0277–5387(94)E0133–X

SOLUTION AND SOLID-STATE NMR STUDIES OF MeHg^{II} AND RSHg^{II} (R = Me, Et) COMPLEXES WITH PYRAZOLYL-CONTAINING LIGANDS

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Abstract—The solid state and solution NMR spectra of the tetrakis(pyrazol-1-yl) borate (L^a) and tris(3,5-dimethylpyrazol-1-yl) hydroborate (L^b) ligands and their complexes with MeHg^{II} and RSHg^{II} (R = Me, Et) are reported. The solid state ^{13}C and ^{15}N solid state NMR spectra of the MeHgL^a complex are consistent with the reported X-ray structure. The close similarity of the spectral data shown by MeHgL^a and MeSHgL^a suggests that the two species have the same structure. In order to confirm this hypothesis, the structure of MeSHgL^a has been determined by single crystal X-ray diffraction. The chemical shift anisotropy (CSA) of ^{199}Hg resonance is too large in these T-shaped complexes and does not allow the observation of the ^{199}Hg resonance under cross polarisation–magic angle spinning (CPMAS) experimental mode. On the other hand ^{199}Hg CPMAS NMR spectra were obtained for the complexes with the L^b ligand. The reduced ^{199}Hg CSA value together with the information gained from the ^{13}C and ^{15}N CPMAS NMR spectra suggest a tetra coordination around mercury in these complexes. The tight co-ordination mode shown by complexes with the L^b ligand is reflected in a decrease in the thiol intermolecular exchange rate in solution. This decreased ligand lability allows the detection of $^3J_{Hg-H}$ couplings (inside HgSCH$_3$ and HgSCH$_2$CH$_3$ moieties) in the low temperature NMR limiting spectra.

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In dealing with the interaction of Hg^{II} and $MeHg^{II}$ with biomolecules it has been pointed out that a coordination mode in which mercury has a coordination number higher than two is of great biological interest (*i.e.* in the situation involved in the Hg–MerR biosensor).[1] On the grounds of the fundamental importance of mercury toxicology, there is a need for models with such a coordination environment to further elucidate this kind of interaction. However, in the solution state the mercury complexes are very labile and this makes it difficult to assess the actual structural coordination mode.[2,3]

In order to investigate models in which the mercury shows a coordination number higher than two, we undertook a solid-state NMR approach which would bear some advantages: (i) any ligand exchange process that may take place in solution is frozen so that only a static situation is considered; (ii) the lattice structure may stabilise the coordination frame around the metallic centre more effectively than a solution environment does. In this sense a solid-state model can be more suitable than a solution state in simulating the interaction between mercury containing species and a proteic substrate.

The flexible polypyrazolylborate ligands[4] were chosen because their electronic and steric properties are highly responsive to ring or boron substitution. Moreover, the pyrazolylborate moiety has been exploited as a model for histidine residues in potentially biomimetic complexes.[4d-f]

EXPERIMENTAL

The compounds under investigation were prepared according to the procedure reported in Ref. 5. The ^1H and ^{13}C solution NMR spectra were recorded on a Jeol EX 400 spectrometer operating at 399.6 MHz and 100.4 MHz respectively. The solid-state NMR experiments were performed on a Jeol GSE 270 (6.34 T) spectrometer. Cylindrical 6 mm o.d. zirconia rotors with a sample volume of 120 μl were employed with a spinning speed in the range from 4.0 to 5.5 kHz. For all samples the magic angle was carefully adjusted from the ^{79}Br MAS (magic angle spinning) spectrum of KBr by minimising the linewidth of the ssb's from the satellite transitions. High resolution solid-state ^{13}C, ^{15}N and ^{199}Hg NMR were recorded at 67.8, 27.4 and 48.3 MHz respectively using the cross polarisation–magic angle spinning (CPMAS) technique. Contact times and recycle times were adjusted sample by sample by considering their structure. At least 12 h of accumulation were required to obtain a reasonable signal-to-noise ratio for ^{15}N and ^{199}Hg NMR spectra. Conditions and scale reference for ^{15}N measurements

were refined by using a 90% isotopically enriched $^{15}NH_4NO_3$ sample. The operating conditions for the ^{199}Hg spectra were refined using $(CH_3COO)_2Hg$. The scale was set giving a value of -2490 ppm to the isotropic peak of mercury acetate.

