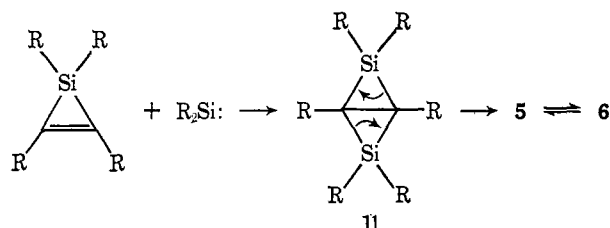


substituted disilylene generators and work toward this goal is now in progress. A final problem concerns the origin of **6**. It is possible that silylene adds to the π -bond of a silacyclopropene to produce an intermediate disilabicyclo[1.1.0]butane (**11**). Such a molecule could thermally rearrange to **5**, and we are experimentally checking this possibility at this time.



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Crystal and Molecular Structure of an Osmium Bispyridine Ester of Adenosine

Sir:

Organic complexes of osmium(VI), apart from their inherent interest as metal-organic complexes in inorganic chemistry, have become of biochemical interest because they have been reported to form a heavy atom derivative of transfer ribonucleic acid (tRNA).¹ We wish to report the X-ray diffraction structure determination of a bis(pyridine)osmate(VI) ester of adenosine.² We believe that the stereochemistry observed in this compound may serve as a model of one mode of binding of osmium to tRNA in the heavy atom derivatives used in the structure determination of tRNA.^{1b,3,4}

The preparation of crystals of the adenosine bis(pyridine)osmate complex proceeded from the observation that ribonucleosides, as well as other cis diols, form 1:1 addition complexes with OsO₃py₂ in water-pyridine solution.^{5,6} OsO₃py₂ (118.7 mg), prepared from OsO₄ by reduction with ethanol according to Criegee, *et al.*,⁶ and 80.1 mg of adenosine (Sigma) were dissolved in 4.5 ml of water-pyridine (2:1, v/v) and kept for several hours at 4° in the dark. The progress of the reaction was followed by thin-layer chromatography on Merck Cellulose F plates in 2-propanol-concentrated ammonium hydroxide-water (50:1:49, v/v). The osmate ester appeared after drying of the plate as a gray-brown spot ($R_f = 0.21$). After completion of the reaction the

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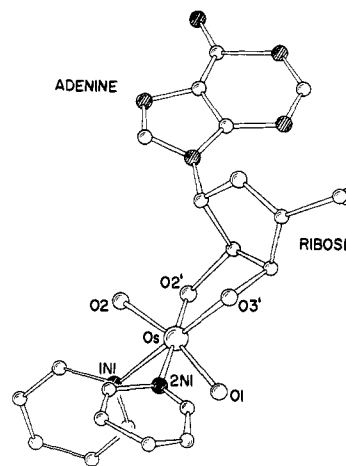


Figure 1. Molecular structure of bis(pyridine)osmate(VI) ester of adenosine. Selected distances (Å) and angles (deg) are listed with errors in parentheses: O(3')-Os, 1.99 (5); O(2')-Os, 1.91 (5); O(1)-Os, 1.78 (4); O(2)-Os, 1.78 (4); 1N(1)-Os, 2.24 (6); 2N(1)-Os, 2.11 (7); 1N(1)-Os-2N(1), 91 (3)°; 1N(1)-Os-O(3'), 178 (3)°; 2N(1)-Os-O(3'), 87 (3)°; O(2')-Os-O(3'), 90 (3)°; O(2)-Os-1N(1), 90 (3)°; O(2')-Os-2N(1), 178 (3)°; O(1)-Os-O(2), 164 (3)°. The nitrogen atoms have diagonal shading.

product was isolated by evaporation of the solvent. It was redissolved in a few drops of water-pyridine (1:1) and crystallized on cooling in the form of brown lamellar plates and needles (yield 125 mg, 65%).

The problem of finding a suitable crystal for data collection proved extremely difficult despite repeated recrystallizations; the crystals formed tight aggregates, were quite brittle, and exhibited a high degree of mosaic spread as well as thermal diffuse scattering. During preliminary X-ray photographic investigations, no crystal could be found which failed to exhibit both undue mosaic spread and thermal diffuse scattering; however, we decided to attempt data collection anyway. The diffraction photographs indicated that the crystal belongs to the orthorhombic space group $P2_12_12_1$, as determined by its systematic absences; the cell constants were $a = 7.84$, $b = 12.28$, and $c = 23.71$ Å. Data were collected using a modified Picker FACS I diffractometer at 8° with an ω -stepscan; 2243 unique reflections were collected to a resolution of approximately 0.7 Å. In at least one direction the mosaic spread caused some reflections to be appreciably wider than the counter (528 mm from crystal) could accommodate, hence these reflections were "clipped" to substantially less than their true value.

