Figure 1. Such a shift results in a decrease in the magnitude of D.[8,12] In order that the spectrum continue to fit a Hamiltonian, the separation between the z lines must decrease in a parallel fashion. Figures 1 and 2d show very clearly the decreasing separation between the z lines as the temperature is raised.[15]

What is the nature of the new state of trimethylenemethane? Theoretical estimates[16] of the difference in energy between the planar (0,0,0) and perpendicular (0,0,90) triplet trimethylenemethanes (1) range from 8[16a] and 10[16b] to approximately 17[16c,d,e] kcal/mol. It may be argued that even the lowest of these values is too great to account satisfactorily for a transformation in which it appears that rapid equilibration or averaging occurs near −150 °C. While the theoretical results can in no way alone be taken to rule out the (0,0,90) form as a possibility, they do encourage a search for alternative possible states of the triplet (I) which might be accessible under the conditions of the experiments described above.

In their recent theoretical examination of trimethylenemethane (I), Yarkony and Schaefer[13c] noted that when the $^3A_2'$ ground state of trimethylenemethane was described as the $^3B_2$ state of C_{2v} symmetry, the energy was not changed.[17] No further discussion of the $^3B_2$ state has occurred and there have been no predictions that it might represent a stable minimum on any reaction pathway of the triplet 1. It is intriguing to speculate, however, that the temperature dependent splitting of the xy lines might be the result of the reversible interconversion of the $^3B_2$ and $^3A_2'$ states. Such an averaging between states of D_{3h} and C_{2v} symmetry would provide an explanation for the observed temperature dependent splitting. It would also lead to an understanding of the decrease in the D value. Thus, if the molecule is transformed from D_{3h} to C_{2v} symmetry by way of an E' vibration, this would entail not only contraction of the central bond angle but also lengthening of the opposing carbon–carbon bond.[18] The net effect would be an increased average separation between the two unpaired electrons and a consequent decrease in the value of D.[12] However, it is not intuitively obvious and it is correspondingly unsettling, that what appears to be a normal vibrational mode, the contraction of the bond angle at the central carbon atom of 1, should lead to a potential minimum. *If* so, this symmetry-breaking step would add a bizarre new dimension to the chemical and spectroscopic attributes of trimethylenemethane (1).[19]

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(2) The four lines are the $\Delta m = 1$ lines appearing at 2993, 3118, 3368, and 3502 G at −175 °C. There is, of course, a fifth line in the spectrum, the $\Delta m = 2$ line at 1618 G, which is not shown in any of the figures. The latter peak is relatively little changed in appearance over the temperature range examined in the present study.

(3) The x and y axes are taken to be those lying in the horizontal plane of the molecule; the z axis is that normal to the horizontal plane. For each one of the Cartesian coordinates x, y, and z, two $\Delta m = 1$ lines are generated, giving rise, when the three axes are distinct from one another, to a total of six lines.[4]

(4) W. A. Yager, E. Wasserman, and R. M. R. Cramer, *J. Chem. Phys.*, **37**, 1148 (1962).

(5) Prepared by condensation of acetaldehyde-d_4 (more readily available than acetaldehyde-1-d_1) with formaldehyde-d_2 yielding pentaerythritol-d_8. The latter was then converted to methylenecyclopropane-d_6 by published procedures.[6] The isotopic purity of the methylenecyclopropane-d_6 was high; the final product contained 96% C_4D_6 and 4% C_4HD_5.

(6) A Mooradian and J. B. Cloke, *J. Am. Chem. Soc.*, **67**, 942 (1945); J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *Ibid.*, **75**, 3344 (1953); B. C. Anderson, *J. Org. Chem.*, **27**, 2720 (1962).

(7) (a) K. Takeda, H. Yoshida, K. Hayashi, and S. Okamura, *Bull. Inst. Chem. Res. Kyoto Unit.*, **45**, 55 (1967); (b) T. Yamaguchi, M. Irie, and H. Yoshida, *Chem. Lett.*, 975 (1973); (c) H. Yoshida and O. Edlund, *Chem. Phys. Lett.*, **42**, 107 (1976).

(8) Over the temperature range −196 to −155 °C, the xy lines in the spectrum of I-d_6 broaden from 9 to 17 G and the z lines move toward the center of the spectrum by approximately 10 G.

(9) The temperature range over which the splitting occurs is that in which trimethylenemethane (i) closes to methylenecyclopropane at a measurable rate.[10] Lowering the temperature restores the original spectrum, with the xy-lines unsplit, but it is accompanied by some loss in intensity due to the ring-closure reaction. Even with the loss in intensity in the higher temperature reaches, it is still possible to demonstrate many reversible cycles of the splitting in the xy lines. When the triplet spectrum described above (Figure 1) is allowed to decay completely, there remains a very weak apparently more stable (less reactive) triplet spectrum ($D = 0.025$, $E = 0$ cm^{-1}) which differs from that described above in being almost completely unresponsive to temperature. This observation will be described in more detail shortly.[10]

(10) P. Dowd and M. Chow, to be submitted for publication.

