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$^{1}H\{^{15}N\}$ heteronuclear correlation and ^{15}N cross-polarized magic angle spinning NMR studies of the coordination modes in Zn(II) chloride complexes with purine and methylpurines

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Abstract

The $^{1}H\{^{15}N\}$ heteronuclear correlation and ^{15}N cross-polarized magic angle spinning NMR spectra of purine (**1**) were measured. The Zn(II) chloride complexes with **1**, 7-methylpurine (**2**) and 9-methylpurine (**3**) were synthesised and studied by analytical methods, far-IR and ^{15}N NMR. The formulae of ZnL_2Cl_2 (L = **1**) and $[ZnLCl_2]_n$ (L = **2**, **3**) were found. The formation of Zn(II)–N coordination bonds resulted in 3–15 ppm low-frequency shifts of the respective ^{15}N NMR signals: N-7 for **1**; N-1, N-9 for **2**; N-1, N-7 for **3**.

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1. Introduction

Purine (**1**), 7-methylpurine (**2**) and 9-methylpurine (**3**) (Fig. 1) are well known heterocycles studied by NMR [1].

The data on their ^{15}N chemical shifts (in such solvents as H_2O/D_2O, aqueous NaOH, aqueous D_2SO_4, dmso-d_6, CF_3COOH, HSO_3F) and their $^{2}J_{NH}$ coupling constants were obtained by one-dimensional NMR techniques [2–5]. In this work we present the $^{1}H\{^{15}N\}$ heteronuclear correlation and ^{15}N cross-polarized magic angle spinning (CPMAS) spectra of **1**, as well as the results of a HSQC-HECADE experiment allowing for precise calculation of both $^{2}J_{NH}$ and $^{4}J_{NH}$ values.

Compounds **1**–**3** possess several potential N-donor metallation sites and easily form complexes with transition metals [6–13]. Their NMR studies involved mainly ^{1}H measurements of aqueous solutions containing **1**–**3** and such ions as Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+} [14–17]. The equilibrium of N(1), N(7) and N(9)-coordinated forms was generally suggested and supported by selective broadening of ^{15}N signals in the paramagnetic Cu^{2+} +**1** system [18]. In the following we focus on the complexes of Zn(II). Previous one-dimensional ^{15}N NMR measurements with the ligands mentioned above were performed for unidentified species in dmso-d_6 solutions of $ZnCl_2$, $CdCl_2$, $HgCl_2$ [19]. We now report the $^{1}H\{^{15}N\}$ heteronuclear correlation spectra for well-defined Zn(II) chloride complexes of **1**–**3**, dissolved in dmf-d_7 or dmso-d_6.

Three types of Zn(II) coordination compounds, formed in aqueous or ethanol solutions of $ZnCl_2$ and **1**, were described. Speca et al. [6] reported $[Zn(purine)Cl_2]_n$ as the main product from the reaction of $ZnCl_2$ with **1** in absolute ethanol and suggested its di-, oligo- or polymeric structure with N-3, N-9 bridges. Laity and Taylor [20] obtained, by evaporation of a water solution of $ZnCl_2$, **1** and diluted HCl, monomeric $Zn(purine)_2Cl_2$

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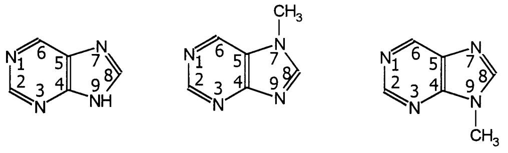

purine (**1**) 7-methylpurine (**2**) 9-methylpurine (**3**)

Fig. 1. Purine (**1**), 7-methylpurine (**2**) and 9-methylpurine (**3**).

and proved by X-ray analysis its N-7 monodentate coordination. Sheldrick [21] reported the X-ray structure of another species, Zn(purinium)Cl_3, protonated at N-1 and Zn-metallated at N-7, this compound being isolated from a more concentrated HCl solution.

