After removal of redundant and space group forbidden data, 3113 reflections were considered observed [$I > 3.0\sigma(I)$]. The structure was solved for heavy-atom positions with MULTAN80.[26] Initial refinement of heavy-atom positions was completed in centric space group $P2/a$. While locations for the oxo atoms, one acetate, and the methyl carbon atoms attached to tin were readily apparent from a difference Fourier synthesis and these positions were stable to refinement, the positioning of the remaining acetate group was not possible. Positions located failed to refine or refined to chemically unreasonable positions. When atomic coordinates were refined in the acentric cell Pa the positions of two acetate groups, unrelated by a center of symmetry, were clearly apparent. Thus refinement was completed in the acentric cell. However, the coordinates of the majority of the atoms of the asymmetric unit remain related by the removed center of symmetry, and thus problems of correlation of parameters complicate refinement. This difficulty appears in the temperature parameters for methyl groups of acetate ions and in bond distances involving these atoms. The positioning of tin and oxygen atoms appears well established. Successive least squares/difference Fourier cycles allowed location of the remainder of the non-hydrogen atoms. Refinement of scale factor, positional, and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. The use of the acentric space group, Pa, was justified by the noncentric relationship of carboxylates O31, O32, C31, C32 and O41, O42, C41, C42 (Table II) although the rest of the molecule is nearly centrosymmetric. Hydrogen positions were not apparent from a difference Fourier synthesis calculated after final anisotropic refinement of all non-hydrogen parameters. The final cycle of refinement [function minimized $\sum(|F_o| - |F_c|)^2$] led to a final agreement factor, $R = 4.7\%$, $R = (\sum||F_o| - |F_c||)/\sum|F_o|100$. Anomalous dispersion corrections were made for Sn. Scattering factors were taken from Cromer and Mann.[27] Unit weights were used until the final cycles of refinement when a weight $= 1/\sigma F$ was applied; $R_w = 5.4$. Tables of anisotropic thermal parameters, F_o, and F_c and calculated equations of planes are available as supplementary material.

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(27) Cromer, D. T.; Mann, I. B. *Acta Crystallogr.* **1968**, *A24*, 321.

Registry No. $Me_2Sn(OAc)_2$, 13293-57-7; $Me_2Sn(laurate)_2$, 5926-79-4; $[Me_2Sn(OAc)]_2O$, 2179-99-9.

Supplementary Material Available: Tables of anisotropic thermal parameters and calculated equations of planes (3 pages); tables of F_o and F_c (23 pages). Ordering information is given on any current masthead page.

Metal-Stabilized Rare Tautomers of Nucleobases. 1. Iminooxo Form of Cytosine: Formation through Metal Migration and Estimation of the Geometry of the Free Tautomer

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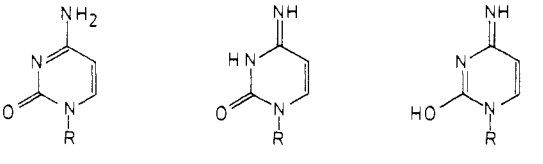
Abstract: A way is presented according to which the geometry of rare nucleobase tautomers is estimated by (i) preparing metal complexes of the rare tautomers, (ii) determining the crystal structure of the metal complex as accurately as possible, and (iii) "subtracting" the effect of the metal on the ligand geometry. The preparation, crystal structures, and spectroscopic (^{1}H NMR, Raman) properties of two modifications of a complex of Pt^{IV} with the model nucleobase 1-methylcytosine (1-MeC), *trans,trans,trans*-$[Pt(NH_3)_2(OH)_2(C_5H_7N_3O)_2](NO_3)_2\cdot 2H_2O$, is reported. In the two compounds, neutral 1-MeC ligands are coordinated to Pt through the deprotonated exocyclic N4′ positions with N3 protonated. Thus the 1-MeC ligands are in the rare iminooxo tautomer form of cytosine. **5a** crystallizes in the triclinic space group $P\bar{1}$ with $a = 5.819$ (2) Å, $b = 7.178$ (2) Å, $c = 13.626$ (7) Å, $\alpha = 90.72$ (4)°, $\beta = 105.82$ (3)°, $\gamma = 94.02$ (8)°, $V = 545.9$ Å^3, and $Z = 1$. **5b** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.892$ (1) Å, $b = 11.496$ (1) Å, $c = 11.010$ (1) Å, $\beta = 100.05$ (2)°, $V = 1108.2$ Å^3, and $Z = 2$. The structures were refined to $R = 0.020$, $R_w(F) = 0.020$ in **5a** and $R = 0.040$, $R_w(F) = 0.045$ in **5b** on the basis of 1911 (**5a**) and 2525 (**5b**) independent reflections. The geometries of the 1-MeC ligands in **5a** and **5b** differ from that of the normal, uncomplexed 1-MeC tautomer with significant differences in C4–N4′ and N1–C2 bond lengths (shorter in **5**), in N3–C4 and C2–N3 bond lengths (longer in **5**), as well as in ring angles at positions 2, 3, and 4. The effect of Pt^{IV} on the geometry of the cytosine ring is suggested to be minimal and essentially restricted to the exocyclic imino group by slightly lengthening the C4–N4′ bond. Formation of **5** occurs in three distinct steps, all of which have been detected in solution, and the respective species have been isolated: (i) Pt coordination via N3, (ii) chelate formation through N3 and N4′ with elimination of H_2O from the complex, and (iii) addition of H_2O to the complex with reformation of Pt–OH and opening of the Pt–N3 bond. The acidity of the rare 1-MeC tautomer in its Pt^{IV} complexed form (deprotonation at N3) has been determined as ca. 5.8 (pK_{a1}) and 8.2 (pK_{a2}).