(11) P. Dowd and K. Sachdev, *J. Am. Chem. Soc.*, **89**, 715 (1967).

(12) Stated more fully: in the spectrum of an n-fold symmetric triplet ($n \geq 3$), the separation between the xy lines is a characteristic of the triplet called the zero-field parameter D. Ordinarily expressed in units of wavenumbers (cm^{-1}), the D value is generally taken as a measure of the magnitude of the dipolar interaction between the unpaired electrons. The D value for trimethylenemethane (I) is 0.025 cm^{-1} at 196 °C. For all randomly oriented triplet molecules, the separation between the two z lines is required to be $2D$. Thus, a splitting of the xy lines, if it is the result of site nonequivalence reflected in the D value, must also be manifested by splitting, to the same extent, of the z lines.

(13) In hexafluorobenzene the spectra were weaker than those obtained from samples of neat methylenecyclopropane-d_6, and the effect of changing the matrix is to decrease somewhat the stability of the diradical I-d_6 in the critical temperature region.

(14) The zero-field parameter E is obtained from the triplet spectrum and is one-third of the separation between the x and y lines. E is generally taken as a measure of the asymmetry of the triplet molecule, being zero for molecules in which the x axis is equivalent to the y axis (threefold or higher symmetry axis) and taking on nonzero values for molecules in which the x axis is not equivalent to the y axis.

(15) All of the samples examined, including those in hexafluorobenzene and tetrahydrofuran, and those prepared starting with 3-methylenecyclobutanone showed the same temperature dependent variation in the D value as that shown in Figures 1 and 2b. The decrease in the D value has also been noted recently by others,[7c] and the change ascribed, on the basis of no other evidence, to molecular out-of-plane vibrations.

(16) (a) M. J. S. Dewar and J. S. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971); (b) J. Olsen and S. Kang, *J. Mol. Struct.*, **9**, 315 (1971); (c) D. R. Yarkony and H. F. Schaefer, *J. Am. Chem. Soc.*, **96**, 3754 (1974); (d) W. Hehre, L. Salem, and M. Wilcott, *ibid.*, **96**, 4328 (1974); (e) J. H. Davis and W. A. Goddard, *ibid.*, **98**, 303 (1976).

(17) Although explicit point was not made of it, the state diagrams of Davis and Goddard[16e] and of W. T. Borden, *Tetrahedron Lett.*, 259 (1967), carry the implication that the $^3A_2'$ and $^3B_2$ states should be considered to be close in energy.

(18) F. A. Cotton, "Chemical Applications of Group Theory", 2nd ed, Wiley, New York, N.Y., p 297.

(19) A referee has suggested that the temperature dependent splitting of the xy lines might arise through wide amplitude torsional motion of the methylene groups. He has proposed that such a motion in the E mode will confer an average C_{2v} geometry on the (D_{3h}) ground state. The referee prefers this explanation because it neither requires a new electronic state which is almost degenerate with the ground state nor two potential minima associated with the same normal mode. While we cannot rule out such an explanation, the proposal that one electronic state (the D_{3h} ground state) can take on an average C_{2v} character through one torsional mode seems most unusual. It ignores the other 23 vibrational modes and makes tenuous the idea that discrete molecular electronic states can be classified and characterized according to a single average symmetry.

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Synthesis and Crystal Structure of *cis*-Diammineplatinum α-Pyridone Blue

Sir:

The blue compounds formed from aqueous solutions of platinum(II) in the presence of amides have been a subject of

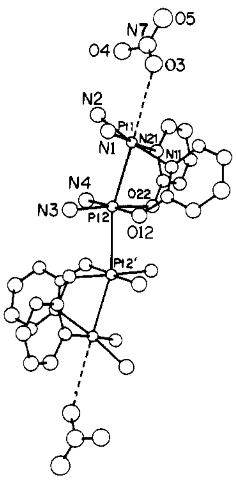
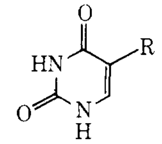
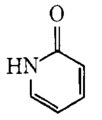


Figure 1. Structure of $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_5$ showing the 40% probability thermal ellipsoids and omitting noncoordinated nitrate ions and hydrogen atoms. Carbon atoms are not labeled. Primed atoms are related to unprimed atoms by a crystallographically required[12] center of symmetry.

