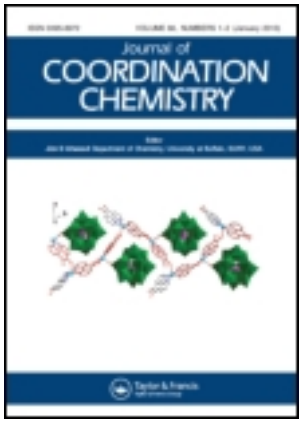

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Mercury(II) cyanide complexes with alkyldiamines: solid-state/solution NMR, computational, and antimicrobial studies

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Mercury(II) cyanide complexes with alkyldiamines: solid-state/solution NMR, computational, and antimicrobial studies

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Mercury cyanide complexes of alkyldiamines (**1**–**6**), $[Hg(L)(CN)_2]$ (where L = *en* (1,2-diaminoethane), *pn* (1,3-diaminopropane), *N*-Me-*en*, *N*, *N*′-Me_2-*en*, *N*, *N*′-Et_2-*en*, and *N*, *N*′-ipr_2-*en*), have been synthesized and characterized by elemental analysis, IR, ^{13}C, and ^{15}N solution NMR in DMSO-d_6, as well as ^{13}C, ^{15}N, and ^{199}Hg solid-state NMR spectroscopy. Complexes **1** and **2** have been studied computationally, built and optimized by GAUSSIAN03 using DFT at B3LYP level with LanL2DZ basis set. Binding modes of *en* and *bn* (where *bn* = 1,4-diaminobutane) toward $Hg(CN)_2$ are completely different. Complexes with *en* and *pn* show chelating binding to Hg(II), while *bn* behaves as a bridging ligand to form a polymeric structure, $[Hg(CN)_2\text{-}bn]_\infty$ [B.A. Al-Maythalony, M. Fettouhi, M.I.M. Wazeer, A.A. Isab. *Inorg. Chem. Commun.*, **12**, 540 (2009).]. The solution ^{13}C NMR of the complexes demonstrates a slight shift of the $-C{\equiv}N$ (0.9 to 2 ppm) and $-C{-}NH_2$ (0.25 to 6 ppm) carbon resonances, while the other resonances are relatively unaffected. ^{15}N labeling studies have shown involvement of alkyldiamine ligands in coordination to the metal. The principal components of the ^{13}C, ^{15}N, and ^{199}Hg shielding tensors have been determined from solid-state NMR data. Antimicrobial activity studies show that the complexes exhibit higher antibacterial activities toward various microorganisms than $Hg(CN)_2$.

Keywords: Mercury cyanide complexes; Solid-state NMR; ^{13}C, ^{15}N, ^{199}Hg NMR

1. Introduction

Coordination chemistry of mercury(II) receives attention due to concerns regarding its environmental and toxicological impacts [1–3]. There have been many approaches to elucidating the nature and geometry of the coordination sphere around mercury using X-ray crystallography as well as solution and solid-state NMR including ^{199}Hg NMR [4–9]. A large number of Hg(II) complexes with thione and thiolate ligands [10–20] have been reported due to the importance of these ligands in biological chemistry and their

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high affinity for Hg(II) [21]. We have reported spectroscopic and structural characterization of Ag(I)–, Au(I)–, Cd(II)–, and Hg(II)-cyanide complexes with various thiones and selenones [12, 22–30]. Some of these studies have resulted in correlation of ^{199}Hg solid-state NMR parameters and the structure of the complexes [11, 12]. Such information is of value in investigation of mercury coordination environments where structural data are not readily obtainable by other methods [31].

Recently, we reported the structural characterization of [$Hg(CN)_2$-*bn*] (*bn* = 1,4-diaminobutane) employing ^{13}C, ^{15}N, and ^{199}Hg cross-polarization-magic angle spinning (CPMAS) NMR spectroscopy and X-ray crystallography [1]. This complex was polymeric with *bn* bridging between two metal centers. In addition, mercury cyanide complex with ethylenediamine was reported by Ahuja *et al.* [32]. However, neither NMR nor computational characterization was reported in their work. Motivated by our continued search to better understand the chemical and physical behavior of mercury cyanide complexes [12, 29, 30], we have synthesized mercury(II) cyanide complexes with a range of diamines such as *en* (1,2-diaminoethane), *pn* (1,3-diaminopropane), and *N*-substituted– (*N*-Me-*en*) as well as *N, N′*-disubstituted– (*N, N′*-Me_2-en, *N, N′*-Et_2-en, and *N, N′*-ipr_2-*en*) alkyldiamines and characterized them by solution as well as solid-state NMR with labeled (^{15}N) ligands. The computationally built structures for two of the complexes are also presented here. In addition, we have investigated the antibacterial activities of the prepared complexes. The proposed structures of the complexes prepared in this study are given in scheme 1.

