Cite this: *Chem. Commun.*, 2015, 51, 8488

Received 23rd March 2015,
Accepted 10th April 2015

DOI: 10.1039/c5cc02423d

www.rsc.org/chemcomm

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

Takenori Dairaku,^{‡a} Kyoko Furuita,^{‡b} Hajime Sato,^{‡c} Jakub Šebera,^{‡de} Daichi Yamanaka,^a Hiroyuki Otaki,^a Shoko Kikkawa,^a Yoshinori Kondo,^a Ritsuko Katahira,^b F. Matthias Bickelhaupt,^{fg} Célia Fonseca Guerra,^f Akira Ono,^h Vladimír Sychrovský,^{*d} Chojiro Kojima^{*b} and Yoshiyuki Tanaka^{*ai}

We have observed the 1-bond ¹⁹⁹Hg–¹⁵N J-coupling (¹J(¹⁹⁹Hg,¹⁵N) = 1050 Hz) within the Hg^{II}-mediated thymine–thymine base pair (T–Hg^{II}–T). This strikingly large ¹J(¹⁹⁹Hg,¹⁵N) is the first one for canonical sp²-nitrogen atoms, which can be a sensitive structure-probe of N-mercured 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 ¹⁹⁹Hg 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(¹⁹⁹Hg,¹⁵N) is challenging, owing to the large chemical shift anisotropy (CSA) of ¹⁹⁹Hg and low natural abundance of ¹⁵N.¹⁸ The only ¹J(¹⁹⁹Hg,¹⁵N) value of a linear two-coordinate complex was recorded for (Me₃Si)₂N–Hg^{II}–N(SiMe₃)₂.¹⁹ The ¹J(¹⁹⁹Hg,¹⁵N) values for other coordination modes of ¹⁹⁹Hg are also limited to Hg^{II}–CyDTA (*trans*-1,2-diaminocyclohexane-*NNN'*-tetraacetate)²⁰ and Hg^{II}–(NHMe₂)₂Cl₂²¹ complexes (Tables S1 and S2 in ESI†). However, in all cases, some of important parameters such as structure, ¹⁵N or ¹⁹⁹Hg NMR chemical shifts ($\delta(^{15}\text{N})$ or $\delta(^{199}\text{Hg})$), 2-bond ¹⁵N–¹⁵N J-couplings across Hg^{II}, (²J(¹⁵N,¹⁵N)) or hybridization state of nitrogen atoms always remained unknown. Therefore, a complete ¹⁹⁹Hg/¹⁵N 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 ¹J(¹⁹⁹Hg,¹⁵N), 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 ¹⁹⁹Hg chemical shift $\delta(^{199}\text{Hg})$,²³ the 2-bond ¹⁵N–¹⁵N J-coupling across Hg^{II}, ²J(¹⁵N,¹⁵N)⁶ and $\delta(^{15}\text{N})$ ⁶ were previously determined. Hence, the only missing NMR parameter for characterizing the unique physicochemical properties of the N–Hg^{II} bond is ¹J(¹⁹⁹Hg,¹⁵N). Once it is measured for T–Hg^{II}–T, the T–Hg^{II}–T system will provide a complete J/ δ dataset for ¹⁹⁹Hg/¹⁵N with a reliable structure, and the ¹J(¹⁹⁹Hg,¹⁵N) value may provide a key concept for constructing molecular devices^{8,25–44} from Hg^{II}–DNA complexes.

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

^a Graduate School of Pharmaceutical Sciences, Tohoku University, 6-3 Aza-Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan.