X-ray crystallographic analysis

Crystal data are summarised in Table 1. A crystal of $HgSBN_8C_{13}H_{15}$, obtained from its aqueous solution, was mounted on a Nicolet R_3 automatic four-circle diffractometer using graphite monochromatized Mo-K_α radiation ($\lambda = 0.71069$ Å). The cell parameters were refined by least squares from the angular positions of 40 reflections in the range $15 < 2\theta < 37°$. The data were measured at room temperature for $3.0 < 2\theta < 60°$ from a colourless crystal with approximate dimensions of $0.5 \times 0.38 \times 0.25$ mm, using a $\theta/2\theta$ scan technique. The scan rate was automatically chosen according to the peak intensity in the range 3.0–15.0° min^{-1} and background counts were taken with stationary crystal at each end of the scan and total background time to scan time ratio of 0.5. The data were processed[6] to yield values of I and $\sigma(I)$. The intensities

Table 1. Crystallographic data

Formula	$HgSBN_8C_{13}H_{15}$
Formula weight	526.8
Crystal system	triclinic
Space group	$P1$
a (Å)	8.278(1)
b (Å)	8.856(1)
c (Å)	12.814(2)
α (°)	103.89(1)
β (°)	99.12(1)
γ (°)	105.62(1)
V (Å^3)	852.86
Z	2
D_{calc} (g cm^{-3})	2.052
μ (cm^{-1})	93.433
$F(000)$	500.0
No. of measured reflections	5330
No. of unique reflections	4825
Obsd reflections $I > 3\sigma(I)$	3451
Function minimised	$\Sigma w(F_0-F_c)^2$
Variables refined	217
a, b values in the weight Function:	
$w = 1.0/(a \mid F_0 + bF_0)$	14.38; 0.00947
Final R (isotropic), %	11.92
Final R_w (isotropic), %	16.96
Final R (anisotropic), %	3.45
Final R_w (anisotropic), %	4.86
Goodness of fit, s	0.22

of three standard reflections, measured every 97 reflections throughout the data collections, decayed by about 6.0%. The values of I and $\sigma(I)$ were corrected for Lorentz and polarisation and for shape anisotropy effects. A total of 3451 independent reflections having $I > 3\sigma(I)$ were used in all subsequent calculations.

The mercury atom coordinates were found from a Patterson map, and the remaining atoms were located by successive structure factor calculations and Fourier maps. All non-hydrogen atoms were refined by full-matrix least-squares methods with anisotropic thermal parameters. The hydrogen atoms were idealised (sp^3C—H = 1.08 Å, and sp^2C—H = 1.05 Å)[7] and each H atom was assigned the equivalent isotropic temperature factor of the parent C atom and allowed to ride on it. The final difference Fourier map, with a root-mean-square deviation of electron density of 0.16 e Å^{-3}, showed no peaks with values exceeding 3.0 times the e.s.d. Atomic scattering factors were taken from Ref. 8. Calculations were performed on the new DEC 3500 AXP using the SIR CAOS[9] structure determination package. The positional and thermal parameters, a full list of bond lengths and angles and observed and calculated structure factors are available as supplementary material from the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

In order to accomplish the conditions for high co-ordination around the MeHg^{II} and RSHg^{II} (R = Me, Et) moieties, we dealt with tetrakis(pyrazol-1-yl) borate (L^a) and tris(3,5-dimethyl pyrazol-1-yl) hydroborate (L^b) ligands. In the absence of significant steric effects the ligands should exhibit different donating properties with L^b > L^a since (i) methyl substitution renders 3,5-dimethylpyrazole more basic toward proton by 1.6 pK_a units than the parent pyrazole,[10] and (ii) the [HB(pz)$_2$]-group is more electron releasing than [B(pz)$_3$]-one, as results from a Hammett correlation.[11]

La   Lb
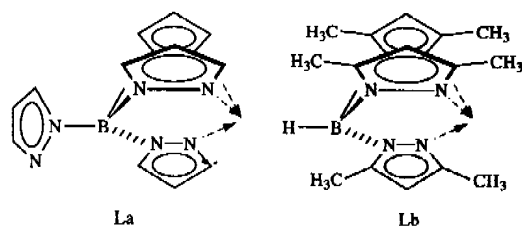
Scheme 1.

