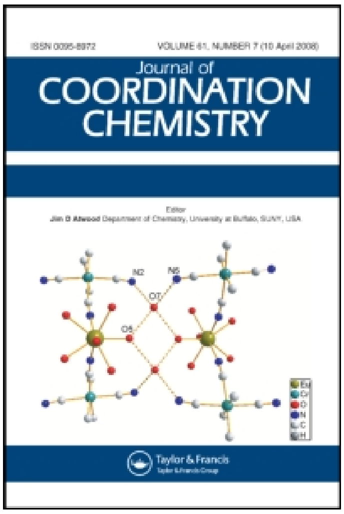


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Solid state and solution NMR studies of some new complexes of mercury selenocyanate with imidazolidine-2-thione and its derivatives

Mohammed I. M. Wazeer[a]; Anvarhusein A. Isab[a]
[a] Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

To cite this Article Wazeer, Mohammed I. M. and Isab, Anvarhusein A.(2007) 'Solid state and solution NMR studies of some new complexes of mercury selenocyanate with imidazolidine-2-thione and its derivatives', Journal of Coordination Chemistry, 60: 24, 2649 — 2657, First published on: 19 September 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701288421

URL: http://dx.doi.org/10.1080/00958970701288421

Journal of Coordination Chemistry
Vol. 60, No. 24, 15 December 2007, 2649–2657

Taylor & Francis
Taylor & Francis Group

Solid state and solution NMR studies of some new complexes of mercury selenocyanate with imidazolidine-2-thione and its derivatives

MOHAMMED I. M. WAZEER* and ANVARHUSEIN A. ISAB*

Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

(*Received 27 November 2006; in final form 15 February 2007*)

Reactions of imidazolidine-2-thione (Imt), 1,3-diazinane-2-thione (Diaz) and 1,3-diazipane-2-thione (Diap) with mercury(II) selenocyanate in acetonitrile resulted in formation of 2 : 1 complexes. Both solid state and solution NMR, confirm the exocyclic sulfur atom to be the donor in all cases. ^{199}Hg shielding tensors and anisotropies were calculated from the solid-state NMR spectra. Based on the solid NMR data a distorted tetrahedral disposition of ligands around mercury is proposed.

Keywords: Mercury(II) complexes; Selenocyanate complexes; Imidazolidine-2-thione; CP MAS NMR studies

1. Introduction

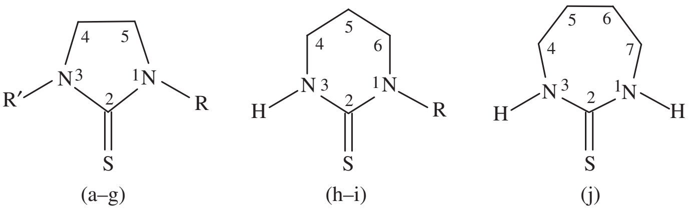
There is considerable interest in solution as well as solid state NMR of heavy metal nuclei, which include the ^{199}Hg NMR [1–3]. A significant number of these studies involve complexes with thiolate ligands, the main interest in this group of compounds being the important role played by such ligands in biological chemistry [4]. We recently reported the solid state NMR of some Hg-selone complexes [5, 6]. These studies resulted in correlation between the ^{199}Hg solid-state NMR parameters and structures of complexes. Such correlations are of value in the investigation of mercury coordination environments where structural data are not readily obtainable by other methods [7]. Since several mercury containing thiolates as well as other complexes are polymeric [8], it was considered desirable to try to establish a more quantitative relationship between solid state NMR and structural parameters and to use this to assist in the interpretation of the data obtained for mercury complexes involving a wider variety of complexes [9].

We have chosen to study a series of complexes of $Hg(SeCN)_2$ with thione ligands. Thiones, which are less basic than thiolate, are of interest because of their similar bonding nature with mercury compared to thiolates that have biological significance [10, 11].