2. Experimental

2.1. *Materials and methods*

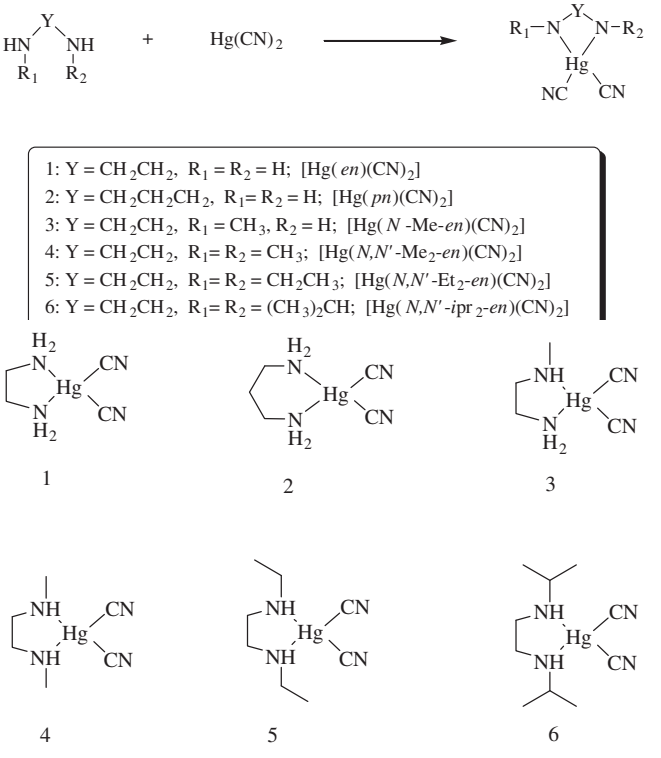
The ^{15}N labeled diamines ligands were obtained from Cambridge Isotope Labs, USA. All other reagents and solvents used were obtained from Aldrich Chemical Co. and used as received. All reactions were carried out under an atmosphere of nitrogen. Elemental analyses were performed on a Perkin Elmer Series 11 (CHNS/O), Analyzer 2400.

2.2. *Synthesis of Hg(II) complexes*

The complexes were prepared by mixing solutions of 3.5 m mol of diamine (e.g., 0.21 g for *en*) and 0.76 g (3.0 m mol) $Hg(CN)_2$ in methanol and refluxing for about 4 h (scheme 1). The resulting colorless solutions were filtered and kept in a refrigerator for crystallization. The products were obtained in good yield. Elemental analysis data are given in table 1.

2.3. *IR studies*

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



Scheme 1. Synthesis of the complexes and their proposed structures.

Table 1. Elemental analyses and melting points of the complexes.

				Found (Calcd)%		
Complexes	Yield (%)	Color	m.p. (°C)	C	H	N
1	77	Gray powder	105	15.50(15.36)	2.78(2.58)	17.79(17.92)
2	69	Gray powder	130	18.63(18.38)	3.23(3.08)	17.27(17.15)
3	82	Gray powder	75–76	17.97(18.38)	3.38(3.08)	17.13(17.15)
4	58	Gray crystal	60–61	20.89(21.15)	3.33(3.55)	16.62(16.44)
5	72	Gray powder	95–96	26.34(26.19)	3.44(3.85)	14.98(15.27)
6	52	White crystal	50–52	29.99(30.42)	4.39(4.59)	14.29(14.19)

2.4. *Solution NMR studies*

All NMR measurements were carried out on a Jeol JNM-LA 500 NMR spectrophotometer at 298 K. ^{13}C NMR spectra were obtained at a frequency of 125.65 MHz with ^{1}H broadband decoupling with chemical shifts reported 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. ^{15}N NMR spectra were recorded at 50.55 MHz using $^{15}NH_4NO_3$ as

external reference, which lies at −358.62 ppm relative to pure $MeNO_2$ [33]. The spectral conditions for ^{15}N were: 32 K data points, 0.721 s acquisition time, 2.50 s delay time, 60° pulse angle, and approx. 5000 scans. The ^{199}Hg NMR signals for the complexes could not be observed in solution perhaps due to low concentration of the complexes on account of their low solubility. Moreover, slow exchange of ligands with DMSO can result in a very broad resonance buried under the noise.

2.5. *Solid-state NMR studies*

Natural abundance ^{13}C solid-state NMR spectra were obtained on a JEOL LAMBDA 500 spectrometer operating at 125.65 MHz, corresponding to a magnetic field of 11.74 T, at 298 K. 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 in the CPMAS experiments. The magic angle spinning rates were from 3000 Hz to 5000 Hz. Carbon-13 chemical shifts were referenced to TMS by setting the high-frequency isotropic peak of solid adamantane to 38.56 ppm. The ^{15}N NMR spectrum was recorded at 50.55 MHz using $^{15}NH_4NO_3$ as external reference, which lies at −358.62 ppm relative to pure $MeNO_2$ [19]. The spectral conditions for ^{15}N were: 32 K data points, 0.721 s acquisition time, 2.50 s delay time, 60° pulse angle, and approx. 5000 scans. The chemical shifts of nitrogen were initially referenced with respect to liquid NH_3, by setting the ^{15}N peak in enriched solid $^{15}NH_4Cl$ to 40.73 ppm [34], and then converted to the standard nitromethane by a shift of −380.0 ppm [19] for ammonia. Solid-state CPMAS $^{199}Hg\{^1H\}$ NMR spectra were obtained at ambient temperature on the same spectrometer operating at a frequency of 89.30 MHz. Contact times of 20 ms were 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 [35] from Me_2Hg). The ^{199}Hg and ^{15}N spectra containing spinning side-band manifolds were analyzed using a computer program WSOLIDS developed at Dalhousie and Tubingen universities [36].

