

# Complexation of Cd(SeCN)<sub>2</sub> with imidazolidine-2-thione and its derivatives: Solid state, solution NMR and anti-bacterial studies

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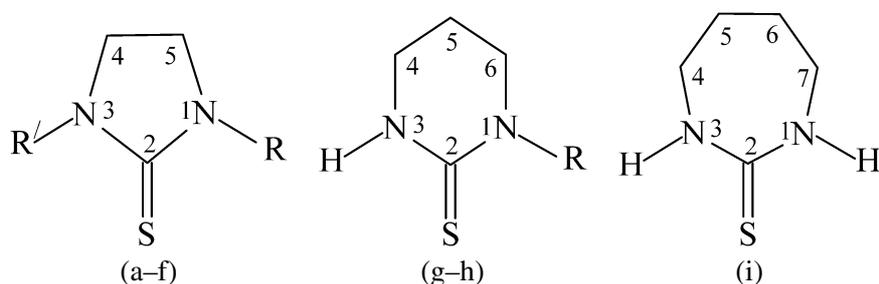
**Abstract.** Reactions of imidazolidine-2-thione (Imt), 1,3-diazinane-2-thione (Diaz) and 1,3-diazipane-2-thione (Diap) with Cd(SeCN)<sub>2</sub> in acetonitrile resulted in the formation of 2:1 tetrahedral complexes. Both solid state and solution NMR, confirm the exocyclic thione atom to be the donor in all cases. <sup>113</sup>Cd shielding tensors and anisotropies were calculated from the solid-state NMR spectra. Based on the solid NMR data, a distorted tetrahedral dispositions of ligands around cadmium is proposed for the Imt complex. However, when the Imt ligand is substituted with one or two R groups (where R = Me, Et or *i*-Pr) forming RImt or R<sub>2</sub>Imt, a five coordinate complex with polymeric structure [(RImt)Cd(SeCN)<sub>2</sub>]<sub>∞</sub> or [(R<sub>2</sub>Imt)Cd(SeCN)<sub>2</sub>]<sub>∞</sub> is observed. Antibacterial studies of some of the complexes were carried out.

Keywords: Cadmium(II) complexes, selenocyanate complexes, imidazolidine-2-thione, CP MAS NMR studies

## 1. Introduction

The coordination chemistry of cadmium(II) has received increased attention, in part due to concerns regarding its impact on the environment and its toxicological effects in marine microorganisms [1–3] and cadmium complexation by metallothioneins [4,5]. Although <sup>113</sup>Cd NMR studies have been performed on many thiolate ligand complexes, and this nucleus has a rich history in the literature as a metallobioprope [6,7] there are, in fact, very few reports of <sup>113</sup>Cd NMR measurements on complexes containing SeCN<sup>-</sup> containing ligands [8]. The cadmium complexes present a significant advantage over their zinc counterparts from the structural characterization point of view, since <sup>113</sup>Cd NMR spectroscopy stands a sensitive probe of the coordination sphere of the cadmium ion. It has developed into a useful probe of metal environments in metallo-proteins because Cd<sup>2+</sup> may often be exchanged for other divalent metals such as Zn<sup>2+</sup> in proteins [9–12]. Further, Cd<sup>2+</sup> may often be exchanged for other divalent metals such as

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- (a)  $\text{R}=\text{R}'=\text{H}$ ; Imidazolidine-2-thione (Imt)  
 (b)  $\text{R}=\text{C}_2\text{H}_5$ ,  $\text{R}'=\text{H}$ ; N-ethylimidazolidine-2-thione (EtImt)  
 (c)  $\text{R}=\text{C}_3\text{H}_7$ ,  $\text{R}'=\text{H}$ ; N-propylimidazolidine-2-thione (PrImt)  
 (d)  $\text{R}=\textit{i}\text{-C}_3\text{H}_7$ ,  $\text{R}'=\text{H}$ ; N-(*i*-propyl)imidazolidine-2-thione (*i*-PrImt)  
 (e)  $\text{R}=\text{CH}_3$ ,  $\text{R}'=\text{CH}_3$ ; N,N'-dimethylimidazolidine-2-thione ( $\text{Me}_2\text{Imt}$ )  
 (f)  $\text{R}=\text{C}_3\text{H}_7$ ,  $\text{R}'=\text{C}_3\text{H}_7$ ; N,N'-diisopropylimidazolidine-2-thione (*i*-Pr<sub>2</sub>Imt)  
 (g)  $\text{R}=\text{H}$ ; 1,3-diazinane-2-thione (Diaz)  
 (h)  $\text{R}=\text{C}_2\text{H}_5$ ; N-ethyl-1,3-diazinane-2-thione (EtDiaz)  
 (i) 1,3-diazepane-2-thione (Diap)

Scheme 1.