E-mail: tanaka@mail.pharm.tohoku.ac.jp

^b Institute for Protein Research, Osaka University, 3-2 Yamadaoka, Suita, Osaka 565-0871, Japan. E-mail: kojima@protein.osaka-u.ac.jp

^c Application, Bruker BioSpin K.K., 3-9 Moriya-cho, Kanagawa-ku, Yokohama, Kanagawa 221-0022, Japan

^d Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Flemingovo náměstí 2, 16610, Praha 6, Czech Republic. E-mail: vladimir.sychrovsky@uochb.cas.cz

^e Institute of Physics, Academy of Sciences of the Czech Republic, v.v.i., Na Slovance 2, CZ-182 21 Prague 8, Czech Republic

^f Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling (ACMM), VU University Amsterdam, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

^g Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands

^h Department of Material & Life Chemistry, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama, Kanagawa 221-8686, Japan

ⁱ Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770-8514, Japan. E-mail: tanakay@ph.bunri-u.ac.jp

† Electronic supplementary information (ESI) available: Additional information as noted in text. See DOI: 10.1039/c5cc02423d

‡ These authors contributed equally to this work.

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 $\text{DMSO}-d_6$ 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 $\text{DMSO}-d_6$ 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 $^1J(^{199}\text{Hg}, ^{15}\text{N})$, 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 $^1J(^{199}\text{Hg}, ^{15}\text{N})$ 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 $[\text{thymidine} + \text{HgO} \rightarrow \text{T-}\text{Hg}^{\text{II}}\text{-T} + \text{H}_2\text{O}]$ 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 ($\text{DMSO}-d_6$) (Fig. 1). The ^{199}Hg NMR signal was successfully observed as a triplet resonance at $\delta(^{199}\text{Hg}) = -1784$ ppm, with the absolute 1J -value $|^1J(^{199}\text{Hg}, ^{15}\text{N})| = 1050$ Hz (Fig. 1 and Table 1). The observed $\delta(^{199}\text{Hg})$ 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 $\delta(^{15}\text{N}) = 184$ 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 $^1J(^{199}\text{Hg}, ^{15}\text{N})$.

The $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ value of 1050 Hz for T- Hg^{II} -T was strikingly larger than the 1J -coupling of $(\text{Me}_3\text{Si})_2\text{N-}\text{Hg}^{\text{II}}\text{-N}(\text{SiMe}_3)_2$ (316.2 Hz),¹⁹

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

Ligand	Method	N-hybrid ^a	$ ^1J_{\text{HgN}} ^b$	$\delta(^{199}\text{Hg})^c$
Thymine ^d	Experiment	sp^2	1050	−1784
	Theory ^e	sp^2	931 ^f	−1848
$\text{N}(\text{SiMe}_3)_2$ ^g	Experiment	$\text{sp}^2\text{-like}^h$	316.2 ⁱ	−992 ^j
	Theory ^e	$\text{sp}^2\text{-like}^h$	278.4 ^f	−827

^a Hybridization state of nitrogen atoms. ^b The “absolute” 1-bond ^{199}Hg - ^{15}N - J -coupling, $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$, 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 $^1J(^{199}\text{Hg}, ^{15}\text{N})$ and $\delta(^{199}\text{Hg})$ 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 $\delta(^{199}\text{Hg})$ and $^1J_{\text{HgN}}$ 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 $(\text{Me}_3\text{Si})_2\text{N-}\text{Hg}^{\text{II}}\text{-N}(\text{SiMe}_3)_2$ 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 $^{15}\text{N}^6$ and $^1\text{H}^{54}$ 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†).

Hg^{II} -CyDTA complexes (365.7–395.5 Hz),²⁰ and $\text{Hg}^{\text{II}}\text{-(NHMe}_2)_2\text{Cl}_2$ (14.7 Hz)²¹ (Table 1 and Tables S1 and S2 in ESI†). Thus, the observed $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ value for T- Hg^{II} -T is the largest of all 1J -values reported to date.

