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Metal Ion Coordination to the Exocyclic Amine in a Pyrimidine Complex. Structure of (1-Methylcytosinato)pentaammineruthenium(III) Hexafluorophosphate, $[Ru(NH_3)_5(1\text{-}MeCyt^-)](PF_6)_2$

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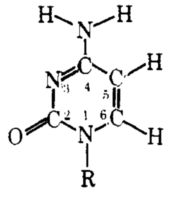
Abstract: The crystal and molecular structure of (1-methylcytosinato)pentaammineruthenium(III) hexafluorophosphate(V), $[Ru(NH_3)_5(C_5H_6N_3O)](PF_6)_2$, has been determined from three-dimensional X-ray data collected on an automatic diffractometer. The metal-pyrimidine complex crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a cell of dimensions $a = 14.760$ (10) Å, $b = 7.734$ (4) Å, $c = 8.779$ (5) Å, $\alpha = 90.19$ (3); $\beta = 99.56$ (3); and $\gamma = 89.98$ (4)°. Full-matrix, least-squares refinement of the structure using 3326 independent intensities has converged to a final, conventional R factor of 0.068. The crystals consist of isolated, monomeric units of $[Ru(NH_3)_5(1\text{-}MeCyt)]^{2+}$ cations which are surrounded by PF_6 anions. The molecular structure of the cation shows that the 1-methylcytosine anion is bound to ruthenium through the deprotonated exocyclic amine nitrogen atom. This is the first crystallographic example of metal coordination to an exocyclic amine of any purine or pyrimidine. The coordination around the ruthenium(III) center is roughly octahedral, the inner coordination sphere consisting of the five ammine nitrogen atoms with Ru-N bond lengths in the range 2.108 (7) to 2.136 (8) Å and the pyrimidine amine nitrogen atom with associated Ru-N distance of 1.983 (9) Å. This latter distance is short and is indicative of very strong σ bonding between the metal and the pyrimidine ligand.

Introduction

Crystallographic studies of transition-metal complexes of purines, pyrimidines, nucleosides, and nucleotides have been performed in recent years in order to gain an understanding of metal ion interactions with DNA.[1,2] Some metal ions stabilize double-helical DNA while others destabilize it,[3] and some metal ion complexes inhibit DNA replication[4] while others do not.



I

a, R = CH_3 (1-methylcytosine)
b, R = ribose (cytidine)
c, R = ribose 5'-monophosphate (CMP)
d, R = ribose 5'-triphosphate (CTP)

Crystallographic studies of metal complexes of derivatives of cytosine (Cyt) in which N(1) is blocked, I, including 1-methylcytosine (1-MeCyt), cytidine (Cyd), cytidine 5′-monophosphate (CMP), and cytidine 5′-triphosphate (CTP), nearly all demonstrate metal binding to N(3). The lone exception to this "rule" is the CMP complex of Mn(II), in which the only base atom to which the metal binds is O(2).[5] In several other complexes, varying degrees of metal-O(2) interaction in addition to the strong metal-N(3) binding have been noted, from a strong interaction in $[Ag(1\text{-}MeCyt)(NO_3)]$[6] to very weak contacts in complexes of mercury(II), copper(II), cadmium(II), and zinc(II).[1,7-10] Several other complexes, however, exhibit only the metal-N(3) bond noted above,[1,11-15] or that bond in conjunction with metal-phosphate interactions. Metal ion interactions with O(2) are not surprising, of course, since CNDO/2 molecular orbital calculations[16] based on the solid-state structure of cytidine[17] show that O(2) is more basic

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than N(3). For cytidine, O(2) has a net residual negative charge of −0.43 electron, while N(3) has −0.34 electron, and N(4) has only −0.25 electron. Indeed, metal chelation to N(3) and O(2) has been suggested as the reason for the strong binding of some transition-metal ions to DNA.[18] While N(3) coordination predominates over O(2) coordination in the crystallographic studies cited, this may in part be due to the choice of metal ions examined to date.

