



Cation-controlled formation of N,N' -dialkylimidazolium cadmium–thiocyanate complexes: synthesis and structural characterization

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Received 4 June 2002; received in revised form 3 September 2002; accepted 25 September 2002

Abstract

Three new N,N' -dialkylimidazolium salts of cadmium–thiocyanate, $[\text{EtMeIm}]_2[\text{Cd}_2(\text{SCN})_6]$ (**2**), $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2][\text{Cd}(\text{SCN})_4]$ (**3**), $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3][\text{CdBr}_3(\text{SCN})](\text{NO}_3)$ (**4**) have been prepared, and their crystal structures have been determined by X-ray diffraction. Crystal data: **2**, monoclinic, $C2/c$, $a = 18.349(4) \text{ \AA}$, $b = 7.8667(18) \text{ \AA}$, $c = 21.399(5) \text{ \AA}$, $\beta = 110.346(4)^\circ$, $V = 2896.1(11) \text{ \AA}^3$, $Z = 4$, and $R1 = 0.0561$; **3**, monoclinic, $C2/c$, $a = 20.347(7) \text{ \AA}$, $b = 14.029(5) \text{ \AA}$, $c = 9.380(3) \text{ \AA}$, $\beta = 112.034(6)^\circ$, $V = 2482.1(15) \text{ \AA}^3$, $Z = 4$, and $R1 = 0.0397$; **4**, hexagonal, $P6_3$, $a = b = 10.7634(8) \text{ \AA}$, $c = 16.0315(17) \text{ \AA}$, $V = 1608.4(2) \text{ \AA}^3$, $Z = 2$, and $R1 = 0.0569$. Compound **2** consists of triply bridged infinite one-dimensional cadmium–thiocyanate chains, and two independent cadmium atoms are octahedrally coordinated in $2N4S$ and $4N2S$ geometry, respectively. In **3**, the cadmium atom is octahedrally coordinated with two *cis* N -bonded monodentate NCS^- ligands and four bridging SCN^- in a S *trans* to S , and N *trans* to N coordination fashion, and thus form doubly bridged infinite one-dimensional chains. Whereas **4** is mononuclear, consisting of a discrete $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3]^{3+}$ cation, a nitrate, and $[\text{CdBr}_3(\text{SCN})]^-$ ion, and each cadmium(II) ion is coordinated to three bromide and one nitrogen atom of SCN^- ion. The structures of these compounds are dictated by the imidazolium cations.

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Keywords: Cation control; Imidazolium; Thiocyanate; Cadmium complexes; Crystal structures

1. Introduction

The N,N' -dialkylimidazolium salts (also called ionic liquids) are receiving growing interests recently since they have proved to be good solvents, and their deprotonated forms (i.e., heterocyclic carbene) reacts with many transition metals [1, 2]. The interests also arise from their distinct physicochemical properties and potential applications in electrochemistry [3], extraction technology [4], and as liquid crystals [5]. A few dialkylimidazolium salts with the formula $[\text{RR}'\text{Im}][\text{MX}_n]$ have been recently prepared and characterized [6, 7]. Recently, it has been reported that some hybrid materials involving polymeric anionic cadmium–

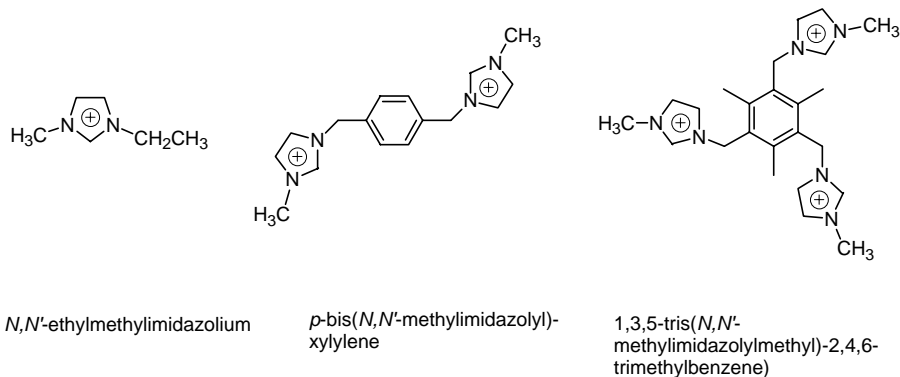
thiocyanate exhibit anisotropic physical properties such as NLO behavior [8–14]. The arrangement and alignment of one-dimensional coordination polymer chains dominate their physical properties such as optoelectronic and luminescence. Imidazolium salts are easily prepared, and their size and symmetry can be easily tuned by changing the N -substituents. Thus, the utilization of imidazolium salts affords the opportunity to explore the role of the counter cations in the arrangement and alignment of the cadmium–thiocyanate chains [15].

In this paper, we report the synthesis, characterization and single-crystal X-ray structure of the imidazolium salts, $[\text{EtMeIm}]_2[\text{Cd}_2(\text{SCN})_6]$ ($\text{EtMeIm} = N$ -ethyl- N' -methylimidazolium) (**2**), $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2][\text{Cd}(\text{SCN})_4]$ ($[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2 = p$ -bis(N,N' -methylimidazolyl)xylylene]) (**3**), and $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3][\text{CdBr}_3(\text{SCN})](\text{NO}_3)$ ($[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3 = 1,3,5$ -tris(N,N' -methyl-

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imidazolylmethyl)-2,4,6-trimethylbenzene] (**4**). The imidazolium cations used are shown in Chart 1.