The osmium atom was located by Patterson methods, and all other atoms were placed in subsequent Fourier refinements. Least-squares refinement of the structure using anisotropic temperature factors for the osmium atom and isotropic temperature factors for all other atoms lowered the crystallographic R factor to 0.108. The use of anisotropic temperature factors on all atoms does not improve this figure significantly according to the Hamilton R test.⁷ The final structure is depicted in Figure 1, with the packing of the structure in the unit cell depicted in Figure 2.⁸

A few structural observations are immediate; the osmium binds as an osmate ester to the 2'-3' cis diol of

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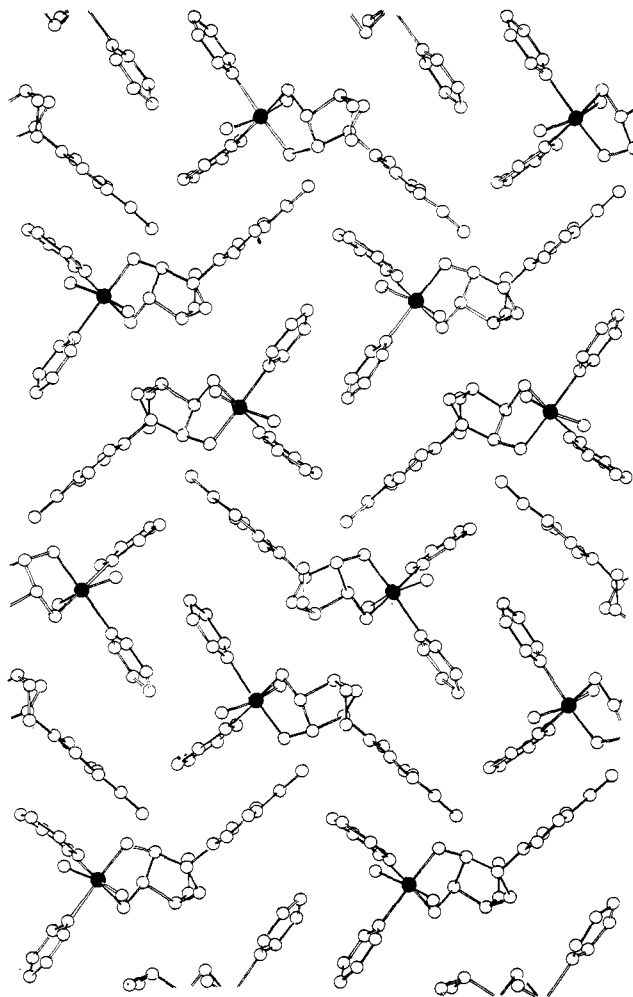


Figure 2. Projection of the crystal structure of bis(pyridine)osmate(VI) ester of adenosine along the a axis. The osmium atom is shaded black.

the adenosine molecule, and the entire complex assumes an octahedral coordination with the two osmyl groups trans to one another; this was anticipated on spectral evidence by Griffith and Rosetti.⁹ The nucleoside is in the syn conformation, rather than the usually preferred anti conformation which is found in the free nucleoside.¹⁰⁻¹² The glycosidic torsion angle ($\chi = 121^\circ$), while slightly out of the normal range for syn β -purine nucleosides, is similar to that observed for formycin¹³ and virazole¹⁴ and ψ ¹⁵ the C(4')-C(5') conformation angle is 55° . The furanose ring is in an envelope (²E) conformation C(2') endo; the phase angle of pseudorotation (P) is 166° and the amplitude of pucker is 32° .¹⁶ Essentially, these parameters agree, to within the limits of reliability of the data, with the profile considered typical of syn β -purine nucleosides.¹⁷

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The packing in the unit cell is partially determined by parallel stacking of the first pyridine ring and the adenine, separated by about 3.5 \AA from molecules related by symmetry. A hydrogen bond of length 2.9 \AA between O(5') and N(6) in symmetry-related molecules may stabilize the syn conformation. The constraints of parallelism between the adenine and first pyridine rings hold this first pyridine ring perpendicular to the plane of O(2'), O(3'), 1N1, and 2N1. The second pyridine ring stacks parallel to a symmetry-related copy of itself. This pyridine ring seems free to rotate slightly about its Os-2N1 axis since systematically shortened and elongated bonding distances characteristic¹⁸ of such rotation are observed.

From a study of this structure, we infer that the osmium binding observed in yeast phenylalanine tRNA may occur primarily at the location of the only free cis diol, at the 3'OH end of the molecule.⁴ However, two different hydroxyl groups in the correct position along the tRNA chain might also bind an osmium, provided that these hydroxyl groups are close enough. Subsequent work on the osmium heavy atom derivatives of tRNA make it seem likely that the 3'OH end of tRNA is indeed the primary osmium binding site, while other minor binding sites are observed which could correspond to other modes of ligand binding.⁴

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Influence of Solvation Factors on Acidity. Thermodynamics of Hydration of a Series of Meta- and Para-Substituted Phenols^{1,2}

Sir:

Volumes and entropies of ionization ($\Delta \bar{V}_1^\circ$ and $\Delta \bar{S}_1^\circ$, respectively) appear to be valuable quantities in understanding the nature and degree of solute-solvent interaction.³⁻⁷ It has recently been reported that the differ-

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