

Figure 1. ^{13}C NMR spectra at 100 MHz illustrating the progress of the reaction catalyzed by UV endo V. Spectrum A was recorded before the addition of enzyme, and spectra B through E were recorded 1.75, 5.25, 12.25, and 24 h after the addition of enzyme. The resonance at 72 ppm is associated with the 2-carbon of the glycerol present in the storage buffer for uracil-DNA glycosylase, the resonance at 62 ppm is associated with the primary alcohol carbons of both the glycerol and the ethylene glycol present in the storage buffer for UV endo V, and the resonance at 171 ppm is associated with (ammonium) formate contaminating the heteroduplex; these resonances serve as convenient intensity standards during the course of the reaction.

likely that the adducts we have detected are derived from addition of these to the α,β -unsaturated aldehyde.¹⁸ While the formation of such adducts does not alter our conclusion that the mechanism of the UV endo V catalyzed reaction involves a β -elimination mechanism, it does provide an explanation for the previously reported observation that more than one product is obtained from the action of endo III on abasic sites.⁵

Our observations on the cleavage of abasic sites in DNA catalyzed by UV endo V and those previously reported for the cleavage catalyzed by endo III⁵ illustrate that the enzymatic cleavage of phosphate ester bonds can proceed by C–O as well as P–O bond scission. Further studies of the mechanism of the β -elimination reaction catalyzed by UV endo V are in progress.

Acknowledgment. We thank Professor Errol C. Friedberg, Stanford University Medical Center, for his gift of an expression

(16) The ^{13}C NMR chemical shifts of the 1-carbons of ethanol, 3-methylbutanol, and 3,3-dimethylbutanol are 57.0, 60.2, and 58.9 ppm, respectively: *Carbon-13 NMR Spectra Data*; Verlag Chemie: New York, 1979.

(17) The uracil-DNA glycosylase is stored in a buffer containing dithiothreitol, and UV endo V is stored in a buffer containing 2-mercaptoethanol.

(18) The ^{13}C NMR chemical shift of carbon-1 in 1-(methylthio)cyclohexane is 44.9 ppm: Eliel, E. L.; Kandasamy, D. *J. Org. Chem.* **1976**, *41*, 3899–3904.

plasmid for UV endo V. This research was supported by NIH GM-34572 to J.A.G and NIH GM-34573 to J.A.G. and P.H.B.

Supplementary Material Available: ^{13}C NMR spectra of the adducts formed by addition of nucleophiles to the α,β -unsaturated aldehyde enzymatic product (1 page). Ordering information is given on any current masthead page.

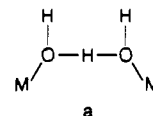
The Amido–Ammine Bridging Ligand (H_5N_2^-)

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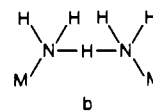
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The role of very strong O–H–O hydrogen bonds in coordination chemistry, especially in the hydrolysis of metal ions, has been revealed in recent years.^{2,3} An H_2O ligand of one metal atom may interact with an OH ligand of another metal atom by means of a very short (<2.50 Å) and centered hydrogen bond to form an (H_3O_2^-) bridging ligand (a) between the metal atoms. The



central role of this ligand in the structure of hydroxoqua and related complexes has been reviewed recently.³ The mechanism and steric course of *olation* (formation of μ -(OH) bridges between metal atoms) was shown to be controlled by the configuration of the H_3O_2 bridges in the reacting species.⁴ The exceptional acidity of chromium(III) diols such as $[(\text{H}_2\text{O})_4\text{Cr}(\text{OH})_2\text{Cr}(\text{H}_2\text{O})_4]^{4+}$ was ascribed to stabilization of the deprotonated species by formation of an H_3O_2 bridge (in addition to the two OH bridges).^{5,3} This assumption was recently confirmed by a single-crystal X-ray study.⁶

An ammine analogue of a di- μ -(OH) metal complex, the di- μ -amidobis[tetraammineplatinum(IV)] ion, $[(\text{NH}_3)_4\text{Pt}(\text{NH}_2)_2\text{Pt}(\text{NH}_3)_4]^{6+}$, was shown to be very acidic,⁷ with a $\text{p}K_1 = 1.9$, compared to $[\text{Pt}(\text{NH}_3)_6]^{4+}$ with $\text{p}K_1 = 7.0$. This remarkable acidity was first ascribed to deprotonation of a bridging amido ligand, but an NMR study ruled out this possibility^{7,8} and supported the conclusion that deprotonation occurred at a *terminal* ammine ligand, located above the $\text{Pt}(\text{NH}_2)_2\text{Pt}$ plane, i.e., in a *cis* position relative to the two amido bridges.⁸ Stabilization of such a deprotonated species may be achieved by strong hydrogen bonding of the terminal amido nitrogen with the ammine ligand of the second Pt atom located above the $\text{Pt}(\text{NH}_2)_2\text{Pt}$ plane, i.e., by formation of an (H_5N_2^-) bridging ligand (b), which is the ammine analogue of (H_3O_2^-).