$\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Mg}^{2+}$ , in proteins and  $^{113}\text{Cd}$  NMR spectroscopy has been developed into a useful probe of metal environments in metallo-proteins [10,12]. Our goal is to expand NMR studies of  $^{113}\text{Cd}$  to include thione and selenone containing ligands [14,15].

Our previous reports on such cadmium(II) chloride complexes have utilized the ligands imidazoline-2(3H)-thione (Imt), and its derivatives all of which have similar structures, with the first possessing a five-membered thioamide  $\text{N}-\text{C}=\text{S}(-\text{N})$  heterocycle. Both N- and/or S-coordination is possible with these ambidentate ligands, as well as thione–thiol tautomers. However, although N-coordination was suggested earlier for some of the complexes from infrared spectroscopic studies, it has been confirmed crystallographically that coordination is via the exocyclic sulfur, predominantly in the thione form, with a reduction in the  $\pi$ -electron density of the exocyclic  $\text{C}=\text{S}$  bond [14,16–20].

Herein we now report the coordination chemistry of the thione ligands (see Scheme 1) with cadmium(II) selenocyanate.

## 2. Experimental

### 2.1. Chemicals

$\text{CdCl}_2$ , Acetone, acetonitrile and  $\text{DMSO-d}_6$  were obtained from Fluka Chemical Co. All the thiones were synthesized according to the procedure described earlier [20].  $\text{KSe}^{13}\text{CN}$  was bought from Isotech Chemical Co., USA.

## 2.2. Preparation of complexes

CdCl<sub>2</sub> (10 mmol) was dissolved in a minimal amount of water and KSe<sup>13</sup>CN (~5% <sup>13</sup>C label 20 mmol) was also dissolved in minimum amount of water under N<sub>2</sub> gas. On mixing the two solutions, Cd(Se<sup>13</sup>CN)<sub>2</sub> immediately got precipitated.

The thione ligands (20 mmol) were dissolved in minimum amount of MeOH with 10 mmol Cd(Se<sup>13</sup>CN)<sub>2</sub>. In the case of poorly soluble ligands, acetonitrile was added to achieve complete solubility. Both solutions were mixed and stirred for about 30 min. The precipitates were collected and dried under vacuum. Yields of 55–65% were obtained. Five of the nine complexes were obtained in the solid form, the elemental analyses of which are given in Table 1. The rest four could not be isolated in the solid state and therefore, only their solution NMR is being carried out. We were able to crystalline only one complex [(Me<sub>2</sub>Imt)Cd(SeCN)<sub>2</sub>]<sub>∞</sub> for which we publish a data, since it provided a very unusual stereochemistry [21].

## 2.3. Spectroscopic measurements

The measurements of solid-state IR and solution NMR were recorded as described in the literature [14,15]. The chemical shifts of ligands along with corresponding complexes are given in Table 2.

Table 1  
Elemental analysis of LCd(SeCN)<sub>2</sub> and L<sub>2</sub>Cd(SeCN)<sub>2</sub> complexes

Complex	Found (Calcd) %				m.p. (°C)
	C	H	N	S	
(Imt) <sub>2</sub> Cd(SeCN) <sub>2</sub>	18.52 (18.24)	2.46 (2.30)	16.33 (15.96)	12.66 (12.18)	133–135
(Et-Imt)Cd(SeCN) <sub>2</sub>	19.33 (18.58)	2.65 (2.23)	12.45 (12.37)	7.38 (7.07)	111–114
(Me <sub>2</sub> Imt)Cd(SeCN) <sub>2</sub>	19.01 (18.58)	2.38 (2.23)	12.08 (12.37)	7.37 (7.07)	156–158
( <i>i</i> -Pr <sub>2</sub> Imt)Cd(SeCN) <sub>2</sub>	26.44 (25.97)	3.85 (3.57)	11.72 (11.01)	9.39 (9.13)	118–122
(Diaz) <sub>2</sub> Cd(SeCN) <sub>2</sub>	22.17 (21.65)	3.00 (2.91)	16.00 (15.15)	12.55 (11.56)	98–101

Table 2  
Selected IR absorption (cm<sup>-1</sup>) for free ligands and their LCd(SeCN)<sub>2</sub> and L<sub>2</sub>Cd(SeCN)<sub>2</sub> complexes

Species	ν(C=S)	ν(NH <sub>2</sub> )	ν(CN) of Cd(SeCN) <sub>2</sub>
KSeCN	–	–	2073
Cd(SeCN) <sub>2</sub>	–	–	2361
Imt	510	3200	–
(Imt) <sub>2</sub> Cd(SeCN) <sub>2</sub>	500	3368	2077
Et-Imt	–	3200	–
(EtImt)Cd(SeCN) <sub>2</sub>	500	3442	2155
Me <sub>2</sub> Imt	520	–	–
(Me <sub>2</sub> Imt)Cd(SeCN) <sub>2</sub>	490	–	2114, 2037
<i>i</i> -Pr <sub>2</sub> Imt	518	–	–
( <i>i</i> -Pr <sub>2</sub> Imt)Cd(SeCN) <sub>2</sub>	485	–	2107
EtDiaz	505	3210	–
(EtDiaz)Cd(SeCN) <sub>2</sub>	495	3305	2115
Diaz	510	3200	–
(Diaz) <sub>2</sub> Cd(SeCN) <sub>2</sub>	490	3442	2119, 2089