We have performed the $ZnCl_2$+**1** reaction in 96% ethanol. Although the conditions were similar to those described by Speca et al. [6], a coordination compound of the formula Zn(purine)$_2Cl_2$ (**1a**), analogous to that described by Laity and Taylor [20] was obtained. The identity of both species was proven by us using X-ray powder diffraction. On the other hand, the Zn(II) chloride complexes with **2** and **3** revealed the formulae of Zn(7-methylpurine)Cl_2 (**2a**) and Zn(9-methylpurine)Cl_2 (**3a**).

Compounds **1a**–**3a** were studied by us using $^1H\{^{15}N\}$ two-dimensional NMR methods (GHSQC, GHMQC), in order to determine the metallation sites and Zn(II)-induced ^{15}N coordination shifts. For **1a**, the ^{15}N CPMAS and far-IR spectra in the solid phase as well as ^1H NMR, UV–Vis and conductivity measurements in aqueous solutions were also performed.

2. Experimental

2.1. Materials

The chemicals used for syntheses were $ZnCl_2$ (POCh Gliwice, Poland, 98–99%) and **1**, 2,6-dihydroxy-3,7-dimethylpurine, 5-amino-4,6-dichloropyrimidine (Aldrich, 97–99%).

2.2. Methods

$^1H\{^{15}N\}$ NMR spectra were measured with a Varian INOVA 500 MHz spectrometer, equipped with a Nalorac Z-SPEC IDG 500-5HT gradient probe. The resonance frequencies were 499.805 MHz for ^1H and 50.664 MHz for ^{15}N, the reference standards being TMS and external CH_3NO_2, respectively. The solvents were dmf-d_7 (**1**, **1a**) and dmso-d_6 (**2**, **3**, **2a**, **3a**), the concentrations being 0.1 M. The temperature was 303 K. The ^1H one-dimensional NMR spectra of aqueous solutions (D_2O) of **1** and **1a** were measured with a Varian Gemini-XL 200 MHz spectrometer.

The $^1H\{^{15}N\}$ NMR spectra of **2**, **3**, **2a** and **3a** were performed using gradient-enhanced heteronuclear multiple-quantum correlation (GHMQC) [22] with the following parameters: $\pi/2$ pulse lengths of 8.0 μs for ^1H, 24.5 μs for ^{15}N; relaxation delay 1.5 s; long-range couplings evolution delay 50 ms ($J = 10$ Hz); sweep width 10 ppm in F2 and 240 ppm in F1; 1024 experiments in t1; 2K points in t2; quadrature detection in t2; linear prediction to 2048 and zero filling up to 4K real points in F1 with sine bell apodisation in both dimensions.

The $^1H\{^{15}N\}$ NMR spectra of **1** and **1a** were detected using gradient-enhanced heteronuclear single-quantum correlation (GHSQC) [23], the conditions being analogous to those of the GHMQC measurements and completed by echo-antiecho in t1 and apodisation with $\pi/2$-shifted squared sine bell in both dimensions.

Compounds **1** and **1a** were also studied by $^1H\{^{15}N\}$ GHSQC-HECADE, a GHSQC-based two-dimensional sequence, allowing for accurate and sensitive determination of heteronuclear coupling constants (J_{NH}) from E.COSY-type cross peaks [24,25]. Sixteen FIDs were coherently added for each echo and anti-echo data set for 256 t1/t1* increments (t1 and t1* being the evolution times of the S-spin chemical shift and heteronuclear couplings, respectively). The maximum t1 value was set to 31.6 ms, t1* incremented up to 126.4 ms, t2 sampled up to 1.02 s (in order to increase the coupling separation: shift differences ratio by a factor of 4). The optimisation was done for a heteronuclear coupling constant of 8 Hz (60 ms delay), the apodisation with $\pi/2$-shifted sine bell in t1 and 1 Hz exponential broadening in t2.