The rare tautomers of the naturally occurring nucleobases have been the subject of numerous studies, both with respect to their possible biological role in base-mispairing and mutagenesis,[2] and their physical properties such as relative energy, geometry, acidity, etc.[3] Apart from detection problems of rare tautomers present in proportions lower than 10^{-4}, a major difficulty with quantum-mechanical calculations on relative energies of tautomers represents the geometry approximation used for the respective tautomer.[4]

Chart I



I II III

(1) (a) Universität Freiburg. (b) Universität Ulm.
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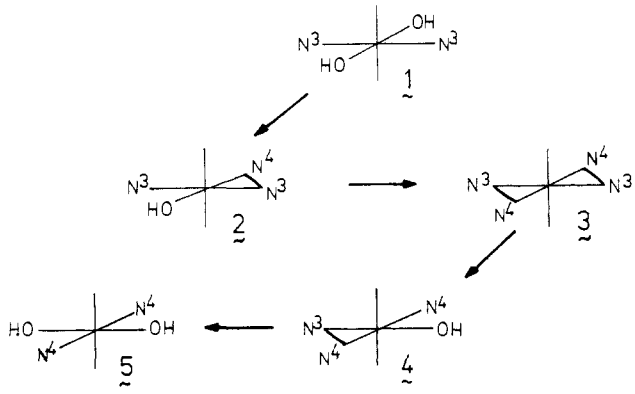
0002-7863/86/1508-6616$01.50/0

Scheme I



Dealing with metal complexes of nucleobases provides an opportunity to isolate rare tautomers in metal-complexed form and, by accounting for the effect of the metal on the ligand geometry, estimate the geometry of the free tautomer to a good approximation.

In an earlier report,[5] we have described the formation of a complex of *cis*-$(NH_3)_2Pt^{II}$ containing the rare iminol tautomer of 1-methylthymine via the reaction sequence (i) N3 deprotonation, (ii) N3 platinum coordination, and (iii) protonation of the anionic ligand at O4. The corresponding complex of 1-methyluracil has recently been characterized by ourselves using X-ray crystallography, as we shall report shortly.[6]

In this paper we describe the formation and the crystal structures of two modifications of a Pt^{IV} complex containing one of the two possible rare cytosine tautomers, the iminooxo form II (Chart I). N1-substituted cytosines can exist in three tautomeric forms, the aminooxo form I, which by far is the preferred species in the solid state, in solution, and in the nucleic acids,[7] the iminooxo form II, estimated to coexist with I in proportions of 10^{-4}–10^{-5},[8] and the iminohydroxo form III, the abundance ratio of which appears to be uncertain. Formation of the title complex *trans,trans,trans*-$[Pt(NH_3)_2(OH)_2(1\text{-MeC-}N^4)_2](NO_3)_2\cdot 2H_2O$ takes place in three distinct steps (i–iii) (Scheme I), two of which (i, ii) have already been described:[9] (i) Pt binding to N3 of 1-MeC (**1**), (ii) intramolecular condensation between a Pt–OH group and $NH_2(4)$ of the 1-MeC ligand, leading to chelate formation through N3 and N4 (**2**, **3**), and (iii) addition of H_2O with cleavage of the Pt–N3 bond and reformation of Pt–OH (**4**, **5**). The described linkage isomerization thus represents a text book example of a metal migration process with starting compound, intermediate, and final product isolated and fully characterized.

Metal binding to the N4 position of cytosine nucleobases has occasionally been observed before, usually in conjunction with simultaneous N3 metalation.[10] There are only few well-established cases with metal ($(NH_3)_5Ru^{3+}$, CH_3Hg^+) binding exclusively through N4 of the *deprotonated* cytosine ligands.[11] The possibility of protonating such species at N3 has been pointed out.[11b]

Table I. Crystallographic Data of **5a** and **5b**

compound	**5a**	**5b**
f_w	673.47	673.47
space group	$P\bar{1}$	$P2_1/c$
a, Å	5.819 (2)	8.892 (1)
b, Å	7.178 (2)	11.496 (1)
c, Å	13.626 (7)	11.010 (1)
α, deg	90.72 (4)	90
β, deg	105.82 (3)	100.05 (2)
γ, deg	94.02 (8)	90
V, Å^3	545.9	1108.2
Z	1	2
d_{calcd}	2.009	2.018
d_{measd}	1.98	2.00
cryst size, mm	0.1 × 0.2 × 0.4	0.3 × 0.5 × 0.5
μ, cm^{-1}	62.3	61.4
θ_{range}, deg	2–25	2–28
no. of unique refl	1911	2669
no. of refl used	1911	2525
in the calcltns no. of params		$F_o > \sigma F_o$
	151	151
R	0.020	0.040
R_w(F)	0.020	0.045