2. Experimental section

2.1. Materials and methods

All the starting materials were reagent grade and used without further purification. Elemental analyses were performed on a PE 240C elemental analyzer. ^1H NMR spectra were acquired on a Bruker AM 400 (400 MHz) spectrometer, using the deuterated solvent as the lock and residual solvent as the internal reference. $[\text{EtMeIm}]\text{Br}$ and $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2]\text{Cl}_2$ were prepared using the published procedure [16].

2.2. Preparation of $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3]\text{Br}_3$, **1**

To a solution of 1,3,5-*tris*(bromomethyl)-2,4,6-trimethylbenzene (4.0 g, 0.01 mol) in 20 mL of toluene was added *N*-methylimidazole (4.1 g, 0.05 mol) slowly. Pale-yellow solid was obtained by adding 20 mL of diethyl ether to the mixture. Yield: 94%. Anal. calcd for $\text{C}_{24}\text{H}_{33}\text{Br}_3\text{N}_6$: C, 44.67; H, 5.15; N, 13.02%. Found: C, 44.33; H, 5.42; N, 12.79%. ^1H NMR (D_2O): 8.71 (s, NCHN, 3H), 7.56, 5.65 (both br. NCHCHN, each 3H), 4.65 (s, CH_2 , 6H), 3.94 (s, NCH₃, 9H), 2.41 (s, ArCH₃, 9H).

2.3. Preparation of $[(\text{EtMeIm})]_2[\text{Cd}_2(\text{SCN})_6]$, **2**

To a mixture of 1 mL of $\text{Cd}(\text{NO}_3)_2$ (1 mol/L) and 3 mL of KSCN (1 mol/L) in water was added *N*-ethyl-*N'*-methylimidazolium bromide (1 mmol). A white precipitate was immediately formed. Addition of acetone to the resulted mixture till all the precipitate was dissolved. Slow evaporation of the pale-yellow solution afforded colorless prisms in 86% yield. Anal. calcd for $\text{C}_{18}\text{H}_{22}\text{Cd}_2\text{N}_{10}\text{S}_6$: C, 27.17; H, 2.79; N, 17.60%. Found: C, 26.96; H, 3.02; N, 17.49%.

2.4. Preparation of $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2][\text{Cd}(\text{SCN})_4]$, **3**

To a mixture of 1 mL of $\text{Cd}(\text{NO}_3)_2$ (1 mol/L) and 3 mL of KSCN (1 mol/L) in water was added $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2]\text{Cl}_2$ (0.5 mmol). A white precipitate was immediately formed. Acetone was added to the above mixture till all the precipitate was dissolved. Slow evaporation of the colorless solution afforded needle-like crystals in 81% yield. Anal. calcd for $\text{C}_{20}\text{H}_{20}\text{CdN}_8\text{S}_4$: C, 39.18; H, 3.29; N, 18.28%. Found: C, 39.06; H, 3.44; N, 18.17%.

2.5. Preparation of $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3][\text{CdBr}_3(\text{SCN})](\text{NO}_3)$, **4**

To a mixture of 1 mL of $\text{Cd}(\text{NO}_3)_2$ (1 mol/L) and 3 mL of KSCN (1 mol/L) in water was added $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3]\text{Br}_3$ (0.33 mmol) in 4 mL of acetone. The mixture was allowed to stand at 5°C. Colorless crystals were grown after a week. Yield: 74%. Anal. calc for $\text{C}_{25}\text{H}_{33}\text{Br}_3\text{CdN}_8\text{O}_3\text{S}$: C, 34.21; H, 3.79; N, 12.77%. Found: C, 33.70; H, 3.82; N, 12.54%.

2.6. Crystallographic data collection and structure determination

Single-crystal X-ray diffraction measurements of all compounds were carried out with a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. The determination of unit-cell parameters and data collections were performed with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Unit-cell dimensions were obtained with least-squares refinements and the structure was solved by direct methods [17, 18]. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 . The hydrogen atoms were added theoretically, and riding

Table 1
Crystal data and structure refinement for **2**, **3**, and **4**

	2	3	4
Empirical formula	C18H22Cd2N10S6	C20H20CdN8S4	C25H33Br3CdN8O3S
Formula weight	397.81	613.08	877.78
Crystal size (mm)	0.17 × 0.27 × 0.81	0.08 × 0.10 × 0.32	0.43 × 0.27 × 0.21
Crystal system	Monoclinic	Monoclinic	Hexagonal
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P6(3)</i>
<i>a</i> (Å)	18.349(4)	20.347(7)	10.7634(8)
<i>b</i> (Å)	7.8667(18)	14.029(5)	10.7634(8)
<i>c</i> (Å)	21.399(5)	9.380(3)	16.0315(17)
β (deg)	110.346(4)	112.034(6)	
<i>V</i> (Å ³)	2896.1(11)	2482.1(15)	1608.4(2)
<i>T</i> (K)	123(2)	293(2)	123(2)
<i>Z</i>	4	4	2
<i>D</i> _{calc} (g/cm ³)	1.825	1.641	1.812
Reflections collected	8340	7477	10276
Reflections unique (<i>R</i> _{int})	3255(0.0497)	2842(0.0556)	2233(0.1174)
Goodness-of-fit	1.029	0.974	1.338
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.0561	0.0397	0.0569
w <i>R</i> 2	0.1502	0.0973	0.1526