2.6. *Computational studies*

The structures of **1** and **2** were optimized using GAUSSIAN03 [37] at DFT/B3LYP level with LANL2DZ basis set [38, 39]. Selected bond lengths and angles are given in table 2.

2.7. *Antibacterial assay*

Antimicrobial activities for **1** and **2** in two different solvents were measured [40, 41] by the minimum inhibitory concentration (MIC) on four microorganisms, Heterotropic plate counts (HPC), *Pseudomonas aeruginos*a, *Fecal Streptococcus*, and *Escherichia coli*. Each analysis was carried out in duplicate to maintain the accuracy. Dosage of each chemical started from 10 μg mL^{-1} and continued until MIC was reached. A maximum dose of 1000 μg mL^{-1} was used as a stopping criterion. The bioactivities were tested and data are shown in table 3.

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2** calculated computationally.

1			
Hg–C	2.208	C–Hg–C	157.89
Hg–N	2.590	N–Hg–N	72.20
C≡N	1.189	C1–Hg–N1	97.45
C–N	1.496	C2–Hg–N1	100.50
C–C	1.541	C–N–Hg	106.87
		Hg–C≡N	175.53
2			
Hg–C4	2.210	C4–Hg–C5	156.36
Hg–C5	2.217	N1–Hg–N2	81.06
Hg–N1	2.568	C4–Hg–N1	100.91
Hg–N2	2.568	C2–Hg–N2	100.91
C≡N	1.188	C1–N2–Hg	112.37
C1–N2	1.497	C3–N1–Hg	112.37
C1–C2	1.544	Hg–C4–N3	176.43

Table 3. Antibacterial activities of mercury(II) complexes evaluated by the MIC (μg mL^{-1}).

Test organism	$Hg(CN)_2$ in water	$Hg(CN)_2$ in DMSO	**1** in water	**1** in DMSO	**2** in water	**2** in DMSO
HPC	>1000	950	850	825	>1000	>1000
P. aeruginosa	950	900	800	750	>1000	>1000
F. streptococcus	>1000	>1000	800	750	975	940
E. coli	850	800	775	720	930	950

3. Results and discussion

3.1. *IR studies*

Selected IR bands for the free ligands, Hg(II) precursor, and the complexes are given in table 4. A sharp band at 3300 cm^{-1} was observed for all the complexes, indicating the presence of diamines. The C≡N stretching frequency of $Hg(CN)_2$ is at 2191 cm^{-1}. For **1**–**6**, only one ν(C≡N) mode was observed at lower frequency compared to $Hg(CN)_2$. For example, in **1**, ν(C≡N) shift is 33 cm^{-1} to lower frequency than the cyanide precursor, consistent with significant back donation of electron density from the metal to empty π^* orbitals of cyanide upon coordination to the diamines. The changes in ν(N–H) between ligands and corresponding complexes are small and within experimental error.

3.2. *Solution NMR studies*

The ^{13}C and ^{15}N NMR chemical shifts of various complexes are summarized in tables 5 and 6 respectively. Upfield ^{13}C NMR chemical shifts were observed with respect to the free ligands. Similar to the polymeric [*bn*-$Hg(CN)_2$] [1], the ^{13}C NMR spectrum of

Table 4. IR frequencies (in cm^{-1}) of diamines and their Hg(II) complexes.

Species	ν(N–H)	ν(C≡N)
$Hg(CN)_2$	–	2191
en	3393	–
1	3398	2158
pn	3282	–
2	3280	2154
N-Me-*en*	3282	–
3	3294	2166
N, *N*′-Me_2-*en*	3288	–
4	3253	2169
N, *N*′-Et_2-*en*	3235	–
5	3245	2166
N, *N*′-*i*pr_2-*en*	3249	–
6	3257	2168

Table 5. ^{13}C NMR chemical shifts of $Hg(CN)_2$-alkanediamine complexes in DMSO-d_6.

Species	C≡N	C–1	C–2	C–3
$Hg(CN)_2$	145.15			
en		45.05		
1	144.24	42.12		
pn		39.86	37.33	
2	143.28	38.02	35.45	
N-Me-*en*		36.26	46.37	
3	144.42	41.48	31.26	
N, *N*′-Me_2-*en*		51.43	36.49	
4	143.28	50.17	35.99	
N, *N*′-*i*pr_2-*en*		48.82	47.57	23.09
6	143.46	49.03	47.11	22.21

Table 6. ^{15}N NMR chemical shifts (in ppm) of $Hg(CN)_2$-alkanediamine complexes in DMSO-d_6.

Species	$\delta(^{15}N)$
pn HCl	−343.12
2	−363.52
4	−363.19
6	−362.34

[*en*-$Hg(CN)_2$] shows no significant shift in cyanide signal upon complexation with *en*, while a downfield shift of around 3 ppm was observed for the *en* carbons. This shift may be due to the flow of electron density from C to N, in the complexes [10, 13, 24, 28, 42, 43]. The ^{15}N NMR signal of **2** is shifted downfield compared to that of *pn*. However, no significant shift difference was observed between the complexes. For example,

Table 7. Solid-state ^{13}C, ^{15}N, and ^{199}Hg isotropic chemical shifts (δ_{iso}) and principal shielding tensors (σ_{xx}) of Hg(II)-cyanide complexes with alkyldiamines.

