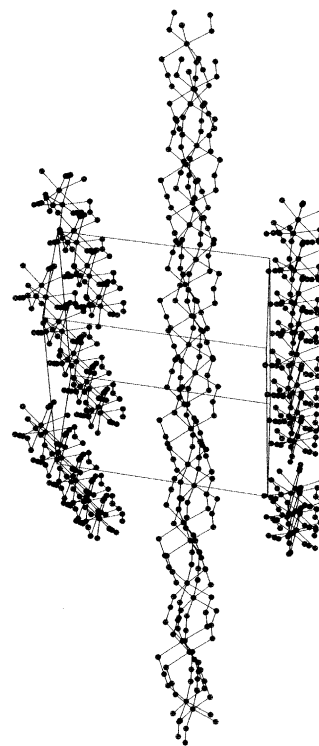


FIG. 4. A perspective view approximately parallel to the crystallographic *c*-axis of the stacking layers in **4**. The imidazolium cations and solvent molecules were omitted for clarity. Note that the 1-D chains form AB layers and run approximately perpendicularly.

The layers and chains are separated by *N,N'*-dicyclohexylimidazolium cations and acetone molecules, and the cations interact with the anionic infinite chains through a weak C(8)–H(8)⋯S(5) (2.749 Å) hydrogen bond. It is noted that the more acidic C(7)–H(7) does not have close contact with either S or N atoms of SCN[−] ions. Probably, the very weak hydrogen bonds also play some role in the unique orientation and stacking of the infinite chains.

In summary, we have prepared two novel *N,N'*-dialkylimidazolium cadmium–thiocyanate inorganic–organic hybrid compounds. The dialkylimidazolium cations act as the spacers and controllers, which dominate the arrangement and alignment of the anionic [Cd₂(SCN)₆]^{2−} chains. And a novel crystallization pattern for [(Cy₂Im)₂][Cd₂(SCN)₆] \cdot C₃H₆O is discovered when bulkier imidazolium cations is used as the spacer. The coordination solid, [(Cy₂Im)₂][Cd₂(SCN)₆] \cdot C₃H₆O is unique among the known 1-D cadmium–thiocyanate polymers so far as the chain arrangement is concerned.

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