Table 2
Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
C(1)	1165(3)	9570(9)	4151(3)	33(1)
C(2)	533(4)	7209(8)	1280(3)	36(1)
C(3)	625(3)	11401(7)	1539(3)	28(1)
C(4)	2277(7)	4460(20)	4128(9)	148(9)
C(5)	1280(5)	3374(10)	3346(4)	52(2)
C(6)	1062(7)	3912(10)	3832(4)	64(3)
C(7)	1684(10)	5401(16)	4927(5)	118(6)
C(8)	1941(12)	4140(20)	5442(9)	142(7)
C(9)	2507(6)	3590(20)	3012(9)	204(14)
Cd(1)	0	8790(1)	2500	24(1)
Cd(2)	0	10000	0	27(1)
N(1)	−1019(3)	10177(8)	411(2)	39(1)
N(2)	439(4)	7791(8)	762(3)	46(1)
N(3)	453(3)	10856(6)	1968(2)	28(1)
N(4)	1638(5)	4547(10)	4324(3)	76(3)
N(5)	2053(4)	3728(11)	3530(5)	87(3)
S(1)	1401(1)	8713(3)	3549(1)	42(1)
S(2)	669(1)	6335(2)	2012(1)	42(1)
S(3)	861(1)	12234(3)	931(1)	48(1)

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

on the concerned atoms and refined with fixed thermal factors. Crystallographic data and experimental details for structural analyses are summarized in Table 1. The atomic coordinates of compounds **2**, **3**, and **4** are given in Tables 2–4.

3. Results and discussion

3.1. Preparation of the complexes

Interest in these inorganic–organic hybrid materials was raised by the observation that some cadmium–

Table 3
Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for **3**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
C(1)	3954(2)	7998(2)	8207(3)	22(1)
C(2)	5813(2)	5434(2)	11125(3)	22(1)
C(3)	1946(2)	6276(2)	8137(3)	20(1)
C(4)	2168(2)	6203(2)	6030(4)	22(1)
C(5)	2792(2)	6199(2)	7228(3)	24(1)
C(6)	877(2)	6215(2)	5676(3)	23(1)
C(7)	424(2)	6225(2)	6626(3)	20(1)
C(8)	217(1)	5373(2)	7078(3)	21(1)
C(9)	212(2)	7080(2)	7066(3)	24(1)
C(10)	3172(2)	6270(2)	10126(3)	27(1)
Cd(1)	5000	6284(1)	7500	19(1)
N(1)	4473(1)	7461(2)	8130(3)	29(1)
N(2)	4413(1)	5130(2)	8293(3)	31(1)
N(11)	2646(1)	6246(2)	8547(3)	20(1)
N(12)	1641(1)	6254(1)	6615(3)	18(1)
S(1)	3354(1)	8746(1)	8303(1)	26(1)
S(2)	6150(1)	6235(1)	10308(1)	23(1)

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

thiocyanate coordination polymers exhibit promising NLO properties. The combination of dialkylimidazolium (ionic liquid) and cadmium–thiocyanate complexes may create new physicochemical properties. The imidazolium halide can be easily prepared by either the quarterization of *N*-alkylimidazole with organic halide or the condensation of glyoxal, paraformaldehyde, and primary amines. Three imidazolium salts of cadmium–thiocyanate were prepared by metathesis reactions between cadmium–thiocyanate anions and imidazolium halide in water. They are isolated as white or pale-yellow

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**

Atom	x	y	z	U_{eq}^a
Br(1)	8822(1)	5731(1)	1540(1)	40(1)
C(1)	6667	3333	-891(12)	25(3)
C(2)	6678(9)	4635(8)	4269(4)	31(1)
C(3)	7981(9)	4638(8)	4253(4)	34(2)
C(4)	9353(11)	6009(10)	4191(6)	47(2)
C(5)	6695(11)	6036(9)	4350(5)	43(2)
C(6)	7807(9)	8299(9)	3478(6)	41(2)
C(7)	6314(11)	6287(9)	2828(5)	46(2)
C(8)	7654(9)	8628(9)	2664(6)	44(2)
C(9)	6385(14)	7242(11)	1418(7)	62(3)
Cd(1)	6667	3333	1051(1)	30(1)
N(1)	6667	3333	-410(20)	61(5)
N(2)	6965(8)	6841(7)	3560(4)	35(1)
N(3)	6743(8)	7344(7)	2283(4)	41(2)
N(4)	10000	10000	488(5)	45(2)
O(1)	8881(17)	9250(30)	109(12)	149(13)
S(1)	6667	3333	-2030(3)	62(2)

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

solids. The formation of $[\text{EtMeIm}]_2[\text{Cd}_2(\text{SCN})_6]$ (**2**) is expected since the $[\text{Cd}(\text{SCN})_3]^-$ chain is commonly formed at the Cd/SCN ratio of 3 [15]. In the case of $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2]^{2+}$, the complex of the formula $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2][\text{Cd}(\text{SCN})_4]$ (**3**) was obtained as the sole isolated compound at the same Cd/SCN ratio. Surprisingly, when $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3]^{3+}$ was employed under the same reaction conditions, $[\text{CdBr}_3(\text{SCN})]^{2-}$ is the only identified cadmium species. Their composition was determined by elemental analysis, and further confirmed by X-ray diffraction analysis.

3.2. X-ray crystal structure of $[\text{EtMeIm}]_2[\text{Cd}_2(\text{SCN})_6]$, **2**

The structure of compound **2** is shown in Fig. 1, and selected bond lengths and angles are collected in Table 5. The cadmium and thiocyanate ions form triply bridged one-dimensional infinite polymeric chains; two independent Cd atoms are octahedrally coordinated in a $4N2S$ and $2N4S$ coordination environment, respectively. This is quite different from other one-dimensional infinite cadmium–thiocyanate polymers, in which the cadmium atoms are normally 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 Cd center, dictated by *trans* effect [8, 18, 19]. The average Cd–S and Cd–N lengths are 2.721 and 2.319 Å, the average Cd–S–C and Cd–N–C angles are 97.87° and 146.93° , respectively which are consistent with those of other reported cadmium–thiocyanate compounds [8–15]. The N–C–S bridging ligands are almost linear with an average angle

