Structural and Computational Studies of 1-Methyl-2-thiocytosine and its Coordination Mode in a Dinuclear Platinum(IV) Complex $[(PtMe_3)_2(\mu\text{-}1\text{-MeSCy-}1\kappa N^3,1{:}2\kappa^2 S)_2][BF_4]_2$

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X-Ray diffraction analysis of 1-methyl-2-thiocytosine (1-MeSCy, **1**) revealed that its crystals contain two structurally very similar independent molecules (A, B). These molecules are connected through a complex network of hydrogen bonds. Centrosymmetric di- and tetrameric units AA′ and BAA′B′, respectively, are formed through N–H···N hydrogen bonds (N4a···N3a′ 3.019(4) Å, AA′; N4a···N3b 2.988(4) Å, BAA′B′), and the tetrameric units are connected through N–H···S hydrogen bonds. The arrangement of A and B molecules found in crystals of **1** was confirmed by DFT calculations up to tetrameric BAA′B′ units, yielding similar equilibrium structures, and the energies of the N–H···N hydrogen bonds between A and A′ and A and B were calculated to be about 10 kcal mol^{-1}. Reaction of 1-MeSCy (**1**) with $[PtMe_3(Me_2CO)_3][BF_4]$ (**2**) led to the formation of the ionic dinuclear complex $[(PtMe_3)_2(\mu\text{-}1\text{-MeSCy-}1\kappa N^3,1{:}2\kappa^2 S)_2][BF_4]_2$ (**3**) which was fully characterized by NMR (^{1}H, ^{13}C, ^{195}Pt) and IR spectroscopy, ESI mass spectrometry and microanalysis. A single-crystal X-ray diffraction analysis of **3** confirmed the dinuclear structure of the complex. The complex cation consists of a central $[Pt_2(\mu\text{-}S)_2]$ core having bound the 1-methyl-2-thiocytosine ligands in a $1\kappa N^3,1{:}2\kappa^2 S$ coordination mode in a face-to-face arrangement, the thionucleobase ligands being present as the amino-thione tautomer.

Key words: Thionucleobases, Platinum Complexes, Hydrogen Bonding, Single-crystal X-Ray Diffraction Analysis, DFT Calculations

Introduction

Thionucleobases and thionucleosides can be found in many biological processes. 2-Thiouracil has been found in t-RNA of *E. coli* bacteria [1]. Furthermore, the nucleosides of 4-thiouracil and 2-thiocytosine are present in t-RNA of several sources [2 – 5]. Further insight into the function of these compounds can be achieved by investigations of model compounds. The most simple models for these nucleosides are the derivatives methylated at the position next to the carbohydrate moiety. They should exist in the same tautomeric form as the requisite nucleosides. Depending on the solvent, thionucleobases can exist as many different tautomers. For 2-thiocytosine, in particular, it has been found that in aqueous solution and polycrystalline films the thione-amino tautomer is the predominant species [6 – 9]. In accordance with these observations the thione-amino form is present in crystals of 2-thiocytosine [10]. Methylation of a nucleobase limits the number of possible tautomers and may severely influence the resulting hydrogen bonding pattern. Metal coordination of thionucleobases is also of particular interest [11], especially because the coordination behavior of thionucleobases has not been studied as extensively as that of the naturally occurring oxygen analogs. It has been shown that metal thionucleobase complexes exhibit interesting bioactive properties [12]. Here we report the crystal structure of 1-methyl-2-thiocytosine (**1**) as well as the synthesis and the crystal structure of its ionic, dinuclear platinum(IV) complex $[(PtMe_3)_2(\mu\text{-}1\text{-MeSCy-}1\kappa N^3,1{:}2\kappa^2 S)_2][BF_4]_2$ (**3**).

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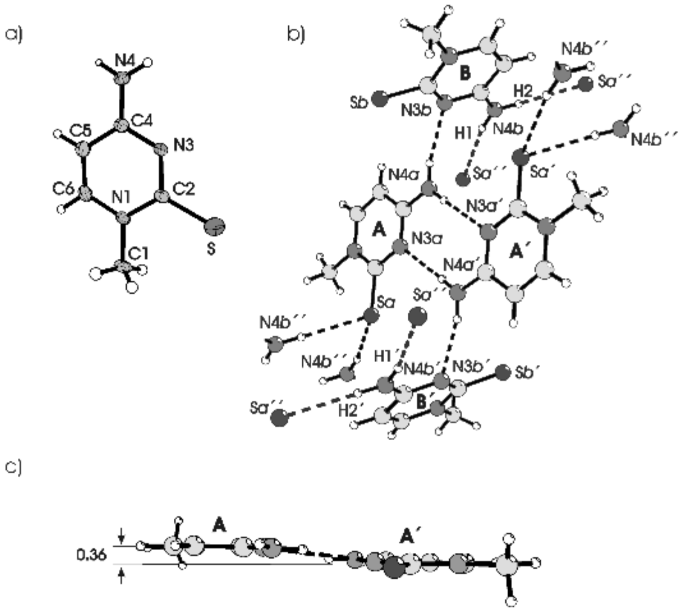


Fig. 1. a) Molecular structure of one of the two crystallographically independent monomeric 1-methyl-2-thiocytosine units in crystals of **1**. The displacement ellipsoids are drawn at the 30 % probability level. b) Hydrogen bonding in crystals of **1**. All atoms which do not belong to the BAA′B′ unit are doubly primed. c) Side view of the centrosymmetric AA′ dimer (1-MeSCy)$_2$.

Results and Discussion

Crystal structure of 1-methyl-2-thiocytosine (1)

Colorless needles of 1-methyl-2-thiocytosine (1-MeSCy, **1**) were obtained from an ethanol solution. The compound crystallizes in the centrosymmetric space group $P2_1/n$. The crystals contain two crystallographically independent molecules of 1-MeSCy (A, B) which are structurally very similar (Fig. 1 and Table 1). Within the 3σ criterion all corresponding bonds in A and B as well as most of the angles are equivalent.