---

*Corresponding authors. Email: miwazeer@kfupm.edu.sa; aisab@kfupm.edu.sa

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701288421



(a) R = R′ = H; Imidazolidine-2-thione (Imt)
(b) R = CH_3, R′ = H; N-methylimidazolidine-2-thione (MeImt)
(c) R = C_2H_5, R′ = H; N-ethylimidazolidine-2-thione (EtImt)
(d) R = C_3H_7, R′ = H; N-propylimidazolidine-2-thione (PrImt)
(e) R = *i*-C_3H_7, R′ = H; N-(*i*-propyl)imidazolidine-2-thione (*i*-PrImt)
(f) R = CH_3, R′ = CH_3; N,N′-dimethylimidazolidine-2-thione (Me2Imt)
(g) R = C_2H_5, R′ = CH_3; N-ethyl-N′-methylimidazolidine-2-thione (EtMeImt)
(h) R = H; 1,3-diazinane-2-thione (Diaz)
(i) R = C_2H_5; N-ethyl-1,3-diazinane-2-thione (EtDiaz)
(j) 1,3-Diazipane-2-thione (Diap)

Scheme 1.

2. Experimental

2.1. *Chemicals*

Methanol, acetone and DMSO-d_6 were obtained from Fluka Chemical Co. The thione ligands were synthesized according to the procedure described in the literature (by addition of CS_2 to diamines in ether and then heating the resulting adduct at 100°C for 2–3 h, followed by crystallization in methanol) [12]. $KSe^{13}CN$ (where ^{13}C is ~98%) is obtained from Isotec, USA.

2.2. *Synthesis of $Hg(Se^{13}CN)_2$ complex*

One equivalent of $HgCl_2$ and two equivalents of $KSe^{13}CN$ are separately dissolved in minimum distilled water, flushed with N_2 gas then mixed. The mixture was stirred for 1 h under N_2 gas, filtered and dried, the precipitate giving a yield of about 80%.

2.3. *Synthesis of the complexes*

The complexes were prepared by adding thiones in acetonitrile to $Hg(Se^{13}CN)_2$ solution in acetone in the molar ratio of 2 : 1 and stirring for 15–20 min [5, 6]. The resulting white precipitates were filtered and washed with acetone, giving 55 to 60% yield. Only four complexes gave solid powder, all other complexes were deliquescent in nature and only their solution NMR studies were carried out; IR and CP MAS NMR studies could not be carried out. Elemental analysis of the four complexes is given in table 1.

Table 1. Elemental analyses of $L_2Hg(SeCN)_2$ complexes.

Complex	Found (Calcd)%				m.p. (°C)
	C	H	N	S	
$(Imt)_2Hg(SeCN)_2$	16.02 (15.63)	1.78 (1.79)	14.01 (13.67)	10.33 (10.43)	144–146
$(Me_2Imt)_2Hg(SeCN)_2$	22.00 (21.48)	3.12 (3.00)	12.88 (12.53)	9.40 (9.56)	110–113
$(iPr_2Imt)_2Hg(SeCN)_2$	31.04 (30.67)	4.84 (4.63)	10.92 (10.73)	8.00 (8.19)	88–92
$(Diaz)_2Hg(SeCN)_2$	19.00 (18.68)	2.88 (2.51)	14.0 (13.71)	9.75 (9.98)	132–134

2.4. *Spectroscopic measurements*

The solid state IR spectra of the ligands and their mercury(II) complexes were recorded on a Perkin Elmer FTIR 180 spectrophotometer using KBr pellets over the range 4000–400 cm^{-1}.

All NMR measurements were carried out on a Jeol JNM-LA 500 NMR spectrophotometer at 297 K. The ^1H NMR spectra were recorded at a frequency of 500.00 MHz. The ^{13}C NMR spectra were obtained at a frequency of 125.65 MHz with ^1H broadband decoupling and relative to TMS. The spectral conditions were: 32 k data points, 0.967 s acquisition time, 1.00 s pulse delay and 45° pulse angle. The ^{77}Se NMR spectra were recorded at 95.35 MHz, using 160 millisecond acquisition time, 2.00 s pulse delay. The ^{77}Se NMR chemical shifts were measured relative to external SeO_2 at 1301 ppm.