Complex	Nucleus	δ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$[a]	η[b]
$[Hg(CN)_2]$	^{13}C (CN)	–					
	^{199}Hg	−1396					
1	^{13}C(CN)	163.7	282.22	192.84	13.94	267	0.600
	^{15}N	−125.2					
	^{15}N(*en*)	−315.5					
	^{199}Hg	−503	30.79	−555.35	−985.61	1016	0.805
4	(i) ^{13}C (CN)	145.3	291.9	207.7	−63.7	355.6	0.53
	(ii) ^{13}C (CN)	143.5	274.8	235.8	−80.1	354.9	0.78
	(i) ^{15}N (CN)	−92.5	110.3	110.3	−498.3	608.3	1.00
	(ii) ^{15}N (CN)	−95.9	101.1	101.1	−489.9	590.9	1.00
	^{15}N (*en*)	−348.5					
	^{119}Hg	−311.5					
5	(i) ^{13}C (CN)	142.9	214.5	214.5	−0.39	214.9	1.00
	(ii) ^{13}C (CN)	145.8	217.4	217.4	2.50	214.9	1.00
	(i) ^{119}Hg	−365.7	157.5	−306.9	−947.7	1105.2	0.16
	(ii) ^{119}Hg	−371.6	159.5	−332.5	−942.0	1101.5	0.11
6	^{13}C (CN)	146.5	249.1	249.1	−58.7	307.9	1.00
	^{15}N (CN)	−91.9	72.7	72.7	−421.0	493.7	1.00
	^{15}N (*en*)	−316.3	−29.4	−408.6	−1074.4	1045.4	0.28
	^{119}Hg	−504.3					

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

^{15}N NMR chemical shift of ethylenediamine ring nitrogen atoms in **4** and **6** is very similar to that of the propylenediamine ring in **2**.

3.3. *CPMAS NMR characterization*

Table 7 shows solid-state NMR data for the complexes studied. ^{199}Hg signals in the complexes are 1000 ppm deshielded from those in $Hg(CN)_2$, in keeping with the change in geometry and coordination of two nitrogen atoms to ^{199}Hg (figures 1 and 2). This is clear confirmation that the complexes are formed. As reported for some mercury cyanide/chloride double salts, these complexes have a see-saw effective coordination geometry based upon linear coordination [44] (2+2 according to Gredenic [45]). The C–Hg–C bond angles in their complexes are 150–160°. The Hg anisotropies are 2300–3400 ppm. In earlier studies [12] on $Hg(CN)_2$ complexes with imidazolidine-2-thiones and its derivatives, the anisotropies of ^{199}Hg are 1400–2000 ppm and have been rationalized in terms of stronger coordination of sulfur compared to chloride, making the C–Hg–C angle less than 150; i.e. closer to a highly distorted tetrahedral geometry. The C–Hg–C bond angle for **1** described here is 157.89° and diamine is weakly coordinated. So, the ^{199}Hg anisotropies in the complexes under study here are 1000 ppm, perhaps indicating weaker binding of diamines to $Hg(CN)_2$; that is also indicated by the calculated structural parameters.

Carbon-13 and nitrogen-15 CPMAS spectra show two distinct resonances for CN (figures 3–5), for **4** and **5**, indicating two chemically different environments for CN. This suggests that two distinct molecules may exist in a unit cell, or one CN is H-bonded and

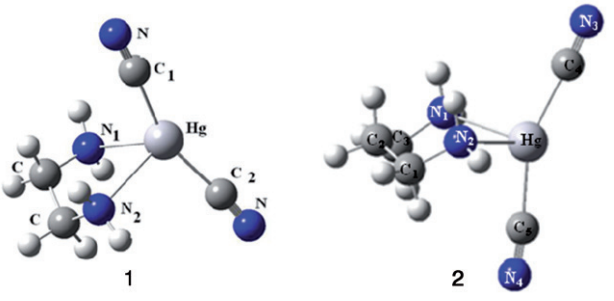


Figure 1. Computationally optimized structure of the complexes **1** and **2** by GAUSSIAN03 at DFT/ B3LYP level with LanL2DZ basis set.

