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# ARTICLE TYPE

# 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 ($^1J(^{199}$Hg,$^{15}$N) = 1050 Hz) within the Hg$^{II}$-mediated thymine–thymine base pair (T–Hg$^{II}$–T). This strikingly large $^1J(^{199}$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 $^1J(^{199}$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 $|^1J(^{199}$Hg,$^{15}$N)| value of a linear two-coordinate complex was recorded for (Me$_3$Si)$_2$N–Hg$^{II}$–N(SiMe$_3$)$_2$.[19] The $|^1J(^{199}$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$_2$)$_2$Cl$_2$[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$^{II}$, ($^2J(^{15}$N,$^{15}$N)) or hybridization state of nitrogen atoms always remained unknown. Therefore, a complete $^{199}$Hg/$^{15}$N NMR $J/\delta$ dataset for a structurally well-defined compound has never been recorded so far.

In this sense, the T–Hg$^{II}$–T base pair (Figure 1) provides an excellent platform for studying $^1J(^{199}$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$^{II}$, $^2J(^{15}$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 $^1J(^{199}$Hg,$^{15}$N). Once it is measured for T–Hg$^{II}$–T, the T–Hg$^{II}$–T system will provide a complete $J/\delta$ dataset for $^{199}$Hg/$^{15}$N with a reliable structure, and the $^1J(^{199}$Hg,$^{15}$N) value may provide a key concept for constructing molecular devices[8,25-44] from Hg$^{II}$-DNA complexes.

To measure $^1J(^{199}$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 $^1J(^{199}$Hg,$^{15}$N) owing to exchange broadening. Considering these facts, we determined the $^1J(^{199}$Hg,$^{15}$N) value by using a thymidine-Hg$^{II}$-thymidine complex (T-Hg$^{II}$-T). 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$_2$O] followed by H$_2$O evaporation.[24] The resulting pure $^{15}$N-labeled T–Hg$^{II}$–T was subjected to $^{199}$Hg NMR measurements in dimethyl sulfoxide-d6 (DMSO-d6) (Figure 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 (Figure 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 (Figure 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 (Figure S1 in ESI†). Thus, the splitting of the $^{199}$Hg resonance shown in Figure 1a should be interpreted as $^1J(^{199}$Hg,$^{15}$N).
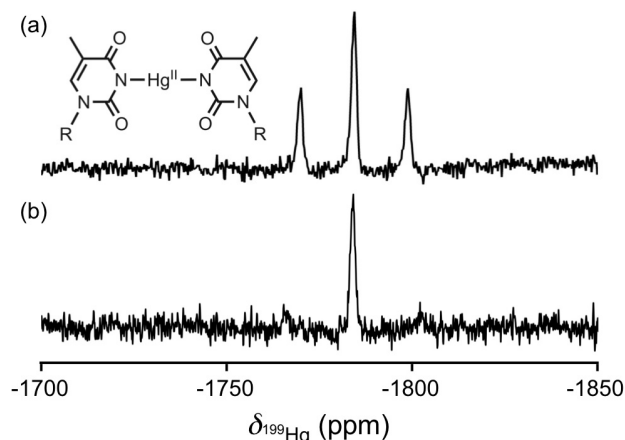


**Figure 1.** One-dimensional $^{199}$Hg NMR spectrum (71.667 MHz for $^{199}$Hg frequency) of the thymidine-Hg$^{II}$-thymidine complex (25 mM) in DMSO-d6 under natural abundance $^{199}$Hg (16.84%). (a) The 1D $^{199}$Hg NMR spectrum without $^{15}$N-decoupling. (b) The 1D $^{199}$Hg NMR spectrum with $^{15}$N-decoupling. The $^{199}$Hg NMR chemical shifts are displayed with respect to dimethylmercury (0 ppm) using 1 M HgCl$_2$ in DMSO-d6 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.

The $|^1J(^{199}$Hg,$^{15}$N)| value of 1050 Hz for T–Hg$^{II}$–T was strikingly larger than the $^1J$-coupling of (Me$_3$Si)$_2$N–Hg$^{II}$–N(SiMe$_3$)$_2$ (316.2 Hz),[19] Hg$^{II}$–CyDTA complexes (365.7–395.5 Hz),[20] and Hg$^{II}$–(NHMe$_2$)$_2$Cl$_2$ (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.

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$_3$Si)$_2$N–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$_3$Si)$_2$N-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$_3$Si)$_2$N–Hg$^{II}$–N(SiMe$_3$)$_2$ were strikingly different (Table 1). However, this may be because the sp$^2$-like N-hybridization in (Me$_3$Si)$_2$N-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$_2$N-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 (Figure S1 and Table S1 in ESI†). From these facts, the N-hybridization state of (Me$_3$Si)$_2$N-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$_3$Si)$_2$N–Hg$^{II}$–N(SiMe$_3$)$_2$.

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

| Ligand | Method | N-hybrid[a] | $\|^1J_{HgN}\|$[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$_3$Si)$_2$N–Hg$^{II}$-N(SiMe$_3$)$_2$ complex. [h] See Supporting Discussion for details. [i] Reference 19 [j] Reference 53. For chemical shift referencing see the footnote to Table S1 in ESI†. It should be noted that $^{15}$N[6] and $^1$H[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†).

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 (Tables S3 in ESI†). The $|^1J(^{199}$Hg,$^{15}$N)| value of 278.4 Hz calculated for (Me$_3$Si)$_2$N–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$_3$Si)$_2$N–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.

## Conclusions

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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## Notes and references

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