Natural abundance ^{13}C solid-state NMR spectra were obtained on a JEOL LAMBDA 500 spectrometer operating at 125.65 MHz (11.74 T), at ambient temperature of 25°C. Samples were packed into 6 mm zirconium oxide 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 in the CPMAS experiments. The magic angle spinning rates were from 2 to 5 kHz. Carbon chemical shifts were referenced to TMS by setting the high frequency isotropic peak of solid adamantane to 38.56 ppm. Solid state cross-polarization magic-angle spinning (CPMAS) $^{199}Hg\{^1H\}$ NMR spectra were obtained at ambient temperature on the same spectrometer operating at a frequency of 89.30 MHz. Contact time of 20 ms was used with a proton pulse width of 6 μs, with a recycle delay of 10 s. Approximately 5000 FIDs were collected and transformed with a line broadening of 100 Hz. Chemical shifts were referenced using an external sample of solid $[Hg(DMSO)_6](O_3SCF_3)_2$ ($\delta\,Hg = -2313$ ppm from Me_2Hg) [13]. CP MAS ^{77}Se spectra were obtained on the same instrument operating at a frequency of 95.35 MHz. The contact time of 5 ms with proton pulse width of 6.0 μs, and a recycle delay of 12 s were used. Approximately 5000 scans were employed. ^{77}Se chemical shifts are referenced using an external solid ammonium selenate sample ($\delta_{Se} = 1040.2$ ppm relative to liquid Me_2Se at 23°C) [14]. Center band signals were located by varying the spinning speed. The CPMAS spectra (^{199}Hg and ^{77}Se) containing spinning side-band manifolds were analysed using a program based on Maricq and Waugh and developed by Durham University, UK, using an iterative method, to yield shielding tensor values [15]. Calculated tensor values and the isotropic chemical shifts are shown in table 3. Errors in

Table 2. Selected IR absorption (cm^{-1}) for free ligands and their $L_2Hg(SeCN)_2$ complexes.

Species	ν(C=S)	$\nu(NH_2)$	ν(CN) of $Hg(SeCN)_2$
$Hg(SeCN)_2$	–	–	2140, 2130[a]
Imt	510	3200	–
$(Imt)_2Hg(SeCN)_2$	423	3425	2115
Me_2Imt	520	–	–
$(Me_2Imt)_2Hg(SeCN)_2$	490	–	2114, 2037
iPr_2Imt	518	–	–
$(iPr_2Imt)_2Hg(SeCN)_2$	485	–	2107
Diaz	510	3200	–
$(Diaz)_2Hg(SeCN)_2$	490	3371	2119, 2089

[a] From ref. [9].

the shielding tensor parameters for ^{77}Se are considered high (±30 ppm) because of the high noise level and base line correction. Errors in ^{199}Hg tensors are estimated to be around 20 ppm.

3. Results and discussion

The complexes were synthesized by reacting $Hg(SeCN)_2$ with thiones in 1 : 2 ratio; C, H, N and S analyses are given in table 1.

3.1. *IR spectroscopic studies*

Selected IR spectroscopic vibration bands for the free ligands and their mercury(II) complexes are given in table 2. The ν(C=S) vibration, which occurs around 500 cm^{-1} for the free ligands, shifts to lower frequency upon complexation, as for other thione complexes [16, 17]. Another important vibrational band observed in IR spectra of the thiones is the ν(NH), which appears around 3200 cm^{-1}. Upon coordination to $Hg(SeCN)_2$ this band shifts to higher wave number, with some exceptions. The presence of a band around 3200 cm^{-1} 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 2140, 2130 cm^{-1} corresponding to CN^- stretch are observed in the IR spectra of $Hg(SeCN)_2$ [9]. For the complexes of PrImt, Me_2Imt, MeEtImt, Diaz, EtDiaz and Diap, only one ν(CN) mode was observed, at lower frequency (by approx. 150 cm^{-1}) compared to free $Hg(SeCN)_2$. For the rest of the complexes, two stretching bands (asymmetric and symmetric) are observed for CN^-, characteristic of $[Hg(SeCN)_2]$.

3.2. *^{1}H and ^{13}C NMR solution studies*

The ^{1}H and ^{13}C NMR chemical shifts of the complexes in DMSO-d_6 are summarized in table 3. In ^{1}H NMR spectra of the complexes, the N–H signal of thiones becomes less intense upon coordination and shifted downfield by 0.5–1.1 ppm from their positions in

Table 3. ^{1}H and ^{13}C NMR chemical shifts of thiones and their selenocyanomercury(II) complexes in DMSO-d_6.