(1) (a) Universitaet des Saarlandes. (b) The Hebrew University of Jerusalem.

(2) (a) Ardon, M.; Bino, A. *J. Am. Chem. Soc.* **1983**, *105*, 7748–7750. (b) Ardon, M.; Bino, A. *Inorg. Chem.* **1985**, *24*, 1343–1347. (c) Ardon, M.; Bino, A.; Jackson, W. G. *Polyhedron* **1987**, *6*, 181–187. (d) Ardon, M.; Bino, A.; Michelsen, K.; Pedersen, E. *J. Am. Chem. Soc.* **1987**, *109*, 5855–5856.

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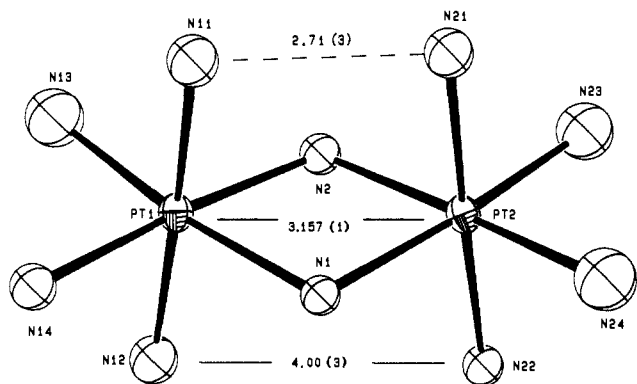


Figure 1. The structure and dimensions of $[(\text{NH}_3)_3\text{Pt}(\text{NH}_2)_2(\text{H}_5\text{N}_2^-)\text{Pt}(\text{NH}_3)_3]^{5+}$ as found in **1**. The N-H-N bond in the H_5N_2^- bridge is represented by the dashed line: average Pt-N (terminal in plane) 2.08 (2) Å; Pt(1)-N(11), 2.03 (2) Å; Pt(2)-N(21), 2.06 (2) Å; Pt(1)-N(12), 2.08 (2) Å; Pt(2)-N(22) 2.14 (2) Å; average Pt-N (bridge) 2.08 (2) Å.

We have confirmed this assumption by a single-crystal X-ray study of $[(\text{NH}_3)_3\text{Pt}(\text{NH}_2)_2(\text{N}_2\text{H}_5)\text{Pt}(\text{NH}_3)_3](\text{ClO}_4)_5 \cdot 4\text{H}_2\text{O}$, compound **1**.⁹ The structure of the complex is presented in Figure 1. Some striking features of this complex ion are revealed by comparing it with the fully protonated ion, as found in $[(\text{NH}_3)_4\text{Pt}(\text{NH}_2)_2\text{Pt}(\text{NH}_3)_4]\text{Cl}_6 \cdot 2\text{DMSO}$, compound **2**.⁷ The

(9) Single crystals of $[(\text{NH}_3)_3\text{Pt}(\text{NH}_2)_2(\text{N}_2\text{H}_5)\text{Pt}(\text{NH}_3)_3](\text{ClO}_4)_5 \cdot 4\text{H}_2\text{O}$ were obtained by evaporation, at room temperature, of a solution of **2** which had been partly neutralized with NaOH to pH 5.6 (pK_2 of **2** is 7.17). Compound **1** is triclinic, space group $P\bar{1}$ with $a = 9.564$ (2) Å, $b = 17.588$ (3) Å, $c = 9.464$ (1) Å, $\alpha = 91.95$ (3)°, $\beta = 119.32$ (3)°, $\gamma = 83.68$ (2)°, $V = 1379$ (1) Å³, and $Z = 2$. The structure was refined by least-squares methods by using 3714 unique reflections with $I > 3\sigma(I)$ to a conventional R factor of 7.4%.