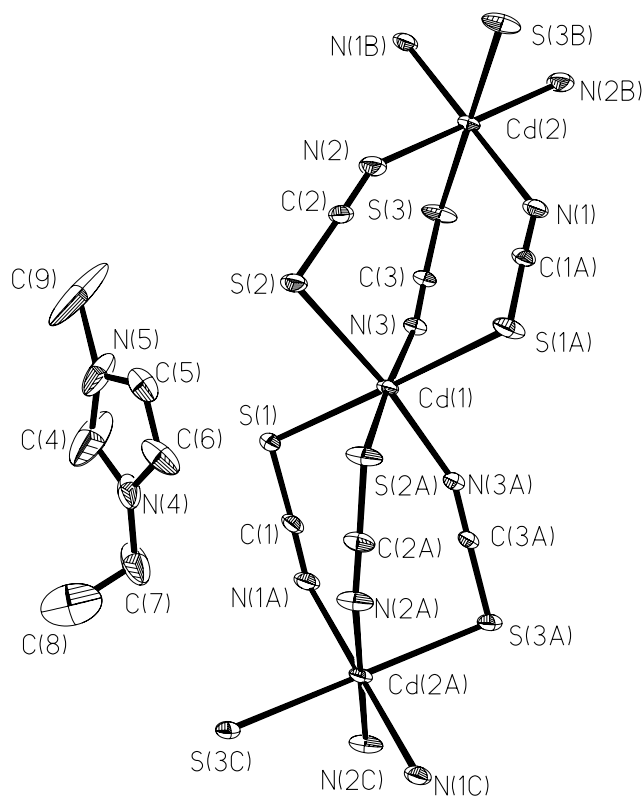


Fig. 1. ORTEP drawing of **2** with thermal ellipsoids at 30% probability level. The hydrogen atoms are omitted for clarity.

Table 5

Selected bond lengths (Å) and angles (deg) for **2**

Cd(1)–S(1)	2.7635(16)	Cd(1)–S(2)	2.6865(16)
Cd(1)–N(3)	2.300(5)	Cd(2)–N(1)	2.331(5)
Cd(2)–N(2)	2.327(6)	Cd(2)–S(3)	2.7130(17)
C(1)–N(1)#1	1.162(8)	C(2)–N(2)	1.154(8)
C(3)–N(3)	1.150(7)	C(1)–S(1)	1.642(6)
C(2)–S(2)	1.649(6)	C(3)–S(3)	1.644(5)
N(1)#1–C(1)–S(1)	178.1(5)	N(2)–C(2)–S(2)	178.7(6)
N(3)–C(3)–S(3)	178.3(6)	N(3)–Cd(1)–N(3)#1	90.1(2)
N(3)–Cd(1)–S(2)#1	173.33(12)	N(3)–Cd(1)–S(2)	91.29(13)
S(2)#1–Cd(1)–S(2)	88.09(8)	N(3)–Cd(1)–S(1)#1	90.46(12)
S(2)–Cd(1)–S(1)#1	95.19(6)	N(3)–Cd(1)–S(1)	91.32(12)
S(2)–Cd(1)–S(1)	82.98(6)	S(1)#1–Cd(1)–S(1)	177.48(8)
N(2)–Cd(2)–N(2)#2	180.0	N(2)–Cd(2)–N(1)#2	95.3(2)
N(2)–Cd(2)–N(1)	84.7(2)	N(1)#2–Cd(2)–N(1)	180.0(3)
N(2)–Cd(2)–S(3)#2	90.13(17)	N(1)–Cd(2)–S(3)#2	88.68(15)
N(2)–Cd(2)–S(3)	89.87(17)	N(1)–Cd(2)–S(3)	91.32(15)
S(3)#2–Cd(2)–S(3)	180.00(6)	C(1)#1–N(1)–Cd(2)	135.9(5)
C(2)–N(2)–Cd(2)	150.2(5)	C(3)–N(3)–Cd(1)	154.7(4)
C(1)–S(1)–Cd(1)	101.7(2)	C(2)–S(2)–Cd(1)	97.5(2)
C(3)–S(3)–Cd(2)	94.4(2)		

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

of 178.4° , and the average C–S and C–N bond lengths of 1.634 and 1.151 Å, respectively.

As far as the alignments of chains are concerned, the cadmium atoms are triply bridged by SCN^- ions, and