L^a complexes

In Fig. 1 we report the ^{13}C NMR spectra (trace a: solid state; trace b: solution) of the MeHgL^a complex.[12, 13] In solution the four pyrazolyl groups are clearly equivalent and give rise to three ^{13}C resonances at 141.6, 135.8 and 105.5 ppm, respectively. In the solid state[14] there are more ^{13}C resonances for the pyrazolyl rings (C$_5$ appears the most affected) to suggest that they interact in a different way with the methyl mercury ion.

On comparing the solution and the solid-state ^{13}C NMR spectra of the MeHgL^a complex other differences concern the methyl resonance, whose up-field shift (from 3.7 to 7.5 ppm) is accompanied by a large increase in the $^1J_{Hg-C}$ coupling constant (from 1697 Hz in solution to 1997 Hz in the solid). Such a behaviour of the Hg–C coupling constant[15] is not well understood at this stage and it appears to reflect both solvation effects as well as changes in the interactions at the metallic centre occurring in the solid state as a result of the crystal packing.

The ^{15}N CPMAS NMR spectra are very informative.[16] The ^{15}N NMR spectrum of L^a clearly distinguishes the two types of nitrogen atoms in the pyrazolyl group. The N-1 resonances fall at -154 ppm whereas N-2 afforded two signals at -79 and -85 ppm, respectively. The appearance of two N-2 resonances is likely due to the packing effect which makes those sites two by two crystallographically non-equivalent.[14] Upon co-ordination to the MeHg moiety the absorption pattern assigned to N-2 resonances changes markedly giving rise to four resonances at -68, -77, -97 and -110 ppm, respectively, whereas only one of the N-1 resonances differentiates substantially from the remaining three (at -154 ppm) by showing a new absorption at -162 ppm. The resonances at -97 and -110 ppm appear broader than those at -68 and -72 ppm, probably as a consequence of a direct interaction with mercury. Owing to the poor S/N ratio of these ^{15}N spectra, it is not possible to observe the expected ^{199}Hg satellite sub-spectra which should account for 16% of the intensity of each N-2 resonance.

The body of observations made on the basis of ^{13}C and ^{15}N NMR spectra is fully consistent with the results from the X-ray structure of the McHgL^a complex[13] which revealed the co-ordination of two nitrogen atoms to define a T-shaped coordination of the mercury as depicted in Scheme 2.

The length of the stronger N—Hg bond is 2.07(4) Å, with a 169(2)° N—Hg—C angle, while the weaker Hg—N' bond is 2.65(4) Å, with a N'—Hg—C angle of 112(1)°. The weaker interaction may be considered as an "interfering" one
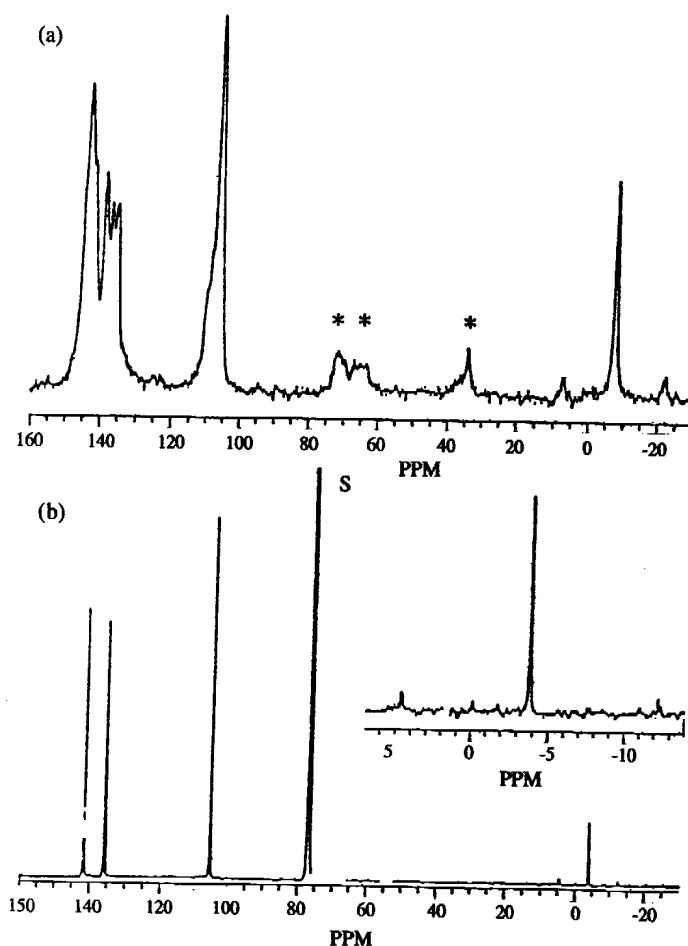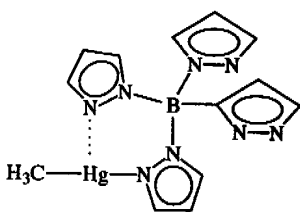
Fig. 1. ^{13}C NMR spectra of MeHgL^a. (a) In the solid state under CPMAS technique (* represent spinning sidebands). Experimental conditions : spinning speed 4.9 kHz, recycle time 6 s, contact time 3.5 ms. (b) In CDCl$_3$ solution.