While a wide variety of metal ions is used in studies of the binding behavior of N(1)-blocked cytosine derivatives, one transition metal that is infrequently utilized is ruthenium in either the 2+ or 3+ oxidation state. The advantages of employing this metal have been documented by Clarke,[19a] and the differences in reactivity of Ru(II) and Ru(III) ammine complexes result in very interesting and potentially useful biological selectivity and activity. Spectroscopic results[19] indicate that Ru(III) ammine complexes have a different mode of base binding from most other metal ion–cytosine complexes. In order to examine the mode of binding of ruthenium(III) ammine complexes to cytosine derivatives, we have undertaken an X-ray crystallographic study of the complex (1-methylcytosinato)pentaammineruthenium(III) hexafluorophosphate(V), $[Ru(NH_3)_5(1\text{-}MeCyt^-)](PF_6)_2$; the results of that study are reported here.

Experimental Section

X-ray Data Collection. A sample of the complex was generously donated to us by Professor M. J. Clarke. Crimson crystals of relatively poor quality were obtained from this sample. Preliminary photographic examination of the crystals by precession and Weissenberg photography suggested that they belong to the monoclinic system, but a thorough analysis of the intensity data demonstrated that they are actually triclinic, the space group being either $P\bar{1}$ or $P1$; successful refinement of the structure in the former space group suggests that this assignment is correct. The cell constants, obtained by least-squares methods, are a = 14.760 (10) Å, b = 7.734 (4) Å, c = 8.779 (5) Å, α = 90.19 (3)°, β = 99.56 (3)°, and γ = 89.98 (4)°. The density of the crystals as measured by flotation in a bromoform-carbon tetrachloride solution is 2.01 g cm^{-3}, which is in good agreement with the calculated value of 2.03 g cm^{-3}, assuming two formula units per cell. Thus, in space group $P\bar{1}$, no crystallographic symmetry is imposed on the molecules.

Diffraction data were collected on a Picker four-circle automatic diffractometer equipped with molybdenum radiation and a graphite monochromator. The wavelength was assumed to be λ(Mo $K\alpha_1$) 0.709 26 Å. A trapezoidal crystal bounded by the faces (100), ($\bar{1}$00), (001), (00$\bar{1}$), (0$\bar{1}$0), and (21$\bar{1}$) and mounted along the b axis was used for data collection. The crystal dimensions are 0.07 × 0.50 × 0.26 mm in the a, b, and c directions, respectively. The data were collected at a takeoff angle of 1.5° by the θ–2θ scan technique in the range $2\theta \leq 60°$ with a scan rate of 2° (2θ) min^{-1} for data with 2θ(Mo) $\leq 45°$ and 1° (2θ) min^{-1} for data with 2θ(Mo) $> 45°$. To allow for the presence of both $K\alpha_1$ and $K\alpha_2$ radiations, the reflections were scanned from 0.80° (2θ) below the calculated $K\alpha_1$ peak to 0.80° (2θ) above the calculated $K\alpha_2$ peak. Stationary-counter, stationary-crystal background counts were taken at both ends of every scan; these were of 10-s duration for data with $2\theta \leq 45°$, and 20 s for data with $2\theta > 45°$. Throughout data collection the intensities of three standard reflections were monitored after every 100 reflections. These intensities remained constant within the limits of the scintillation counter.

Data reduction was carried out using the method described by Ibers and co-workers.[20] After correction for background radiation, the intensities, I, were assigned standard deviations according to the formula

$$\sigma(I) = [C + 0.25(ts/tb)^2(\mathrm{BH} + \mathrm{BL}) + (pI)^2]^{1/2}$$

where the quantities have their usual definitions[20] and a value of 0.05 was assigned to the correction factor, p. The intensities and their standard deviations were corrected for Lorentz-polarization effects and absorption. The absorption coefficient[21a] for this compound with Mo $K\alpha$ radiation is 10.6 cm^{-1}, and the observed transmission coefficients ranged only from 1.05 to 1.48. A total of 5708 independent reflections were processed of which 4993 had $I \geq 3\sigma(I)$. Only these latter data were considered to be observed and used in subsequent calculations. Since we had reason from our experience with other data sets collected at this time to believe that the very weak data were unreliable, we elected to reject all data with fewer than 100 recorded counts. Hence, we were left with 3326 independent observations.