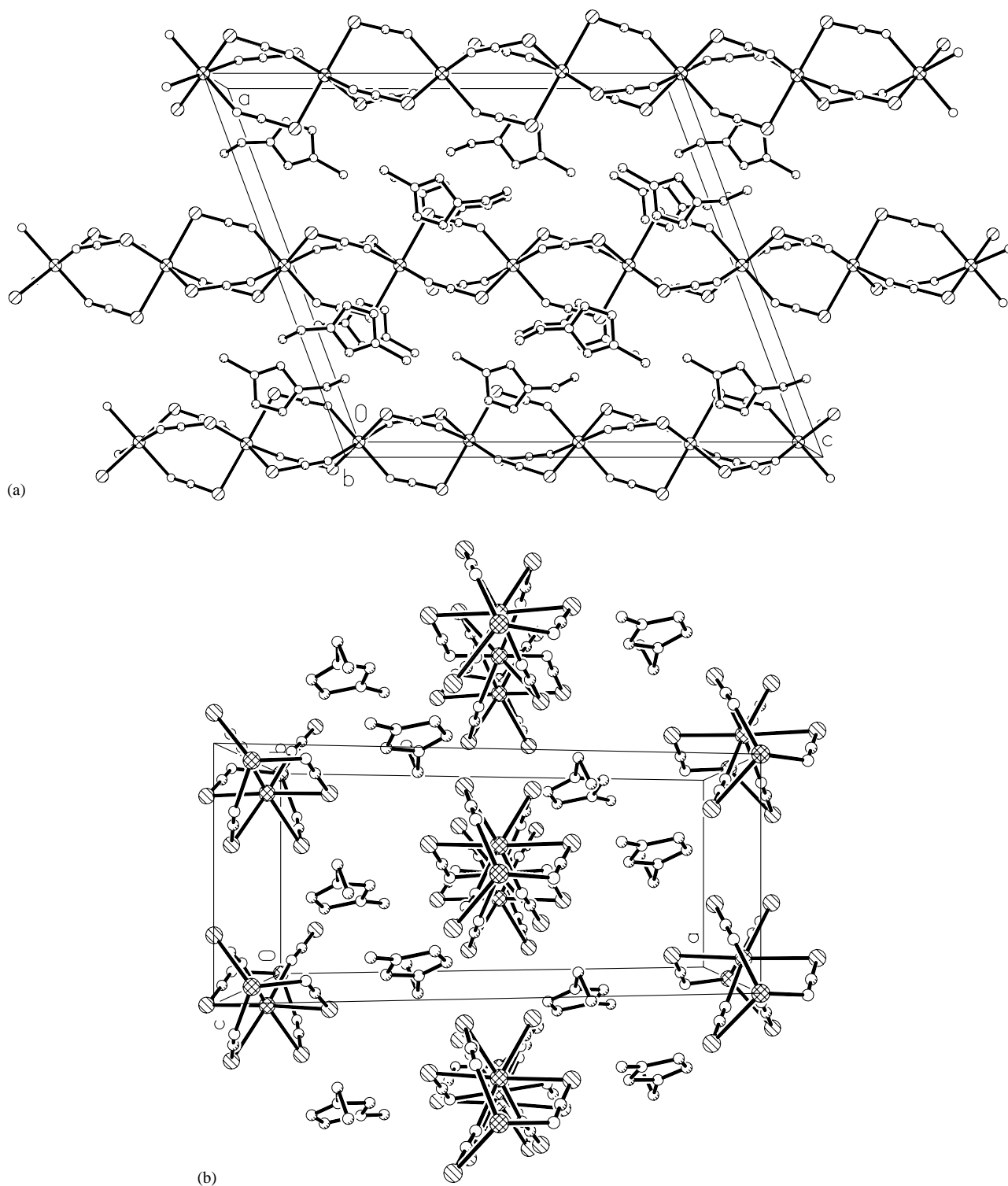


Fig. 2. Perspective view of the stacking of the infinite $[\text{Cd}(\text{SCN})_3]^-$ chains: (a) along the crystallographic a -axis and (b) along the crystallographic c -axis.

thus form infinite zigzag chains. The $\text{Cd}\cdots\text{Cd}$ distance is $\sim 5.385 \text{ \AA}$, and the $\text{Cd}\cdots\text{Cd}\cdots\text{Cd}$ angle is 164.72° , respectively. The adjacent chains are parallel to each other running along the crystallographic a -axis (Fig. 2(a)). The infinite chains form approximate hex-

agonal array along the crystallographic c -axis, and three neighboring chains consist of triangular channels, which are occupied by imidazolium cations, as shown in Fig. 2(b). The imidazolium cations interact with anionic cadmium–thiocyanate chains through weak hydrogen

bonding, C(4)–H(4)⋯S(1) (2.893 Å) and electronic interactions. Hexagonal arrangement is also adopted by anionic $[\text{Cd}(\text{SCN})_3]^-$ chains in $[(12\text{C}_4)_2\text{Na}][\text{Cd}(\text{SCN})_3]$ [8, 10], $[\text{R}_4\text{N}][\text{Cd}(\text{SCN})_3]$ [19, 20].

3.3. X-ray crystal structure of $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2][\text{Cd}(\text{SCN})_4]$, **3**

X-ray diffraction analysis revealed that $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2][\text{Cd}(\text{SCN})_4]$ (**3**) consist of infinite one-dimensional chains of repeated $[\text{Cd}(\text{SCN})_4]^{2-}$ units and discrete $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2]^{2+}$ cations. Within the anionic chain, each cadmium atom is octahedrally coordinated with two *cis* *N*-bonded monodentate NCS^- ligands and four bridging SCN^- in a *S trans* to *S*, and *N trans* to *N* coordination manner. Fig. 3 shows the ORTEP plots of the cation and $[\text{Cd}(\text{SCN})_4]^{2-}$ anion. Selected bond lengths and angles are summarized in Table 6. The Cd–N [2.295(3) Å] bond lengths of the monodentate SCN^- is the same as that of the bridging SCN^- [2.295(3) Å], whereas the C–N and C–S bond lengths of monodentate SCN^- are slightly longer and shorter than those of the bridging SCN^- in the same compound, respectively. In general, all the bond lengths and angles are in the normal range as those in other cadmium–thiocyanate compounds. Although 4*N*2*S*-hexacoordinated doubly bridged cadmium compounds are known [19, 21–26]. Compound **3** is the first example of cadmium–thiocyanate complexes having two *cis* monodentate SCN^- ions.