Experimental Section

Preparation. *trans,trans,trans*-$[Pt(NH_3)_2(OH)_2(1\text{-MeC-}N^4)_2](NO_3)_2\cdot 2H_2O$ was obtained in two modifications, **5a** and **5b**, by keeping an aqueous solution of *trans,trans,trans*-$[Pt(NH_3)_2(OH)_2(1\text{-MeC-}N^3)_2](NO_3)_2$ (**1**)[9] (330 mg in 5 mL of H_2O, pH 4.3, stoppered flask) for 40–50 h at 70–80 °C. During this time, the solution changed from colorless via intensely yellow to finally pale yellow with no change in pH. Cooling the resulting solution to 3 °C or slow evaporation gave 205 mg of **5a** (colorless columns) and, at a later stage, 40 mg of **5b** (colorless cubes). Occasionally, and especially with shorter reaction times, yellow crystals of the bis(chelate) **4** were isolated as well. ^1H NMR studies showed that the interconversion of **3** → **5** is practically quantitative after 4 h at 100 °C. Anal. Calcd for $[Pt(NH_3)_2(OH)_2(C_5H_7N_3O)_2](NO_3)_2\cdot 2H_2O$ (**5a**): C, 17.83; H, 3.90; N, 20.80; Pt, 28.96. Found: C, 17.65; H, 3.99; N, 20.97; Pt, 29.0. No elemental analysis was performed for **5b** which was identical with **5a** according to its IR spectrum, as verified by the X-ray structure determination.

Attempts to replace the OH ligands in **5a** by Cl^- through HCl treatment (50 mg of **5a** in 3 mL of 1 N HCl, 5 min at 85 °C, cooling to 22 °C) were unsuccessful and gave the colorless chloride analogue of **5** only (no Pt–Cl stretching mode in the IR). Anal. Calcd for $[Pt(NH_3)_2(OH)_2(C_5H_7N_3O)_2]Cl_2\cdot 2H_2O$ (**5c**): C, 19.36; H, 4.23; N, 18.06; Cl, 11.43. Found: C, 19.95; H, 4.21; N, 18.15; Cl, 11.16.

Instruments used for the spectroscopic studies (IR, Raman, and ^1H NMR) and the potentiometric titration were as previously reported.[12]

Crystallography. The X-ray measurements were carried out at room temperature by using a Philips PW-1100 single crystal diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Crystal data and experimental details are summarized in Table I. The cell dimensions for **5a** were calculated from 22 reflections ($15° < \theta < 22°$) and for **5b** from 12 reflections ($16° < \theta < 20°$) centered on the diffractometer. Intensities were measured by using $\theta/2\theta$ scans. Lp and (in a later stage) empirical absorption corrections were applied by using the program of Walker and Stuart.[13] The coordinates of the Pt atoms were taken from a three-dimensional Patterson map. The other non-hydrogen atoms were localized by subsequent ΔF syntheses. With **5a** all hydrogen atoms were localized. They were included in the F_c calculations but not refined. In **5b** some of the hydrogen atoms were found from the ΔF map. They were ignored during the structure determination, however. The non-hydrogen atoms were refined with anisotropic thermal parameters. Atomic parameters and the equivalent isotropic temperature factors (calculated from the U_{ij} values by $U_{eq} = {}^1/_3\Sigma_i\Sigma_j a_i^* a_j^* \mathbf{a}_i\mathbf{a}_j$) for **5a** are given in Table II (for hydrogen atoms an isotropic temperature factor of 0.08 was assumed), those for **5b** in Table III. Complex scattering factors for neutral atoms were taken from ref 14 and 15. For the calculations, the SHELX program package[16] was used.

(4) See, e.g.: (a) ref 3, pp 221–230 and literature cited. (b) Czerminski, R.; Lesyng, B.; Pohorille, A. *Int. J. Quantum Chem.* **1979**, *16*, 605, 1141.
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(6) Lippert, B.; Schöllhorn, H.; Thewalt, U., to be submitted for publication.
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(8) (a) Reference 3, p 211. (b) Morita, H.; Nagakura, S. *Theor. Chim. Acta* **1968**, *11*, 279.
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(10) (a) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 1111. (b) Prizant, L.; Rivest, R.; Beauchamp, A. L. *Can. J. Chem.* **1981**, *59*, 2290. (c) Häring, U. K.; Martin, R. B. *Inorg. Chim. Acta* **1983**, *78*, 259. (c) Charland, J. P.; Simard, M.; Beauchamp, A. L. *Inorg. Chim. Acta* **1983**, *80*, L57. (d) McConnell, B. *J. Am. Chem. Soc.* **1982**, *104*, 1723.
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(12) See, e.g.: (a) Raudaschl-Sieber, G.; Lippert, B. *Inorg. Chem.* **1985**, *24*, 2426. (b) Schöllhorn, H.; Raudaschl-Sieber, G.; Müller, G.; Thewalt, U.; Lippert, B. *J. Am. Chem. Soc.* **1985**, *107*, 5932. (c) Reference 9b.
(13) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.
(14) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.
(15) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Table II. Positional Parameters and Temperature Factors (Å²) for **5a**

