$\alpha$-pyridone blue. The metal–metal distances in the sulfate (2.446 Å), $\alpha$-pyridonate (2.779 and 2.885 Å), and pyrophosphate (3.22 and 3.11 Å) bridged complexes reflect the extent of metal–metal bonding and are correlated with differences in their formal oxidation states, 3.0, 2.25, and 2.0, respectively.[19]

*cis*-Diammineplatinum $\alpha$-pyridone blue is unstable in neutral or alkaline solutions, judging by the diminution with time of the broad visible absorption band ($\lambda_{max}$ 685 nm). The color of aqueous solutions of the compound is instantly discharged by excess chloride ion and by reducing (dithionite, borohydride) or oxidizing (peroxide) agents. These reactions should be noted in conjunction with attempts to explain the antitumor activity of the platinum pyrimidine blues.

The bridged oligomeric structure involving partially oxidized platinum atoms found in the present study most likely embodies features shared by all amide containing platinum blues.[20-22] Moreover, the ability of *cis*-diammineplatinum(II) to bond to the exocyclic keto oxygen atom of the deprotonated $\alpha$-pyridone ligand requires that a similar binding mode be given serious consideration for the interaction of the antitumor drug *cis*-dichlorodiammineplatinum(II) with DNA, RNA, and their constituents.[24]

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(10) On occasion, a purple solution formed upon addition of nitric acid and sodium nitrate. Following similar isolation procedures, purple-black microcrystals were obtained, aqueous solutions of which have a broad absorption band centered at $\lambda_{max}$ 525 nm with a shoulder at 675 nm. Chemical analysis suggests the formulation $Pt_5(C_5H_4ON)_2(NH_3)_2(NO_3)_{16}$. Anal. Calcd: C, 5.49; H, 0.64; N, 12.79; O, 36.53; Pt, 44.55. Found: C, 5.50; H, 0.49; N, 12.83; O, 36.37; Pt, 44.72.
(11) Chemical analysis. The sample used in the x-ray study analyzed as follows: C, 14.72; H, 2.63; N, 14.35; calcd for $PtC_5H_{10}N_{4.25}O_{4.75}$, C, 14.99; H, 2.52; N, 14.85; O, 18.96; Pt, 48.68. Analytical data for a separately prepared sample are: C, 14.70; H, 2.90; N, 13.95; O, 19.70; Pt, 48.60. These data fit the formula $PtC_5H_{10}N_{4.25}O_{4.75}(H_2O)_{0.25}$ (calcd: C, 14.82; H, 2.61; N, 14.67; O, 19.74; Pt, 48.14). The crystal structure reveals channels of nitrate ions that might accommodate an extra water molecule per unit cell.[12]
(12) X-ray analysis. Dark blue platelets, obtained from solution prior to filtration, were air-dried and mounted on glass rods. The compound crystallizes in the triclinic system with the following unit cell dimensions: $a$ = 10.220 (4) Å, $b$ = 11.256 (5) Å, $c$ = 9.547 (4) Å, $\alpha$ = 106.29 (2)°, $\beta$ = 93.95 (3)°, $\gamma$ = 73.64 (3)°, $V$ = 1011.4 Å$^3$, M = 400.8, $\rho_{obsd}$ = 2.62 (2) g/cm$^3$, $\rho_{calcd}$ = 2.631 g/cm$^3$ for $Z$ = 4 formula units. Using 3548 unique observed reflections collected with Mo K$\alpha$ ($\lambda$ 0.7107 Å) radiation out to $2\theta = 55°$ on a computer controlled four-circle diffractometer, the structure was solved by standard heavy atom Patterson and Fourier methods. Refinement with anisotropic temperature factors for platinum and isotropic $B$'s for all other atoms has converged at a current value of 0.068 for the discrepancy index $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. The space group has been taken as $P\bar{1}$, and attempts to refine the structure in $P1$ are currently in progress. Five nitrate anions are in the unit cell, one of which is disordered across a crystallographic center of symmetry. Full details will be reported at a later date.
(13) Nonbonded ammine contacts of this kind would tend to destabilize a doubly $\alpha$-pyridonate bridged complex of *trans*-diammineplatinum.
(14) Integration of the broad electron spin resonance spectrum ($g_{av} \sim 2.2$) of a frozen (80 K) solution of the compound gave 0.8 ± 0.2 unpaired electrons per four platinum atoms. This result agrees with the crystallographic analysis which requires 1.0 unpaired electrons per four platinum atoms.
(15) An isomer of the doubly bridged cis complex having the $\alpha$-pyridonate ligands related by a $C_2$ symmetry axis (each platinum would then have two ammines, one oxygen, and one deprotonated nitrogen atom in its coordination sphere) would be stable but, for steric reasons, would not be expected to oligomerize further.
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(20) "A polymeric structure involving acetamido-bridges" was in fact proposed for platinum blue by Gillard and Wilkinson in 1964.[2]
(21) Uracil and thymine might use both keto oxygen atoms and the deprotonated nitrogen atom (**1**) to link three platinum atoms. Another variation would be an oligomeric structure in which every pair of adjacent platinum atoms is bridged by an amidate ligand but in which no double bridging occurs.
(22) Studies of the blue product obtained in the reaction of trimethylacetamide with $(CH_3CN)_2PtCl_2$ were interpreted in terms of the platinum(IV) formulation $[(CH_3)_3CCONH)_2PtCl_2]$.[3] X-ray photoelectron spectra of this compound are not consistent with the presence of tetravalent platinum, however.[23] It is possible that the blue trimethylacetamide complex is also a mixed valent oligomer.
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(24) Chelation of *cis*-$[(R_3N)_2PtCl_2]$ at the O6–N7 site of guanine has been evoked previously.[25] The present results suggest bridging at O6 and deprotonated N1 as an alternative binding mode for *cis*-diammineplatinum with guanine.
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## Experimental Electron Density Distribution of Sodium Hydrogen Diacetate. Evidence for Covalency in a Short Hydrogen Bond