Cadmium atoms are bridged by two SCN^- ions, one of them is *S*-coordinated and other is *N*-coordinated to the same metal atom, thus form a infinite polymeric zigzag chain structure, with Cd⋯Cd distances of 5.914 Å. The infinite $[\text{Cd}(\text{SCN})_4]^{2-}$ zigzag chains align in a parallel manner (Fig. 4(a)), resulting in a space group *C2/c*. The H(3) and H(4) of the imidazolium ring forms hydrogen bonds with S atoms of coordinated SCN^- ions. Probably, the weak hydrogen bonding interactions, C3–H(3)⋯S(1) (2.7573 Å) and C(4)–H(4)⋯S(1) (2.8752 Å), play some role in the formation of the unique chain polymer. The atoms of doubly bridging SCN^- ions, together with the cadmium ion on

Table 6
Selected bond lengths (Å) and angles (deg) for **3**

Cd(1)–N(1)	2.295(3)	Cd(1)–N(2)	2.295(3)
Cd(1)–S(2)	2.7916(10)	C(2)–S(2)	1.648(3)
C(1)–N(1)	1.162(4)	C(2)–N(2)#1	1.151(4)
C(1)–S(1)	1.637(3)		
N(1)–C(1)–S(1)	179.2(3)	N(2)#1–C(2)–S(2)	179.0(3)
N(2)–Cd(1)–N(2)#3	90.32(15)	N(2)–Cd(1)–N(1)	90.95(11)
N(2)#3–Cd(1)–N(1)	176.30(8)	N(1)–Cd(1)–N(1)#3	88.00(13)
N(2)–Cd(1)–S(2)#3	86.25(7)	N(1)–Cd(1)–S(2)#3	84.85(7)
N(1)#3–Cd(1)–S(2)#3	97.18(7)	N(2)–Cd(1)–S(2)	91.77(7)
N(1)#3–Cd(1)–S(2)	84.85(7)	S(2)#3–Cd(1)–S(2)	177.19(3)
C(1)–N(1)–Cd(1)	167.3(2)	C(2)#1–N(2)–Cd(1)	171.1(2)
C(2)–S(2)–Cd(1)	96.17(10)		

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y + 2, -z + 1$; #2 $-x, y, -z + 3/2$; #3 $-x + 2, y, -z + 1/2$.

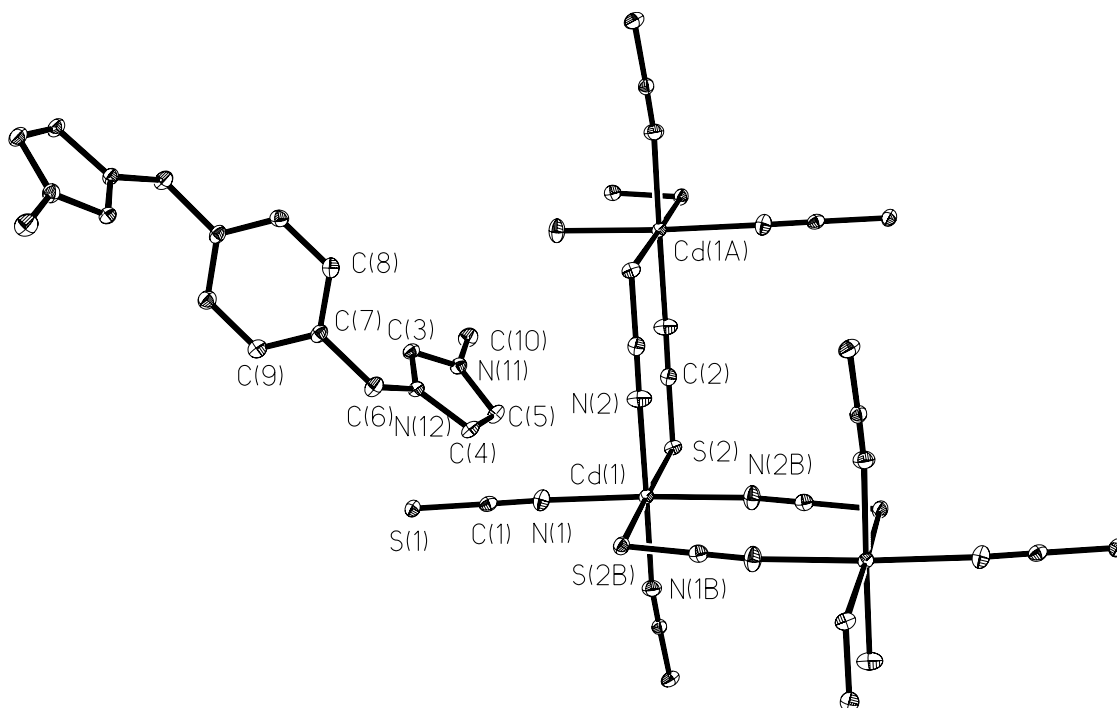


Fig. 3. ORTEP drawing of **3** with thermal ellipsoids at 30% probability level. The imidazolium cation, hydrogen atoms are omitted for clarity.