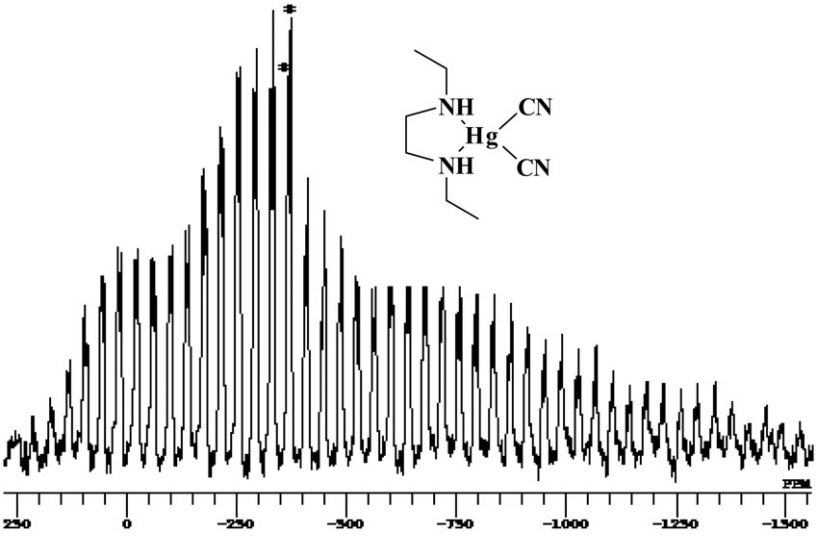


Figure 2. ^{199}Hg CPMAS spectrum of **5**. The isotropic peaks are denoted by *.

the other is free [1, 46]. The nitrogen resonances in CN show skew values of 1.00 indicating that axial symmetry is maintained, whereas the carbon resonances show skew values less than 1.00. The ^{15}N signals from $-NH_2$ are slightly overlapped with CN sidebands and we can only pick out one type of resonance for this nucleus.

3.4. *Computational analysis*

The computationally optimized structures of **1** and **2** are shown in figure 6; selected bond lengths and angles of the optimized structures are presented in table 2. In both complexes, Hg exhibits severely distorted tetrahedral geometry completed by two nitrogen atoms of diamines and two cyanides. The Hg–N and Hg–C bond distances and most of the bond angles are in agreement with those observed in other reported

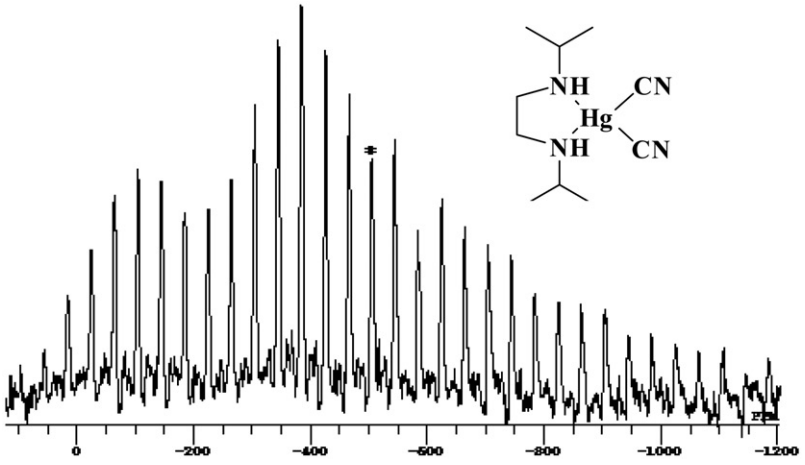


Figure 3. ^{199}Hg CPMAS spectrum of **6**. The isotropic peaks are denoted by *.

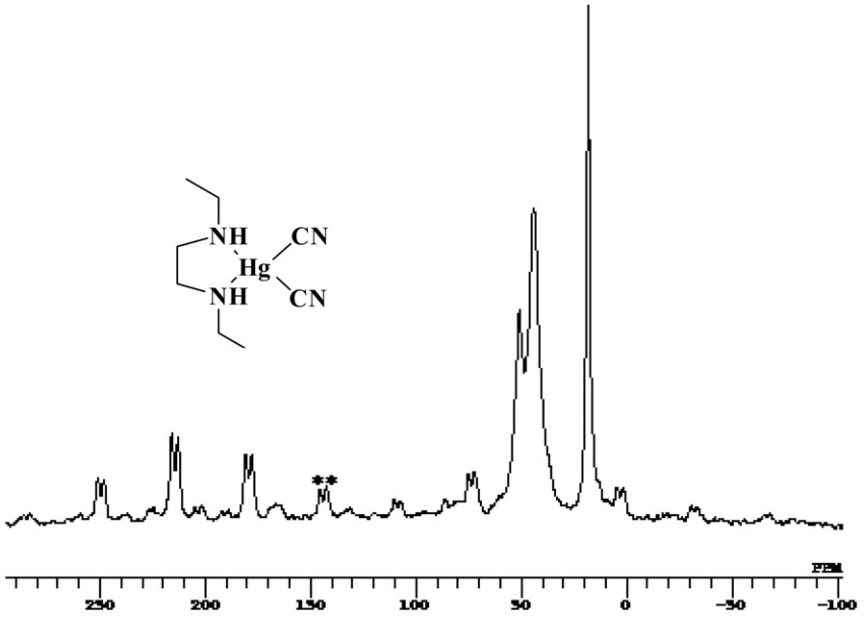


Figure 4. ^{13}C CPMAS spectrum of **5**. The isotropic peaks denoted by *.