Solution and Refinement of the Structure. The structure was solved (with some difficulty owing to the pseudosymmetry) by the heavy-atom method.[22] The ruthenium and both phosphorus atoms were located in a three-dimensional Patterson function, and the remaining nonhydrogen atoms were located from subsequent difference Fourier summations. Anisotropic refinement of these atoms gave values of the usual residuals $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and R_2 (or weighted R factor) $= [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.109 and 0.180, respectively. In all calculations of F_c the atomic scattering factors were taken from ref 21b; the effects of the anomalous dispersion of ruthenium and phosphorus were included in the calculation, the values of $\Delta f'$ and $\Delta f''$ being taken from ref 21c. Attempts to locate the hydrogen atoms and to vary their thermal parameters were only partially successful. In the case of the ammine groups only one or two hydrogen atoms were found and successfully varied for each nitrogen atom. The geometry at the ammine nitrogen atoms was expected to deviate from perfect tetrahedral geometry owing to the size of the metal ion relative to that of hydrogen, and this would result in expanded Ru–N–H angles and compressed H–N–H angles. The positions of any ammine hydrogen atoms that were not immediately found in a difference Fourier map were calculated assuming a similar Ru–N–H bond angle to that for the hydrogen atom which was found. The calculated positions were then adjusted to correspond to nearby maxima of electron density. Most of the 1-MeCyt$^-$ hydrogen atoms were located in a difference Fourier map. One methyl hydrogen atom could not be found and its position was calculated by assuming tetrahedral geometry at the methyl carbon atom. The ammine and methyl hydrogen atoms were assigned fixed isotropic thermal parameters, B, of 12.0 Å^2, ligand hydrogen atom H4 was given a fixed value of 4.0 Å^2, and ligand hydrogen atoms H5 and H6 were given fixed values of 8.0 Å^2.

In the final cycle of least squares there were 3326 observations and 262 variables; no parameter shifted by more than 0.5σ, which is taken as evidence of convergence. The final values of R_1 and R_2 were calculated to be 0.068 and 0.093, respectively. A final difference Fourier map showed a peak of 4.7 e Å^{-3} in the vicinity of the ruthenium atom. Other peaks as high as 1.8 e Å^{-3} were also found in the vicinity of the ruthenium atom. There was a peak of 3 e Å^{-3} which was near no atom in the structure and which did not make any chemical or structural sense. We attribute these peaks to some error in our absorption correction or to random errors in our data.

The atomic positional parameters obtained from the last cycle of least squares, along with their standard deviations as estimated from the inverse matrix, are presented in Table I. Lists of the atomic thermal parameters and the observed and calculated structure amplitudes are available.[23]

Description of the Structure. The crystal structure of $[Ru(NH_3)_5(1\text{-}MeCyt^-)](PF_6^-)_2$ consists of monomeric units of the cationic ruthenium complex which are surrounded by PF_6^- anions. The individual ions pack in the cell in such a manner as to give approximate monoclinic symmetry, which is broken only by the orientation of the 1-MeCyt$^-$ ligands. The 1-MeCyt$^-$ moiety acts as a monodentate ligand; hence, ruthenium is six coordinated with approximately octahedral geometry. The Ru-ammine nitrogen bond lengths are in the range 2.108 (7) to 2.136 (8) Å. These values are all slightly greater than that of 2.104 (4) Å in the tetrafluoroborate salt of $[Ru(NH_3)_6]^{3+}$ but shorter than those of 2.144 (4) Å in the iodide salt of the corresponding ruthenium(II) complex,[24] and are comparable with the Ru(III)–N distances reported for other complexes.[25,26] Magnetic susceptibility measurements[19a] confirm that ruthenium is in the 3+ oxidation state. The cis bond angles around ruthenium are in the range 86.9–93.1°, while the smallest trans angle is 177.9°. The manner in which the 1-MeCyt$^-$ ligand is situated relative to the ammine ligands causes the contraction of the NA1–Ru–NA2 angle and the concomitant expansion of the NA2–Ru–NA3 and NA1–Ru–NA4 bond angles from 90°. The contraction of the NA1–Ru–NA2 angle is probably due to hydrogen-bonding effects between N3 of 1-MeCyt$^-$ and the two ammine nitrogens. A view of the cation is shown in Figure 1.