*Sir:*

In a typical hydrogen bond, the oxygen to oxygen distance is ~2.8 Å with the hydrogen located ~1 Å from one of the oxygens. In solids, however, considerable variation exists in O···O lengths, and examples are found which range down to a lower limit of ~2.4 Å.[1] As the O···O distance decreases, the O—H distance increases until the hydrogen may be symmetrically located ~1.2 Å from each oxygen. Since both O—H bonds are now equal, the extent of covalency (in contrast to the largely electrostatic interaction of "long" hydrogen bonds) is of great interest.[2]

The electron density distribution in a crystal may be obtained by combining accurate x-ray intensity measurements with neutron diffraction results.[3] Quantitative comparisons between experimental charge density measurements and extended basis set, ab initio theoretical calculations have recently been made.[3b] We report here a low temperature x-ray and neutron diffraction study of the bonding in the short, symmetrical hydrogen bond of sodium hydrogen diacetate.

Recent experimental electron density studies on several compounds (glycylglycine,[4a] $\alpha$-glycine,[4b] 2-amino-5-chloropyridine,[4c] and formamide[4d]) containing normal X—H···Y hydrogen bonds show a lack of charge buildup between the X—H donor and the acceptor Y, relative to isolated atoms. Theoretical calculations of the change in electron density on dimerization of various simple molecules ($HCONH_2$,[5a] HF,[5b] and $H_2O$[5c]) predict a similar charge distribution between donor and acceptor.