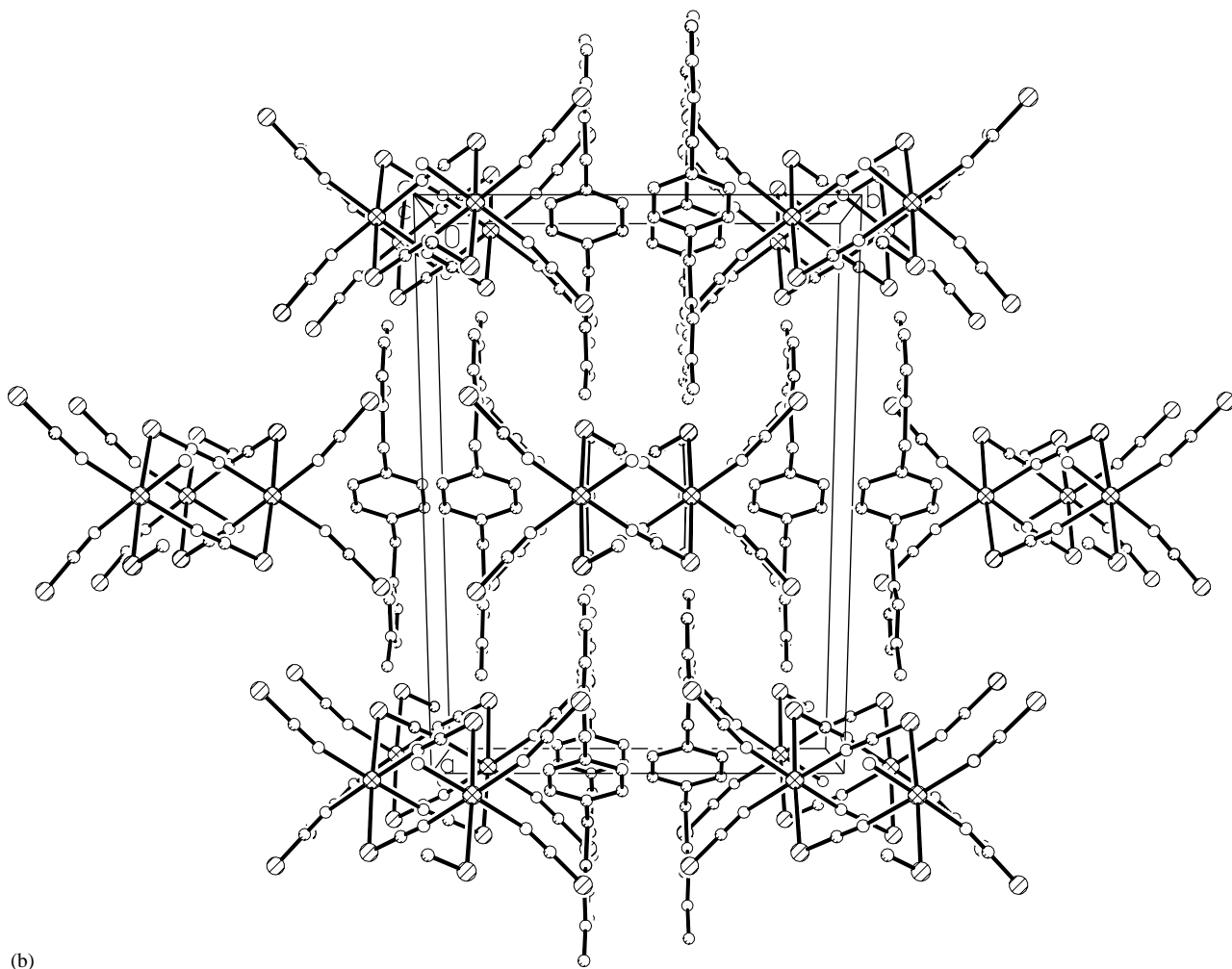
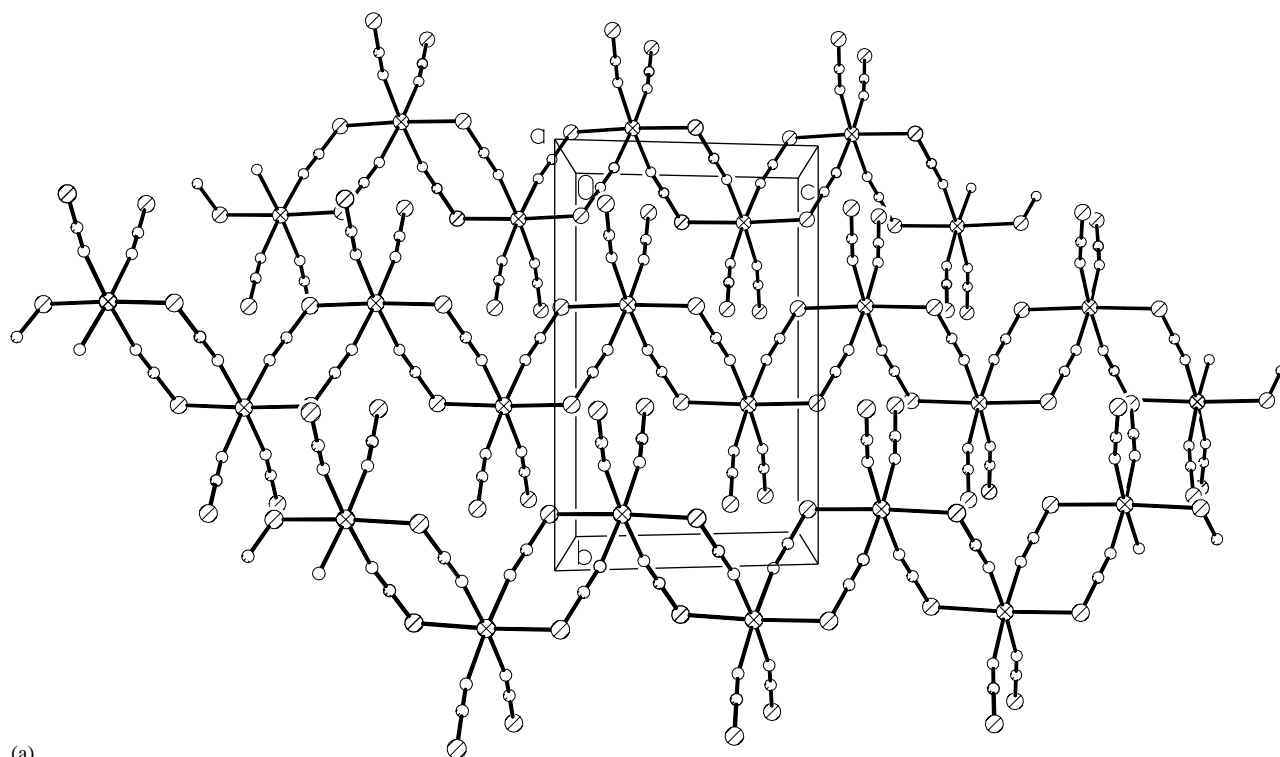


Fig. 4. Perspective view of the stacking of the infinite $[\text{Cd}(\text{SCN})_4]^{2-}$ chain: (a) along the crystallographic a -axis and (b) along the crystallographic c -axis.

both sides, constitute an eight-membered ring. As shown in Fig. 4(b), the $[\text{Cd}(\text{SCN})_4]^{2-}$ chains form tetragonal channels running along the crystallographic c -axis. The channels are filled by the $[\text{C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2]^{2+}$ cations.