In crystals of **1** a network of hydrogen bonds connects the monomeric molecules A and B. Basically, two molecules of A build up a centrosymmetric dimer AA′ through two N4*a*–H···N3*a*′ hydrogen bonds (Fig. 1, Table 1). The AA′ dimer is not planar, but the monomers are shifted parallel by 0.36 Å. Such a shift by as much as 1.41 Å was also found in crystals of 1-methylcytosine [13, 14]. The N4*a*H$_2$ amino groups generate further hydrogen bonds to N3*b* (Table 1). Thus, a centrosymmetrical tetrameric unit BAA′B′ is formed. The B molecules are nearly perpendicular to the AA′ dimers (interplanar angle: 86.4(8)°). Interestingly, the N4*a*–H vector forms an angle of 34.9° with the pyrimidine plane of molecule B. Thus, in the hydrogen bond N4*a*–H···N3*b* the lone pair of electrons on N3*b* is not directed towards the central H atom. In addition, the sulfur atoms S*a* act as hydrogen acceptors for the amino groups N4*b*H$_2$ of the B molecules yielding N–H···S hydrogen bonds (Fig. 1, Table 1). On the other hand, the interaction of the sulfur atom S*b* with C6*b*–H groups (S*b*···C6*b* 3.663(4) Å, S*b*···H 2.73 Å) is found to be in the border range of weak hydrogen bonds [15, 16].

Table 1. Selected bond lengths and angles of molecules A and B[a] and structural parameters of hydrogen bonds in crystals of 1-MeSCy (**1**) (distances in Å, angles in deg).

C1–N1	1.477(3)/1.475(4)	C4–N4	1.327(3)/1.338(4)
C2–N1	1.381(3)/1.390(3)	C4–C5	1.423(4)/1.422(4)
C2–S	1.702(3)/1.692(3)	C5–C6	1.338(4)/1.335(4)
C2–N3	1.344(3)/1.343(3)	C6–N1	1.371(3)/1.358(4)
C4–N3	1.343(3)/1.334(3)		
C1–N1–C2	121.5(2)/121.3(3)	S–C2–N3	119.1(2)/121.0(2)
C2–N3–C4	120.9(2)/120.4(2)	N4–C4–N3	117.8(2)/118.1(2)
S–C2–N1	121.3(2)/119.6(2)	C4–C5–C6	117.5(3)/116.5(3)

D-H··A	N4*a*-H··N3*a*′	N4*a*-H··N3*b*	N4*b*-H1··S*a*″	N4*b*-H2··S*a*″
D···A	3.019(4)	2.988(4)	3.493(4)	3.463(4)
D–H	0.87	0.87	0.88	0.91
H···A	2.16	2.14	2.64	2.55
D–H···A	174	165	164	173

[a] The first value refers to molecule A and the second value to molecule B.

The geometrical parameters of the four hydrogen bonds discussed (Table 1) are in accord with data given in the literature [17, 18]. Thus, for N–H···N(sp^2) hydrogen bonds the median of the N···N distances was found to be 3.023 Å (lower/upper quartile: 2.967/3.091 Å, for 1253 observations). For N–H···S=C hydrogen bonds the median of the N···S

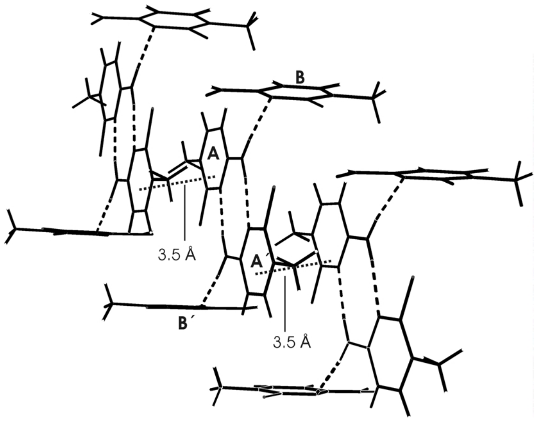


Fig. 2. Packing of molecules A and B and π-π stacking (···) between A and A′ molecules in crystals of **1**.

distances proved to be 3.467 Å (lower/upper quartile: 3.408/3.551 Å, for 1873 observations) [17].

In crystals of **1** the dimeric units AA′ and the monomeric units B are packed in infinitive strands like a "staircase", as shown in Fig. 2. Within the AA′ strands an interplanar ring distance of 3.5 Å and a displacement angle of 17.5° between pairs of pyrimidine rings of A indicate a stabilization through π-π stacking and/or C–H-π stacking [19]. Though a relatively short interplanar distance of 3.0 Å between the molecules in the B strands was found, a displacement angle of 59.9° of the B molecules suggests the absence of significant stabilization through π-π/C–H-π interactions.

Quantum-chemical calculations

To gain insight into the strength of the hydrogen bonds that are found in crystals of 1-methyl-2-thiocytosine (**1**), DFT calculations (using the B3LYP hybrid functional and 6-31++G(d,p) basis sets) of the monomeric 1-MeSCy **1m**, the doubly N4–H···N3′ hydrogen-bonded dimer **1d** and the tetramer **1t**, having two further monomers attached to **1d** through N4–H···N3′ hydrogen bonds, were performed. The equilibrium structures are shown in Fig. 3, selected structural parameters are given in Table 2. As Table 2 reveals, the involvement of **1m** in a hydrogen-bonded system gives rise to only small structural changes.

Dimer **1d** and tetramer **1t** can be regarded as models for the dimer AA′ and the tetramer BAA′B′ found in the solid-state structure of **1**. As shown in Table 2, there is good agreement of the calculated (**1t**) and the experimental structure (**1**). The most obvious difference is that the dimeric units AA′ in **1d** and **1t** were calculated to be (nearly perfectly) planar (greatest deviation from the mean plane: 0.003 Å for N4*a*/N4*a*′), whereas in **1** the two halves of the dimer are shifted parallel by 0.36 Å (see Fig. 1). Furthermore, in the tetramer **1t** the interplanar angle between the central dimeric unit (AA′) and its attached monomers (B/B′) is found to be 36.9°, whereas in the solid-state structure of **1** the B/B′ units are nearly perpendicular to the dimeric unit AA′ (86.4(8)°). A tetrameric structure **1t′**, obtained by a restricted optimization such that the interplanar angle between the AA′ unit and the B/B′ molecules found in the experimental structure (86.4°) is obtained, proved to be only 6.2 kcal mol^{-1} higher in energy than the equilibrium structure **1t**. As found in the experimental structure of **1**, the free electron pair of N3*b* in the calculated structure **1t** is not pointing directly towards the central H atom. However, the calculated angle between the N4*a*–H vector and the mean plane of the pyrimidine ring (22.8°) is remarkably smaller than in crystals of **1** (34.9°). This can be accounted for by further hydrogen bonds (N–H···S) and also π–π stackings in crystals of **1** that were not taken into consideration in the calculations.