The ^{15}N CP MAS spectra of **1** and **1a** were measured with a Bruker AVANCE-DRX 500 MHz spectrometer using a Bruker MASVTN500SB BL4 probehead and 4 mm zirconia rotors. A 10 kHz spinning speed was applied. A ramp [26] was implemented on the proton channel of the cross-polarization pulse sequence. A ^1H decoupling rf field strength of 73.5 kHz (3.4 μs $\pi/2$ pulse length) and a two pulse phase-modulation decoupling sequence [27] were applied. The following parameters were used: frequency 50.689 MHz; spectral width 23 kHz; contact time 6 ms; acquisition time 15 ms for **1** and 25 ms for **1a**; relaxation delay 300 s for **1** and 30 s for **1a**; number of acquisitions 196 for **1** and 476 for **1a**. The spectra were referenced to solid glycine and recalculated to nitromethane ($\delta(NH_2$ in glycine$) = -347.6$ ppm).

The X-ray powder diffractogram of **1a** was recorded with a Philips X-Pert Pro diffractometer, whereas that of Laity's compound, Zn(purine)$_2Cl_2$ [20], was simulated with a SHELX-97 computer program [28]. The far-IR spectra of **1a**–**3a** were measured in the 400–100 cm^{-1} range with a Perkin–Elmer Spectrum 2000 FT-IR spectrometer using polyethylene discs. The UV–Vis spectra of **1** and **1a** were detected in 0.1 M aqueous solutions with a Hewlett-Packard 8453 spectrophotometer. The conductivity measurements were performed with an Elmetron CX-732 conductometer. The amount of C, H, N in **1a**–**3a** was determined by elemental analysis, whereas that of Zn by titration with EDTA (after mineralization).

2.3. *Syntheses*

The synthesis of **2** from 2,6-dihydroxy-3,7-dimethylpurine and **3** from 5-amino-4,6-dichloropyrimidine followed literature procedures [19]. Compound **1a** was obtained from $ZnCl_2$ and **1** in 96% EtOH, whereas **2a**, **3a** from $ZnCl_2$ and **2**, **3** in water. The white precipitates were filtered after 24 h, washed with EtOH and dried in air. The elemental analyses revealed the formulae of $Zn(purine)_2Cl_2$ for **1a** (*Anal*. Calc. for $C_{10}H_8Cl_2N_8Zn$/Found)—C, 31.9/32.0; H, 2.1/2.0; N, 29.8/30.2; Zn, 17.4/17.5% and $Zn(methylpurine)Cl_2$ for **2a**, **3a** (*Anal*. Calc. for $C_6H_6Cl_2N_4Zn$/Found for **2a**/Found for **3a**)—C, 26.6/26.5/26.8; H, 2.2/2.3/2.4; N, 20.7/20.5/20.5, Zn 24.2/24.0/24.0%.

3. Results and discussion

3.1. *$^1H\{^{15}N\}$ NMR spectra of* ***1–3***

The $^1H\{^{15}N\}$ GHSQC spectrum of **1** (in dmf-d_7) is presented in Fig. 2.

We observe the following $^{15}N-^1H$ correlations via two bonds: N-1 with H-2 and H-6; N-3 with H-2; N-7 with H-8; N-9 with H-8. Some weaker $^{15}N-^1H$ spin–spin interactions via four bonds, N-3 with H-6 and H-8, have also been detected. These results allow for an unambiguous assignment of ^{15}N signals, identical with that known from one-dimensional NMR experiments [5], their chemical shifts decreasing in order N-1 > N-3 > N-7 > N-9. It is worth noting that N-7 and N-9 correlate in the same way. They can be easily distinguished, however, as the latter nitrogen possess a higher shielding constant due to its pyrrole-type character [1].

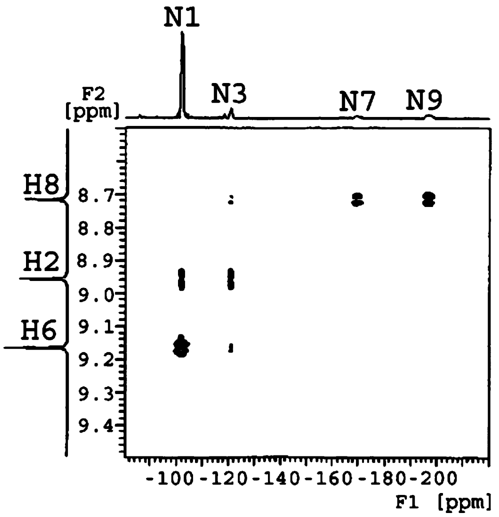

Fig. 2. $^1H\{^{15}N\}$ GHSQC spectrum of **1** (in dmf-d_7).