atom	x	y	z	u
		Cation		
Pt	0.0000 (0)	0.0000 (0)	0.0000 (0)	0.016 (1)
N10	0.2312 (5)	−0.2073 (4)	0.0169 (2)	0.026 (2)
O10	0.2806 (4)	0.1850 (3)	0.0106 (2)	0.024 (2)
N1	0.5441 (6)	0.2581 (5)	0.3859 (2)	0.031 (2)
C1′	0.7417 (10)	0.3447 (8)	0.4695 (3)	0.048 (4)
C2	0.5598 (7)	0.2793 (5)	0.2880 (3)	0.027 (3)
O2′	0.7300 (5)	0.3627 (4)	0.2678 (2)	0.040 (2)
N3	0.3686 (6)	0.1978 (4)	0.2129 (2)	0.026 (2)
C4	0.1816 (6)	0.0917 (5)	0.2291 (2)	0.022 (2)
N4′	0.0230 (5)	0.0096 (4)	0.1512 (2)	0.023 (2)
C5	0.1717 (7)	0.0758 (5)	0.3318 (3)	0.028 (3)
C6	0.3526 (8)	0.1604 (5)	0.4055 (3)	0.030 (3)
H1	0.2158 (0)	0.2803 (0)	−0.0352 (0)	
H2	0.3074 (0)	−0.2270 (0)	0.0840 (0)	
H3	0.1488 (0)	−0.3134 (0)	−0.0209 (0)	
H4	0.3726 (0)	−0.1706 (0)	−0.0033 (0)	
H5	0.7540 (0)	0.4907 (0)	0.4549 (0)	
H6	0.7128 (0)	0.3079 (0)	0.5360 (0)	
H7	0.9137 (0)	0.2775 (0)	0.4714 (0)	
H8	0.3642 (0)	0.2200 (0)	0.1425 (0)	
H9	−0.1019 (0)	−0.0571 (0)	0.1595 (0)	
H10	0.0460 (0)	−0.0191 (0)	0.3428 (0)	
H11	0.3612 (0)	0.1564 (0)	0.4797 (0)	
		Nitrate Anion		
N20	0.5582 (6)	0.7561 (5)	0.2856 (2)	0.032 (3)
O20	0.5951 (7)	0.8051 (6)	0.2039 (2)	0.053 (3)
O21	0.3722 (6)	0.6595 (5)	0.2856 (3)	0.053 (3)
O22	0.7052 (7)	0.8071 (7)	0.3670 (2)	0.059 (4)
		Water		
O30	0.0554 (6)	0.4682 (4)	−0.1295 (2)	0.039 (2)
H12	0.0329 (0)	0.5147 (0)	−0.1747 (0)	
H13	−0.0691 (0)	0.4190 (0)	−0.1791 (0)	

Table III. Positional Parameters and Temperature Factors (Å²) for **5b**

atom	x	y	z	U
		Cation		
Pt	0.5000 (0)	0.5000 (0)	0.5000 (0)	0.016 (1)
O10	0.4406 (4)	0.6684 (2)	0.4816 (2)	0.024 (2)
N10	0.2909 (5)	0.4723 (4)	0.5475 (4)	0.026 (3)
N1	0.1730 (4)	0.6633 (3)	0.0533 (3)	0.027 (3)
C1′	0.0739 (5)	0.7338 (4)	−0.0393 (4)	0.034 (4)
C2	0.2313 (4)	0.7110 (3)	0.1645 (4)	0.022 (3)
O2′	0.2114 (4)	0.8137 (2)	0.1904 (3)	0.029 (2)
N3	0.3171 (3)	0.6396 (3)	0.2515 (3)	0.021 (2)
C4	0.3446 (6)	0.5250 (4)	0.2311 (5)	0.023 (3)
N4′	0.4214 (4)	0.4619 (4)	0.3209 (3)	0.024 (3)
C5	0.2854 (9)	0.4767 (5)	0.1133 (6)	0.034 (5)
C6	0.2031 (6)	0.5487 (4)	0.0292 (4)	0.031 (4)
		Nitrate Anion		
N20	0.2396 (5)	0.3042 (3)	−0.1833 (4)	0.035 (3)
O20	0.2701 (4)	0.2655 (3)	−0.0775 (3)	0.041 (3)
O21	0.3302 (6)	0.2882 (3)	−0.2550 (4)	0.057 (4)
O22	0.1171 (5)	0.3544 (4)	−0.2179 (4)	0.071 (5)
		Water		
O30	−0.0484 (4)	0.5415 (4)	0.6657 (4)	0.052 (4)

Results and Discussion

Formation and Spectroscopic Properties. Formation of the complex **5** was initially observed while studying the solution behavior of *trans,trans,trans*-$[Pt(NH_3)_2(OH)_2(1\text{-MeC-}N^3)_2](NO_3)_2$, **1**. As previously described,[8b] brief warming of an aqueous solution of **1** leads to formation of **2** and **3**. As has now been found, prolonged warming of **1** or heating of **3** gives new ^1H NMR resonances which unambiguously can be assigned to complex **5** containing 1-MeC ligands platinated at N4. The chemical shifts

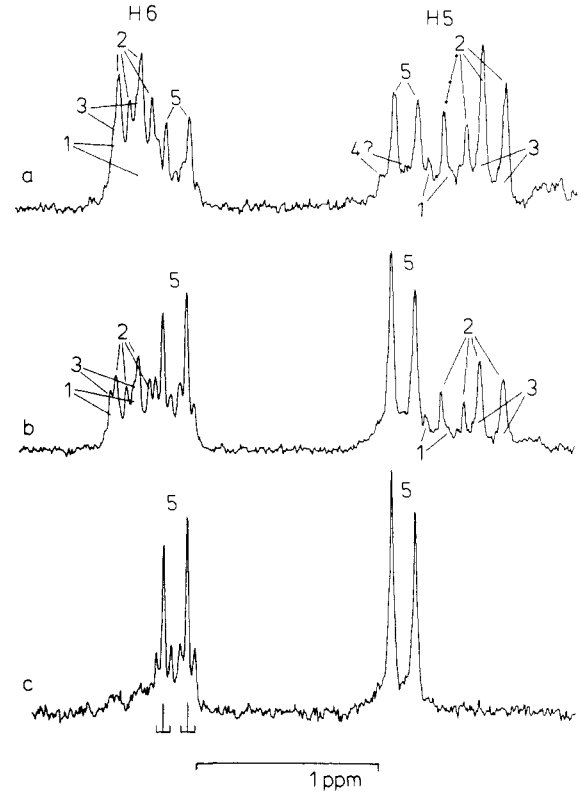
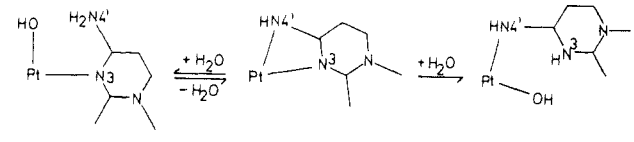