The hexafluorophosphate anions have geometries that compare favorably to other structures containing PF_6^-.[27-29] P–F bond distances range from 1.56 to 1.61 Å, cis bond angles vary from 88.4 to 93.1°,

Table I. Atomic Positional Parameters in $[Ru(NH_3)_5(1\text{-}MeCyt^-)](PF_6)_2$

atom	x	y	z
Ru	0.1974 (1)	0.2356 (1)	−0.1942 (1)
P1	−0.2654 (2)	0.2618 (3)	−0.3247 (3)
P2	−0.0254 (2)	−0.2560 (3)	−0.2550 (3)
F11	−0.3249 (6)	0.2646 (11)	−0.1919 (11)
F21	−0.1755 (6)	0.2577 (12)	−0.1960 (13)
F31	−0.2019 (11)	0.2604 (9)	−0.4505 (13)
F41	−0.3528 (12)	0.2554 (15)	−0.4510 (15)
F51	−0.2657 (6)	0.0567 (8)	−0.3232 (9)
F61	−0.2623 (6)	0.4695 (8)	−0.3234 (8)
F12	0.0845 (5)	−0.2754 (10)	−0.2210 (8)
F22	−0.0191 (5)	−0.1090 (8)	−0.1256 (8)
F32	−0.1338 (5)	−0.2340 (9)	−0.2881 (9)
F42	−0.0159 (5)	−0.1133 (9)	−0.3821 (8)
F52	−0.0292 (6)	−0.4047 (9)	−0.3826 (8)
F62	−0.0332 (6)	−0.3943 (8)	−0.1272 (8)
NA1	0.1941 (6)	0.0357 (9)	−0.0287 (9)
NA2	0.1837 (6)	0.0390 (9)	−0.3633 (9)
NA3	0.1994 (7)	0.4312 (10)	−0.3605 (9)
NA4	0.2107 (7)	0.4335 (10)	−0.0244 (9)
NA5	0.0513 (5)	0.2572 (9)	−0.2235 (9)
N4	0.3326 (6)	0.2111 (12)	−0.1745 (11)
C4	0.3846 (7)	0.0629 (12)	−0.1812 (12)
N3	0.3471 (5)	−0.0922 (9)	−0.1673 (9)
C2	0.3939 (6)	−0.2401 (11)	−0.1798 (10)
O2	0.3594 (5)	−0.3847 (8)	−0.1663 (8)
N1	0.4846 (6)	−0.2286 (11)	−0.2056 (11)
C1	0.5312 (10)	−0.3908 (19)	−0.2219 (21)
C6	0.5269 (8)	−0.0683 (15)	−0.2115 (17)
C5	0.4781 (8)	0.0772 (15)	−0.2014 (19)
H4[a]	0.343	0.320	−0.171
H5	0.508	0.178	−0.211
H6	0.586	−0.062	−0.222
H11	0.501	−0.451	−0.329
H12	0.525	−0.465	−0.138
H13	0.595	−0.370	−0.222
HA11	0.177	0.057	0.061
HA12	0.148	−0.053	−0.060
HA13	0.244	−0.024	0.008
HA21	0.221	−0.048	−0.342
HA22	0.131	−0.009	−0.354
HA23	0.195	0.071	−0.453
HA31	0.161	0.514	−0.382
HA32	0.254	0.503	−0.344
HA33	0.217	0.414	−0.460
HA41	0.191	0.534	−0.040
HA42	0.220	0.423	0.060
HA43	0.277	0.498	−0.008
HA51	0.014	0.254	−0.162
HA52	0.012	0.359	−0.254
HA53	0.008	0.198	−0.273

[a] Hydrogen atom parameters were not varied.