Here we investigate the correlation between $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ value and N-hybridization state. Within the compounds whose $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ were reported, T- Hg^{II} -T and $(\text{Me}_3\text{Si})_2\text{N-}\text{Hg}^{\text{II}}\text{-N}(\text{SiMe}_3)_2$ possess the linear two-coordinate structure, and their $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ values can be compared. Regarding the N-hybridization state of $(\text{Me}_3\text{Si})_2\text{N-}\text{Hg}^{\text{II}}\text{-N}(\text{SiMe}_3)_2$, 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 rule⁴⁵ (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 $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ are insufficient for us to correlate between $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ and N-hybridization, due to the lack of the 1J -values for $\text{N}(\text{sp})\text{-}\text{Hg}^{\text{II}}$ and $\text{N}(\text{sp}^3)\text{-}\text{Hg}^{\text{II}}$ bonds.

As a further investigation, $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ values for the “ sp^2 nitrogen” in T- Hg^{II} -T and “ sp^2 -like nitrogen” in $(\text{Me}_3\text{Si})_2\text{N-}\text{Hg}^{\text{II}}\text{-N}(\text{SiMe}_3)_2$ were strikingly different (Table 1). However, this may be because the sp^2 -like N-hybridization in $(\text{Me}_3\text{Si})_2\text{N-}\text{Hg}^{\text{II}}\text{-N}(\text{SiMe}_3)_2$ might be different from the “canonical sp^2 nitrogen” in T- Hg^{II} -T. This possibility was also inferred from $^{14}/^{15}\text{N}$ NMR spectroscopic data,⁴⁶ where the ^{14}N NMR chemical shift for the $\text{Si}_2\text{N-}\text{Hg}^{\text{II}}\text{-NSi}_2$ linkage showed a rather sp^3 -like value ($\delta(^{14}\text{N}) = 66.2$ ppm,⁴⁶ Table S1 in ESI†). By contrast, $\delta(^{15}\text{N})$ 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 $(\text{Me}_3\text{Si})_2\text{N-}\text{Hg}^{\text{II}}\text{-N}(\text{SiMe}_3)_2$ can't be unambiguously assigned (see also Supporting discussion in ESI† for details). However, on the basis of the investigations mentioned above, the $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ value might be a sensitive NMR parameter for detecting differences in the fine electronic structures of T- Hg^{II} -T and $(\text{Me}_3\text{Si})_2\text{N-}\text{Hg}^{\text{II}}\text{-N}(\text{SiMe}_3)_2$.

We then quantum chemically computed $|^1J(^{199}\text{Hg}, ^{15}\text{N})| = 931 \text{ Hz}$ and $\delta(^{199}\text{Hg}) = -1848 \text{ ppm}$ 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 $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ and $\delta(^{199}\text{Hg})$ values agree well with the experimental data (Table 1). With reference to the theoretical values given by Bagno and Saielli ($|^1J(^{199}\text{Hg}, ^{15}\text{N})| = 670 \text{ Hz}$, $\delta(^{199}\text{Hg}) = -1727 \text{ ppm}$),⁵⁰ the theoretical $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ value was refined by using the complex where it was actually recorded (Table S3 in ESI†). The $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ value of 278.4 Hz calculated for (Me₃Si)₂N-Hg^{II}-N(SiMe₃)₂ also agreed satisfactorily with experiment (316.2 Hz).¹⁹ The signs of $^1J(^{199}\text{Hg}, ^{15}\text{N})$ for T-Hg^{II}-T and (Me₃Si)₂N-Hg^{II}-N(SiMe₃)₂ were both “–” theoretically (Table S4 in ESI†).

In order to investigate the correlation between $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ values and N-hybridization states theoretically, we further analyzed the theoretical $^1J(^{199}\text{Hg}, ^{15}\text{N})$. The calculated $^1J(^{199}\text{Hg}, ^{15}\text{N})$ 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 $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ in the future, although it should be experimentally explored.