The deformation density is the difference between the ex-

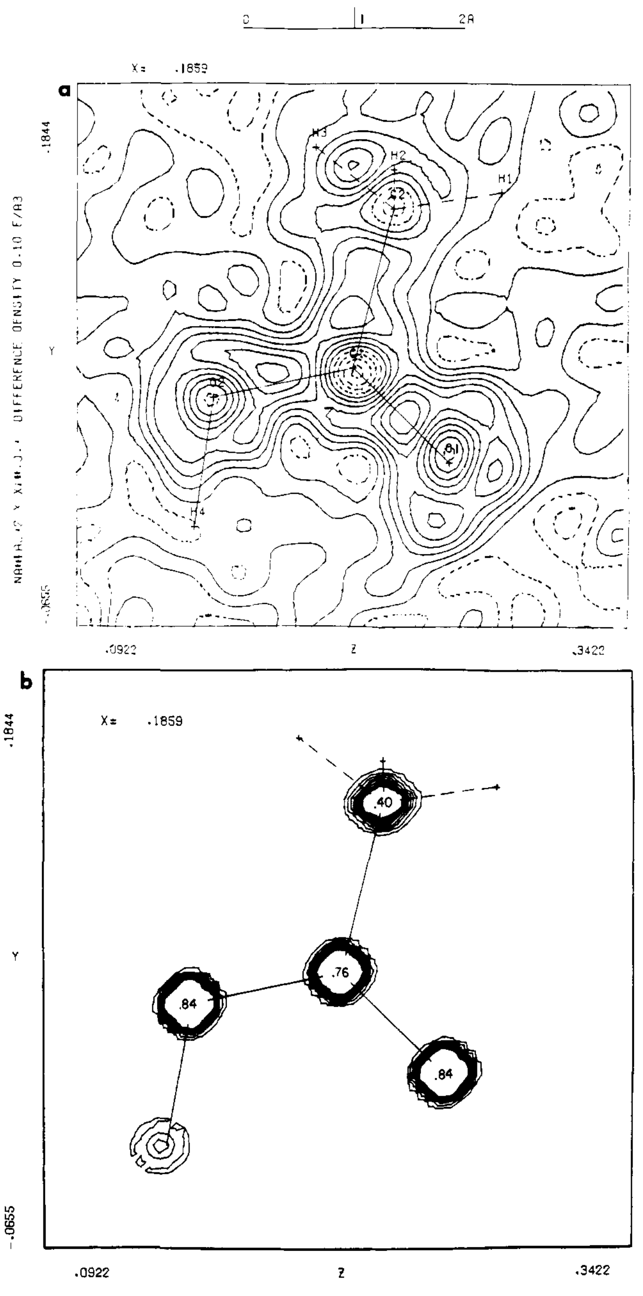

**Figure 1.** (a) Experimental deformation density ($\Delta\rho_{X-X}$) in the plane of the acetate ion. Contours at 0.1 e/Å$^3$, negative contours broken. (b) Error distribution in the deformation density: contours at 0.01 e/Å$^3$, lowest contour at 0.07 e/Å$^3$. Highest contours omitted and labeled with maximum values.