Scheme 2.

on an essentially linear N—Hg—C coordinating pattern ; then, from a ^{199}Hg solid-state NMR point of view, we deal with a very anisotropic environment which is expected to have a huge chemical shift dispersion.[17] As a matter of fact, our trials to obtain the ^{199}Hg CPMAS NMR spectrum of MeHgL^a were unsuccessful.

We then considered the analogous derivative, MeSHgL^{a5} to ascertain if the introduction of the MeS — group would cause changes in the coor-

dination ability of the L^a ligand. The ^{13}C spectrum of MeSHgL^a complex shows four resonances in CDCl$_3$ solution (C$_3$ at 142.0, C$_5$ at 135.9, C$_4$ at 105.8 and S—CH$_3$ at 11.6 ppm, respectively) and a higher number in the solid state. Again the more affected resonance is C$_5$ which is split into two equally intense signals at 137.6 and 135.9 ppm. The S—CH$_3$ resonance shows the largest shift as it resonates at 15.1 ppm in the solid state. The ^{15}N CPMAS spectrum shows two close resonances for the two N$_2$ not involved in the coordination to mercury (at −68.6 and −72.9 ppm) and two resonances for the N$_2$ atoms interacting with mercury (at −95.7 and −122.6 ppm). The four N$_1$ resonances fall in a single broad absorption at −158.5 ppm. The close similarity between the spectral patterns shown by MeHgL^a and MeSHgL^a unambiguously suggests that the two species have the same structure. We confirmed this hypothesis by performing the X-ray structure analysis of a crystal of MeSHgL^a.

Description of the molecular structure of

Table 2. Relevant bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

HG(1)—S(1)	2.330(2)		B(1)—N(3)	1.558(9)	
HG(1)—N(2)	2.434(8)		B(1)—N(5)	1.53(1)	
HG(1)—N(4)	2.141(7)		B(1)—N(7)	1.519(8)	
HG(1)—S(1')	3.025(2)		S(1)—C(13)	1.81(1)	
B(1)—N(1)	1.551(8)				
N(4)—HG(1)—N(2)		84.3(2)	N(5)—B(1)—N(7)		109.5(5)
S(1)—HG(1)—N(2)		111.7(2)	N(2)—N(1)—B(1)		118.5(6)
S(1)—HG(1)—N(4)		161.7(2)	C(1)—N(1)—N(2)		109.9(7)
S(1')—HG(1)—N(2)		87.0(2)	C(1)—N(1)—B(1)		131.6(8)
S(1')—HG(1)—S(1)		91.8(1)	HG(1)—N(2)—N(1)		117.5(4)
S(1')—HG(1)—N(4)		98.2(2)	C(3)—N(2)—N(1)		105.7(8)
C(13)—S(1)—HG(1)		99.8(5)	C(3)—N(2)—HG(1)		136.8(8)
C(13)—S(1)—HG(1')		92.5(4)	B(1)—N(3)—N(4)		120.3(6)
N(1)—B(1)—N(3)		109.9(5)	C(4)—N(3)—B(1)		131.5(8)
N(1)—B(1)—N(5)		110.2(6)	C(4)—N(3)—N(4)		108.2(6)
N(1)—B(1)—N(7)		107.8(5)	HG(1)—N(4)—N(3)		121.6(4)
N(3)—B(1)—N(5)		110.3(5)	C(6)—N(4)—N(3)		107.3(8)
N(3)—B(1)—N(7)		109.2(5)	C(6)—N(4)—HG(1)		130.3(7)

