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Direct detection of the mercury–nitrogen bond in the thymine–Hg^{II}–thymine base-pair with ^{199}Hg NMR spectroscopy†

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We have observed the 1-bond ^{199}Hg–^{15}N *J*-coupling ($^{1}J(^{199}Hg,^{15}N)$ = 1050 Hz) within the Hg^{II}-mediated thymine–thymine base pair (T–Hg^{II}–T). This strikingly large $^{1}J(^{199}Hg,^{15}N)$ is the first one for canonical sp^2-nitrogen atoms, which can be a sensitive structure-probe of N-mercurated compounds and a direct evidence for N-mercuration.

Mercury-199 NMR spectroscopy is used to probe coordination modes, coordinating elements, and the nature of metals in biomolecules.[1] Within the ^{199}Hg NMR data, those for N–Hg bonds are of particular importance as metals in proteins and in DNA/RNA molecules frequently interact with nitrogen atoms. Moreover, the N–Hg^{II} bond formation in the Hg^{II}-mediated thymine–thymine base pair (T–Hg^{II}–T) corresponds to an irregular "deprotonative" N-mercuration in water of a bulk proton source.[2–7] In addition, extraordinary thermal stability with a positive reaction entropy was observed for N–Hg^{II}–N bonding in a DNA duplex.[8–12] The stability of the Hg–DNA complex can be explained partly owing to the metallophilic attraction between Hg atoms in consecutive T–Hg^{II}–T base pairs, and the metallophilic attraction itself is a recent hot topic of inorganic chemistry.[13–17]

Despite such biological/chemical importance, N–Hg^{II} bonds remained uncharacterized. Particularly, the measurements of $^{1}J(^{199}Hg,^{15}N)$ is challenging, owing to the large chemical shift anisotropy (CSA) of ^{199}Hg and low natural abundance of ^{15}N.[18] The only $|^{1}J(^{199}Hg,^{15}N)|$ value of a linear two-coordinate complex was recorded for $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$.[19] The $|^{1}J(^{199}Hg,^{15}N)|$ values for other coordination modes of ^{199}Hg are also limited to Hg^{II}–CyDTA (*trans*-l,2-diaminocyclohexane-*NNN′N′*-tetraacetate)[20] and Hg^{II}–$(NHMe_2)_2Cl_2$[21] complexes (Tables S1 and S2 in ESI†). However, in all cases, some of important parameters such as structure, ^{15}N or ^{199}Hg NMR chemical shifts ($\delta(^{15}N)$ or $\delta(^{199}Hg)$), 2-bond ^{15}N–^{15}N *J*-couplings across Hg^{II}, ($^{2}J(^{15}N,^{15}N)$) or hybridization state of nitrogen atoms always remained unknown. Therefore, a complete $^{199}Hg/^{15}N$ NMR J/δ dataset for a structurally well-defined compound has never been recorded so far.

In this sense, the T–Hg^{II}–T base pair (Fig. 1) provides an excellent platform for studying $^{1}J(^{199}Hg,^{15}N)$, as its chemical and 3-dimensional (3D) structures have been solidly determined[3,6,7,12,22] and historically accumulated data[2–4,23,24] are available. Regarding the NMR parameters of the T–Hg^{II}–T base pair, the ^{199}Hg chemical shift $\delta(^{199}Hg)$,[23] the 2-bond ^{15}N–^{15}N *J*-coupling across Hg^{II}, $^{2}J(^{15}N,^{15}N)$[6] and $\delta(^{15}N)$[6] were previously determined. Hence, the only missing NMR parameter for characterizing the unique physicochemical properties of the N–Hg^{II} bond is $^{1}J(^{199}Hg,^{15}N)$. Once it is measured for T–Hg^{II}–T, the T–Hg^{II}–T system will provide a complete J/δ dataset for $^{199}Hg/^{15}N$ with a reliable structure, and the $^{1}J(^{199}Hg,^{15}N)$ value may provide a key concept for constructing molecular devices[8,25–44] from Hg^{II}–DNA complexes.

To measure $^{1}J(^{199}Hg,^{15}N)$ in T–Hg^{II}–T, its highly soluble ^{15}N-labeled complex is crucial for $^{199}Hg/^{15}N$ signal detection. In addition, Hg^{II}–ligand exchanges must be suppressed to avoid the disappearance of $^{1}J(^{199}Hg,^{15}N)$ owing to exchange broadening. Considering these facts, we determined the $^{1}J(^{199}Hg,^{15}N)$ value by using a thymidine–Hg^{II}–thymidine complex (T–Hg^{II}–T).