Table 2. Calculated parameters (distances in Å, angles in deg) of the monomeric 1-MeSCy (**1m**), the twofold hydrogen-bridged dimer of the type AA′ (**1d**) and the tetrameric unit of the type BAA′B′ (**1t**). For comparison, the corresponding experimentally measured values in crystals of **1** are given.

	1m	**1d**	**1t**	**1**
C2–N1	1.420	1.411	1.402/1.410[a]	1.381(3)/1.390(3)[a]
C2–S	1.678	1.689	1.702/1.686	1.702(3)/1.692(3)
C2–N3	1.357	1.351	1.350/1.356	1.344(3)/1.343(3)
C4–N3	1.323	1.341	1.345/1.332	1.343(3)/1.334(3)
C4–N4	1.361	1.338	1.339/1.358	1.327(3)/1.338(4)
N1–C2–N3	117.5	118.0	118.8/118.0	119.7(2)/119.4(2)
C2–N3–C4	121.6	122.4	121.3/121.7	120.9(2)/120.4(2)
N4···N3′		2.948	3.063/3.161[b]	3.019(4)/2.988(4)[b]
N4–H		1.032	1.027/1.015	0.87/0.87
H···N3′		1.916	2.038/2.200	2.16/2.14
N4–H···N3′		179.4	175.3/157.3	174/165

[a] The first value refers to molecules A and the second value to molecules B; [b] the first value refers to hydrogen bonds in the dimers AA′ and the second value to the hydrogen bonding within units AB.

The strength of intermolecular hydrogen bonds, ΔH_{hb}, is defined as the enthalpy of the reaction

$$\text{X–H}\cdots\text{Y} \longrightarrow \text{X–H} + |\text{Y}$$

when all components are in their equilibrium conformations. The energies for the reactions

$$\mathbf{1d} \rightarrow 2\,\mathbf{1m} \quad\text{and}\quad \mathbf{1t} \rightarrow \mathbf{1d} + 2\,\mathbf{1m}$$

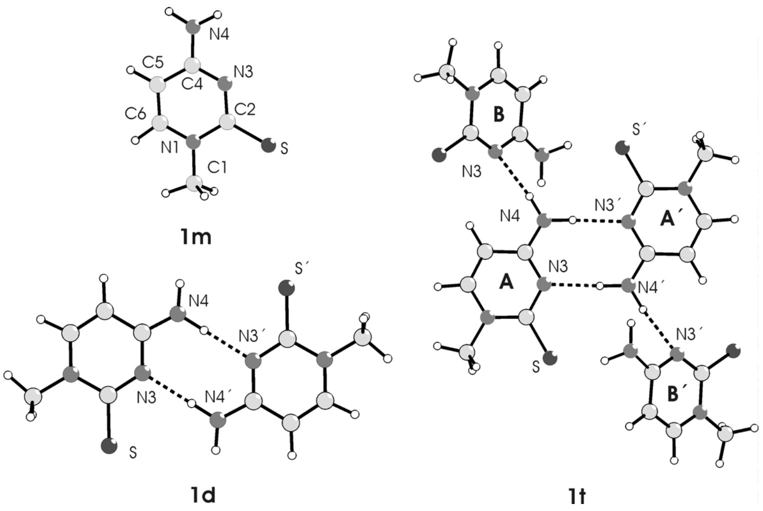
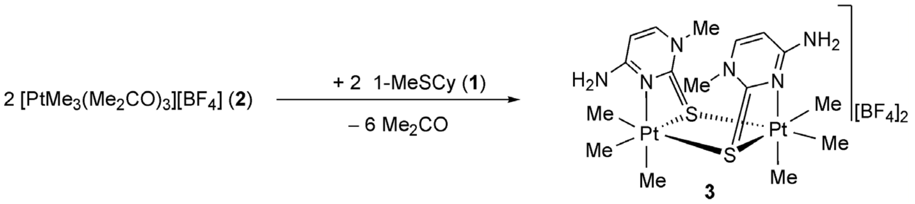


Fig. 3. Calculated equilibrium structures of the monomeric 1-MeSCy (**1m**), the twofold hydrogen-bonded dimer of the type AA′ (**1d**) and the tetrameric unit of the type BAA′B′ (**1t**).



Scheme 1.

were found to be endothermic by 20.2 and 21.7 kcal mol^{-1}, respectively. Considering basis BSSE set superposition errors [20], values of 19.4 and 19.6 kcal mol^{-1}, respectively, were obtained. Thus, both types of the N4–H···N3′ hydrogen bonds, namely those building up the dimers and tetramers, are of approximately the same strength (about 10 kcal mol^{-1} per hydrogen bond). Thus, these hydrogen bonds are stronger than those in gaseous water dimers (5.0 kcal mol^{-1}) [20, 21] which are benchmarks for hydrogen bonds. Classifying hydrogen bonds with respect to their energies [22] (weak < 4, moderate 4–15, strong 14–40 kcal mol^{-1}) they have to be regarded as moderate.

Synthesis and spectroscopic characterization of [(PtMe$_3$)$_2$(μ-1-MeSCy-1κN^3,1:2$\kappa^2 S$)$_2$][BF$_4$]$_2$ (3)

[PtMe$_3$(Me$_2$CO)$_3$][BF$_4$] (**2**) [23] was reacted with 1-methylthiocytosine (**1**) in acetone solution to yield [(PtMe$_3$)$_2$(μ-1-MeSCy-1κN^3,1:2$\kappa^2 S$)$_2$][BF$_4$]$_2$ (**3**) (Scheme 1). The slightly air- and moisture-sensitive complex was isolated in 56 % yield. By contrast, the analogous reaction with 2-thiocytosine led to the formation of several products. Complex **3** was fully characterized by ^{1}H, ^{13}C and ^{195}Pt-NMR spectroscopy, as well as by ESI-MS spectrometry, IR spectroscopy, and X-ray diffraction analysis. Table 3 shows the ^{1}H and ^{13}C-NMR data of [(PtMe$_3$)$_2$(μ-1-MeSCy-1κN^3,1:2$\kappa^2 S$)$_2$][BF$_4$]$_2$ (**3**). A remarkably downfield shift for the signals of H5 and the respective carbon atom C5 by 0.44 and 4.8 ppm, respectively, is observed. Moreover, the doublet of H5 exhibits platinum satellites ($^4J_{\mathrm{Pt,H}}$ = 11.6 Hz) indicating the involvement of N3 in platinum coordination [24]. The signals of H6/C6 are also shifted to lower field but to a lesser extent (0.25/1.0 ppm), and no platinum satellites

Table 3. ^{1}H and ^{13}C NMR data (δ in ppm, J in Hz) of 1-MeSCy (**1**) and [(PtMe$_3$)$_2$(μ-1-MeSCy-1κN^3,1:2$\kappa^2 S$)$_2$] (**3**) in CD$_3$OD.