complexes [1, 29, 30, 47]. In both **1** and **2**, the Hg–C distance is slightly longer than in $Hg(CN)_2$ (2.015(3) Å) [48]. The C–Hg–C angles in **1** and **2** are 157.89° and 156.36°, respectively, much larger than the normal tetrahedral value of 109.5°. These large angles are counter balanced by the very small N–Hg–N bond angles of 72.20° and 81.06° for **1** and **2**, respectively. This tetrahedral distortion as well as somewhat longer Hg–N distances than those in $[Hg(CN)_2$-*bn*$]_n$ indicate weak binding of diamine to Hg(II). The C–Hg–N bond angles in **1** and **2** are 97.45 and 100.91, respectively. In comparison to *bn* (1,4-diaminobutane), which formed a linear polymeric complex $[Hg(CN)_2$-*bn*$]_n$ [1], the

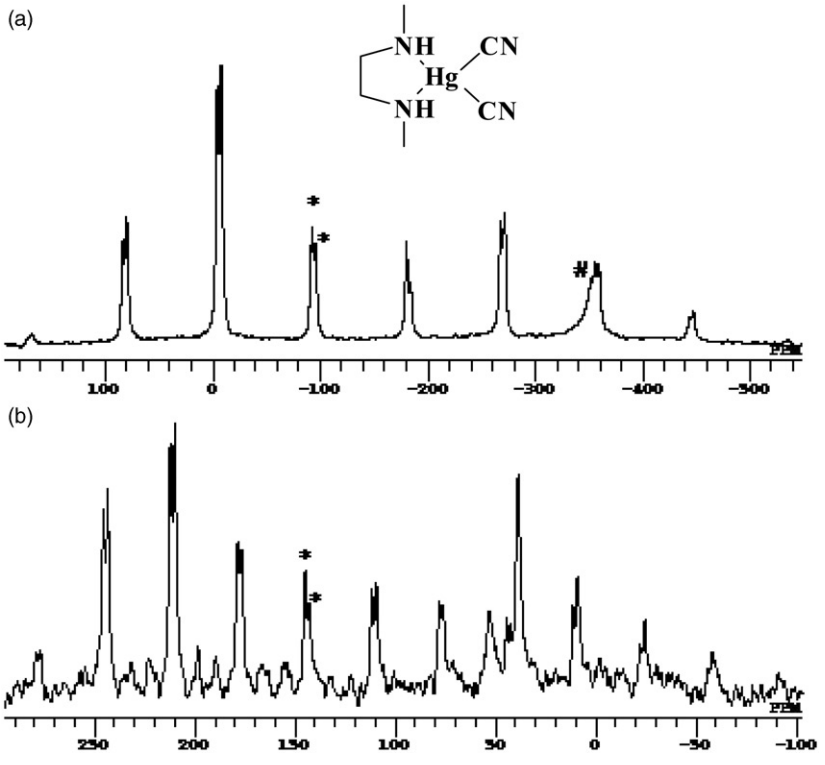


Figure 5. (a) ^{15}N and (b) ^{13}C CPMAS spectra of **4**. The isotropic peaks are denoted by * and the NH resonance is denoted by #.

diamines used in this study, *en* and *pn* form chelates, **1** and **2**. As indicated by the N–Hg–N bond angles, the chelate formed by *pn* is less strained than that of *en*.

3.5. *Bioactivity studies*

The antibacterial activities of $Hg(CN)_2$ and two of its complexes, estimated by MIC ($\mu g\,mL^{-1}$), are given in table 3. Complex **1** in DMSO is particularly effective in inhibiting the growth of tested bacteria. Compound **2** shows some activity against two of the microbes, but in general was highly resistant against all four bacteria. A comparison between the activity of **1** and **2** against the most sensitive organism, *E. coli*, shows that the minimum concentration increased from 775 $\mu g\,mL^{-1}$ to 930 $\mu g\,mL^{-1}$ in water and 720 to 950 $\mu g\,mL^{-1}$ in DMSO as we move from **1** to **2**. The greater activity of **1** may be related to a more strained ring of the chelate so that the ligand could be easily replaced by biological ligands.

4. Conclusion

In this study, we have synthesized and characterized a number of $Hg(CN)_2$ complexes [(L)$Hg(CN)_2$] (where L = *en, pn, N*-Me-*en, N, N′*-Me_2-*en, N, N′*-Et_2-*en*,