Figure 1. ^1H NMR spectra (D_2O, H5, and H6 resonances only) of the bis(chelate) **3** (20 mg/0.5 mL). (a) After 50 min at 100 °C the mixture contains predominantly **2**, followed by **5**, **3**, **1**, and possibly **4**. (b) After 2.5 h at 100 °C **5** is the major compound in the mixture, followed by **2**, **3**, and **1**. (c) After 4 h at 100 °C the solution contains exclusively compound **5**. Heating of an aqueous solution of **1** eventually leads to **5** as the exclusive product as well.

Scheme II



(D_2O) of **5** with respect to species **1**, **2**, and **3**[8b] are as follows: H5 highest downfield (δ 6.16 ppm) with unresolved ^{195}Pt coupling ($^4J \leq 2$ Hz), H6 highest upfield (δ 7.41 ppm) with well resolved ^{195}Pt coupling ($^5J = 4.4$ Hz), CH_3 almost unchanged (δ 3.38 ppm). In Me_2SO-d_6, shifts of **5** are somewhat different (CH_3, 3.29; H5, 6.11; H6, 7.50). The resonance at 7.26 ppm with ^{195}Pt satellites ($J = 12.5$ Hz) is tentatively assigned to N(4′)H. Protons due to OH, NH_3, N(3)H, and H_2O are not observed individually but rather give rise to an averaged, broad, and unresolved resonance around 5.7 ppm. As can be seen from Figure 1, the bis(chelate) **3** equilibrates initially with **2** and **1** but eventually gives the thermodynamically most stable endproduct **5**

$$\mathbf{1} \rightleftharpoons \mathbf{2} \rightleftharpoons \mathbf{3} \rightleftharpoons \mathbf{4} \rightarrow \mathbf{5}$$

Thus, although chelate opening takes place in two different ways in the beginning (Scheme II), the equilibrium is shifted toward the most stable product **5**. The expected intermediate **4**, containing one chelating (N^3,N^4) and one terminal (N^4) cytosine ligand, has not unambiguously been detected in the NMR spectra,[17] which suggests that it does not accumulate in the reaction mixture but rather quickly converts to **5**.

Figure 2 shows sections of the solid state Raman spectra of **1**, **2**, **3**, and **5**. The Raman-intense ring-stretching mode which, in free 1-methylcytosine, is at 1276 cm^{-1}, is characteristically shifted, depending on the Pt^{IV} binding site: with monodentate binding

(16) Sheldrick, G. M. SHELX, *Program for Crystal Structure Determination*; University of Göttingen: Göttingen, 1976.

(17) A weak resonance at 6.28 ppm (Figure 1a) might originate from species 4 which should have both two doublets for H5 and H6.

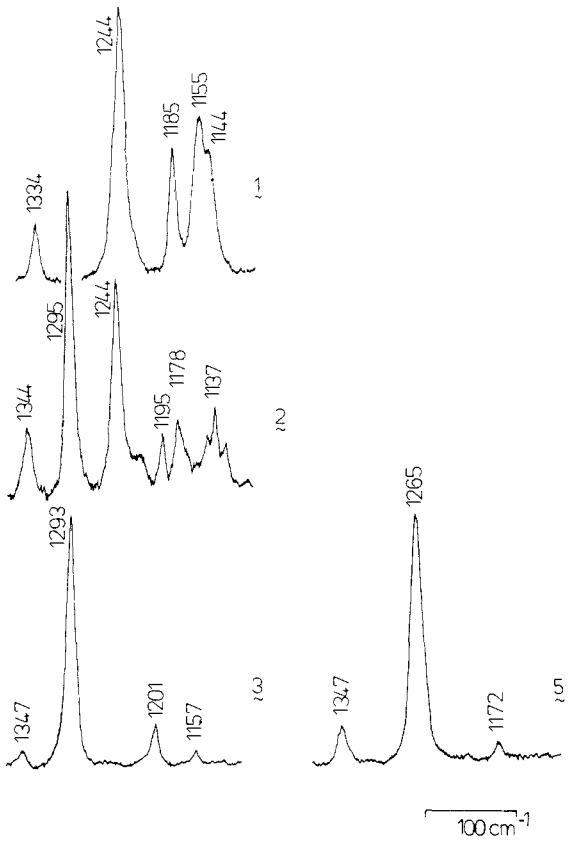


Figure 2. Sections of the Raman spectra (solid state) of complexes **1**, **2**, **3**, and **5** with characteristic ring-stretching modes in the range 1240–1300 cm^{-1}. Slit widths were 6 cm^{-1}, power (Kr, 647.1 nm) 20 mW (**2**, **3**) – 130 mW (**1**).

through N3, it is around 1240 cm^{-1}, with N3,N4′ chelation around 1295 cm^{-1}, and with monodentate binding through N4′ at 1265 cm^{-1}. In compound **2**, which contains two differently bound cytosine ligands (N3,N4′ chelate and N3), two ring-stretching modes are observed, at 1295 and 1244 cm^{-1}. These examples further confirm previous findings on the usefulness of Raman spectroscopy in differentiating metal binding patterns with heterocyclic ring systems, although the respective sensitive ring modes may vary.[18]