Species	N–H	$Hg(Se^{13}CN)_2$	C-2	^{199}Hg	^{77}Se
$KSe^{13}CN$	–	116.64	–		−273.52
$Hg(Se^{13}CN)_2$	–	103.02*	–	−1651	−87.50
Imt	7.98	–	183.44	–	
$(Imt)_2Hg(Se^{13}CN)_2$	8.68	106.31	178.48	a	−168
EtImt	7.99	–	182.05		
$(EtImt)_2Hg(SeCN)_2$	8.67	106.20	180.94	−2053	−173
PrImt	7.99	–	182.55	–	
$(PrImt)_2Hg(SeCN)_2$	8.66	106.11	176.72	−2056	−172
i-PrImt	7.96	–	181.44		
(*i*-PrImt)$_2$Hg(SeCN)$_2$	8.15	106.08	175.78	−2059	−173
Me_2Imt	–	–	182.90	–	
$(Me_2Imt)_2Hg(SeCN)_2$	–	105.22	179.74	a	−168
Et_2Imt	–	–	181.00	–	
$(Et_2Imt)_2Hg(SeCN)_2$	–	106.11	178.00	−2086	−168
i-Pr$_2$Imt	–				
(*i*-Pr$_2$Imt)$_2$Hg(SeCN)$_2$	–	109.54	179.79	a	−210
Diaz	7.81		175.62		
$(Diaz)_2Hg(Se^{13}CN)_2$	8.71	107.63 107.58	169.10	a	−196
EtDiaz	7.89		176.05		
$(EtDiaz)_2Hg(SeCN)_2$	8.6	106.50	169.88	a	a
Diap	7.76	–	187.91		
$(Diap)_2Hg(SeCN)_2$	8.12	106.78	183.64	a	−227

^{199}Hg is referenced from $HgCl_2$ in DMSO −1562 ppm.

[a] Could not observe.

* $^{1}J(^{13}C–^{77}Se)$ 124 Hz for $Hg(Se^{13}CN)_2$ and $^{1}J(^{13}C–^{77}Se)$ 137 Hz for the free $KSe^{13}C^{15}N$ in DMSO-d_6.

free ligands. Deshielding of the N–H proton is related to an increase of the π electron density in the C–N bond upon complexation [18–20]. The appearance of N–H signal in ^{1}H NMR shows that the ligands coordinate in the selone form in solution [19, 20].

In all complexes, the C-2 resonance of thiones appears upfield by 4 ppm compared to free ligands (table 3) as observed for other complexes of Ag(I) and Au(I) with thiones [16, 17, 20]. 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 [16, 19].

The ^{13}C NMR shift difference for the C-2 resonance of thiones upon complexation is related to the strength of the metal-selenium bond [18]. The C-2 shift of 6 ppm is the highest in $[(Diaz)_2Hg(SeCN)_2]$ showing that the Hg–S bond in $[(Diaz)_2Hg(SeCN)_2]$ should be the strongest among these complexes. A similar observation was made for the $[(DiapSe)_2HgCl_2]$ complex, where the C-2 NMR shift was observed to be the highest among several complexes studied for the various $(selone)_2HgCl_2$ complexes. This observation indicates that for Imt, Diaz and Diap with five-, six- and seven-member rings, respectively, the six-member ring forms a more stable complex with $Hg(SeCN)_2$.

3.3. ^{77}*Se solution NMR studies*

^{77}Se NMR seems to be the most effective technique for characterizing these complexes because in ^{77}Se NMR a large upfield shift is observed for all the ligands upon complexation. On coordination of $SeCN^-$ with Hg(II), selenium resonances are

Table 4. Solid-state ^{119}Hg, ^{77}Se and ^{13}C isotropic chemical shifts (δ_{iso}) and principal shielding tensors (σ_{xx})[a] of the complexes.