Empirically, the $\delta(^{199}\text{Hg})$ 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 $\delta(^{199}\text{Hg})$ with the ionicity of the X-Hg^{II} bond (high ionicity → up-field shift of $\delta(^{199}\text{Hg})$),⁵¹ Unfortunately, owing to both a paucity of experimental $\delta(^{199}\text{Hg})$ values for a linear two-coordinate N-Hg^{II}-N linkage and the uncertain N-hybridization state in (Me₃Si)₂N-Hg^{II}-N(SiMe₃)₂, the correlation between $\delta(^{199}\text{Hg})$ and the N-hybridization state of Hg^{II}-linked nitrogen also remains obscure. Nevertheless, the highly up-field-shifted $\delta(^{199}\text{Hg})$ value for T-Hg^{II}-T among those of N-mercurated compounds suggests that N(sp²)-Hg^{II}-N(sp²) 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 $\delta(^{199}\text{Hg})$ 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 metalloproteins¹ and metallo-DNA/RNA.

Accordingly, ^{199}Hg NMR parameters, especially $^1J(^{199}\text{Hg}, ^{15}\text{N})$, 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 $^1J(^{199}\text{Hg}, ^{15}\text{N})$ 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 $|^1J(^{199}\text{Hg}, ^{15}\text{N})|$ value of 1050 Hz has been reported for canonical sp²-hybridized nitrogen for the first time. From this result, the T-Hg^{II}-T system provides a comprehensive and reliable $^{199}\text{Hg}/^{15}\text{N}$ NMR dataset for probing the Hg^{II} environment in N-mercurated compounds. This newly observed $^1J(^{199}\text{Hg}, ^{15}\text{N})$ coupling can be used for detecting N-Hg bond formations and precisely characterizing these bonds.

This work was performed using the NMR spectrometer under the Cooperative Research Program of the Institute for Protein

Research, Osaka University. This work was supported by the Platform for Drug Discovery, Informatics, and Structural Life Science from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This work was supported by grants-in-aid for Scientific Research (A) (24245037 to A.O. and Y.T.), (B) (24310163 to Y.T. and C.K.), (C) (18550146 to Y.T.) from MEXT, Japan; a Human Frontier Science Program (HFSP) Young Investigator Grant from HFSP, France (Y.T. and V.S.); and GAČR (P205/10/0228 and 16-12465S to V.S.) from the Czech Republic. T.D. and K.F. are the recipients of a Research Fellowship for Young Scientists from the Japan Society for the Promotion of Science (JSPS). Y.T. and V.S. were further supported by an Invitation Fellowship for Research in Japan (Short-Term) from JSPS. F.M.B. and C.F.G. were supported by the National Research School Combination – Catalysis (NRSC-C) and the Netherlands Organization for Scientific Research (NWO-CW and NWO-EW).