A comparison of the UV spectra of **1** and **5** (Supplementary Material) shows that N3 platination has relatively little effect on the position of the absorption maximum of the free ligand (273 nm) and causes only a slight bathochromic shift of 3 nm (ϵ 7150 per 1-MeC). In contrast, the absorption maximum of **5** is substantially shifted to lower energy (λ_{max} 292 nm, ϵ 16 050 per 1-MeC; shoulder at 305 nm). Deprotonation reverses this effect in part (λ_{max} 284 nm, ϵ 13 350 per 1-MeC). The absorptions of **5** at 292 and 305 nm are not affected by an increase in temperature (20–80 °C) or by MeOH (up to 75% by volume), thus pointing against a feasible tautomer equilibrium of the kind

$$Pt(II) \rightleftharpoons Pt(III)$$

Potentiometric titration of **5** with NaOH (Supplementary Material) gave two endpoints around pH 7.1 and 9.6 after addition of 1 and 2 equiv of base with pK_a values of ca. 5.8 and 8.2 for the following equilibria

$$[Pt(NH_3)_2(OH)_2(1\text{-}MeC)_2]^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [Pt(NH_3)_2(OH)_2(1\text{-}MeC)(1\text{-}MeC^-)]^{+} \overset{+H^+}{\underset{-H^+}{\rightleftharpoons}} Pt(NH_3)_2(OH)_2(1\text{-}MeC^-)_2$$

Considering the cycle outlined in Scheme III, with the experimentally determined pK_a of 16.7 for the amino group deprotonation of the aminooxo tautomer I,[19] and the estimated tautomeric ratio[8] I:II $\simeq 10^5$, the acidity of the rare tautomer II can be calculated according to

$$pK_{II,II^-} = (pK_{I,II^-}) - (pK_{I,II})$$

as 12.7. This means that Pt^{IV} coordination to the imino nitrogen at the 4-position makes the proton at N3 more acidic by 6.9 and 4.5 log units, respectively. The observed acidification, which is a consequence of the positive charge of the metal and the relative close proximity between Pt and the acidic proton H8 (2.82 Å in the solid state), is somewhat lower than that reported for the $(NH_3)_3Ru^{III}$ complex containing N4′ bound 1-MeC[11b] but clearly larger than the acidification of the amino protons of 1-MeC (form I) with a Pt^{II} electrophile coordinated at N3.[20]

Crystal Structure. Figure 3 depicts the crystal structure of *trans,trans,trans*-$[Pt(NH_3)_2(OH)_2(1\text{-}MeC\text{-}N^4)_2](NO_3)_2\cdot 2H_2O$, **5a**. The cation geometry of the second modification **5b** is very similar. Table IV lists interatomic distances and angles of the Pt coordination spheres. Geometries of the anions, hydrogen bond distances and angles, possible hydrogen bonding interactions, and conformational data are given in the Supplementary Material.

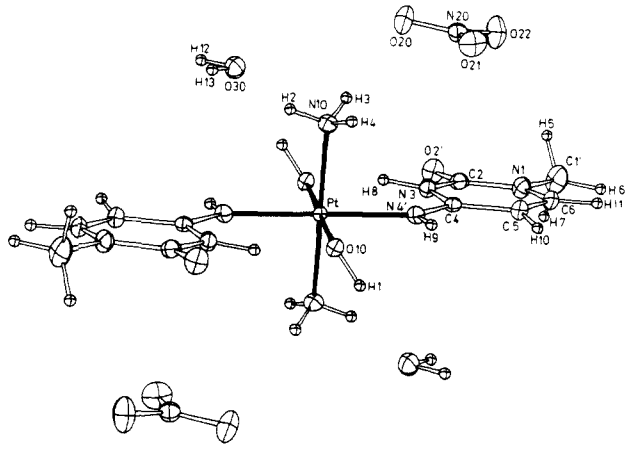


Figure 3. View of *trans,trans,trans*-$[Pt(NH_3)_2(OH)_2(1\text{-}MeC\text{-}N^4)_2](NO_3)_2\cdot 2H_2O$ (modification **5a**). The geometry of the cation of **5b** is virtually identical.

Scheme III

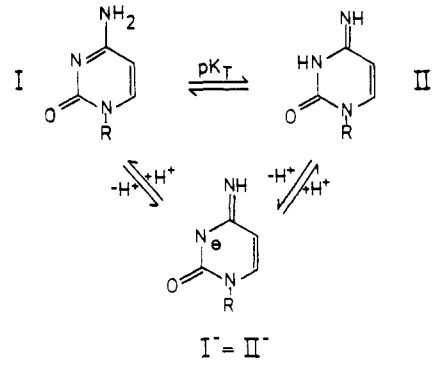


Table IV. Interatomic Distances (Å) and Angles (deg) about the Pt

	5a	5b
Pt–O10	2.003 (3)	2.008 (3)
Pt–N10	2.049 (3)	2.042 (5)
Pt–N4′	2.028 (3)	2.022 (4)
O10–Pt–N10	88.0 (1)	86.6 (2)
O10–Pt–N4′	95.2 (1)	94.0 (2)
N10–Pt–N4′	92.3 (1)	92.3 (2)

(18) See, e.g.: Faggiani, R.; Lippert, B.; Lock, C. J. L. *Inorg. Chem.* **1982**, *21*, 3210 and references cited therein.