	1		**3**	
	δ_{H}	δ_{C}[b]	δ_{H} ($^2J_{\mathrm{Pt,H}}$)	δ_{C}
H5/C5[a]	6.09	97.0	6.53	101.8
H6/C6	7.73	146.8	7.98	147.8
N1–CH$_3$	3.72	43.3	3.64	40.7
C2		180.6		184.4
C4		160.5		160.4
PtMe$_3$			1.22(75.5)[c]	−7.3

[a] Numbering scheme according to Fig. 1a; [b] due to insufficient solubility of 1-MeSCy (**1**) the chemical shifts of **1** in [D$_6$]DMSO are given; [c] at −50 °C: 1.189/1.194 ppm (74.7/81.5).

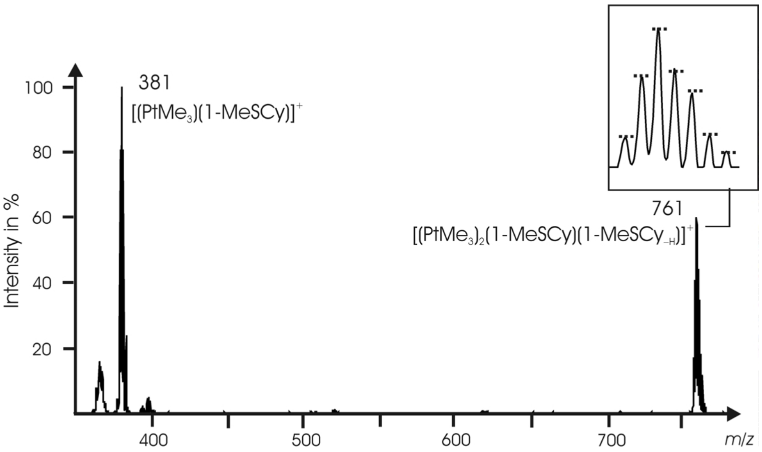


Fig. 4. Full scan mass spectrum of $[(PtMe_3)_2(\mu\text{-1-MeSCy-1}\kappa N^3\text{,1:2}\kappa^2 S)_2][BF_4]_2$ (**3**). Inset: isotopic pattern of the molecular ion $[PtMe_3(1\text{-MeSCy})(1\text{-MeSCy}_{-H})]^+$ at $m/z = 761$ showing the expected intensities due to the isotopic composition in horizontal bars.

are found. The shift of the signal for C2 by 3.8 ppm to lower field indicates the sulfur coordination to the platinum(IV) atom. Thus, from the NMR experiments a $\kappa N^3,\kappa S$ coordination could be derived, as definitely established by X-ray diffraction measurement (see below). For the protons of the three methyl ligands at room temperature only one sharp signal flanked by platinum satellites is found, whereas at −50 °C a splitting into at least two singlets, flanked by platinum satellites, becomes apparent (Table 3).

ESI-MS measurements using acetone solutions have confirmed the presence of a dinuclear cation $[(PtMe_3)_2(1\text{-MeSCy})(1\text{-MeSCy}_{-H})]^+$ at $m/z = 761$ (Fig. 4). The isotopic pattern has been found to be characteristic for a monocation containing two platinum atoms [natural isotopic composition: ^{190}Pt (0.01 %), ^{192}Pt (0.79 %), ^{194}Pt (32.9 %), ^{195}Pt (33.8 %), ^{196}Pt (25.3 %) and ^{198}Pt (7.2 %)] in good agreement with calculated data. Furthermore, at $m/z = 381$ the monocation $[PtMe_3(1\text{-MeSCy})]^+$ has been found. Collision-induced dissociation (CID) experiments have shown that this peak is also formed by fragmentation of the isolated parent ion $[(PtMe_3)_2(1\text{-MeSCy})(1\text{-MeSCy}_{-H})]^+$.

Table 4. Selected bond lengths and angles of $[(PtMe_3)_2(\mu\text{-1-MeSCy-1}\kappa N^3\text{,1:2}\kappa^2 S)_2]$ (**3** · 1.5 C_6H_6) (distances in Å, angles in deg).

Pt1–C1	2.057(6)	Pt1–S1	2.551(2)	Pt2–S1	2.525(2)
Pt1–C3	2.055(8)	Pt1–S2	2.501(2)	Pt2–S2	2.542(2)
Pt2–C4	2.062(8)	Pt1–N4	2.257(5)	S1–C7	1.737(7)
Pt2–C5	2.047(6)	Pt2–N1	2.243(5)	S2–C12	1.726(7)
C1–Pt1–C2	87.7(4)	S1–C7–N1	114.2(5)	S2–Pt1–N4	66.0(1)
C3–Pt1–N4	166.7(3)	C4–Pt2–C5	87.7(3)	Pt1–S1–Pt2	92.56(6)
S1–Pt2–N1	65.4(1)	C6–Pt2–N1	166.8(3)	Pt1–S2–Pt2	93.34(6)

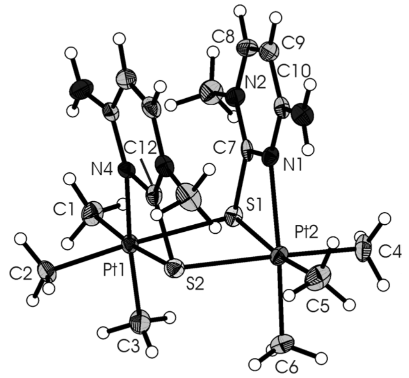


Fig. 5. Molecular structure of the cation of one enantiomer in crystals of $[(PtMe_3)_2(\mu\text{-1-MeSCy-1}\kappa N^3\text{,1:2}\kappa^2 S)_2][BF_4]_2$ (**3** · 1.5 C_6H_6). The displacement ellipsoids are drawn at the 30 % probability level.