MeSHgL[a]. A perspective drawing of this compound under study is shown in Fig. 2. Selected interatomic bond lengths and angles are reported in Table 2. The co-ordination geometry at the Hg atom is "T-shaped", with the two Hg—N bonds significantly different, similar to that already observed in the MeHgL[a] compound.[13] The Hg and the coordinated atom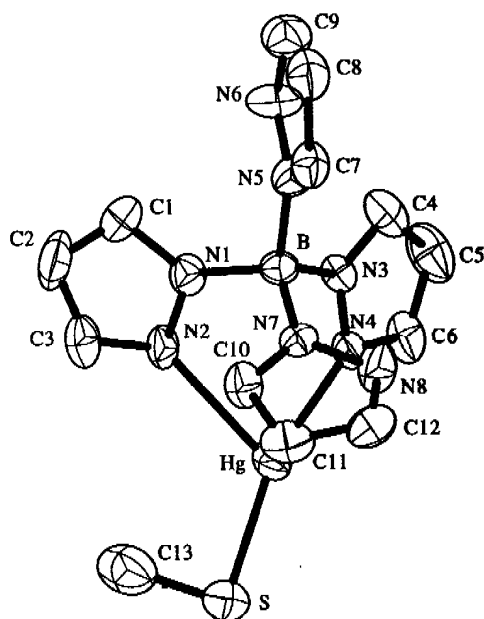s lie almost in a plane (the maximum deviation from the least-squares plane through them is 0.11 Å for the Hg atom). The distance from the Hg to the S atom of the centrosymmetric molecule, 3.025(2) Å, is shorter than the van der Waals sum of the radii and the S atom is placed perpendicularly to the coordination plane. Taking into account this intermolecular interaction, the coordination sphere about the Hg atom can be roughly described as a distorted tetrahedron, and the two centrosymmetric molecules can be considered forming a dimeric unit, as shown by Fig. 3.

The co-ordination of the B atom is quite normal and the four pyrazolyl five-membered rings are planar within the limits of experimental error (the maximum deviation of an atom in a ring from the least squares plane is 0.008 Å). The six-membered HgN_4B ring can be regarded as boat form having the Hg and the B atoms out of the best plane

Fig. 2. Molecular structure of MeSHgL[a] and labelling scheme drawn with 50% thermal ellipsoids.
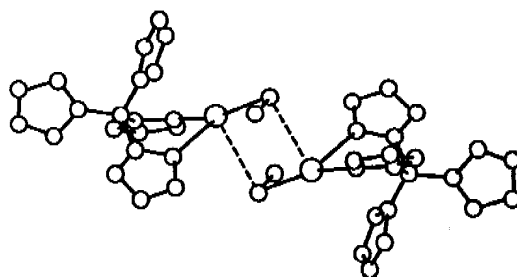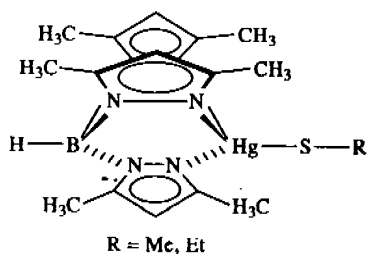

Fig. 3. Packing of the molecules of MeSHgL[a] in the unit cell. Short contacts are shown by broken lines.

through the four N atoms 0.87 and 0.72 Å respectively.