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Table V. Comparison of 1-MeC Geometries (Distances in Å, Angles in deg)

	5a	5b	1-MeC[a]
N1-C1′	1.475 (6)	1.469 (6)	1.464 (2)
N1-C2	1.370 (6)	1.359 (6)	1.395 (2)
C2-O2′	1.219 (6)	1.235 (5)	1.234 (2)
C2-N3	1.378 (5)	1.385 (5)	1.358 (2)
N3-C4	1.353 (5)	1.365 (7)	1.332 (2)
C4-N4′	1.303 (5)	1.318 (7)	1.336 (2)
C4-C5	1.421 (5)	1.424 (9)	1.422 (2)
C5-C6	1.344 (6)	1.356 (8)	1.334 (2)
C6-N1	1.365 (6)	1.380 (6)	1.357 (2)
C1′-N1-C6	121.0 (4)	120.4 (4)	121.5 (1)
C1′-N1-C2	117.7 (4)	119.4 (4)	118.5 (1)
C6-N1-C2	121.3 (4)	120.1 (4)	120.1 (1)
O2′-C2-N1	123.1 (4)	123.1 (4)	118.6 (1)
O2′-C2-N3	121.7 (4)	119.4 (4)	122.4 (1)
N1-C2-N3	115.1 (4)	117.5 (4)	118.0 (1)
C2-N3-C4	125.4 (3)	123.4 (4)	120.0 (1)
N4′-C4-N3	119.0 (4)	119.5 (5)	117.8 (1)
N4′-C4-C5	123.8 (4)	121.9 (5)	120.1 (1)
N3-C4-C5	117.2 (3)	118.5 (5)	121.8 (1)
Pt-N4′-C4	132.0 (3)	131.2 (4)	
C4-C5-C6	117.8 (4)	117.0 (6)	117.2 (1)
C5-C6-N1	122.9 (4)	123.4 (5)	121.8 (1)

[a] Reference 23.

In both compounds, the centrosymmetric cations are of *all* trans geometry, with the cytosine ligands monodeprotonated and platinated at N4′ and protonated at N3. The platinum atom and the proton at N3 are syn to each other. The coordination spheres of the Pt atoms are completed by two NH_3 and two OH groups. Pt–N (trend toward somewhat shorter Pt–N4(1-MeC) bonds as opposed to Pt–NH_3) and Pt–O distances are normal for Pt^{IV} complexes,[21] and angles about Pt, though deviating significantly from the ideal 90°, are not unusual for Pt^{IV} complexes containing heterocyclic rings with exocyclic groups.[9,22] Nitrate geometries are normal.

Hydrogen bonding in **5a** (cf. Supplementary Material) involves all three protons of the NH_3 ligands, the proton of the hydroxo group, the two water protons, and the imino proton at N4′ of the 1-MeC ring as donors, with nitrate oxygens, the water oxygen, and O2′ of 1-MeC acting as acceptors. In **5b**, there is an additional weak hydrogen bond between N(3)H and a nitrate oxygen.

Geometry of 1-MeC. In Table V interatomic distances and angles of the 1-methylcytosine ligands in **5a** and **5b** are given and compared with the data for the normal aminooxo tautomer of 1-MeC.[23] With the data for **5a** being somewhat more accurate than those for **5b**, in the following the comparison between 1-MeC (form I) and the 1-MeC (form II) ligand in **5** will be restricted to the **5a** product. As can be seen, significant differences[24] in bond lengths exist for C4–N4′ (shorter in **5a** by 0.033 Å, corresponding to 6.1σ), for N1–C2 (shorter in **5a** by 0.025 Å, 4σ), N3–C4 (longer in **5a** by 0.021 Å, 3.9σ), and C2–N3 (longer in **5a** by 0.20 Å, 3.7σ). Significant differences are also observed when ring angles are compared: C2–N3–C4 increases in **5a** by 5.4° (17σ), N3–C4–C5 decreases in **5a** by 4.6° (15σ), O2′–C2–N1 increases by 4.5° (11σ), N4′–C4–C5 increases by 3.4° (8σ), and N1–C2–N3 decreases by 2.9° (7σ). Two of these differences are readily rationalized: the decrease in C4–N4′ bond length (1.303 (5) Å in **5a**) as compared to 1.336 (2) Å in 1-MeC (form I) clearly reflects the increase in double-bond character of this group. The increase of the internal ring angle at N3 from 120.0 (1)° in 1-MeC (normal tautomer I) to 125.4 (3)° in **5a**, on the other hand, is a consequence of the protonation of the N3 site of the 1-MeC ligand in 5a.[25]

A comparison of the cytosine geometry in **5a** with that of the deprotonated 1-MeC ligand in $[(NH_3)_5Ru(1\text{-}MeC^-\text{-}N^4)]^{2+}$,[11c] and the preferred tautomer I reveals the following: (i) Deprotonation of the N4′ metalated cytosine ring leads to a lengthening[37] of C4–N4′ relative to **5a** (0.087 Å, 7σ) and relative to free 1-MeC (0.054 Å, 5.4σ). (ii) The ring angles of the deprotonated cytosine ligand in the Ru complex are close to those of the 1-MeC tautomer I. Differences relative to **5a** do not exceed the 4σ level and refer to angles affected in **5a** as well. The effect of the negative charge in the cytosine ring of the Ru complex thus may be described as "smoothing" the large differences in angles existing between tautomer I and the platinated tautomer II.

Effect of Metal on Ring Geometry. The usefulness of the concept of estimating the geometry of a tautomer on the basis of its complexed form has its limitation in the understanding of the influence of the metal on the heterocyclic ring. A second difficulty, inherent to any discussion of structural parameters, refers to crystal packing effects.