#### 2.4. Solid-state NMR

Natural abundance <sup>113</sup>Cd, <sup>13</sup>C and <sup>77</sup>Se solid state NMR spectra were obtained on a JEOL LAMBDA 500 spectrometer operating at 110.85, 125.65 and 95.35 MHz respectively, corresponding to a magnetic field of 11.74 T, at ambient temperature of 25°C. Samples were packed into 6 mm zirconia rotors. Cross polarization and high power decoupling were employed. Pulse delay of 7.0 s and a contact time of 5.0 ms were used for cadmium and carbon observations in the CP MAS experiments, whereas the pulse delay of 10 s and a contact time of 6.0 ms were used in the selenium observation. The magic angle spinning rates were from 3000 to 5000 Hz. The cadmium chemical shifts were referenced using a secondary reference Cd(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O, by setting the peak to -100 ppm relative to 0.1 M Cd(ClO<sub>4</sub>)<sub>2</sub> aqueous with ionic strength of 4.5, whose chemical shift was taken to be 0.0 ppm [22]. The same Cd(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O sample was used to set up the Hartmann–Hahn condition for the CPMAS experiments. <sup>13</sup>C chemical shifts were referenced to TMS by setting the high frequency isotropic peak of solid adamantane to 38.48 ppm. The selenium chemical shifts were referenced using the secondary reference (NH<sub>4</sub>)<sub>2</sub>SeO<sub>4</sub>, by setting the <sup>77</sup>Se peak to +1040.2 ppm relative to (CH<sub>3</sub>)<sub>2</sub>Se [23]. The center peaks were differentiated from the spinning side-bands by recording the spectra at two different spinning speeds. The <sup>113</sup>Cd and <sup>77</sup>Se spectra containing spinning side-band manifolds were analyzed using a computer program WSOLIDS developed at Dalhousie and Tubingen universities [24]. The calculated <sup>113</sup>Cd shielding tensors are shown in Table 4.

#### 2.5. Test bacterial strains

Standard type culture of *Escherichia coli* (MTCC 443), *Klebsiella pneumoniae* (MTCC 109), *Pseudomonas aeruginosa* (MTCC 1688), *Salmonella typhi* (MTCC 733) and *Staphylococcus aureus* (MTCC 737) were obtained from Microbial Type Culture Collection (MTCC) Chandigarh India.

#### 2.6. Material and method

The agar well diffusion technique [25] was used to screen the antibacterial activity. *In vitro* antibacterial activities were screened by using nutrient agar plates obtained from Himedia (Mumbai). The plates were prepared by pouring 20 ml of molten media into a sterile Petri dish and allowed to solidify for 5 min. A sterile cork borer of diameter 6.0 mm was used to make wells in the agar plates. Inoculums were swabbed uniformly on the surface of agar plates. 0.1 mg/well were loaded on 6.00 mm diameter well. The plates were allowed to stand for 1 h for diffusion then incubated at 37°C for 24 h. At the end of incubation, inhibition zones were measured.

### 3. Results and discussion

#### 3.1. IR studies

Selected IR spectroscopic vibration bands for the free ligands and their cadmium(II) complexes are given in Table 2. The  $\nu(\text{C}=\text{S})$  vibration, which occurs around 500 cm<sup>-1</sup> for the free ligands, shifts towards lower frequency upon complexation, in accordance with the data observed for the other thione complexes [26,27]. Another important vibrational band observed in IR spectra of the thiones is the  $\nu(\text{NH})$ , which appears around 3200 cm<sup>-1</sup>. Upon coordination to Cd(SeCN)<sub>2</sub> this band shifts to higher

wave numbers with some exceptions. The presence of a band around 3200 cm<sup>-1</sup> in free ligands as well as in the complexes indicates the existence of the thione form of the ligands in the solid state.

One or two bands around 2361 cm<sup>-1</sup> corresponding to CN<sup>-</sup> stretch are observed in the IR spectra of the complexes. For the complexes of Imt, *i*-PrImt, Me<sub>2</sub>Imt, EtImt, Diaz and Diap, one or two  $\nu$ (CN) mode were observed, which appeared at lower frequency (by ~280–240 cm<sup>-1</sup>) compared to free Cd(SeCN)<sub>2</sub>.