The ^{15}N chemical shifts of **1** (Table 1), recorded in dmf-d_7, differ not more than 2 ppm from those found in dmso-d_6 [4,5]. The $^{15}N-^1H$ coupling constants, determined from the HSQC-HECADE spectrum, are as follows: $^2J_{N1H2} = 15.3$, $^2J_{N1H6} = 10.8$, $^2J_{N3H2} = 15.2$, $^2J_{N7H8} = 10.9$, $^2J_{N9H8} = 10.0$, $^4J_{N3H6} = 1.4$, $^2J_{N3H8} = 1.5$ Hz. The values of $^2J_{NH}$ differ less than 1 Hz from the literature data [5], whereas those of $^4J_{NH}$ do not exceed a typical [29] magnitude of 1.5 Hz.

The $^1H\{^{15}N\}$ GHMQC spectra of **2** and **3** have been performed in dmso-d_6, the ^{15}N chemical shifts (Table 1) being identical with those described in literature [4,5].

3.2. *Spectroscopic properties of* ***1a–3a***

3.2.1. *X-ray powder diffraction and far-IR studies of* ***1a–3a***

In spite of many attempts, we were not able to obtain monocrystals of **1a**, suitable for X-ray analysis. Therefore, we have measured the X-ray powder diffractogram of **1a** and compared it with that simulated for Laity's compound, $Zn(purine)_2Cl_2$, based on the published atomic coordinates [20]. The most intensive reflections, measured at 15.5°, 20.8°, 26.0°, 27.3° (2θ angles), appear also in the simulation (Fig. 3), allowing for a conclusion that both complexes are one species.

In the far-IR spectrum of **1a** two strong absorption bands at 321 and 303 cm^{-1} have been detected. They derive, most likely, from the Zn–Cl stretching vibrations, typical for pseudotetrahedral monomeric molecules of the ZnL_2Cl_2 type [30]. The noted ν_{ZnCl} frequencies are similar to those reported for $Zn(pyridine)_2Cl_2$ (329, 297 cm^{-1}) [31] or $Zn(imidazole)_2Cl_2$ (304, 291 cm^{-1}) [32]. The far-IR spectra of **2a** and **3a** are more difficult to interpretate due to the broad absorp-

Table 1
The ^{15}N chemical shifts (ppm) of **1**–**3** and **1a**–**3a** (coordination shifts in parentheses)

Compound	N-1	N-3	N-7	N-9
1 [a]	−101.9	−120.9	−169.3	−196.7
1a [a]	−110.7	−121.4	−179.6	−199.1
	(−8.8)	(−0.5)	(−10.3)	(−2.4)
2 [b]	−102.3	−109.4	−237.6	−137.0
2a [b]	−106.6	−110.8	−235.2	−146.8
	(−4.3)	(−1.4)	(+2.4)	(−9.8)
3 [b]	−103.4	−130.0	−140.8	−230.8
3a [b]	−106.4	−128.7	−155.8	−228.2
	(−3.0)	(+1.3)	(−15.0)	(+2.6)

[a] In dmf-d_7.

[b] In dmso-d_6.

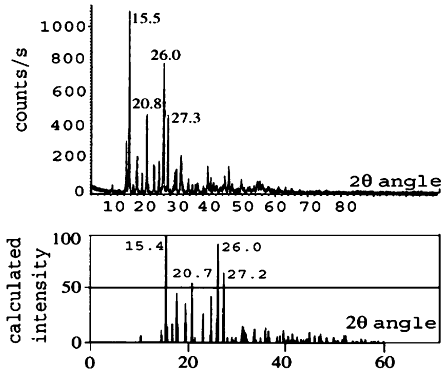

Fig. 3. X-ray powder diffractogram of **1a** (top) and simulation for Laity's compound (bottom).

tion band in the 150–350 cm^{-1} range, associated most likely with the polymeric structure of both complexes.