Notes and references

1. L. M. Utschig, J. W. Bryson and T. V. O'Halloran, *Science*, 1995, **268**, 380–385.
2. S. Katz, *Biochim. Biophys. Acta*, 1963, **68**, 240–253; references cited therein.
3. L. D. Kosturko, C. Folzer and R. F. Stewart, *Biochemistry*, 1974, **13**, 3949–3952.
4. Z. Kuklenyik and L. G. Marzilli, *Inorg. Chem.*, 1996, **35**, 5654–5662.
5. Y. Miyake, H. Togashi, M. Tashiro, H. Yamaguchi, S. Oda, M. Kudo, Y. Tanaka, Y. Kondo, R. Sawa, T. Fujimoto, T. Machinami and A. Ono, *J. Am. Chem. Soc.*, 2006, **128**, 2172–2173.
6. Y. Tanaka, S. Oda, H. Yamaguchi, Y. Kondo, C. Kojima and A. Ono, *J. Am. Chem. Soc.*, 2007, **129**, 244–245.
7. T. Uchiyama, T. Miura, H. Takeuchi, T. Dairaku, T. Komuro, T. Kawamura, Y. Kondo, L. Benda, V. Sychrovský, P. Bouř, I. Okamoto, A. Ono and Y. Tanaka, *Nucleic Acids Res.*, 2012, **40**, 5766–5774.
8. A. Ono and H. Togashi, *Angew. Chem.*, 2004, **116**, 4400–4402 (*Angew. Chem., Int. Ed.*, 2004, **43**, 4300–4302).
9. H. Torigoe, A. Ono and T. Kozasa, *Chem. – Eur. J.*, 2010, **16**, 13218–13225.
10. H. Torigoe, Y. Miyakawa, A. Ono and T. Kozasa, *Thermochim. Acta*, 2012, **532**, 28–35.
11. J. Šebera, J. Burda, M. Straka, A. Ono, C. Kojima, Y. Tanaka and V. Sychrovský, *Chem. – Eur. J.*, 2013, **19**, 9884–9894.
12. H. Yamaguchi, J. Šebera, J. Kondo, S. Oda, T. Komuro, T. Kawamura, T. Daraku, Y. Kondo, I. Okamoto, A. Ono, J. V. Burda, C. Kojima, V. Sychrovský and Y. Tanaka, *Nucleic Acids Res.*, 2014, **42**, 4094–4099.
13. P. Pykkö, *Chem. Rev.*, 1997, **97**, 597–636.
14. F.-A. Polonius and J. Müller, *Angew. Chem.*, 2007, **119**, 5698–5701 (*Angew. Chem., Int. Ed.*, 2007, **46**, 5602–5604).
15. L. Benda, M. Straka, Y. Tanaka and V. Sychrovský, *Phys. Chem. Chem. Phys.*, 2011, **13**, 100–103.
16. L. Benda, M. Straka, V. Sychrovský, P. Bouř and Y. Tanaka, *J. Phys. Chem. A*, 2012, **116**, 8313–8320.
17. S. Kumbhar, S. Johannsen, R. K. O. Sigel, M. P. Waller and J. Müller, *J. Inorg. Biochem.*, 2013, **127**, 203–210.
18. J. Mason and R. J. Goodfellow, in *Multinuclear NMR*, ed. J. Mason, Plenum Press, New York, 1987, ch. 12 & 21.
19. P. Bernatowicz, S. Szymański and B. Wrackmeyer, *J. Phys. Chem. A*, 2001, **105**, 6414–6419.
20. E. H. Curzon, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1980, 721–725.
21. S. S. Al-Showiman, *Inorg. Chim. Acta*, 1988, **141**, 263–274.
22. J. Kondo, T. Yamada, C. Hirose, I. Okamoto, Y. Tanaka and A. Ono, *Angew. Chem.*, 2014, **126**, 2417–2420 (*Angew. Chem., Int. Ed.*, 2014, **53**, 2385–2388).
23. A. R. Norris and R. Kumar, *Inorg. Chim. Acta*, 1984, **93**, 33–35.
24. E. Buncel, C. Boone, H. Joly, R. Kumar and A. R. Norris, *J. Inorg. Biochem.*, 1985, **25**, 61–73.
25. K. Tanaka and M. Shionoya, *J. Org. Chem.*, 1999, **64**, 5002–5003.
26. H. Weizman and Y. Tor, *J. Am. Chem. Soc.*, 2001, **123**, 3375–3376.