### 3.2. Solution NMR studies

The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of the complexes in DMSO-d<sub>6</sub> are summarized in Table 3. In <sup>1</sup>H NMR spectra of the complexes, the N–H signal of thiones became less intense upon coordination and shifted downfield by 0.7–1.0 ppm from their positions in free ligands. Deshielding of the N–H proton is related to an increase of the  $\pi$ -electron density in the C–N bond upon complexation [27,28]. The appearance of N–H signal shows that the ligands are coordinating to cadmium(II) via a thione group.

In all complexes, the C-2 resonance of thiones appears upfield by 1–2 ppm compared to free ligands in accordance with the data observed for other complexes of copper(I), silver(I) and gold(I) with heterocyclic thiones [29]. The upfield shift is attributed to a lowering of the >C=S bond order upon coordination and a shift of N→C electron density producing partial double bond character in the C–N bond [28,29]. A small shift of one ppm is observed in other carbon atoms, which shows that nitrogen atoms are not involved in coordination. In the complexes of Imt and its derivatives a deshielding effect is observed at C-4/5, while in Diaz complex a deshielding effect is observed at C-4 and C-6, but C-5 bears a shielding effect. The deshielding at C-4/6 is due to an increase in  $\pi$  character of the C–N bond.

Table 3

<sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of thiones and their selenocyanocadmium(II) complexes in DMSO-d<sub>6</sub>

Species	N–H	Cd(Se <sup>13</sup> CN) <sub>2</sub>	C-2	<sup>77</sup> Se
KSe <sup>13</sup> CN	–	116.64	–	273
Cd(Se <sup>13</sup> CN) <sub>2</sub>	–	118.54	–	281
Imt	7.98	–	183.44	–
(Imt) <sub>2</sub> Cd(Se <sup>13</sup> CN) <sub>2</sub>	8.32	117.47	181.51	279
EtImt	7.99	–	182.05	–
(EtImt)Cd(SeCN) <sub>2</sub>	8.56	117.80	180.11	278
PrImt	7.99	–	182.55	–
(PrImt)Cd(SeCN) <sub>2</sub>	8.32	118.25	182.00	279
<i>i</i> -PrImt	7.96	–	181.44	–
( <i>i</i> -PrImt)Cd(SeCN) <sub>2</sub> <sup>a</sup>	8.03	–	180.24	278
Me <sub>2</sub> Imt	–	–	182.90	–
(Me <sub>2</sub> Imt)Cd(SeCN) <sub>2</sub>	–	117.79	180.89	279
<i>i</i> -Pr <sub>2</sub> Imt	–	–	180.31	–
( <i>i</i> -Pr <sub>2</sub> Imt)Cd(SeCN) <sub>2</sub>	–	117.44	179.95	276
EtDiaz	7.89	–	176.05	–
(EtDiaz)Cd(SeCN) <sub>2</sub>	8.66	117.85	174.22	275
Diaz	7.81	–	175.62	–
(Diaz) <sub>2</sub> Cd(Se <sup>13</sup> CN) <sub>2</sub>	8.22	117.35	172.86	277
Diap	7.76	–	187.91	–
(Diap) <sub>2</sub> Cd(SeCN) <sub>2</sub>	8.06	117.40	184.59	276

<sup>a</sup>Could not observe.

The shift difference for the C-2 resonance of thiones upon complexation is related to the strength of the metal–sulfur bond [27]. The smallest C-2 shift of less than 1 ppm was detected in [(*i*-Pr<sub>2</sub>Imt)Cd(SeCN)<sub>2</sub>], while the highest one was found in [(Diap)<sub>2</sub>Cd(SeCN)<sub>2</sub>] showing that the Cd–S bond should be the strongest for [(Diap)<sub>2</sub>Cd(SeCN)<sub>2</sub>] among these complexes. It can be seen from Table 3 that as the ring size of the ligand is increased the shift difference at C-2 also increases. Thus Diap forms more stable complexes with Cd(SeCN)<sub>2</sub> compared to Imt and Diaz. A similar pattern was observed for thione complexes of AgCN [30].

In the CN region of the <sup>13</sup>C NMR spectrum, a sharp singlet was observed at 118.54 ppm for Cd(SeCN)<sub>2</sub> complex and less than 1 ppm shift was observed for all [ $>C=S-Cd-(Se^{13}CN)_2$ ] complexes. This is probably due to the three bonds difference between the cadmium(II) and the <sup>13</sup>CN group. Therefore, the chemical shift difference between the free and bound complexes are less than one ppm.