Compound	Nucleus	δ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	η
$Hg(SeCN)_2$[b]	119Hg	−1760	503	1337	3440	2520	0.50
$(Me_2Imt)_2Hg(SeCN)_2$	^{119}Hg (i)	−800.1	1035	841	523	−415	0.70
	^{119}Hg (ii)	−898.5	1159	925	610	−431	0.82
	^{77}Se (i)	−162					
	^{77}Se (ii)	−170					
	^{77}Se (iii)	−182					
	^{77}Se (iv)	−193					
	^{13}C (C=S)	177.2	−237	−190	−103	−110	0.63
	(CN)	107.2	−220	−204	101	−322	0.10
$(Diaz)_2Hg(SeCN)_2$	^{119}Hg	−662.3	431	613	941	419	0.65
	^{77}Se(i)	−227	−65	−54	799	858	0.03
	^{77}Se(ii)	−235	−75	−65	845	916	0.03
	^{13}C (C=S)	176.2					
	(CN)	104.2	−215	−198	99	−312	0.12

[a] Isotropic shielding, $\sigma_i = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; $\Delta\sigma = \sigma_{33} - 0.5(\sigma_{11} + \sigma_{22})$; $\eta = 3(\sigma_{22} - \sigma_{11})/2\Delta\sigma$; [b] Ref. [9].

shielded by 186 ppm. This very large shielding provides clear evidence for selenium binding to mercury(II). A decrease in the upfield shift from 42 to 123 ppm was observed for the various complexes as shown in table 3. Symmetrical substitution for the ligands gave the same ^{77}Se NMR shift, e.g. $(Imt)_2Hg(SeCN)_2$, $(Me_2Imt)_2Hg(SeCN)_2$, $(Et_2Imt)_2Hg(SeCN)_2$ gave resonances at −168 ppm except (i-$Pr_2Imt)_2Hg(SeCN)_2$ which gave ^{77}Se NMR shift at −210 ppm. However, monosubstitution gave a resonance at 173 ppm e.g. $(Imt)_2Hg(Se^{13}CN)_2$, $(EtImt)_2Hg(SeCN)_2$ and (i-$PrImt)_2Hg(SeCN)_2$. These observations suggest that there is a trend in the ^{77}Se NMR shift for mono and disubstituted Imt ligands.

We measured ^{199}Hg NMR spectra for the complexes reported in table 3 because of the low solubility of these complexes. There is a shift of about 400 ppm when thiones bind to $Hg(SeCN)_2$. The chemical shifts fall between −2053 to −2086 ppm and no clear trend was observed; therefore, some solid ^{199}Hg NMR spectra were measured and discussed below.

3.4. *Solid-state NMR studies*

The chemical shifts and shielding tensor parameters obtained from spinning side band analyses for ^{119}Hg, ^{77}Se and ^{13}C NMR are shown in table 4, along with data for $Hg(SeCN)_2$ [9]. The ^{77}Se spectra of $(Me_2imt)_2Hg(SeCN)_2$ were of too low signal-to-noise to carry out reliable spinning side band analysis and hence only the isotropic shifts are reported. ^{199}Hg CP MAS NMR spectrum of $(Me_2imt)_2Hg(SeCN)_2$ is shown in figure 1 and the ^{77}Se CPMAS spectrum of $(Diaz)_2Hg(SeCN)_2$ is shown in figure 2.

While solid-state ^{199}Hg NMR spectroscopy reports of thiolate complexes are somewhat common [21], those of selone complexes are scarce. The only solid-state ^{199}Hg NMR study reported so far is for the linear complex mercury(II)selenocyanate [9]. The reported isotropic ^{199}Hg chemical shifts for $HgCl_2$, $Hg(SCN)_2$ and $Hg(SeCN)_2$ are −1625, −1300, and −1760 ppm, respectively, and adding thiolate groups to mercury tends to have a deshielding effect. The chemical shift of Hg nucleus is determined by the