3.4. X-ray crystal structure of $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3][\text{CdBr}_3(\text{SCN})](\text{NO}_3)$, **4**

The structure of the complex $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3][\text{CdBr}_3(\text{SCN})](\text{NO}_3)$, together with the atomic numbering scheme, is shown in Fig. 5. Important bond distances and angles are given in Table 7. The structural study shows that the complex is mononuclear, consisting of a discrete $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3]^{3+}$ cation, a nitrate and $[\text{CdBr}_3(\text{SCN})]^{2-}$ ion. The nitrate ion was not well solved possibly due to severe disorder, although the diffraction data were repeatedly collected. Each cad-

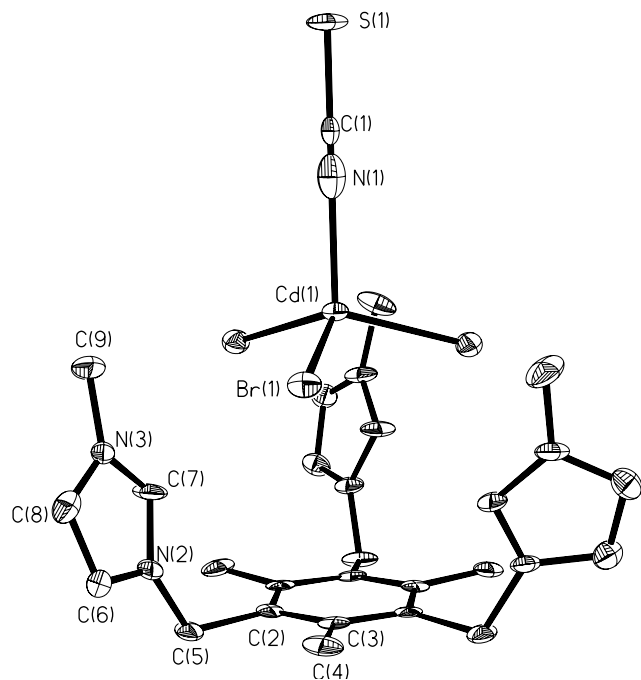


Fig. 5. ORTEP drawing of **4** with thermal ellipsoids at 30% probability level. The hydrogen atoms and nitrate are omitted for clarity.

Table 7
Selected bond lengths (Å) and angles (deg) for **4**

Cd(1)–N(1)	2.221(19)	Br(1)–Cd(1)	2.5756(10)
C(1)–N(1)	1.12(2)	C(1)–S(1)	1.582(14)
N(1)–C(1)–S(1)	180.000(3)	N(1)–Cd(1)–Br(1)	107.43(3)
Br(1)–Cd(1)–Br(1)#1	111.43(3)	C(1)–N(1)–Cd(1)	180.000(3)

Note: Symmetry transformations used to generate equivalent atoms: #1 $-y+1, x-y+1, z$; #2 $-x+y, -x+1, z$; #3 $-y, x-y, z$; #4 $-x+y, -x, z$.

mium(II) ion is coordinated to three bromide ions and one nitrogen atom of SCN^- ion. The bond distances and angles of imidazolium cation are all in normal range. The C–S bond distance [1.582(14) Å] is much shorter than those in **2** and **3**; the Cd–N [2.221(19) Å] distance is slightly shorter than those in **2** and **3**. Whereas the Cd–Br bond distance [2.5756(10) Å] is much shorter than that in the polymeric $[\text{CdBr}_2(\text{H}_2\text{biim})]$ [2.7020(13) Å and 2.8921(11) Å] [27], $[\text{CdLBr}_2]$ ($L = 2\text{-formylpyrrole thiosemicarbazone}$, [2.589(1) and 2.637(1) Å] [28], but matches that in $[\text{CdBr}_2L_2]$ [$L = \text{Ph}_3\text{P}^+(\text{CH}_2)_3\text{CO}_2^-$, 2.580 (2) Å] [29]. An interesting structural feature of complex **4** is that the imidazolium cation, $[\text{C}_6\text{Me}_3(\text{CH}_2\text{ImMe})_3]^{3+}$ displays a crown-like conformation, and the $[\text{CdBr}_3(\text{SCN})]^{2-}$ anion constitute a tripod clothes stand.

In summary, the three inorganic–organic hybrid materials have been characterized by X-ray crystallographic diffraction. The N,N' -dialkylimidazolium cadmium–thiocyanate complexes were prepared under the same conditions. The structural analyses clearly reveal that the variation of the imidazolium cations led to three quite different complexes. It suggests that the different imidazolium cations direct the formation of this kind of complexes, the arrangement of chains, and the coordination motif. It illustrates that the size, symmetry as well as the charge number of the cations play important role in the assembly of cadmium–thiocyanate complexes.

4. Supplementary materials

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. –169280, –175403, and –175404 for compounds **2–4**, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgments

The authors are grateful to the National Natural Science Foundation of China for financial support.

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