The <sup>77</sup>Se NMR chemical shift difference between free and bound resonances was also within 2–5 ppm range for all the complexes reported here indicating very similar environment for most of the complexes in solution. However, a large <sup>77</sup>Se NMR upfield shift is observed for several thione ligands upon complexation with Hg(SeCN)<sub>2</sub> [31]. On coordination of free ligand SeCN<sup>−</sup> with Hg(II), selenium resonances are shielded by 186 ppm. This very large shielding provides a clear evidence for strong selenium binding to mercury(II). This is probably due to the soft acid–soft base interaction of Hg(II)–Se containing complexes, which normally forms stronger complex compared to Cd(II)–Se containing complexes [32].

### 3.3. Solid state NMR

The <sup>113</sup>Cd and <sup>77</sup>Se CPMAS NMR spectra, respectively, for complexes [(Me<sub>2</sub>Imt)Cd(SeCN)<sub>2</sub>]<sub>∞</sub> and [Imt<sub>2</sub>Cd(SeCN)<sub>2</sub>] are shown in Figs 1 and 2. The isotropic peaks are indicated by an asterisk. The calculated chemical shift tensors are given in Table 4, along with the span, Ω, which describes the breadth of the chemical shift tensor and skew, κ, describing the shape of the powder pattern. The thione <sup>13</sup>C isotropic shift in the complexes moves to lower frequency by about 4–5 ppm upon complexation, compared to free ligand. This also confirms that the thione form is retained in the complex in the solid state.

Two selenium isotropic peaks were observed for (Me<sub>2</sub>Imt), (EtImt) and (EtDiaz) complexes, where as only one center peak was observed for the (Imt) complex (Fig. 2). The two Se resonances can arise due to structural inequivalence or due to two molecules in the unit cell. Since only one Cd resonance was observed we can rule out the later scenario. The two chemically different environments for the two selenium atoms in the (Me<sub>2</sub>Imt) complex was borne out by the slightly different bond lengths for the two Cd–Se bonds, shown by the X-ray studies [21]. As expected, both Se environments are far from being axially symmetric (κ = ±1.00) after coordination to Cd. The values of <sup>77</sup>Se isotropic chemical shift, span and skew for solid KSeCN are −282.6 ppm, 874 ppm and 0.89 respectively [33]. Based on these data, the selenium atom with longer Cd–Se distance was assigned to the selenium resonance with the higher skew value.

According to our previous study [21] cadmium(II) selenocyanate reacts with N,N'-dimethylimidazolidine-2-thione (Me<sub>2</sub>Imt) at a 1:1 ratio forming a polymeric [(Me<sub>2</sub>Imt)Cd(SeCN)<sub>2</sub>]<sub>∞</sub> complex. The metal ion is bonded to one imidazolidine thione through the sulfur atom, two selenocyanate ions through their selenium atoms and two other selenocyanates through their nitrogen atoms. The metal complex coordination sphere Cd[SSe<sub>2</sub>N<sub>2</sub>] adopts a distorted trigonal bipyramidal geometry with