*Crystal structure of $[(PtMe_3)_2(\mu\text{-1-MeSCy-1}\kappa N^3\text{,1:2}\kappa^2 S)_2][BF_4]_2$ (**3** · 1.5 C_6H_6)*

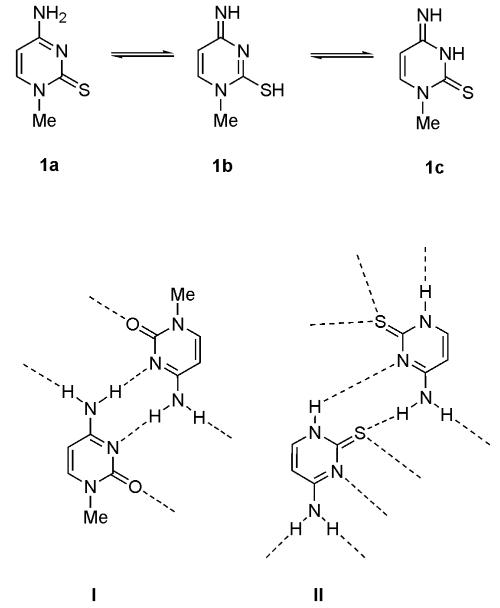
Colorless crystals of **3** · 1.5 C_6H_6 were obtained from acetone solutions layered with benzene and ether. The complex crystallizes as the racemate in the space group $P2_1/c$. The crystals consist of the dinuclear cation $[(PtMe_3)_2(\mu\text{-1-MeSCy-1}\kappa N^3\text{,1:2}\kappa^2 S)_2]^{2+}$, two $[BF_4]^-$ anions and one and a half benzene solvate molecules. The molecular structure of the cation of one enantiomer is shown in Fig. 5. Selected bond lengths and angles are given in Table 4. The primary donor sets of the octahedrally coordinated platinum atoms $[PtC_3NS_2]$ are built up of three methyl ligands in *facial* arrangement and two μ-1-methyl-2-thiocytosine-1κN^3,1:2$\kappa^2 S$ ligands. The central $[Pt_2(\mu\text{-}S)_2]$ core is slightly hinged (Pt1–S1···S2–Pt2: 168.2°). The two 1-methyl-2-thiocytosine ligands are arranged face-to-face, with the dinuclear molecule exhibiting C_2 symmetry in rough approximation. The distance between the heterocyclic ligands (3.4 Å) as well as the angle between the centroid-centroid vector and the ring normal (10.4°) indicate stabilization through π-π stacking [19]. The chelating coordination of the 1-methyl-2-thiocytosine ligands leads to the formation of strained four-membered rings (S2–Pt1–N4 66.0(1)°; S1–Pt2–N1 65.4(1)°), giving rise to greater deviations from the ideal octahedral coordination of the platinum atom. Moreover, the coordination of the sulfur atom to the platinum atom leads to a slight elongation of the S1–C7 and S2–C12 bonds (1.737(7)/1.726(7) Å) compared to the respective bond lengths in **1** (1.702(3)/1.692(3) Å). In accordance with the high *trans* influence of the methyl ligands [25] the bridging Pt–S bonds (2.501(2)–2.551(2) Å) are rather long (median: 2.490 Å, lower/upper quartile: 2.477/2.513 Å, for 41 observations [17]) but comparable to those in other dinuclear sulfur-bridged platinum(IV) complexes with *trans* methyl ligands (2.465(2)–2.551(1) Å) [26].

Inspection of the packing motif in crystals of **3** · 1.5 C_6H_6 reveals π-π interactions between the heterocyclic ring N1, N2, C7–C10 and one benzene ring (centroid-centroid distance: 3.6 Å; angle between the centroid-centroid vectors and the ring normals: 23.4°). Furthermore, there are cation-anion interactions formed through N–H···F and C–H···F hydrogen bonds, involving the fluorine atoms of the $[BF_4]^-$ anions.

Conclusions

The possible tautomers of 1-methyl-2-thiocytosine, namely the thione-amino form (**1a**) as the most stable tautomer both in the gas and aqueous phase, the imino-thiol tautomer (**1b**) and the imino-thione tautomer (**1c**) are shown in Scheme 2 [8]. In the present investigations it has been demonstrated that the tautomer **1a** is also present in crystals of **1**. The same holds for the molecular structures of thiocytidine [27] and 2-thiocytosine [10], as shown by previous X-ray diffraction analyses.

The hydrogen bonding pattern in crystals of 1-MeSCy (**1**) was found to be very similar to that in 1-methylcytosine crystals (1-MeCy, see Formula **I** in Scheme 2) [13, 14]. The oxygen analog also forms centrosymmetric dimers through two identical N4–H···N3′ hydrogen bonds. These dimeric units are connected through N4–H···O hydrogen bonds forming ribbons. In crystals of the non-methylated 2-thiocytosine a more complex hydrogen bonding pattern was observed (see Formula **II** in Scheme 2), which is completely different from that in 1-MeSCy (**1**). The central unit is also a dimer, but the two halves are linked unsymmetrically through N1–H···N3′ and N4′–H···S hydrogen bonds. Further weaker N–H···N and N–H···S hydrogen bonds are connecting the dimers yielding ribbons [10].



Scheme 2.

Apart from the $[PtMe_3(bpy)(1\text{-MeSCy-}\kappa S)][BF_4]$ complex reported by us [12], the new compound $[(PtMe_3)_2(\mu\text{-1-MeSCy-1}\kappa N^3\text{,1:2}\kappa^2 S)_2][BF_4]_2$ (**3**) is the first transition metal complex containing 1-methyl-2-thiocytosine ligands. By contrast, a large number of transition metal complexes with the oxygen analog 1-methylcytosine (1-MeCy) are known [28]. In its platinum(II) complexes predominantly N3 coordination is observed [29], and frequently an additional coordination of N4 of the monodeprotonated 1-methylcytosinato ligands to another Pt or Pd center gives rise to the formation of complexes having bridging μ-1-MeCy-1κN^3,2κN^4 ligands [30]. On the other hand, a chelating coordination through N3 and O (1-MeCy-κN^3,κO ligands) in 1-methylcytosine metal complexes analogous to that in complex **3** is rare [31].