- 27 C. Switzer, S. Sinha, P. H. Kim and B. D. Heuberger, *Angew. Chem.*, 2005, **117**, 1553–1556 (*Angew. Chem., Int. Ed.*, 2005, **44**, 1529–1532).
- 28 K. Tanaka, G. H. Clever, Y. Takezawa, Y. Yamada, C. Kaul, M. Shionoya and T. Carell, *Nat. Nanotechnol.*, 2006, **1**, U190–U195.
- 29 G. H. Clever, C. Kaul and T. Carell, *Angew. Chem.*, 2007, **119**, 6340–6350 (*Angew. Chem., Int. Ed.*, 2007, **46**, 6226–6236).
- 30 J. Müller, *Eur. J. Inorg. Chem.*, 2008, 3749–3763.
- 31 A. Ono, S. Cao, H. Togashi, M. Tashiro, T. Fujimoto, T. Machinami, S. Oda, Y. Miyake, I. Okamoto and Y. Tanaka, *Chem. Commun.*, 2008, 4825–4827.
- 32 S. Johannsen, N. Megger, D. Böhme, R. K. O. Sigel and J. Müller, *Nat. Chem.*, 2010, **2**, 229–234.
- 33 A. Ono, H. Torigoe, Y. Tanaka and I. Okamoto, *Chem. Soc. Rev.*, 2011, **40**, 5855–5866.
- 34 E. Meggers, P. L. Holland, W. B. Tolman, F. E. Romesberg and P. G. Schultz, *J. Am. Chem. Soc.*, 2000, **122**, 10714–10715.
- 35 S. Atwell, E. Meggers, G. Spraggon and P. G. Schultz, *J. Am. Chem. Soc.*, 2001, **123**, 12364–12367.
- 36 E. Meggers, *Curr. Opin. Chem. Biol.*, 2007, **11**, 287–292.
- 37 M. K. Schlegel, L.-O. Essen and E. Meggers, *J. Am. Chem. Soc.*, 2008, **130**, 8158–8159.
- 38 K. Tanaka, A. Tengeiji, T. Kato, N. Toyama and M. Shionoya, *Science*, 2003, **299**, 1212–1213.
- 39 G. H. Clever, S. J. Reitmeier, T. Carell and O. Schiemann, *Angew. Chem.*, 2010, **122**, 5047–5049 (*Angew. Chem., Int. Ed.*, 2010, **49**, 4927–4929).
- 40 T. Carell, C. Behrens and J. Gierlich, *Org. Biomol. Chem.*, 2003, **1**, 2221–2228.
- 41 T. Ito, G. Nikaido and S. I. Nishimoto, *J. Inorg. Biochem.*, 2007, **101**, 1090–1093.
- 42 J. Joseph and G. B. Schuster, *Org. Lett.*, 2007, **9**, 1843–1846.
- 43 L. Q. Guo, N. Yin and G. N. Chen, *J. Phys. Chem. C*, 2011, **115**, 4837–4842.
- 44 H. Isobe, N. Yamazaki, A. Asano, T. Fujino, W. Nakanishi and S. Seki, *Chem. Lett.*, 2011, **40**, 318–319.
- 45 H. A. Bent, *Chem. Rev.*, 1961, **61**, 275–311.
- 46 O. Just, D. A. Gaul and W. S. Rees, Jr., *Polyhedron*, 2001, **20**, 815–821.
- 47 G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931–967.
- 48 M. Swart, C. Fonseca Guerra and F. M. Bickelhaupt, *J. Am. Chem. Soc.*, 2004, **126**, 16718–16719.
- 49 J. M. Fonville, M. Swart, Z. Vokacova, V. Sychrovský, J. E. Šponer, J. Šponer, C. W. Hilbers, F. M. Bickelhaupt and S. S. Wijmenga, *Chem. – Eur. J.*, 2012, **18**, 12372–12387.
- 50 A. Bagno and G. Saielli, *J. Am. Chem. Soc.*, 2007, **129**, 11360–11361.
- 51 D. Rehder, *Coord. Chem. Rev.*, 1991, **110**, 161–210.
- 52 Y. Tanaka and A. Ono, *Dalton Trans.*, 2008, 4965–4974.
- 53 A. E. Wetherby, Jr., S. D. Benson and C. S. Weinert, *Inorg. Chim. Acta*, 2007, **360**, 1977–1986.
- 54 Y. Tanaka, H. Yamaguchi, S. Oda, M. Nomura, C. Kojima, Y. Kondo and A. Ono, *Nucleosides, Nucleotides Nucleic Acids*, 2006, **25**, 613–624.
- 55 S. S. Lemos, D. U. Martins, V. M. Deflon and J. Elena, *J. Organomet. Chem.*, 2009, **694**, 253–258.