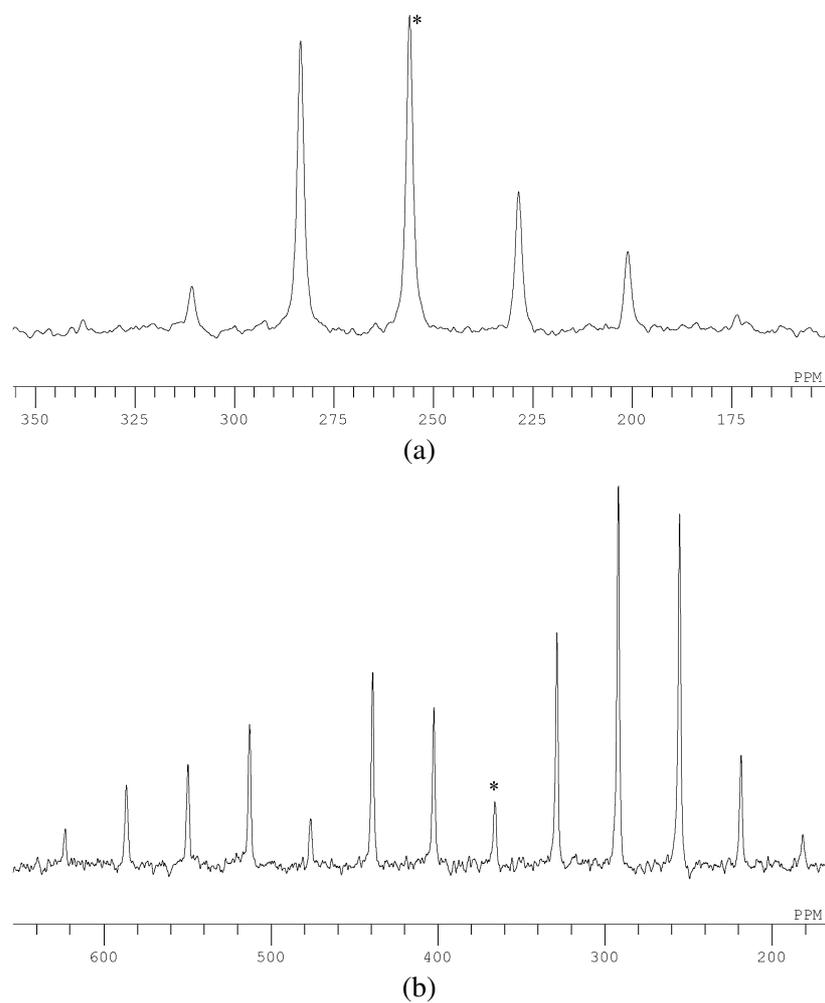


Fig. 1.  $^{113}\text{Cd}$  CPMAS spectra of (a)  $(\text{Imt})_2\text{Cd}(\text{SeCN})_2$  and (b)  $[(\text{Me}_2\text{Imt})\text{Cd}(\text{SeCN})_2]_\infty$ . The center peak is denoted by “\*”.

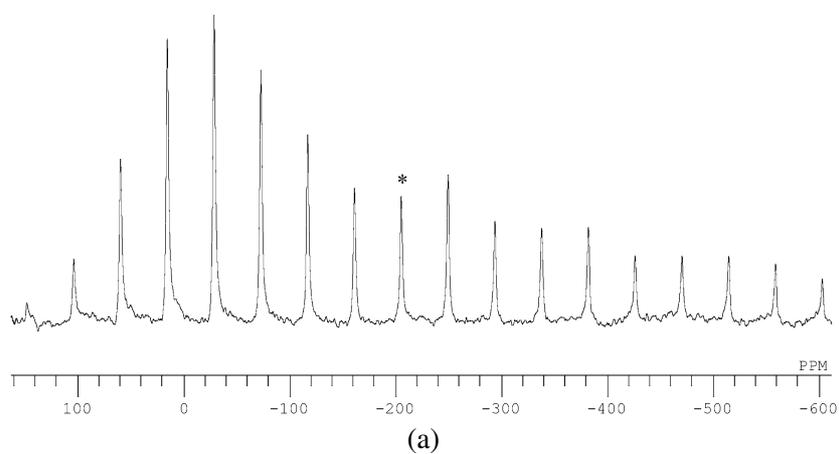


Fig. 2.  $^{77}\text{Se}$  CPMAS spectra of (a)  $(\text{Imt})_2\text{Cd}(\text{SeCN})_2$  and (b)  $[(\text{Me}_2\text{Imt})\text{Cd}(\text{SeCN})_2]_\infty$ . The center peaks are denoted by “\*”.

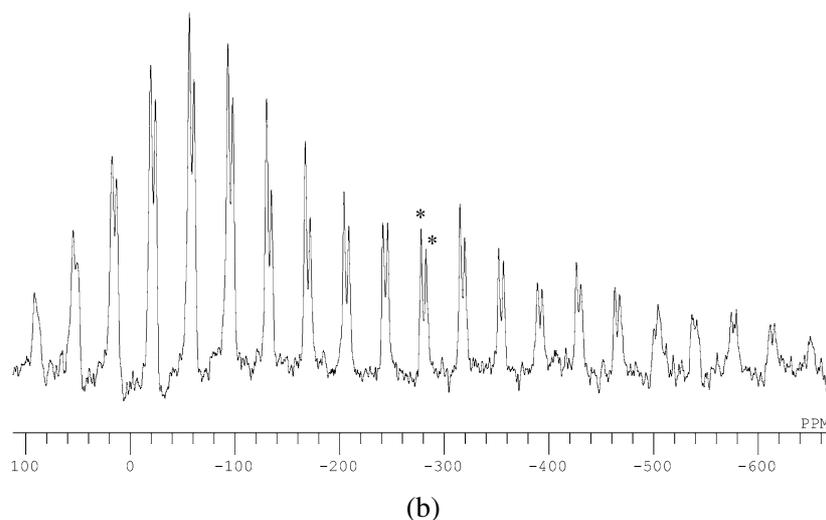


Fig. 2. (Continued).

Table 4

Solid-state <sup>113</sup>Cd, <sup>77</sup>Se and <sup>13</sup>C isotropic chemical shifts ( $\delta_{\text{iso}}$ ) and principal chemical shift tensors ( $\delta_{xx}$ ) of the complexes