Table II. Internuclear Distances (Å) and Angles (deg) in $[Ru(NH_3)_5(1\text{-}MeCyt^-)](PF_6)_2$

atoms	distance	atoms	distance
Ru-NA1	2.132 (7)	P1-F11	1.572 (8)
Ru-NA2	2.108 (7)	P1-F21	1.594 (10)
Ru-NA3	2.110 (7)	P1-F31	1.562 (9)
Ru-NA4	2.119 (7)	P1-F41	1.556 (11)
Ru-NA5	2.136 (8)	P1-F51	1.587 (7)
Ru-N4	1.983 (9)	P1-F61	1.606 (6)
N1-C1	1.45 (1)	P2-F12	1.606 (7)
N1-C2	1.40 (1)	P2-F22	1.597 (6)
C2-O2	1.24 (1)	P2-F32	1.589 (7)
C2-N3	1.35 (1)	P2-F42	1.595 (6)
N3-C4	1.34 (1)	P2-F52	1.597 (7)
C4-N4	1.39 (1)	P2-F62	1.571 (7)
C4-C5	1.43 (1)		
C5-C6	1.35 (2)		
C6-N1	1.39 (1)		
Angles in $[Ru(NH_3)_5(1\text{-}MeCyt^-)]^{2+}$ Cations			
NA1-Ru-NA2	86.9 (3)	Ru-N4-C4	129.2 (7)
NA1-Ru-NA3	179.1 (3)	N4-C4-N3	119.9 (9)
NA1-Ru-NA4	93.1 (3)	N4-C4-C5	119.7 (9)
NA1-Ru-NA5	90.1 (3)	C5-C4-N3	120.4 (10)
NA1-Ru-N4	90.5 (4)	C4-N3-C2	121.9 (9)
NA2-Ru-NA3	92.3 (3)	N3-C2-O2	122.1 (9)
NA2-Ru-NA4	179.8 (3)	N3-C2-N1	118.4 (8)
NA2-Ru-NA5	89.7 (3)	O2-C2-N1	119.5 (8)
NA2-Ru-NA4	88.3 (4)	C2-N1-C1	116.3 (9)
NA3-Ru-NA4	87.6 (3)	C2-N1-C6	120.7 (9)
NA3-Ru-NA5	89.4 (3)	C1-N1-C6	123.0 (10)
NA3-Ru-N4	90.0 (4)	N1-C6-C5	119.6 (10)
NA4-Ru-NA5	90.1 (3)	C6-C5-C4	118.8 (10)
NA4-Ru-N4	91.9 (4)		
NA5-Ru-N4	177.9 (3)		
Angles in PF_6^- Anions			
F11-P1-F21	88.7 (5)	F12-P2-F22	89.8 (4)
F11-P1-F31	177.2 (7)	F12-P2-F32	179.2 (4)
F11-P1-F41	91.7 (8)	F12-P2-F42	89.6 (4)
F11-P1-F51	90.1 (4)	F12-P2-F52	88.9 (4)
F11-P1-F61	90.2 (4)	F12-P2-F62	89.8 (4)
F21-P1-F31	88.5 (7)	F22-P2-F32	89.5 (4)
F21-P1-F41	177.0 (6)	F22-P2-F42	90.2 (4)
F21-P1-F51	88.6 (5)	F22-P2-F52	178.6 (9)
F21-P1-F61	89.9 (5)	F22-P2-F62	88.8 (4)
F31-P1-F41	91.1 (9)	F32-P2-F42	90.0 (4)
F31-P1-F51	90.3 (4)	F32-P2-F52	91.8 (4)
F31-P1-F61	89.4 (4)	F32-P2-F62	90.7 (4)
F41-P1-F51	88.4 (5)	F42-P2-F52	90.3 (4)
F41-P1-F61	93.1 (5)	F42-P2-F62	178.8 (6)
F51-P1-F61	178.5 (7)	F52-P2-F62	90.7 (4)

Table III. Probable A-H···B Hydrogen Bonds in $[Ru(NH_3)_5(1\text{-}MeCyt^-)](PF_6)_2$