The heterocyclic rings in **3** have been found to be in a face-to-face arrangement, as in the neutral dinuclear complexes of the type $[(PtMe_3)_2(\mu$-S^N-

$1\kappa N,1{:}2\kappa^2S)_2]$ [26], with the geometrical parameters (Pt–S and C–S bond lengths, Pt1–S1···S2–Pt2 dihedral angle, π–π stacking) in the same order of magnitude. Thus, the synthesis of $[(\mathrm{PtMe_3})_2(\mu$-1-MeSCy-$1\kappa N^3,1{:}2\kappa^2S)_2][\mathrm{BF_4}]_2$ (**3**) has provided another example of the versatile coordination modes of thionucleobase models.

Experimental Section

General considerations

The synthesis of $[(\mathrm{PtMe_3})_2(\mu$-1-MeSCy-$1\kappa N^3$,-$1{:}2\kappa^2S)_2][\mathrm{BF_4}]_2$ (**3**) was performed under argon using standard Schlenk techniques. Acetone was dried over phosphorus pentoxide. Benzene and diethyl ether were dried over Na benzophenone. All solvents were distilled prior to use. NMR spectra were obtained with Varian UNITY 500 and Gemini 2000 spectrometers using solvent signals (^{1}H and ^{13}C-NMR spectroscopy) as internal references and $\mathrm{Na_2[PtCl_6]}$ ($\delta(^{195}\mathrm{Pt}) = 0$ ppm) as external reference. IR spectra were recorded on a Galaxy Mattson FT IR spectrometer, using KBr pellets. Microanalyses were performed by the University of Halle microanalytical laboratory using a CHNS-932 (LECO) instrument. The ESI mass spectrum was obtained on a Finnigan LCQ spectrometer (Thermo Electron Corp.) using a 10^{-5} M solution of the complex in acetone under the following conditions: flow 8 μL/min, positive ion polarity mode, ESI spray voltage 4.1 kV; capillary temperature 200 °C; capillary voltage 34 V; tube lens offset 10 V; sheath gas $\mathrm{N_2}$; damping gas He. The CID experiments were carried out in the mass analyzer region with use of He as the collision gas and by applying a resonance excitation RF voltage (varying from 0 to 5 V, peak-to-peak). The masses, charge states and isotopic envelopes of the parent and fragment ions (CID) were established by applying the zoom-scan mode (high resolution < 0.2, 10 a. m. u. width). 1-Methyl-2-thiocytosine (**1**) [32] and $[(\mathrm{PtMe_3I})_4]$ [33] were prepared according to the literature. All other chemicals were purchased from commercial sources.

*Spectroscopic characterization of 1-methyl-2-thiocytosine (**1**) and synthesis of $[(\mathrm{PtMe_3})_2(\mu$-1-MeSCy-$1\kappa N^3,1{:}2\kappa^2S)_2][\mathrm{BF_4}]_2$ (**3**)*

*1-Methyl-2-thiocytosine (**1**)*

Yield: 1.2 g (70 %). – ^{1}H-NMR (400 MHz, $\mathrm{CD_3OD}$): $\delta = 7.73$ (d, $^3J_{\mathrm{H,H}} = 7.3$ Hz, 1H, H6), 6.09 (d, $^3J_{\mathrm{H,H}} = 7.3$ Hz, 1H, H5), 3.72 (s, 3H, NCH_3). – ^{1}H-NMR (400 MHz, [D$_6$]DMSO): $\delta = 7.81$ (d, $^3J_{\mathrm{H,H}} = 7.3$ Hz, 1H, H6), 7.48 (s, br, 1H, NH_2), 7.41 (s, br, 1H, NH_2), 5.98 (d, $^3J_{\mathrm{H,H}} = 7.3$ Hz, 1H, H5), 3.59 (s, 3H, NCH_3). – ^{13}C-NMR (100 MHz, [D$_6$]DMSO): $\delta = 180.6$ (C2), 160.5 (C4), 146.8 (C6), 97.0 (C5), 43.3 (C1). – $\mathrm{C_5H_7N_3S}$ (141.04): calcd. C 42.54, H 5.00, N 29.79; found C 42.55, H 5.29, N 29.31.

Table 5. Crystal data, data collection and refinement parameters of 1-MeSCy (**1**) and $[(\mathrm{PtMe_3})_2(\mu$-1-MeSCy-$1\kappa N^3,1{:}2\kappa^2S)_2][\mathrm{BF_4}]_2$ ($\mathbf{3}\cdot 1.5\ \mathrm{C_6H_6}$).

	1	$\mathbf{3}\cdot 1.5\ \mathrm{C_6H_6}$
Empirical formula	$\mathrm{C_5H_7N_3S}$	$\mathrm{C_{25}H_{41}B_2F_8N_6Pt_2S_2}$
Formula weight	141.20	1053.56
Crystal system/	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
Z	8	4
a, Å	5.9919(8)	10.2340(5)
b, Å	19.343(3)	35.854(2)
c, Å	11.293(7)	9.9832(5)
β, deg	99.14(1)	107.701(6)
V, Å^3	1292.3(8)	3489.7(3)
ρ, g cm^{-3}	1.44	2.01
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	0.4	8.2
$F(000)$, e	592	2012
Scan range, deg	$2.11 \le \theta \le 25.03$	$2.09 \le \theta \le 26.02$
Reciprocal lattice segment *hkl*	$\pm 7, +23, -8 \rightarrow 13$	$\pm 12, \pm 44, -11 \rightarrow 12$
Refl. collected	2473	18975
Refl. independent / R_{int}	2252 / 0.0580	6517 / 0.0675
Data / parameters	2252 / 220	6517 / 413
R_1/wR_2 $[I \ge 2\sigma(I)]$	0.0407 / 0.0943	0.0338 / 0.0670
R_1/wR_2 (all data)	0.0602 / 0.1080	0.0581 / 0.0732
Goodness-of-fit on F^2	1.094	0.934
Largest diff. peak / hole, e Å^{-3}	0.20 / −0.18	1.09 / −0.78

*$[(\mathrm{PtMe_3})_2(\mu$-1-MeSCy-$1\kappa N^3,1{:}2\kappa^2S)_2][\mathrm{BF_4}]_2$ (**3**)*