Lᵇ complexes

By using the Lᵇ ligand we prepared the following complexes: MeHgLᵇ,[18] MeSHgLᵇ and EtSHgLᵇ.[5] The ¹³C NMR spectrum of MeHgLᵇ in CDCl₃ solution consists of six resonances assigned as follows: 147.6 (C₃), 144.3 (C₅), 104.4 (C₄), 13.5 and 13.0 (methyl groups on C₃ and C₅, respectively) and −7.1 ppm (Hg—CH₃). The solid state ¹³C pattern maintains the basic features shown in solution, the main difference being the inability to differentiate the two methyl groups on the pyrazole ring and the splitting of the methyl–mercury resonance in three signals of equal intensity at −7.3, −8.1 and −9.4 ppm, respectively. These findings probably indicate that there are more MeHgLᵇ molecules in the unit cell. Unfortunately attempts to observe solid state ¹⁵N NMR spectra of this complex were unsuccessful.

The situation improved significantly when we moved to the MeSHgLᵇ complex. The ¹³C resonances of the Lᵇ ligand both in the solid and in solution show chemical shifts very close to the values reported above for the MeHgLᵇ complex. The CH₃—S resonance falls at 12.2 and 9.8 ppm in solution and in the solid state, respectively. The comparison between the ¹⁵N CPMAS spectra of the free and complexed Lᵇ ligand was again very diagnostic in assigning the structure of this compound. The ¹⁵N NMR spectra of the free Lᵇ ligand consists of two broad resonances at −81 (N₂) and −155 (N₁) ppm, respectively. Upon coordination to mercury the N₂ resonance shows a marked up-field shift of ∼24 ppm whereas the resonance assigned to N₁ shifts only by 5 ppm in the same direction. The number of resonances clearly indicates that in this complex there are just two types of nitrogen as in the free ligand. The observed coordination shift definitively shows that all three N₂ atoms are involved in the coordination to the MeSHg moiety to give rise to a C₃-like structure as shown in Scheme 3.

The EtSHgLᵇ behaves in a very similar way and the ¹³C CPMAS resonances are observed at $\delta = 153.5$ (C₅), 147.5 and 146.9 (C₃ in the relative ratio 3:1), 110.1 (C₄), 29.3 (CH₂), whereas the methyl groups afford a broad absorption centred at 17.5 ppm. Two signals at $\delta = -160$ (N₁) and −105 ppm (N₂) have been detected in the solid-state ¹⁵N NMR spectrum (Fig. 4). An indirect proof to support the occurrence of the proposed C₃-like structure for RSHgLᵇ (R = Me, Et) is gained by the observation of their ¹⁹⁹Hg CPMAS NMR spectra.[19,20] In fact, such a coordination environment on the Hgᴵᴵ atom would result in an axially symmetrical chemical shift tensor with a σ_{zz} very different from σ_{xx} and σ_{yy}, being the latter two values of comparable magnitudes. As shown in Fig. 5, the spinning side bands manifold very closely resembles the one expected for an axially symmetric species. Moreover, as the sulphur atom is known to have a deshielding effect[21] that has a maximum effect along the direction perpendicular to the metal–sulphur vector, in our proposed C_{3v} symmetry the deshielding effect would concentrate along the directions perpendicular to the symmetry axis, so that $\sigma_{zz} < \sigma_{xx} \sim \sigma_{yy}$ (assuming σ_{zz} aligned with the unique symmetry axis). This expectation is confirmed from the computed values of the indi-
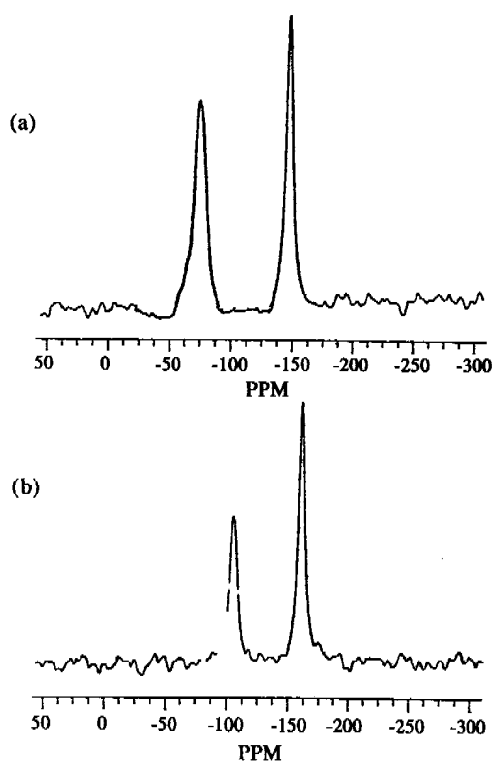

Fig. 4. ¹⁵N CPMAS spectra of (a) Lᵇ ligand and (b) EtSHgLᵇ. Experimental conditions: spinning speed 4.7 kHz, recycle time 12 s, contact time 3.5 ms.