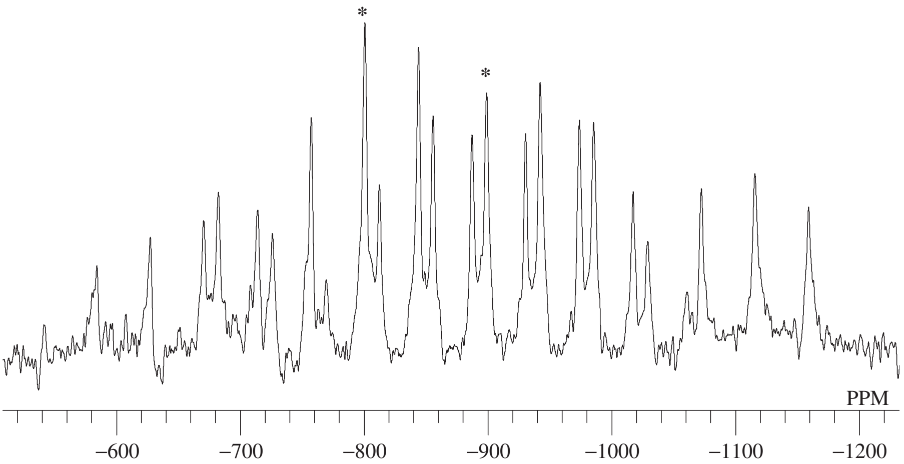


Figure 1. ^{199}Hg CP MAS NMR spectrum of $(Me_2imt)_2Hg(SeCN)_2$. The peaks marked (*) are the isotropic peaks.

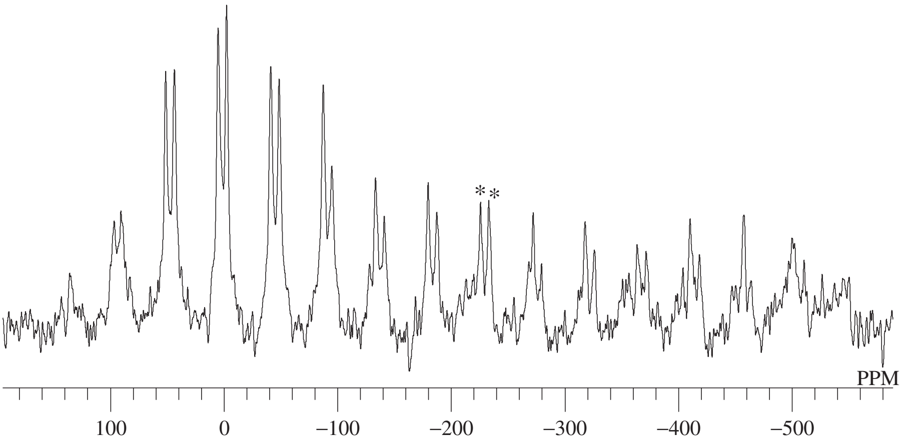


Figure 2. ^{77}Se CP MAS NMR spectrum of $(Diaz)_2Hg(SeCN)_2$. The peaks marked (*) are the isotropic peaks.

arrangement of atoms directly bonded to the Hg atom while the arrangement of the other atoms in the ligand plays a minor role [9]. The presence of two thione ligands will be expected to deshield the Hg nucleus to a great extent and the isotropic chemical shifts observed for the complexes studied here fall in the range −600 to −900 ppm. The linear $Hg(SeCN)_2$ shows a large shielding anisotropy ($\Delta\sigma$) of 2520 ppm [9]. It has been found that the magnitude of the shielding anisotropy of mercury decreases from linear through trigonal planar to a perfect tetrahedral geometry, where it approaches a value of zero. Hence the smaller $\Delta\sigma$ observed (around 400 ppm) for the two complexes is consistent with a distorted tetrahedral disposition of ligands around mercury. The change of sign of $\Delta\sigma$ is due to apparent swapping of σ_{11} and σ_{33} tensor parameters in the two complexes. Moreover, the asymmetry parameter values from 0.65 to 0.82 indicate that the point symmetry of the site occupied by mercury is away from axial symmetry.

Two selenium isotropic peaks were shown by the Diaz complex, presumably due to the two SeCN ligands becoming non-equivalent due to the distorted tetrahedral arrangement of the ligands. However, we observed four isotropic peaks for the Me_2Imt complex. The extra two resonances could be due to site inequivalencies in the crystal structure and needs to be resolved by single crystal X-ray studies. At the moment we are unable to get good single crystals of the complexes. The carbon resonances of the SeCN ligand showed only single isotropic peaks in the two complexes; perhaps this is due to low spread of carbon shifts relative to selenium shifts.