3.2.2. *Aqueous solution of **1a***

The mixture of $ZnCl_2$ and **1** in water did not yield any precipitate, contrary to the case of **2** and **3**, where the insoluble complexes of **2a** and **3a** were rapidly formed. The reason is that **1a**, which easily precipitates in ethanol, is unexpectedly well soluble in water. Its aqueous solution reveals physical and spectroscopic properties identical with those of the $ZnCl_2$ and **1** mixture.

The water solutions of either **1a** or $ZnCl_2+$**1** conduct electricity with molar conductivity characteristic for Zn^{2+} and 2 Cl^-. Their UV–Vis spectra exhibit the same absorption band at 263 nm and the molar absorbance of free **1** [33]. Their ^{1}H NMR spectra, measured in D_2O, are slightly dependent on the concentration (H-8 8.34, H-2 8.65, H-6 8.82 ppm for 0.1 M), being similar to that of pure **1** [34,35].

These observations suggest that monomeric **1a** easily dissociates in water into Zn^{2+}, 2 Cl^- and 2 molecules of **1**. In other words, in aqueous medium **1** has no ability to bind Zn(II) ions. The process of dissociation of **1a** is entirely reversible; however, when water is evaporated, the obtained solid residue appears to be pure **1a**, not the $ZnCl_2+$**1** mixture. Such a behaviour seems to be quite unusual in the case of a coordination compound.

In dmf and dmso, **1a**–**3a** dissolve without dissociation because the respective solutions reveal the conductivity analogous to the pure solvents.

3.2.3. *$^1H\{^{15}N\}$ NMR spectra of **1a**–**3a***

The ^{1}H{^{15}N} GHSQC and GHMQC spectra of **1a**–**3a** were measured in dmf-d_7 or dmso-d_6, **1a** being also studied by HSQC-HECADE. They can be assigned in the same way as those of **1**–**3**, the respective ^{15}N chemical shifts being collected in Table 1 (coordination shifts in parentheses).

For **2a** and **3a** the shielding of two nitrogen atoms: N-1; N-9 (**2a**) and N-1; N-7 (**3a**) has been observed. Because both complexes reveal the formula of $ZnLCl_2$ (L = **2** or **3**), one can assume that the methylpurines behave as bidentate ligands and bridge the Zn(II) ions via N-1 and N-9 (**2a**) or N-1 and N-7 (**3a**). The observed coordination mode differences is the result of blocking the N-7 and N-9 positions, respectively, by a methyl group. Hence di-, oligo- or polymeric structures $(ZnLCl_2)_n$ can be proposed for **2a** and **3a**.

For **1a** the shielding of two nitrogens (N-1 and N-7) occurs as well, but its origin must be different. The X-ray data reveal that the purine rings are N-7 bonded to Zn(II). On the other hand, the absence of N-7/N-9 tautomerism, present in **1**, results in the H-9···N-1′ hydrogen bonds [20]. Assuming that **1a** exists in dmf-d_7 solution in the same form as in the solid state, one can regard the shielding of N-7 and N-1 as the result of Zn(II) coordination and H-bond formation, respectively.

The observed values of Zn(II)-induced ^{15}N coordination shifts (3–15 ppm to lower frequency) are similar or slightly larger than those described for Zn(II) chloride complexes with 1,2,4-triazolo-[1,5α]-pyrimidines (max. 2 ppm) [36,37] or adenosine (2–9 ppm) [38]. It is worth noting that the shielding of Zn(II)-coordinated nitrogen atoms is much larger for the imidazole ring (N-7 and N-9, approximately 10–15 ppm) than for the pyrimidine one (N-1, approximately 3–5 ppm).

The values of J_{NH} coupling constants found for **1a** are similar to those of **1**: $^2J_{N1H2}=14.5$, $^2J_{N1H6}=9.9$, $^2J_{N3H2}=15.0$, $^2J_{N7H8}=11.2$, $^2J_{N9H8}=9.5$, $^4J_{N3H6}=1.8$, $^2J_{N3H8}=1.7$ Hz.