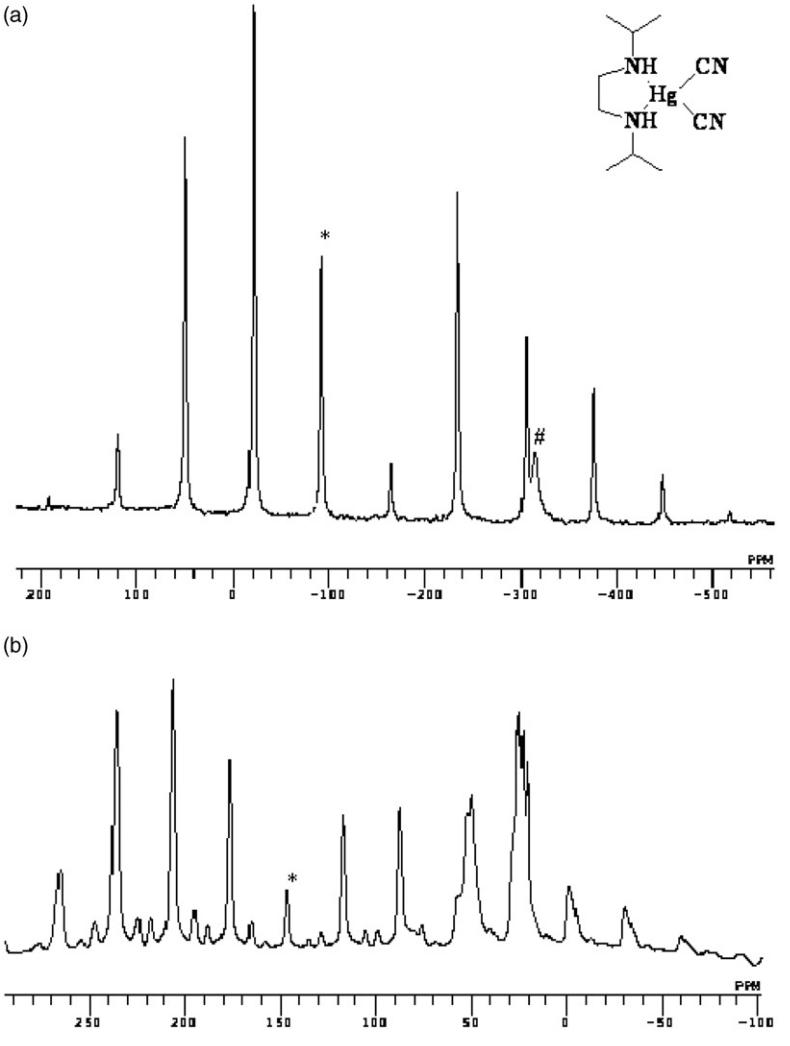


Figure 6. (a) ^{15}N and (b) ^{13}C CPMAS spectra of **6**. The isotropic peaks are denoted by * and the NH resonance is denoted by #.

and *N, N′-i*Pr_2*-en*). According to the elemental analysis data, only one equivalent of alkyldiamine ligand is involved in coordination to form a mercury complex. The ^{13}C solution NMR data clearly indicate that no significant change is observed as the ring size of the metal-chelate increases from five- to six-membered. The ^{15}N labeled NMR studies show involvement of *pn* and *N, N′*-Me_2*-en* for **2** and **4** in coordination to the metal. The antibacterial activities of **1** and **2** are not very significant.