A suspension of $[(\mathrm{PtMe_3I})_4]$ (50.0 mg, 0.04 mmol) and Ag[BF$_4$] (27.0 mg, 0.14 mmol) in acetone (10 mL) was stirred for 30 min in the absence of light. Silver iodide was removed by filtration, and the clear, colorless filtrate was added directly to 1-methyl-2-thiocytosine (19.3 mg, 0.14 mol). After stirring for 2 h the volume was reduced *in vacuo* to 1 mL, and ether (3 mL) was added. The colorless precipitate was isolated, washed with pentane (2 × 2 mL) and dried *in vacuo*. Yield: 72 mg (56 %). IR (KBr): $\nu = 3454$ m, 3352 m, 3111 w, 2961 w, 2899 m, 1792 w, 1650 s, 1537 m, 1506 s, 1400 m, 1368 m, 1215 m, 1081 s, 821 w cm^{-1}. – ^{1}H-NMR (500 MHz, $\mathrm{CD_3OD}$, r. t.): $\delta = 7.98$ (d, $^3J_{\mathrm{H,H}} = 7.5$ Hz, 2H, $H6/H6'$), 6.53 (d, $^3J_{\mathrm{H,H}} = 7.5$ Hz, $^4J_{\mathrm{Pt,H}} = 11.6$ Hz, 2H, $H5/H5'$), 3.64 (s, 6H, NCH_3, NCH_3'), 1.22 (s+d, $^2J_{\mathrm{Pt,H}} = 75.5$ Hz, 18H, Pt(CH_3)$_3$). – ^{1}H-NMR (500 MHz, $\mathrm{CD_3OD}$, −50 °C): $\delta = 8.05$ (d, $^3J_{\mathrm{H,H}} = 7.5$ Hz, 2H, $H6/H6'$), 6.53 (d, $^3J_{\mathrm{H,H}} = 7.5$ Hz, 2H, $H5/H5'$), 3.63 (s, 6H, NCH_3, NCH_3'), 1.194 (s+d, $^2J_{\mathrm{Pt,H}} = 81.5$ Hz, 6H, PtCH_3), 1.189 (s+d, $^2J_{\mathrm{Pt,H}} = 74.7$ Hz, 6H, PtCH_3). – ^{13}C-NMR (125 MHz, $\mathrm{CD_3OD}$): $\delta = 184.4$ ($C2$), 160.4 ($C4$), 147.8 ($C6$), 101.8 ($C5$), 40.7 (NCH$_3$), −7.3 (s+d, br, Pt(CH$_3$)$_3$). – ^{195}Pt-NMR (107 MHz, $\mathrm{CD_3OD}$): $\delta = -2318.4$. – MS ((+)-ESI): m/z (%) = 761 (62) $[(\mathrm{PtMe_3})_2(1\text{-MeSCy})(1\text{-MeSCy}_{-\mathrm{H}})]^+$, 381 (100) $[(PtMe_3)(1\text{-}MeSCy)]^+$. – $C_{16}H_{34}B_2F_8N_6S_2Pt_2$ (938.16): calcd. C 20.47, H 3.65, N 8.96; found C 20.13, H 4.13, N 8.74.

X-Ray crystallography

Single crystals of **1** and **3** · 1.5 C_6H_6, suitable for X-ray diffraction measurements, were obtained by recrystallization from ethanol (**1**) and acetone/benzene (**3** · 1.5 C_6H_6). Intensity data were collected on a STADI (**1**) and a Stoe IPDS diffractometer (**3** · 1.5 C_6H_6) with MoK_α radiation (λ = 0.71073 Å, graphite monochromator) at 293(2) K (**1**) and 220(2) K (**3** · 1.5 C_6H_6). A summary of the crystallographic data, the data collection parameters and the refinement parameters is given in Table 5. A numerical absorption correction was applied for **3** · 1.5 C_6H_6 ($T_{\min}/T_{\max}$ = 0.24 / 0.58). The structures were solved by Direct Methods with SHELXS-97 [34] and refined using full-matrix least-squares routines against F^2 with SHELXL-97 [34]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms in 1-MeSCy (**1**) were found in the difference Fourier map and refined freely, whereas the hydrogen atoms in **3** · 1.5 C_6H_6 were positioned geometrically and refined with isotropic displacement parameters according to the "riding model".

CCDC 761534 and CCDC 761535 contain the supplementary crystallographic data for compounds **1** and **3** · 1.5 C_6H_6. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Quantum-chemical calculations

All DFT calculations were carried out by the GAUSSIAN03 program package [35] using the hybrid functional B3LYP [36] and the basis sets 6-31++G(d,p) as implemented in the GAUSSIAN program. All systems were fully optimized. For the monomeric molecule no symmetry restrictions were applied, whereas the dimeric and tetrameric molecules were calculated in C_i symmetry. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of the normal vibrations. Basis set superposition errors (BSSE) were estimated with counterpoise-type calculations [37].

Supplementary Information

Tables of Cartesian coordinates of atom positions calculated for the equilibrium structures of the monomer **1m**, the hydrogen-bonded dimer **1d** and tetramer **1t** (available online only).

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Supplementary Material to

Structural and Computational Studies of 1-Methyl-2-thiocytosine and its Coordination Mode in a Dinuclear Platinum(IV) Complex $[(PtMe_3)_2(\mu\text{-}1\text{-}MeSCy\text{-}1\kappa N^3,1{:}2\kappa^2 S)_2][BF_4]_2$

Cornelia Vetter, Christoph Wagner, Ralph Kluge, Dirk Steinborn*

ENERGIES AND CARTESIAN COORDINATES OF ATOM POSITIONS OF CALCULATED MOLECULES

Calculation type: B3LYP/6-31++G**

1. 1-MeSCy (monomer) (1m)

File: MeSCy_03.out

E(RB+HF-LYP):	-757.223281659 a.u.
Zero-point vibrational energy:	77.68115 kcal/mol
Sum of electronic and thermal free energies:	-757.133187 a.u.