Complex	Nucleus	$\delta_{\text{iso}}$	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$	$\Omega^a$	$\kappa^b$
Cd(SeCN) <sub>2</sub>	<sup>113</sup> Cd	211.9	322	283	30	291	0.73
	<sup>13</sup> C (CN)	117.0	222	205	-76	298	0.89
	<sup>77</sup> Se	-119.6	53	41	-452	505	0.96
[(Imt) <sub>2</sub> Cd(SeCN) <sub>2</sub> ]	<sup>113</sup> Cd	255.9	303	279	186	118	0.59
	<sup>13</sup> C (C=S)	179.9	247	191	102	145	0.22
	<sup>77</sup> Se	-204.7	98	-30	-682	781	0.67
[(EtImt)Cd(SeCN) <sub>2</sub> ]	<sup>113</sup> Cd	365.0	546	339	210	335	-0.24
	<sup>77</sup> Se (i)	-264.6	117	-51	-859	976	0.66
	(ii)	-269.0	62	-12	-857	919	0.84
	<sup>13</sup> C (C=S)	177.5					
[(Me <sub>2</sub> Imt)Cd(SeCN) <sub>2</sub> ] <sub>∞</sub> <sup>c</sup>	<sup>113</sup> Cd	367.0	635	245	220	415	-0.88
	<sup>77</sup> Se (i)	-277.3	66	-68	-830	896	0.70
	(ii)	-281.9	57	-45	-857	913	0.78
	<sup>13</sup> C (C=S)	177.5					
[(EtDiaz)Cd(SeCN) <sub>2</sub> ]	<sup>113</sup> Cd	381.8	660	280	204	457	-0.67
	<sup>77</sup> Se (i)	-256.1					
	(ii)	-275.0					
	<sup>13</sup> C (C=S)	169.5					

<sup>a</sup> $\Omega = \delta_{11} - \delta_{33}$ ; <sup>b</sup> $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$ ; <sup>c</sup>from Ref. [21].

the chalcogen atoms occupying the equatorial positions and the nitrogen atoms in the axial positions.

For the EtImt and EtDiaz complexes, we suggest a structure similar to that for the Me<sub>2</sub>Imt complex based on the following facts. The high isotropic chemical shift of Cd observed for Me<sub>2</sub>Imt, EtImt and EtDiaz complexes, compared to the isotropic chemical shift of Cd in Cd(SeCN)<sub>2</sub>, is consistent with the

Table 5  
Antibacterial activities of cadmium(II) complexes

Microorganisms	Zone of inhibition				
	Cd(SeCN) <sub>2</sub>	(Me <sub>2</sub> Imt)Cd(SeCN) <sub>2</sub>	(Imt) <sub>2</sub> Cd(SeCN) <sub>2</sub>	(Diaz) <sub>2</sub> Cd(Se <sup>13</sup> CN) <sub>2</sub>	(Diap) <sub>2</sub> Cd(SeCN) <sub>2</sub>
<i>E. coli</i>	25	–	10	10	30
<i>P. aeruginosa</i>	20	15	10	20	10
<i>S. typhi</i>	28	25	25	28	25
<i>S. aureus</i>	20	17	20	18	20
<i>K. pneumoniae</i>	–	–	–	–	–

coordination to one S, two Se and two N atoms. The high span values for cadmium also are consistent with a near axial symmetry for the cadmium environment in these three complexes. However, for the Imt complex, the Cd spectrum (see Fig. 1), shows a low span value and small isotropic shift, implying a very different structure to the other substituted complexes. We suggest a distorted tetrahedral structure based on elemental analysis and the solid state NMR data for this complex.

In the present investigation, the Cd(SeCN)<sub>2</sub> and its complexes revealed antibacterial activity against both gram positive as well as gram negative bacteria. Most the complexes exhibited less antibacterial activity when compared to the Cd(SeCN)<sub>2</sub> except for *K. pneumoniae* which showed resistance to all the compounds tested. The activities of the complexes are summarized in Table 5.

#### 4. Conclusions

In this study, we have shown that Cd(II) forms Cd[SSe<sub>2</sub>N<sub>2</sub>] coordination sphere with Imt containing ligands having N or N,N' substitution, whereas, tetrahedral Cd[S<sub>2</sub>Se<sub>2</sub>] coordination sphere is formed when non-substituted Imt ligands form complexes with Cd(SeCN)<sub>2</sub>. This is reasonable on the basis of increase steric crowding with the substituent on the Imt and Diaz rigs. The <sup>113</sup>Cd, <sup>77</sup>Se CP MAS as well as solution NMR data also provide new insight to a metal environment relevant to biological systems.

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#### References

- [1] T.W. Lane and F.M.M. Morel, *Proc. Natl. Acad. Sci. USA* **97** (2000), 4627.
- [2] H. Strasdeit, *Angew. Chem. Int. Ed.* **40** (2001), 707.
- [3] T.W. Lane, M.A. Saito, G.N. George, I.J. Pickering, R.C. Prince and F.M.M. Morel, *Nature* **435** (2005), 42.
- [4] M. Vasák, *Biodegradation* **9** (1998), 501.
- [5] G. Henkel and B. Krebs, *Chem. Rev.* **104** (2004), 801.
- [6] A.V. Ivanov, A.V. Gerasimenko, O.N. Antzutkin and W. Forsling, *Inorg. Chim. Acta* **358** (2005), 2585 (and references therein).
- [7] A.V. Ivanov, O.V. Loseva, M.A. Ivanov, V.A. Konfederatov, A.V. Gerasimenko, O.N. Antzutkin and W. Forsling, *Russ. J. Inorg. Chem. (Engl. Transl.)* **52** (2007), 1595.
- [8] R.A. Alfred, L.H. Alexander, A.M. Arif and L.M. Berreau, *Inorg. Chem.* **41** (2002), 6790.