R = Me, Et
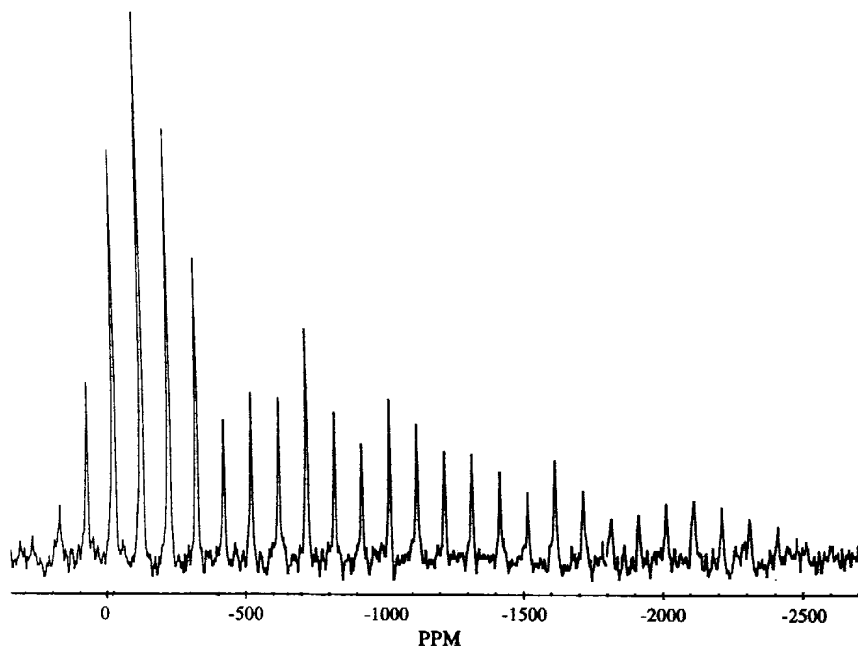
Scheme 3.

Fig. 5. ^{199}Hg CPMAS spectrum of EtSHgL^b (experimental conditions: spinning speed 4.7 kHz, recycle time 6 s, contact time 3 ms).

vidual tensor components and the asymmetry parameters η obtained by the graphical analysis[22] of the spinning sideband manifold: (MeSHgL^b: $\sigma_{xx} = -208$, $\sigma_{YY} = 95$, $\sigma_{zz} = 2457$ ppm, $\sigma_{iso} = 781$ ppm, $\eta = 0.18$; EtSHgL^b: $\sigma_{xx} = -170$, $\sigma_{YY} = 125$, $\sigma_{zz} = 2514$ ppm, $\sigma_{iso} = 823$ ppm, $\eta = 0.17$).

In summary, these findings give further support to the view that ^{199}Hg CPMAS NMR spectra may be observed for those systems whose molecular symmetry is high enough to lower the anisotropy around to ^{199}Hg nucleus to be compatible with the detection capability of the receiver system of the available instrumentation.

The tight coordination found in the solid-state structure of the MeSHgL^b and EtSHgL^b complexes prompted us to see to what extent it may affect their solution lability which is a common feature of mercury complexes. The V.T. ^{1}H NMR spectra (CDCl$_3$ solution) of both complexes show that the intermolecular ligand exchange is frozen out at low temperature as evidenced by the detection of $^3J_{Hg-H}$ coupling constants inside the MeSHg and EtSHg moieties (165 and 180 Hz, respectively). As the temperature is increased, a coalescence process of the satellite sub-spectra is observed, accompanied by a progressive broadening of the resonance of the main isotopomer. Then, at higher temperatures, a sharpening up of the latter signals occurs with the loss of the satellite peaks. As expected for an intermolecular exchange process, the coalescence temperatures are strongly concentration dependent. Since attempts to get the frozen structures for the

mercury complexes of L^a ligand under similar experimental conditions were unsuccessful, we conclude that tetracoordination decreases the kinetic lability thus allowing structural studies of mercury complexes in solution as well.

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