C	-1.99341800	1.57516600	0.00151800
N	-0.67316900	0.93742200	-0.00023600
C	-0.57309500	-0.47942100	-0.00096400
C	0.44747000	1.70766100	0.00054200
N	0.67171500	-1.02061900	0.00027600
S	-1.96100800	-1.42240800	0.00075100
C	1.69737700	1.16597000	-0.00065500
C	1.75694800	-0.26462400	-0.00175800
N	2.95751600	-0.90448400	-0.02657800
H	-2.55884400	1.26289500	-0.87876400
H	-2.55514100	1.26641700	0.88550100
H	-1.85522500	2.65829600	-0.00090800
H	2.58000200	1.79331900	-0.00662800
H	0.28820200	2.78020700	0.00090400
H	3.82054100	-0.40737100	0.11871100
H	2.95246400	-1.90998100	0.06284400

2. $(1\text{-MeSCy})_2$ (dimer of AA' type) (1d)

File: MeSCy_01.out and MeSCy_01bsse.out

E(RB+HF-LYP):	-1514.47877641 a.u.
Zero-point vibrational energy:	157.07258 kcal/mol
Sum of electronic and thermal free energies:	-1514.277264 a.u.
Counterpoise corrected energy:	-1514.477426867834 a.u.
Counterpoise BSSE energy:	0.001349544075 a.u. (0.847 kcal/mol)

C	-5.55121800	0.07138700	0.20016500
N	-4.19622000	0.04438600	-0.35949100
C	-3.07586100	0.04490800	0.49901500
C	-4.02065800	0.01870700	-1.71231500
N	-1.84765200	0.01847300	-0.06206300
S	-3.28779600	0.07802200	2.17435400
C	-2.78739400	-0.00724200	-2.28377900
C	-1.66397500	-0.00707700	-1.39010400
N	-0.40415800	-0.03179200	-1.84067400
H	-5.70874500	-0.79911500	0.84026700
H	-5.68567700	0.96655000	0.81054600
H	-6.26589500	0.06671700	-0.62500700
H	-2.66972300	-0.02731900	-3.35997600
H	-4.92713200	0.02026600	-2.30720600
H	-0.19315700	-0.05031300	-2.82579600
H	0.38449000	-0.03451200	-1.17551500
N	1.84765200	-0.01847300	0.06206300
C	3.07586100	-0.04490800	-0.49901500
C	1.66397500	0.00707700	1.39010400
N	4.19622000	-0.04438600	0.35949100
S	3.28779600	-0.07802200	-2.17435400
C	2.78739400	0.00724200	2.28377900
N	0.40415800	0.03179200	1.84067400
C	5.55121800	-0.07138700	-0.20016500
C	4.02065800	-0.01870700	1.71231500
H	2.66972300	0.02731900	3.35997600
H	0.19315700	0.05031300	2.82579600
H	-0.38449000	0.03451200	1.17551500
H	5.70874500	0.79911500	-0.84026700
H	5.68567700	-0.96655000	-0.81054600
H	6.26589500	-0.06671700	0.62500700
H	4.92713200	-0.02026600	2.30720600

3. (1-MeSCy)$_4$ (tetramer of BAA'B' type) (1t)

File: MeSCY_04neurechner.log and MeSCY_04neurechner_bsse.out

E(RB+HF-LYP) = -3028.95995843 a.u.
Zero-point vibrational energy: 315.38327 kcal/mol
Sum of electronic and thermal free energies: -3028.538912 a.u.
Counterpoise corrected energy: -3028.956639011027 a.u.
Counterpoise BSSE energy: 0.003403365256 a.u. (2.136 kcal/mol)

C	0.32431900	-5.41105500	1.50778400
N	0.31325800	-4.21518400	0.65924400
C	0.18938800	-2.93911500	1.22774600
C	0.43099300	-4.35197700	-0.69878300
N	0.16994100	-1.86297300	0.41363400
S	0.05421200	-2.78674900	2.91748400
C	0.41999700	-3.28379700	-1.53339400
C	0.27485200	-1.99460600	-0.92069300
N	0.23881100	-0.89409500	-1.68334500

H	1.16071900	-5.36869500	2.20847700
H	-0.59874600	-5.46836800	2.08795600
H	0.41817400	-6.28729400	0.86362600
H	0.52645600	-3.39801900	-2.60763000
H	0.53526100	-5.36633700	-1.06625300
H	0.31265200	-0.99958800	-2.69043200
H	0.15279600	0.04440100	-1.27589100
N	-0.36625400	-1.40178100	-4.74421300
N	-0.16994100	1.86297300	-0.41363400
C	0.48906300	-1.95588800	-5.63935700
C	-1.06017500	-0.30134700	-5.02856500
N	0.65539500	-1.31008100	-6.88176600
S	1.34935900	-3.36487300	-5.29523400
C	-0.90268500	0.38660900	-6.27243500
N	-1.95361000	0.13884400	-4.10538700
C	1.58180700	-1.86133800	-7.87653000
C	-0.02737500	-0.16209700	-7.15713900
H	-1.44508800	1.29362800	-6.50580700
H	-1.88239100	-0.30123200	-3.19559700
H	-2.11517000	1.13788700	-4.05738200
H	2.58970900	-1.91067100	-7.45960900
H	1.27873400	-2.87505700	-8.14597400
H	1.56792100	-1.21628600	-8.75692400
H	0.16592300	0.28367800	-8.12610900
C	-0.18938800	2.93911500	-1.22774600
C	-0.27485200	1.99460600	0.92069300
N	-0.31325800	4.21518400	-0.65924400
S	-0.05421200	2.78674900	-2.91748400
C	-0.41999700	3.28379700	1.53339400
N	-0.23881100	0.89409500	1.68334500
C	-0.32431900	5.41105500	-1.50778400
C	-0.43099300	4.35197700	0.69878300
H	-0.52645600	3.39801900	2.60763000
H	-0.31265200	0.99958800	2.69043200
H	-0.15279600	-0.04440100	1.27589100
H	-1.16071900	5.36869500	-2.20847700
H	0.59874600	5.46836800	-2.08795600
H	-0.41817400	6.28729400	-0.86362600
H	-0.53526100	5.36633700	1.06625300
N	0.36625400	1.40178100	4.74421300
C	-0.48906300	1.95588800	5.63935700
C	1.06017500	0.30134700	5.02856500
N	-0.65539500	1.31008100	6.88176600
S	-1.34935900	3.36487300	5.29523400
C	0.90268500	-0.38660900	6.27243500
N	1.95361000	-0.13884400	4.10538700
C	-1.58180700	1.86133800	7.87653000
C	0.02737500	0.16209700	7.15713900
H	1.44508800	-1.29362800	6.50580700
H	1.88239100	0.30123200	3.19559700
H	2.11517000	-1.13788700	4.05738200

H	-2.58970900	1.91067100	7.45960900
H	-1.27873400	2.87505700	8.14597400
H	-1.56792100	1.21628600	8.75692400
H	-0.16592300	-0.28367800	8.12610900