A	H	B	A···B, Å	H···B, Å	A-H···B, deg
NA1	HA13	N3	2.91	2.39	118
NA2	HA21	N3	2.91	2.23	134
NA1	HA12	F12	3.21	2.31	153
NA2	HA22	F42	3.10	2.29	168
NA3	HA33	F61[a]	3.17	2.31	149
NA5	HA52	F52[b]	3.11	2.18	156
NA5	HA52	F62[b]	3.14	2.36	136

[a] $-x$, $1-y$, $-1-z$. [b] x, $1+y$, z.

and the smallest trans bond angle is 177°. The bond distances and angles within the structure are tabulated in Table II. As might be expected, there are several probable hydrogen bonds between the coordinated ammine groups and the PF_6^- anions. These probable hydrogen bonds are listed in Table III.

The outstanding features of the structure are the binding site of Ru to 1-MeCyt⁻ and the shortness of that metal-ligand bond. As seen in Figure 1, ruthenium binds to 1-MeCyt⁻ through the deprotonated exocyclic amine, N4. The length of this Ru-N bond is 1.983 Å, which is substantially shorter than the other Ru-N bonds in the structure; while this shortening might be attributed to some degree of multiple bonding between Ru and N4, it seems more probable that it is a measure of the stronger σ donation of 1-MeCyt⁻ relative to that of NH_3. The apparently lengthened bond trans to N4 (namely, Ru-NA5) may support this conclusion, since this NH_3 ligand is apparently competing less favorably than 1-MeCyt⁻ for σ-electron density. Moreover, the bond length to N4 is comparable to that of 1.86 Å found[30] for the σ donor NO^- ligand in $[Ru(NO)_2Cl(PPh_3)_2]^+$ and is much longer than those of approximately 1.74 Å observed[30-32] in ruthenium(II) complexes of the known π-acceptor ligand NO^+. As noted above, metal coordination to the exocyclic amine of cytidine or adenosine has not previously been substantiated by any X-ray crystal studies, but there are some spectroscopic[19,33] results which do indicate this. Raman difference spectroscopy has been used to investigate the

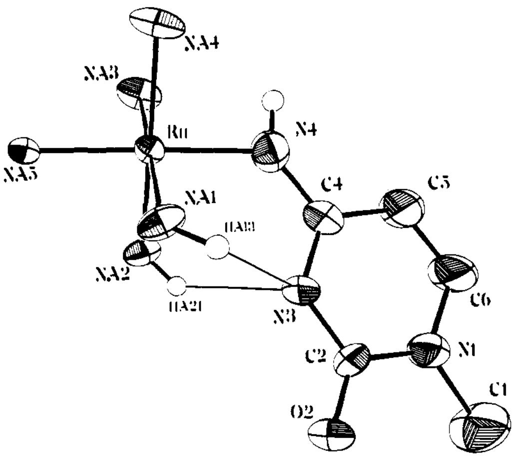

Figure 1. View of the $[Ru(NH_3)_5(1\text{-}MeCyt^-)]^{2+}$ cation in $[Ru(NH_3)_5\text{-}(1\text{-}MeCyt^-)](PF_6)_2$. Most hydrogen atoms are omitted for clarity.

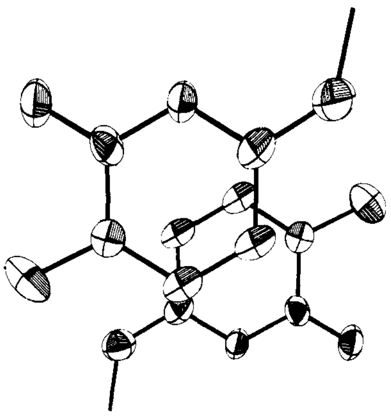

Figure 2. View of the pairwise stacking interaction between pyrimidine rings in $[Ru(NH_3)_5(1\text{-}MeCyt^-)]^{2+}$. The discontinuous bonds from the N(4) atoms show the N(4)-Ru bond directions. The view shown is perpendicular to the mean plane of the rings.