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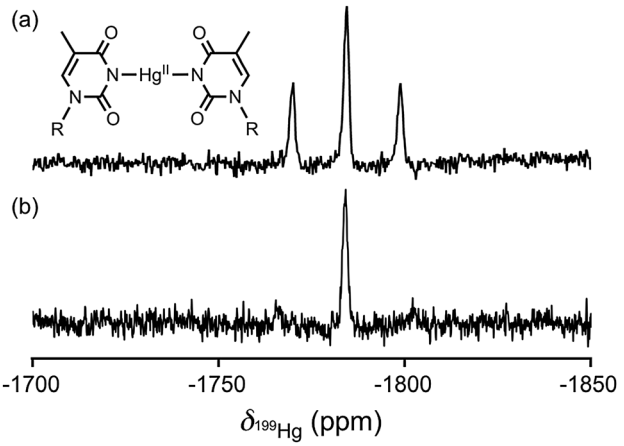

Fig. 1 One-dimensional ^{199}Hg NMR spectrum (71.667 MHz for ^{199}Hg frequency) of the thymidine–Hg^{II}–thymidine complex (25 mM) in DMSO-d_6 under natural abundance ^{199}Hg (16.84%). (a) The 1D ^{199}Hg NMR spectrum without ^{15}N-decoupling. (b) The 1D ^{199}Hg NMR spectrum with ^{15}N-decoupling. The ^{199}Hg NMR chemical shifts are displayed with respect to dimethylmercury (0 ppm) using 1 M $HgCl_2$ in DMSO-d_6 as a secondary reference (−1501 ppm).[55] The chemical structure of the T–Hg^{II}–T is depicted above the spectrum, with "R" denoting ribose.

To confirm if the splitting of the ^{199}Hg resonance is $^1J(^{199}Hg,^{15}N)$, we monitored the disappearance of the splitting upon ^{15}N-decoupling using a special NMR probe for detecting ^{15}N-heteronucleus correlations. Lastly, the derived $^1J(^{199}Hg,^{15}N)$ value was also investigated theoretically with relativistic density functional theory (DFT) including spin–orbit coupling effects.

In this study, we used ^{15}N-labeled thymidine to produce ^{15}N-labeled T–Hg^{II}–T. To suppress the exchange of Hg^{II} ligands, we prepared a sample that contained T–Hg^{II}–T exclusively, without any anion (competitive Hg^{II}–ligands against thymine). Such sample was prepared by the reaction [thymidine + HgO → T–Hg^{II}–T + H_2O] followed by H_2O evaporation.[24] The resulting pure ^{15}N-labeled T–Hg^{II}–T was subjected to ^{199}Hg NMR measurements in dimethyl sulfoxide-d_6 (DMSO-d_6) (Fig. 1). The ^{199}Hg NMR signal was successfully observed as a triplet resonance at $\delta(^{199}Hg) = -1784$ ppm, with the absolute ^1J-value $|^1J(^{199}Hg,^{15}N)| = 1050$ Hz (Fig. 1 and Table 1). The observed $\delta(^{199}Hg)$ value was the same as that observed previously in T–Hg^{II}–T,[23] which ensured successful sampling.

The ^{199}Hg NMR spectrum under ^{15}N-decoupling and ^{15}N NMR spectrum were recorded to exclude the possibility that the observed splitting of the ^{199}Hg signal might arise from a structural polymorphism. Notably, the splitting disappeared upon the ^{15}N-decoupling (Fig. 1b). It should be further noted that this ^{15}N-decoupled ^{199}Hg NMR spectrum can't be recorded with conventionally available probes. This measurement became possible only by using the special probe, which can perform a ^{15}N–^{199}Hg double resonance spectroscopy. In addition, the splitting of the ^{15}N resonance (1050 Hz) was observed as satellite peaks at $\delta(^{15}N) = 184$ ppm in the 1-dimensional ^{15}N NMR spectrum (Fig. S1 in ESI†). Thus, the splitting of the ^{199}Hg resonance shown in Fig. 1a should be interpreted as $^1J(^{199}Hg,^{15}N)$.