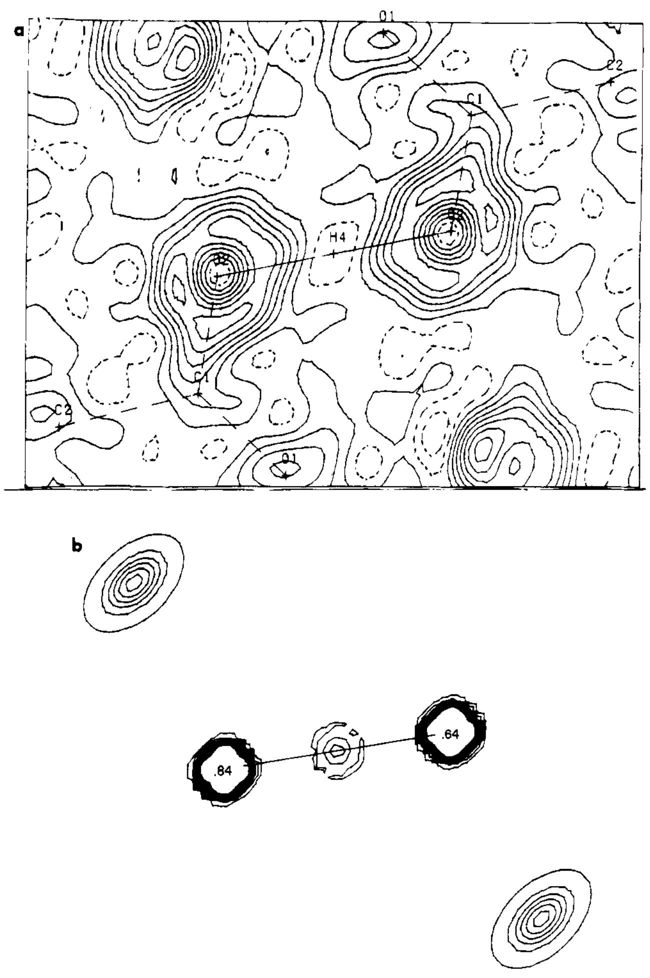

**Figure 2.** (a) Deformation density of the O···H···O hydrogen bond in the plane perpendicular to the twofold axis. Contours as in Figure 1. (b) Error distribution in the deformation density. The peaks off the bond axis are due to a crystallographic threefold axis.

perimental density and the density calculated for an assembly of isolated spherical atoms placed at the nuclear positions. In this function, covalent bonding is indicated by a buildup of density in peaks between atoms. The difference between a charge buildup (expected for covalent bonding) and charge depletion (as found in normal hydrogen bonds) allows assessment of covalency of the bond. Previous room temperature electron density studies on the short hydrogen bonds of pyridine-2,3-dicarboxylic acid[6] and the $H_5O_2^+$ ion in $C_6H_2(NO_2)_3SO_3H{\cdot}4H_2O$[7] and in $C_6H_4(COOH)SO_3H{\cdot}3H_2O$[8] are of limited accuracy and therefore inconclusive.

Sodium hydrogen diacetate ($NaHAc_2$) crystallizes in the cubic space group $Ia3$ with the short hydrogen bond lying across a crystallographic twofold axis. The structure has previously been determined by both x-ray and neutron diffraction.[9] Spectroscopic studies clearly indicate the hydrogen to be in a symmetric single potential well.[10] Single-crystal x-ray intensity measurements were collected on a Picker FACS-I diffractometer at 91 K using Nb filtered Mo K$\alpha$ radiation. A total of 11 037 reflections were measured in the range $0 < \sin\theta/\lambda < 0.86$ Å$^{-1}$. Averaging symmetry related forms gave 1754 unique reflections of which 976 had $I > 3\sigma(I)$. Full-matrix least-squares refinement based on $F$ gave $R(F) = 3.7\%$ and $R_w(F) = 3.8\%$.

To reduce bias in the refined parameters from the valence electron distribution, the x-ray data were refined using only high order measurements ($\sin\theta/\lambda > 0.65$ Å$^{-1}$) for which the scattering is predominantly due to the core electrons. The $\Delta\rho_{X-X}$ deformation density was calculated using high order x-ray parameters and the full x-ray data set. Since hydrogen parameters are not well determined in the high order refinement, they were taken from a parallel 91 K neutron diffraction experiment performed at the Institut Laue Langevin, which is to be described in a later report. The x-ray scale factor was determined by refinement of the full data set with all other parameters fixed at the high-order and neutron values.

In order to judge the significance of features in the deformation maps, it is necessary to estimate the standard deviation of the measured deformation density as a function of position in the crystal. The error distribution has been calculated and plotted as described by Rees[11] including contributions from errors in the x-ray intensity measurements, in the refined parameters, and in the x-ray scale factor. As the error function peaks near the atomic centers, details of the measured density within about 0.25 Å of the heavy atom nuclear positions cannot be considered significant.

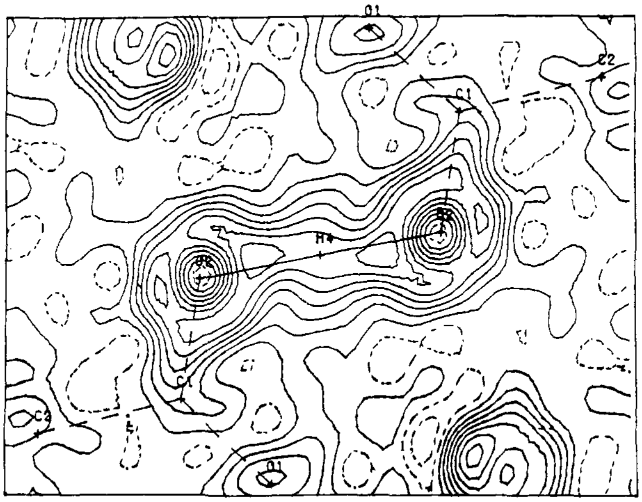

**Figure 3.** Deformation density of the O· · ·H· · ·O bond as in Figure 2, but without subtraction of the hydrogen atom density. Contours as in Figure 1.