separation between the two nitrogen atoms of the (H_5N_2^-) unit is 2.71 (3) Å in **1**, compared with 3.30 Å between the corresponding nitrogen atoms in **2**. The Pt-Pt-N(H_5N_2^-) angles in **1** are approximately 84°, compared with 91° in **2**. This distortion is also reflected by the increase in the separation of the other two extra-planar nitrogen atoms from 3.30 Å in **2** to 4.00 (3) Å in **1** and of the corresponding N-Pt angles from 91° to approximately 98°. The considerable strain imposed by the H_5N_2^- bridge also causes the collapse of the planar $\text{Pt}(\text{NH}_2)_2\text{Pt}$ configuration of **2**. The dihedral angle between the plane defined by Pt(1), N(1), N(2) and the plane defined by Pt(2), N(1), N(2) increases from 0° in **2** to 8.6° in **1**. The (H_5N_2^-) bridging ligand has a very short hydrogen bond at its core; it is 0.5 Å shorter than the sum of the van der Waals radii of two nitrogen atoms¹⁰ and therefore qualifies as a "very strong" hydrogen bond.¹¹ Further investigation of this hydrogen bond will be carried out by neutron diffraction, IR, and NMR studies. The role of the (H_5N_2^-) bridging ligand in *ammine olation* (formation of μ -amido bridges) will also be studied. Evidence for the existence of two (N_2H_5^-) bridges in the doubly deprotonated ion was obtained in a preliminary structural study of $[(\text{NH}_3)_3(\text{NH}_2)\text{Pt}(\text{NH}_2)_2\text{Pt}(\text{NH}_2)(\text{NH}_3)_3]^{4+}$.

Acknowledgment. We are indebted to the fund for Basic Research administered by the Israel Academy of Sciences and Humanities for financial support.

Supplementary Material Available: Tables of atomic positional and thermal parameters for **1** (3 pages). Ordering information is given on any current masthead page.

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Computer Software Reviews

SuperPaint, Version 1.0 p. Silicon Beach Software: P.O. Box 261430, San Diego, CA 92116. List price \$149.95.

SuperPaint is a graphics application for the Macintosh 512K, Plus, SE, XL and II. It occupies 161.5K according to the program information statement, yet when loaded with Switcher, it requires a minimum of 432K and prefers 614K memory. The application disk comes unprotected and can be used with 1 or 2 drives or with a hard disk. Although not designed specifically for chemical applications, SuperPaint would be very useful for creating publication quality drawings. It can input files not only in its own file format but also in the MacPaint format and the PICT format used by MacDraw and other applications. I have successfully transported graphics from MacPaint, MacDraw, and Excel.

SuperPaint has most of the features of MacPaint and MacDraw. Anyone who is familiar with these two applications will immediately feel comfortable with SuperPaint. I have found almost no feature in MacPaint and MacDraw that has been omitted from SuperPaint. The documentation describes SuperPaint as having two superimposed layers: (1) the draw layer, which is object oriented, and (2) the paint layer, which is bit mapped. The two layers may overlap or one may be hidden from the other. One can work in only one layer at a time, but can switch freely between them. Each layer has its own set of drawing tools, many of which accomplish similar functions.

The documentation is well written. It should be clear both to the experienced and the inexperienced Macintosh user. I found the index useful and adequately cross referenced.

Because SuperPaint combined many of the features of MacPaint and MacDraw, I will discuss mainly the differences. There are two sets of fill patterns available in both layers. One of these sets looks fine when printed on either the ImageWriter or the LaserWriter, the other looks fine on the LaserWriter. The latter set of patterns must be created in a draw layer, however, for best quality when printed. In both layers, one can draw circles, ovals, rectangles, and squares from their centers as well

as from the rectangles that enclose them. Also lines can be drawn with different densities in the horizontal and vertical directions. One can rescale either objects or selected rectangles. Rescaling can either increase or decrease the dimensions of the selection. One has available three levels of magnification. In the paint layer, magnification works just like FatBits in MacPaint; however, in the draw layer, it allows positioning and reshaping of objects to the nearest pixel. Automatic scrolling is available when a tool is moved across a window boundary.

In the draw layer when an arc is created, it is drawn having a 90° opening. However, this arc can be edited to have any angle open. Polygons can be created with any number of vertices. Not only can one reposition these vertices but also one can increase the number of vertices as desired.

In the paint layer one can freely rotate a selected rectangle by any angle; the results are often distorted, however. One can also distort a rectangular selection in several ways not available in MacPaint.

SuperPaint allows one to create bit patterns for the LaserWriter at the 300 bit per inch (bpi) resolution. These objects can be edited just as if one were working in a paint layer, but because the screen resolution is only 72 bpi, the image will be an expanded view of what one would see on the LaserWriter. The LaserBits images can be transferred to either the paint or the draw layer. When displayed on the screen or printed on the ImageWriter, the images may be greatly distorted; however, when printed from the draw layer on the LaserWriter, the image prints with 300 bpi resolution. One can transfer images created at 72 bpi resolution (from the paint layer or MacPaint, for example) to the LaserBits editor, but they will be rescaled and, hence, considerably distorted.

Editing at the 300 bpi resolution is quite tedious, but the results can be quite dramatic. An example of the ACS emblem created in LaserBits is given below. I will give a copy of this emblem to anyone wishing to send me a blank disk (Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204). You will be able to paste this