The $|^1J(^{199}Hg,^{15}N)|$ value of 1050 Hz for T–Hg^{II}–T was strikingly larger than the ^1J-coupling of $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$ (316.2 Hz),[19] Hg^{II}–CyDTA complexes (365.7–395.5 Hz),[20] and Hg^{II}–$(NHMe_2)_2Cl_2$ (14.7 Hz)[21] (Table 1 and Tables S1 and S2 in ESI†). Thus, the observed $|^1J(^{199}Hg,^{15}N)|$ value for T–Hg^{II}–T is the largest of all ^1J-values reported to date.

Table 1 Experimental and theoretical ^{199}Hg NMR parameters

Ligand	Method	N-hybrid[a]	$\lvert^1J_{HgN}\rvert$[b]	$\delta(^{199}Hg)$[c]
Thymine[d]	Experiment	sp^2	1050	−1784
	Theory[e]	sp^2	931[f]	−1848
$N(SiMe_3)_2$[g]	Experiment	sp^2-like[h]	316.2[i]	−992[j]
	Theory[e]	sp^2-like[h]	278.4[f]	−827

[a] Hybridization state of nitrogen atoms. [b] The "absolute" 1-bond ^{199}Hg–^{15}N J-coupling, $|^1J(^{199}Hg,^{15}N)|$, in Hz. [c] ^{199}Hg NMR chemical shift in ppm with respect to dimethylmercury (0 ppm). [d] The T–Hg^{II}–T complex. [e] The theoretical calculation (ZORA-SO-B3LYP/TZ2P) in this work. The average values of $^1J(^{199}Hg,^{15}N)$ and $\delta(^{199}Hg)$ were calculated for rotational conformers of thymidine–Hg^{II}–thymidine, because the energy barrier for rotation around the N–Hg^{II}–N axis was smaller than 1.1 kcal mol^{-1}. The calculated $\delta(^{199}Hg)$ and $^1J_{HgN}$ values were therefore averaged over respective rotamers (Table S5 in ESI). [f] The "–" sign was calculated for J-coupling (Table S4 in ESI). [g] The $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$ complex. [h] See Supporting discussion (ESI) for details. [i] Ref. 19. [j] Ref. 53. For chemical shift referencing see the footnote to Table S1 in ESI. It should be noted that $^{15}N^6$ and $^1H^{54}$ chemical shift perturbations for the thymidine–Hg^{II}–thymidine complexation were coherent with those observed for the formation of the T–Hg^{II}–T base-pairs in a DNA duplex (Table S1 in ESI).

Here we investigate the correlation between $|^1J(^{199}Hg,^{15}N)|$ value and N-hybridization state. Within the compounds whose $|^1J(^{199}Hg,^{15}N)|$ were reported, T–Hg^{II}–T and $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$ possess the linear two-coordinate structure, and their $|^1J(^{199}Hg,^{15}N)|$ values can be compared. Regarding the N-hybridization state of $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$, an sp^2-like planar structure of the nitrogen atoms was suggested from the electron diffraction study,[19] which is further supported by Bent's rule[45] (see Supporting discussion in ESI† for Bent's rule). Therefore, the Hg^{II}-bound nitrogen atoms in both samples belong to the sp^2 category basically, and the current data of $|^1J(^{199}Hg,^{15}N)|$ are insufficient for us to correlate between $|^1J(^{199}Hg,^{15}N)|$ and N-hybridization, due to the lack of the ^1J-values for N(sp)–Hg^{II} and N(sp^3)–Hg^{II} bonds.

As a further investigation, $|^1J(^{199}Hg,^{15}N)|$ values for the "sp^2 nitrogen" in T–Hg^{II}–T and "sp^2-like nitrogen" in $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$ were strikingly different (Table 1). However, this may be because the sp^2-like N-hybridization in $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$ might be different from the "canonical sp^2 nitrogen" in T–Hg^{II}–T. This possibility was also inferred from $^{14/15}$N NMR spectroscopic data,[46] where the ^{14}N NMR chemical shift for the Si_2N–Hg^{II}–NSi_2 linkage showed a rather sp^3-like value ($\delta(^{14}N) = 66.2$ ppm,[46] Table S1 in ESI†). By contrast, $\delta(^{15}N)$ for Hg^{II}-linked N3 in T–Hg^{II}–T is 184 ppm, and the value is located within the empirical range for an sp^2-hybridized nitrogen (Fig. S1 and Table S1 in ESI†). From these facts, the N-hybridization state of $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$ can't be unambiguously assigned (see also Supporting discussion in ESI† for details). However, on the basis of the investigations mentioned above, the $|^1J(^{199}Hg,^{15}N)|$ value might be a sensitive NMR parameter for detecting differences in the fine electronic structures of T–Hg^{II}–T and $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$.