In Figure 1, the $\Delta\rho_{X-X}$ deformation density is plotted in the plane of the acetate ion. Peaks are found in the C–O, C–C, and C–H bonds indicating a buildup of electron density in the covalent bonds relative to an assembly of spherical atoms. The peak heights are higher than the ones generally found in room temperature studies (glycylglycine,[4a] for example) due to less smearing by the thermal motion of the molecule at low temperature. The oxygen not involved in the short hydrogen bond ($O_1$) has two lone pair peaks in the plane of the molecule consistent with $sp^2$ hybridization.

Figure 2 shows the $\Delta\rho_{X-X}$ density in the plane perpendicular to the twofold axis containing the $O_2\cdots H\cdots O_2'$ short hydrogen bond. Large peaks (0.48 e Å$^{-3}$, as compared with mean peak heights of 0.65, 0.44, and 0.39 e Å$^{-3}$ for the C–O, C–C, and C–H bonds) are located on each side of the hydrogen near the midpoints of the O–H bonds. Although these peaks merge into the ring of density around $O_2$, they are somewhat further from the nuclear positions than the lone pair peaks on $O_1$ shown in Figure 1 which are ~0.44 Å from the nucleus. It may be noted that these peaks appear more diffuse than commonly observed in normal covalent bonds. There is no significant charge depletion near the hydrogen atom as would be expected for ionic bonding.

The covalent character of the short hydrogen bond is further evident in Figure 3 in which the calculated density of the hydrogen atom has not been subtracted out in the difference density. The error distribution for Figure 3 is essentially the same as Figure 2b. A continuous ridge of electron density about 0.55 e/Å$^3$ high extends along the hydrogen bond from one oxygen to the other. Such a distribution is incompatible with an ionic model.

The early qualitative molecular orbital description by Pimentel[12] of bonding in $HF_2^-$ works remarkably well for the bonding in $NaHAc_2$. Combining the 1s orbital on hydrogen with two oxygen $p\sigma$ orbitals gives three molecular orbitals: a bonding and an antibonding symmetric combination, and a nonbonding antisymmetric combination. Population of the bonding and nonbonding orbitals with two electrons each yields a density distribution in qualitative agreement with the experiment.

A more detailed comparison may be made with the double zeta calculation of $H_5O_2^+$ by Kollman and Allen,[2] who find a node in the bond charge density when the difference between the total density and the $H_2O\cdots H^+\cdots OH_2$ unbonded system is plotted. This node, which is located between the O and $H^+$, is not found in our deformation densities in which spherical atoms are subtracted rather than $H_2O$ molecules with extra density in the lone pair regions. There is no evidence in the experimental distribution for the unique character of short hydrogen bonds as distinguished from ordinary covalent bonds,[2] though both studies indicate a large degree of covalency.

Both experiment and theory show a distinct difference in the distribution of electron density in normal hydrogen bonds and in the short, symmetrical hydrogen bonds. The large number of compounds with hydrogen bonds of intermediate length suggests a continuous change from the long bond in which the electrostatic contribution dominates, to the short bond in which covalent bonding dominates. In this respect, a theoretical analysis of the contributions to the charge redistribution in the short hydrogen bond similar to the study of Yamabe and Morokuma[5c] on "normal" hydrogen bonded systems would be desirable.

While the molecular wave function itself cannot be obtained from measurements of the charge density distribution, the experimental density does indicate the degree of covalent character in bonding and provides an extremely detailed property of the system which any trial wave function must satisfy.

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