Table IV. Least-Squares Plane through 1-MeCyt⁻

atom	*x*	*y*	*z*	Δ, Å
		Plane 1		
		Atoms in the Plane Calculation		
N1	7.4520	−1.7620	−1.7801	0.023
C2	6.0764	−1.8518	−1.5566	−0.006
N3	5.3674	−0.7085	−1.4485	−0.016
C4	5.9410	0.4919	−1.5682	0.021
C5	7.3513	0.6032	−1.7434	−0.003
C6	8.0849	−0.5217	−1.8306	−0.018
		Atoms Not Included in the Plane Calculation		
C1	8.1633	−3.0159	−1.9211	0.065
O2	5.5470	−2.9705	−1.4392	−0.047
N4	5.1640	1.6378	−1.5102	0.070
Ru	3.1981	1.8281	−1.6808	0.513
H4	5.3106	2.4833	−1.4844	0.022
		Plane 2		
		Atoms in the Plane Calculation		
NA1	2.9065	0.2768	−0.2485	0.003
NA2	3.2412	0.3123	−3.1452	−0.003
NA3	3.4694	3.3455	−3.1210	0.003
NA4	3.1470	3.3536	−0.2113	−0.003
		Atom Not Included in the Plane Calculation		
Ru	1.1981	1.8281	−1.6808	−0.007

interaction of CH_3Hg^{II} with cytidine and with 5′-adenosine monophosphate (AMP), and it was determined that at very high pH levels (≥11) methylmercury does "bind" to the amino nitrogen in both cases. In the present case, however, the ruthenium(III) center binds to N(4) of 1-methylcytosine in a complex which is isolated at neutral pH, which may make the present result more biologically significant. Deprotonation of 1-MeCyt occurs during its interaction with $(NH_3)_5Ru^{3+}$ and, given the large number of structures with metal binding to N3, it is possible that Ru first binds to 1-MeCyt at N3, then catalyzes the deprotonation at N4 and finally shifts its binding site from N3 to N4. Evidence for site shifting of this kind has been presented by Clarke in an analogous ruthenium-hypoxanthine system;[34] such a process is normally very slow (half-life is on the order of days) but is fast in the presence of a reductant.[34] Furthermore, it has been shown[19a] that a variety of biological reductants are strong enough to convert Ru(III) into Ru(II). Since the oxidation of Ru(II) to Ru(III) is facile in the presence of O_2, the entire reaction is feasible within a biological system. The conjugate acid of the title complex has a pK_a value of 3.31; by comparison, it has recently been reported [35] that the amino hydrogen atom of a peptide which is coordinated to copper(III) is approximately 12. If Ru in the 3+ oxidation state is catalyzing the deprotonation at N4 by binding to N3 and withdrawing electron density from N4, it would be interesting to determine if the same reaction could be achieved for other systems by oxidizing the metal ion to a higher oxidation state (e.g., Co(II) → Co(III)). While two related structures with Co(III) have been reported,[36,37] both contain adenine ligands coordinated at imidazole nitrogen atoms. Neither of these complexes exhibits the behavior of the ruthenium complex in this study, since no metal ion attached to the imidazole ring of a purine is likely to have much electron-withdrawing power from the $-NH_2$ group on the pyrimidine ring. Hence, in order to achieve the same effect the systems to be studied should be M(III) complexes with cytosine blocked at the N1 position or with adenine blocked at the N7 and N9 positions.

The geometry within the 1-methylcytosine ligand is substantially similar to that observed in other metal structures with this ligand[6,7,11] and in the free ligand itself.[38] The only consistent difference is the C4-N4 bond length, which is 6σ longer in this structure than in other M-(1-MeCyt) complexes and 4σ longer than in the free ligand. This bond lengthening is probably due to metal coordination at N4. All other bond distances and all bond angles are within 2 or 3σ of the corresponding values in the other structure. The ring atoms of the 1-MeCyt⁻ ligand are roughly coplanar, with no atom more than 0.023 Å out of the best least-squares plane through the six positions. This least-squares plane is tabulated in Table IV. The exocyclic atoms are at most 0.07 Å out of the plane, while Ru deviates by more than 0.5 Å. The plane of the cytosine ring forms an angle of 76° with the plane composed of ammine nitrogen atoms NA1, NA2, NA3, and NA4 (Table IV). The only hydrogen bonding that the ligand participates in is from N3 to the ammine hydrogen atoms HA13 and HA21. The geometry of these intramolecular interactions is tabulated in Table III. There are no long-range base-stacking arrangements in this structure but, as is shown in Figure 2, bases do stack in pairs with a separation of 3.47 Å and they are constrained crystallographically to be exactly parallel. The two pyrimidine rings do not overlap completely. Instead, they exhibit the bond-over-ring type of overlap which has been seen in a number of other structures.[39]