3.3. *^{15}N CP MAS spectra of **1** and **1a***

In the ^{15}N CP MAS spectrum of **1** four resonances at −103.3, −115.7, −150.6, −227.6 ppm have been detected (Fig. 4). The two former signals can be assigned

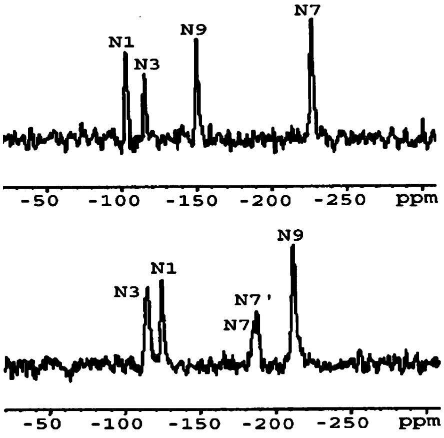

Fig. 4. ^{15}N CP MAS spectra of **1** (top) and **1a** (bottom).

to N-1 and N-3, respectively, by analogy with the spectra measured in dmf-d_7 or dmso-d_6. The two latter peaks must derive from N-7 or N-9 atoms, the more shielded representing the pyrrole-type nitrogen. Because in the solid state the H-7 tautomer is present [39] (contrary to the solutions, for which the H-9 form is more stable [1]), the signal at −227.6 ppm can be assigned to N-7 and that at −150.6 ppm to N-9. It leads to the following order of ^{15}N resonances: N-1 > N-3 > N-9 > N-7 (decreasing the chemical shifts), different from that known for **1** in solution.

The ^{15}N CPMAS spectrum of **1a** exhibits resonances at −115.1, −124.6, −185.8/−188.0, −212.4 ppm (Fig. 4). We can suppose that the signal at −115.1 ppm (close to that at −115.7 ppm in the spectrum of **1**) belongs to N-3, as this nitrogen is not engaged in any intra- or intermolecular interactions in both compounds. The peak at −124.6 ppm probably represents N-1, its 21 ppm low-frequency shift being a consequence of the H-bond formation to H-9 [20]. The signal at −212.4 ppm derives from N-9 as in the case of **1a** it is a pyrrole-type nitrogen [20]. The twin peaks of smaller but similar intensity at −185.8 and −188.0 ppm must represent the same N-7 atom, coordinated by Zn(II). Thus the suggested order of ^{15}N resonances for **1a** is different from that for **1**: N-3 > N-1 > N-7 > N-9 (decreasing the chemical shifts).

The phenomenon of two peaks assigned to N-7 can be explained by a detailed analysis of the X-ray structure of **1a**. Due to the specific packing of molecules in the crystal lattice, the two purine rings in **1a** are not fully equivalent. This effect is especially evident for N-7, for which there are two values of Zn–N bond lengths [Zn–N-7 2.027(3) and Zn–N-7′ 2.033(4) Å] and four Cl–Zn–N angles [112.1(1°), 111.7(1°), 111.4(1°), 107.0(1)°] [20]. Hence N-7 and N-7′ are located in slightly different moieties which results in the presence of two resonances in the ^{15}N CP MAS spectrum. When **1a** is dissolved in dmf-d_7, N-7 and N-7′ become chemically and magnetically equivalent, producing one ^{15}N NMR signal.

4. Conclusions

The Zn(II) chloride complexes with purine, 7-methylpurine or 9-methylpurine differ in stoichiometry and the coordination modes. The reaction of $ZnCl_2$ with purine in ethanol yields monomeric, N-7-coordinated Zn(purine)$_2$Cl$_2$. Analogous syntheses with 7-methylpurine or 9-methylpurine produce di-, oligo- or polymeric compounds of the $[Zn(methylpurine)Cl_2]_n$ type.

The Zn(II) coordination of heterocyclic nitrogens results in 3–15 ppm low-frequency shifts of their ^{15}N NMR signals. This effect indicates N-7; N-1, N-9 and N-1, N-7 nitrogen atoms as the metallation sites in the molecules of purine, 7-methylpurine and 9-methylpurine, respectively. A similar shift of N-1 in Zn(purine)$_2$Cl$_2$, however, seems to be the result of hydrogen bond formation.

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