We then quantum chemically computed $|^1J(^{199}Hg,^{15}N)|$ = 931 Hz and $\delta(^{199}Hg)$ = − 1848 ppm for T–Hg^{II}–T using DFT including relativistic corrections from the zeroth-order regular approximation (ZORA) with spin–orbit (SO) coupling, as implemented in the ADF program[47–49] (see Table 1 and Tables S3–S5 in ESI†). The theoretical $|^1J(^{199}Hg,^{15}N)|$ and $\delta(^{199}Hg)$ values agree well with the experimental data (Table 1). With reference to the theoretical values given by Bagno and Saielli ($|^1J(^{199}Hg,^{15}N)|$ = 670 Hz, $\delta(^{199}Hg)$ = − 1727 ppm),[50] the theoretical $|^1J(^{199}Hg,^{15}N)|$ value was refined by using the complex where it was actually recorded (Table S3 in ESI†). The $|^1J(^{199}Hg,^{15}N)|$ value of 278.4 Hz calculated for $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$ also agreed satisfactorily with experiment (316.2 Hz).[19] The signs of $^1J(^{199}Hg,^{15}N)$ for T–Hg^{II}–T and $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$ were both "−" theoretically (Table S4 in ESI†).

In order to investigate the correlation between $|^1J(^{199}Hg,^{15}N)|$ values and N-hybridization states theoretically, we further analyzed the theoretical $^1J(^{199}Hg,^{15}N)$. The calculated $^1J(^{199}Hg,^{15}N)$ values were dependent on the "Fermi Contact" + "Spin Dipole coupling" (FC + SD) term (Table S4 in ESI†). With the dominance of this FC term, one may find the correlation between the N-hybridization and $|^1J(^{199}Hg,^{15}N)|$ in the future, although it should be experimentally explored.

Empirically, the $\delta(^{199}Hg)$ values are clustered in terms of linked elements, hybridization states, and other factors of Hg^{II}-linked atoms (Table S2 in ESI†). Such phenomena were explained on the basis of the empirical correlation of $\delta(^{199}Hg)$ with the ionicity of the X–Hg^{II} bond (high ionicity → up-field shift of $\delta(^{199}Hg)$),[51] Unfortunately, owing to both a paucity of experimental $\delta(^{199}Hg)$ values for a linear two-coordinate N–Hg^{II}–N linkage and the uncertain N-hybridization state in $(Me_3Si)_2N$–Hg^{II}–$N(SiMe_3)_2$, the correlation between $\delta(^{199}Hg)$ and the N-hybridization state of Hg^{II}-linked nitrogen also remains obscure. Nevertheless, the highly up-field-shifted $\delta(^{199}Hg)$ value for T–Hg^{II}–T among those of N-mercurated compounds suggests that $N(sp^2)$–Hg^{II}–$N(sp^2)$ covalent linkages possess significant ionic character, which agrees with our previous studies (Table 1 and Tables S1 and S2 in ESI†).[7,52] This observation suggests that $\delta(^{199}Hg)$ values can be used as a sensitive indicator for probing the Hg^{II} coordination environment not only in C-mercurated complexes but also in N-mercurated complexes, including metalloproteins[1] and metallo-DNA/RNA.

Accordingly, ^{199}Hg NMR parameters, especially $^1J(^{199}Hg,^{15}N)$, are sensitive parameters for characterizing the electronic structures of N-mercurated complexes and their N–Hg^{II} bonds as well as their Hg atoms. Hence, the $^1J(^{199}Hg,^{15}N)$ value could be a key parameter for predicting the physicochemical properties of N-mercurated complexes and making them into molecular devices, based on a bottom-up approach.

The $|^1J(^{199}Hg,^{15}N)|$ value of 1050 Hz has been reported for canonical sp^2-hybridized nitrogen for the first time. From this result, the T–Hg^{II}–T system provides a comprehensive and reliable $^{199}Hg/^{15}N$ NMR dataset for probing the Hg^{II} environment in N-mercurated compounds. This newly observed $^1J(^{199}Hg,^{15}N)$ coupling can be used for detecting N–Hg bond formations and precisely characterizing these bonds.

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