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Supplementary Material Available: A listing of thermal parameters (U_{ij}'s) and observed and calculated structure amplitudes (21 pages). Ordering information is given on any current masthead page.

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Synthesis and ^{31}P NMR Studies of Unsymmetrical *cis*-Diphosphinoalkenes and Their Complexes with Nickel(II), Palladium(II), and Platinum(II)

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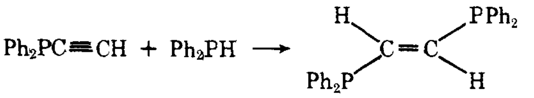
Abstract: Bis(phosphinoalkyne) complexes *cis*-$Cl_2M(Ph_2PC{\equiv}CR)_2$ (M = Pd, Pt; R = CF_3, Ph, *t*-Bu) undergo a facile 1:1 reaction with secondary phosphines HPR′R″ (R′R″ = Ph, C_2H_4CN; R′ = Et, R″ = Ph) to give stereospecifically the *cis*-1,2-diphosphinoalk-1-ene complexes *cis*-$Cl_2M(Ph_2PCH{=}C(R)PR'R'')$. The uncoordinated diphosphinoalk-1-enes may be obtained by treatment of the corresponding Pt(II) complex with excess cyanide ion. Complexes *cis*-$Cl_2Ni(Ph_2PCH{=}C(R)PR'R'')$ are obtained by reaction of *cis*-$Ph_2PCH{=}C(R)PR'R''$ with anhydrous nickel(II) chloride. The free diphosphinoalk-1-enes and their Ni(II), Pd(II), and Pt(II) complexes are characterized by elemental analysis, mass spectrometry, IR, ^{1}H NMR, and ^{31}P NMR spectroscopy. Factors affecting ^{31}P chemical shifts, coordination chemical shifts, and P-P couplings in these systems are discussed.

Introduction

Phosphinoalkynes are potentially bidentate ligands but have been shown[1] to coordinate only through phosphorus in the square planar Pd(II) and Pt(II) complexes *cis*-$X_2M(Ph_2PC{\equiv}CR)_2$ (**1**) (R = alkyl, aryl; X = halogen). Although uncoordinated, the alkyne function in these complexes is activated toward such reactions as hydration,[2] hydrogen halide addition,[3] and acetylene coupling.[4] The prospect of an analogous activation toward addition of the P-H moiety led us to examine the reaction of complexes **1** with secondary phosphines.

The base-catalyzed addition of diphenylphosphine to an uncoordinated phosphinoalkyne (eq 1) has been reported[5] to give stereospecifically the *trans*-1,2-bis(phosphino)alk-1-ene (**2**), a molecule which is unable to act as a chelating ligand by virtue of the rigidity of the olefinic backbone.[6] In contrast, our initial studies showed that the addition of secondary phosphines to coordinated phosphinoalkynes in complexes **1** (eq 2) yielded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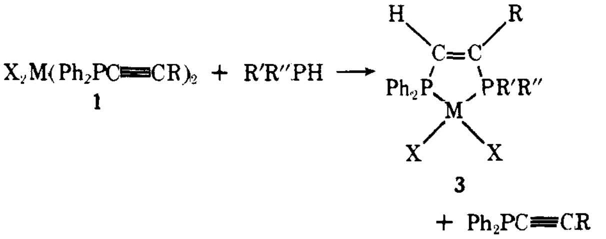
1

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(2)

stereospecifically the *cis*-1,2-diphosphinoalk-1-ene complexes (**3**). Unsaturated, unsymmetrical diphosphines of the type present in complexes **3** are unlikely to be readily obtained by any other route[5,7] and, in view of intense current interest in

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