4. Conclusion

In this study, we have shown that a series of thiones react with $Hg(SeCN)_2$ to form complexes of the type $L_2Hg(SeCN)_2$, in which the ligands exist in thione form both in solution and solid state as indicated by IR and NMR. The ^{13}C and ^{77}Se solution NMR data clearly indicate that as the ring size of the ligand is increased, the chemical shift difference for the free and bound resonance also increases. Thus Diaz forms more stable complexes with mercury(II) compared to Imt. The chemical shifts for different complexes presented here are useful, especially if the ^{77}Se NMR is used to study the metal-ligand interactions in biological systems. ^{199}Hg shielding tensors and anisotropies were calculated from the solid-state NMR spectra. Based on the solid NMR data a distorted tetrahedral disposition of ligands around mercury is proposed.

Acknowledgment

This research was supported by the KFUPM Research Committee under project numbers SABIC 2006-08.

References

[1] H. Fleischer. *Coord. Chem. Rev.*, **249**, 799 (2005).
[2] J.E. Penner-Hahn. *Coord. Chem. Rev.*, **249**, 161 (2005).
[3] J.A. Davies, S. Dutremez. *Coord. Chem. Rev.*, **114**, 201 (1992).
[4] W. Lu, M.J. Stillman. *J. Am. Chem. Soc.*, **115**, 3291 (1993).
[5] A.D. Al-Amri, M. Fettouhi, M.I.M. Wazeer, A.A. Isab. *Inorg. Chem. Comm.*, **8**, 1109 (2005).
[6] A.A. Isab, M.I.M. Wazeer, M. Fettouh, S. Ahmad, W. Ashraf. *Polyhedron*, **25**, 2629 (2006).
[7] J.G. Wright, M.J. Natan, F.M. McDonnell, D.M. Ralston, T.V. O'Halloran. *Prog. Inorg. Chem.*, **38**, 323 (1990).
[8] M.S. Bharara, S. Parkin, D.A. Atwood. *Inorg. Chem.*, **45**, 2112 (2006).
[9] G.A. Bowmaker, A.V. Churakov, R.K. Harris, J.A.K. Howard, D.C. Apperley. *Inorg. Chem.*, **37**, 1734 (1998).
[10] P.D. Akrivos. *Coord. Chem. Rev.*, **213**, 181 (2001).
[11] E. Rodríguez-Fernández, J.L. Manzano, J.J. Benito, R. Hermosa, E. Monte, J.J. Criado. *J. Inorg. Biochem.*, **99**, 1558 (2005).
[12] M.I.M. Wazeer, A.A. Isab, A. El-Rayyes. *Spectroscopy*, **18**, 113 (2004) (and references therein).
[13] J.M. Hook, P.A.W. Dean, L.C.M. van Gorkom. *Magn. Reson. Chem.*, **33**, 77 (1995).
[14] M.J. Collins, C.I. Ratcliffe, J.A. Ripmeester. *J. Magn. Reson*, **68**, 172 (1986).

[15] M. Maricq, J. Waugh. *J. Chem. Phys.*, **70**, 3300 (1979).
[16] A.A. Isab, S. Ahmad, M. Arab. *Polyhedron*, **21**, 1267 (2002).
[17] A.A. Isab, H.P. Perzanowski. *Polyhedron*, **15**, 2397 (1996).
[18] Z. Popovic, G. Pavlovic, D. Matkovic-Calogovic, Z. Soldin, M. Rajic, D. Vikic-Topic, D. Kovacek. *Inorg. Chim. Acta*, **306**, 142 (2000).
[19] S. Ahmad, A.A. Isab, A.P. Arnold. *J. Coord. Chem.*, **56**, 539 (2003).
[20] M.I.M. Wazeer, A.A. Isab. *Spectro. Chim. Acta (A)*, **62**, 880 (2005).
[21] R.A. Santos, E.S. Gruff, S.A. Koch, G.S. Harbison. *J. Am. Chem. Soc.*, **113**, 469 (1991).