Acknowledgments

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References

[1] B.A. Al-Maythalony, M. Fettouhi, M.I.M. Wazeer, A.A. Isab. *Inorg. Chem. Commun.*, **12**, 540 (2009).
[2] L. Prodi, C. Bargossi, M. Montalti, N. Zaccheroni, N. Su, J.S. Bradshaw, R.M. Izatt, P.B. Savage. *J. Am. Chem. Soc.*, **122**, 6769 (2000).
[3] T.F. Baumann, J.G. Reynolds, G.A. Fox. *J. Chem. Soc. Chem. Commun.*, 1637 (1998).
[4] D.J.M. Snelders, M.A. Siegler, L.S. Chrzanowski, A.L. Spek, G. Koten, R.J.M.K. Gebbink. *J. Chem. Soc., Dalton Trans.*, 2588 (2011).
[5] H. Shang, A.X. Zheng, D. Liu, Z.G. Ren, J.P. Lang. *Acta Cryst. C*, **67**, m237 (2011).
[6] D.J.M. Snelders, G. Koten, R.J.M.K. Gebbink. *Chem. Eur. J.*, **17**, 42 (2011).
[7] H. Fleischer. *Coord. Chem. Rev.*, **249**, 799 (2005).
[8] J.E. Penner-Hahn. *Coord. Chem. Rev.*, **249**, 161 (2005).
[9] J.A. Davies, S. Dutremez. *Coord. Chem. Rev.*, **114**, 201 (1992).
[10] A.A. Isab, H.P. Perzanowski. *Polyhedron*, **14**, 2397 (1996).
[11] M.I.M. Wazeer, A.A. Isab. *J. Coord. Chem.*, **60**, 2649 (2007).
[12] M.I.M. Wazeer, A.A. Isab. *Spectrochim. Acta, Part A*, **68**, 1207 (2007).
[13] Z. Popovic, G. Pavlovic, D. Matkovic-Calogovic, Z. Soldin, M. Rajic, D. Vikic-Topic, D. Kovacek. *Inorg. Chim. Acta*, **306**, 142 (2000).
[14] Z. Popovic, Z. Soldin, G. Pavlovic, D. Matkovic-Calogovic, D. Mrvos-Sermek, M. Rajic. *Struct. Chem.*, **13**, 425 (2002).
[15] N.A. Bell, S.J. Coles, C.P. Constable, D.E. Hibbs, M.B. Hursthouse, R. Mansor, E.S. Raper, C. Sammon. *Inorg. Chim. Acta*, **323**, 69 (2001).
[16] T.S. Lobana, R. Sharma, R. Sharma, R. Sultana, R.J. Butcher. *Z. Anorg. Allg. Chem.*, **634**, 718 (2008).
[17] X.Y. Tang, R.X. Yuan, Z.G. Ren, H.X. Li, Y. Zhang, J.P. Lang. *Inorg. Chem.*, **48**, 2639 (2009).
[18] X.Y. Tang, A.X. Zheng, H. Shang, R.X. Yuan, H.X. Li, Z.G. Ren, J.P. Lang. *Inorg. Chem.*, **50**, 503 (2011).
[19] X.Y. Tang, H.X. Li, J.X. Chen, Z.G. Ren, J.P. Lang. *Coord. Chem. Rev.*, **252**, 2026 (2008).
[20] J.X. Chen, W.H. Zhang, X.Y. Tang, Z.G. Ren, Y. Zhang, J.P. Lang. *Inorg. Chem.*, **45**, 2568 (2006).
[21] G.J. Grant, M.E. Botros, J.S. Hassler, D.E. Janzen, C.A. Grapperhaus, M.G. O'Toole, D.G. vanDerveer. *Polyhedron*, **27**, 3097 (2008).
[22] S. Ahmad, A.A. Isab, W. Ashraf. *Inorg. Chem. Commun.*, **5**, 816 (2002).
[23] W. Ashraf, S. Ahmad, A.A. Isab. *Trans. Met. Chem.*, **29**, 400 (2002).
[24] S. Ahmad, A.A. Isab, H.P. Perzanowski. *Can. J. Chem.*, **80**, 1279 (2002).
[25] S. Ahmad, A.A. Isab, A.R. Al-Arfaj, A.P. Arnold. *Polyhedron*, **21**, 2099 (2002).
[26] M.I.M. Wazeer, A.A. Isab, M. Fettouhi. *Polyhedron*, **26**, 1725 (2007).
[27] M. Fettouhi, M.R. Malik, S. Ali, A.A. Isab, S. Ahmad. *Acta Cryst.*, **E66**, 997 (2010).
[28] A.A. Isab, M.I.M. Wazeer, W. Ashraf. *Spectrochim. Acta, Part A*, **72**, 218 (2009).
[29] A.A. Isab, M. Fettouhi, M.R. Malik, S. Ali, A. Fazal, S. Ahmad. *Russ. J. Coord. Chem.*, **37**, 180 (2011).
[30] M. Altaf, H. Stoeckli-Evans, S. Ahmad, A.A. Isab, A.R. Al-Arfaj, M.R. Malik, S. Ali. *J. Chem. Crystallogr.*, **40**, 1175 (2010).
[31] J.G. Wright, M.J. Natan, F.M. McDonnell, D.M. Ralston, T.V. O'Halloran. *Prog. Inorg. Chem.*, **38**, 323 (1990).
[32] I.S. Ahuja, R. Singh. *Inorg. Nucl. Chem. Lett.*, **9**, 289 (1973).
[33] S. Hayashi, K. Hayamizu. *Bull. Chem. Soc. Japan*, **64**, 688 (1991).
[34] W. Kemp. *NMR in Chemistry*, Macmillan Education Ltd., London (1986).
[35] J.M. Hook, P.A.W. Dean, L.C.M. van Gorkom. *Magn. Reson. Chem.*, **33**, 77 (1995).
[36] K. Eichele, R.E. Wasylischen. *Simulation package, (Version 1.4.4)*, Dalhousie University, Canada and University of Tubingen, Germany (2001).
[37] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople. *GAUSSIAN03, Revision B.04*, Gaussian, Inc., Pittsburgh, PA (2003).
[38] N. Zhanpeisov, M. Matsuoka, H. Yamashita, M. Anpo. *J. Phys. Chem. B*, **102**, 6915 (1998).
[39] A. Nicklass, M. Dolg, H. Stoll, H. Preuss. *J. Chem. Phys.*, **102**, 8942 (1995).

[40] K. Nomiya, A. Yoshizawa, K. Tsukagoshi, N.C. Kasuga, S. Hirakawa, J. Watanabe. *J. Inorg. Biochem.*, **95**, 208 (2003).
[41] N.C. Kasuga, K. Sekino, M. Ishikawa, A. Honda, M. Yokoyama, S. Nakano, N. Shimada, C. Koumo, K. Nomiya. *J. Inorg. Biochem.*, **96**, 298 (2003).
[42] M. Fettouhi, M.I.M. Wazeer, A.A. Isab. *Inorg. Chem. Commun.*, **11**, 252 (2008).
[43] S. Ahmad, A.A. Isab, A.P. Arnold. *J. Coord. Chem.*, **56**, 539 (2003).
[44] N.D. Draper, R.J. Batchelor, P.M. Aguir, S. Kroeker, D.B. Leznoff. *Inorg. Chem.*, **43**, 6557 (2004).
[45] D. Gredenic. *Quart. Rev. Chem. Soc.*, **19**, 303 (1965).
[46] A.A. Isab, M.I.M. Wazeer, M. Fettouhi, S. Ahmad, W. Ashraf. *Polyhedron*, **25**, 2629 (2006).
[47] S. Ahmad, H. Sadaf, M. Akkurt, S. Sharif, I.U. Khan. *Acta Cryst. E*, **65**, m1191 (2009).
[48] R.C. Seccombe, C.H.L. Kennard. *J. Organomet. Chem.*, **18**, 243 (1969).