In the large majority of metal–nucleobase complexes characterized by X-ray methods to date, the effects of the metal on bond lengths, bond angles, and ring puckering (planarity) are either very small or even unobservable.[26] This does not refer to sugar conformations (in nucleoside or nucleotide complexes),[27] to metal chelates with nucleobases,[9] and to multinuclear complexes (with the heterocyclic ring usually deprotonated),[28] where structural changes are not uncommon. Clearly, this picture may change somewhat in the future with more and, in particular, more accurate structures of metal–nucleobase complexes available. As to metal binding exclusively to an exocyclic group of a *neutral* nucleobase,[29] the situation applying to our case, only a very limited number of examples are known, e.g., Mn^{II} binding to O2 of 5′-CMP,[30] metal binding to O4 of uracil ligands (Hg^{II},[31] Cu^{II} [32]), and alkali and alkaline earth metals "interactions" with exocyclic oxygens of nucleobases.[33,34] Only with Cu^{II} binding to O4 of 1,3-dimethyluracil is there a statistically significant increase in the bond length (C4–O4) directly associated with the bound metal (from 1.227 (3) Å in the free ligand to 1.246 (4) Å in the complex, 3.8σ).[32] Other bond lengths and angles remain unaffected.

We conclude from the presently available data that the geometry of the free iminooxo tautomer II of 1-methylcytosine is, to a good approximation, identical with that observed in complex **5a**, except for C4–N4′, which should be considered the upper limit of this bond length and most likely is somewhat shorter in the free tautomer, e.g., by 0.01–0.02 Å. The resulting value of 1.28–1.29 Å would be consistent with characteristic C=N double bond

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distances observed for oxamide oxime, for example.[35]

Summary

The results presented here are of interest in two aspects: (1) The migration of Pt^{IV} from N3 to N4′ of a cytosine nucleoase represents a unique example of a linkage isomerization with two intermediates (**2** and **3**) observed in solution, isolated, and characterized. Usually, and in particular with kinetically labile metal complexes, the mechanism of metal migration can be deduced by indirect methods only. Linkage isomerization processes involving metals bound to a nucleobase, which occasionally have been reported,[11b,36] could be of considerable biological significance in that the thermodynamically most stable adduct may behave quite differently from the kinetically favored one. (2) The second point of interest refers to the fact that metal migration from N3 to N4′ is coupled with a concomitant reverse migration of a proton, resulting in a change of tautomeric structure of the ligand. While platinum complexes containing a heterocyclic ring in its unusual tautomer form have been described before,[5,22b] this is the first report of the *structure* of a *rare nucleobase tautomer*. As pointed out, the geometry of the free, uncomplexed tautomer can be estimated to a good approximation from the geometry of the complexed tautomer.

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Registry No. 1, 101152-06-1; **2**, 102149-63-3; **3**, 101181-53-7; **5**, 103639-09-4; 1-MeC, 1122-47-0.

Supplementary Material Available: Listings of atomic parameters, structural details, and potentiometric titration of **5** (8 pages); listings of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Reactions of Iron Atoms with Benzene and Cyclohexadienes in Argon Matrices: Iron–Benzene Complexes and Photolytic Dehydrogenation of Cyclohexadiene

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Abstract: Three cyclic C_6 hydrocarbons—benzene (C_6H_6), 1,4-cyclohexadiene, and 1,3-cyclohexadiene (both C_6H_8)—were codeposited with iron atoms in argon matrices at 12–14 K. When iron atoms were cocondensed with benzene, infrared spectra showed the formation of $Fe(C_6H_6)$, $Fe(C_6H_6)_2$, and $Fe_2(C_6H_6)$ complexes. When iron atoms were codeposited with 1,4-cyclohexadiene, IR spectra showed the formation of $Fe(C_6H_8)$ and $Fe_2(C_6H_8)$ adducts. On photolysis with ultraviolet light the monoiron adduct rearranged to form FeH_2 and benzene in either isolated or adducted states. A similar dehydrogenation reaction was also thought to be observed upon photolysis of the diiron–cyclohexadiene adduct with visible light. 1,3-Cyclohexadiene has been shown to react with iron atoms and dimers in a similar manner. Deuterium isotopic substitution of the three C_6 hydrocarbons was used to obtain confirmatory evidence.

Much recent work has shown that metal atoms, dimers, and small clusters react with other molecules in various surprising ways; matrix isolation spectroscopy has proven to be a powerful tool in studying these reactions.[1-7] One particular area of research has been the selective activation of bonds by metal atoms, as work in this field has immediate application to catalysis and synthesis and can lead directly to a better understanding of chemical reactivity, which has been targeted recently[8] as an important area in chemical research. Recent work in our laboratory has included the study of the codeposition and photolytic reactions of metal atoms with methane,[1] ethylene,[9] acetylene,[10] diazomethane,[11] methanol,[12] and cyclopentadiene.[13]

The results from the iron–cyclopentadiene codeposition study were intriguing: infrared spectra indicated the spontaneous formation of cyclopentadienyliron hydride, the first cyclopentadienyl transition metal hydride detected. One of the reasons for the spontaneous formation of CpFeH (Cp = cyclopentadienyl) was the contribution of aromatic stabilization energy of the Cp anion to the overall ΔH of the reaction ($\Delta H \sim \Delta G$ at low temperatures). It was decided, then, to study the possible reactions of iron atoms with some cyclic C_6 aromatic or near-aromatic

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