- [9] K. McAteer, A.S. Lipton and P.D. Ellis, Cadmium-113 NMR: A surrogate probe for zinc and calcium in proteins, in: *Encyclopedia of Nuclear Magnetic Resonance*, D.M. Grant and R.K. Harris, eds, John Wiley & Sons, New York, 1996, p. 1085 (and reference therein).
- [10] M.F. Summers, *Coord. Chem. Rev.* **86** (1988), 43.
- [11] A.V. Ivanov, A.V. Gerasimenko, A.A. Konzelko, M.A. Ivanov, O.N. Antzutkin and W. Forsling, *Inorg. Chim. Acta* **359** (2006), 3855.
- [12] H. Fleischer, *Coord. Chem. Rev.* **249** (2005), 799.
- [13] M.L. Helm, L.L. Hill, J.P. Lee, D.G. Van Derveer and G.J. Grant, *J. Chem. Soc. Dalton Trans.* (2006), 3534.
- [14] M.I.M. Wazeer, A.A. Isab and M. Fettouhi, *Polyhedron* **26** (2007), 1725.
- [15] A.A. Isab and M.I.M. Wazeer, *J. Coord. Chem.* **58** (2005), 529.
- [16] E.S. Raper, J.R. Creighton, N.A. Bell, W. Clegg and L. Cucurull-Sánchez, *Inorg. Chim. Acta* **277** (1998), 14.
- [17] N.A. Bell, T.N. Branston, W. Clegg, J.R. Creighton, L. Cucurull-Sánchez, M.R.J. Elsegood and E.S. Raper, *Inorg. Chim. Acta* **303** (2000), 220.
- [18] N.A. Bell, T.N. Branston, W. Clegg, L. Parker, E.S. Raper, C.P. Constable and C. Sammon, *Inorg. Chim. Acta* **319** (2001), 130.
- [19] N.A. Bell, S.J. Coles, C.P. Constable, D.E. Hibbs, M.B. Hursthouse, R. Mansor, E.S. Raper and C. Sammon, *Inorg. Chim. Acta* **323** (2001), 69.
- [20] M. Fettouhi, M.I.M. Wazeer and A.A. Isab, *J. Coord. Chem.* **60** (2007), 369 (and references therein).
- [21] M. Fettouhi, M.I.M. Wazeer and A.A. Isab, *Inorg. Chem. Comm.* **11** (2008), 252.
- [22] P.G. Mennit, M.P. Shatlock, V.J. Bartuska and G.E. Maciel, *J. Phys. Chem.* **85** (1981), 2087.
- [23] M.J. Collins, C.I. Ratcliffe and J.A. Ripmeester, *J. Magn. Reson.* **68** (1986), 172.
- [24] K. Eichele and R.E. Wasylischen, W: simulation package, version 1.4.4, Dalhousie University, Canada and University of Tübingen, Germany, 2001.
- [25] V. Navarro, M.I. Villarreal, G. Rojas and X. Lozoya, *J. Ethnopharm.* **53** (1996), 143.
- [26] J.S. Casas, E.G. Martinez, A. Sanchez, A.S. Gonzalez, J. Sordo, U. Casellato and R. Graziani, *Inorg. Chim. Acta* **241** (1996), 117.
- [27] Z. Popovic, G. Pavlovic, D. Matkovic-Calogovic, Z. Soldin, M. Rajic, D. Vikić-Topić and D. Kovacek, *Inorg. Chim. Acta* **306** (2000), 142.
- [28] S. Ahmad, A.A. Isab and M. Arab, *Polyhedron* **21** (2002), 1267.
- [29] U. Bierbach, T.W. Hambly and N. Farrell, *Inorg. Chem.* **37** (1998), 708.
- [30] W. Ashraf, S. Ahmad and A.A. Isab, *Transition Metal Chem.* **29** (2004), 400.
- [31] M.I.M. Wazeer and A.A. Isab, *J. Coord. Chem.* **60** (2007), 2649.
- [32] A.A. Isab, M.I.M. Wazeer, M. Fettouhi, S. Ahmad and W. Ashraf, *Polyhedron* **25** (2006), 2629.
- [33] G.M. Bernard, K. Eichele, G. Wu, G.W. Kirby and R.D. Wasylischen, *Can. J. Chem.* **78** (2000), 614.



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