study since the original report of "Platinblau" in 1908.[1-3] Recent interest in these complexes was sparked by the discovery that aquated products of the antitumor drug *cis*-dichlorodiammineplatinum(II) undergo a slow reaction with polyuracil, uracil, thymine, and related pyrimidines (**1**) to form blue complexes.[4] The platinum pyrimidine blues have antitumor activity of their own[4,5] and are useful electron microscopic stains for DNA.[6] Attempts to crystallize these blue complexes have been largely unsuccessful because they are oligomeric mixtures of varying degrees of hydrolytic instability.[7] With synthetic insights provided by the detailed studies of Lerner[7] and the choice of α-pyridone (**2**) as the amide ligand,[8] we have obtained a crystalline platinum blue and determined its structure by x-ray crystallography.



uracil (R = H)
thymine (R = CH_3) 1



α-pyridone 2

A mixture of *cis*-diammineplatinum(II) hydrolysis products[9] was prepared from 1 mmol of *cis*-$[(NH_3)_2PtCl_2]$ and 2 mmol of silver nitrate in 6 mL of water. After removing the silver chloride by centrifugation, 1 mL of an aqueous solution containing 1 mmol of α-pyridone was added. The yellow solution was adjusted to pH 7 with NaOH and left to stand for 5 days in the dark at 37-40 °C. Up to this point, the procedure closely parallels that employed in the synthesis of the platinum pyrimidine blues.[4] The brown-green (sometimes blue) solution was then adjusted to pH 1 with concentrated nitric acid. An equal volume of a saturated aqueous sodium nitrate solution was then added. Upon standing, the blue solution yielded dark blue[10] crystals which were filtered and washed exhaustively with 100% ethanol. Analytical[11] and x-ray crystallographic[12] data showed the composition to be $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_5$.

Table I. Selected Geometric Features of *cis*-Diammineplatinum α-Pyridone Blue[a]

Distance	Å	Angle	Deg
Pt1-Pt2	2.779	Pt1-Pt2-Pt2'	164.5
Pt2-Pt2'	2.885	Pt2-Pt1-O3	168.2
Pt1-N1	2.06	N1-Pt1-N2	88.5
Pt1-N2	2.06	N3-Pt2-N4	91.6
Pt1-N11	2.09	N1-Pt1-N11	89.3
Pt1-N21	2.01	N2-Pt1-N21	91.8
Pt1-O3	3.30	N3-Pt2-O12	87.4
Pt2-O12	2.06	N4-Pt2-O22	87.8
Pt2-O22	2.02	N11-Pt1-N21	90.1
Pt2-N3	2.02	O12-Pt2-O22	93.2
Pt2-N4	2.08		
N1-N3	3.63		
N2-N4	3.75		

Dihedral Angles Plane A	 Plane B	 Angle, deg
Pt1 coord plane	Pt2 coord plane	28.7
Pt1 coord plane	Pyridone 1	81.0
Pt1 coord plane	Pyridone 2	61.8
Pt2 coord plane	Pyridone 1	62.8
Pt2 coord plane	Pyridone 2	86.2
Pt1-Pt2-N1	Pt1-Pt2-N3	21.7
Pt1-Pt2-N2	Pt1-Pt2-N4	23.9

Hydrogen Bonding[b] Distances, Å				Angle, deg	
N3-H	0.95	H···O22'	1.98	N3-H-O22'	143
N4-H	0.96	H···O12'	1.98	N4-H-O12'	149

[a] Atoms are labeled as in Figure 1. Standard deviations in bond lengths are 0.02 Å and in interbond angles are 0.6° or less. [b] Hydrogen atoms (H) are bonded to the designated ammine nitrogen atoms. Hydrogen atoms were located on difference Fourier maps and have not been refined.

The structure of *cis*-diammineplatinum α-pyridone blue is shown in Figure 1. The geometry is summarized in Table I. Two planar *cis*-diammineplatinum units are bridged by two α-pyridonate ligands. The average N···O bite distance of these ligands (2.31 (3) Å) is shorter than the Pt-Pt bond length of 2.779 Å, and the two coordination planes are canted at an angle of 28.7°. This splaying effect, together with a 23° tortional twist about the Pt1-Pt2 bond axis, permits the nonbonded amine contacts N1-N3 and N2-N4 to average 3.69 Å, a value consistent with the sum of the van der Waals radii.[13] In addition, two α-pyridonate bridged dimers are linked across a crystallographically required[12] center of symmetry by a 2.885 Å platinum-platinum bond that is reinforced by four hydrogen bonds between the coordinated ammines and the oxygen atoms of the α-pyridonate ligands (Table I and Figure 1). Since the unit cell also contains five nitrate ions, the platinum formal oxidation state in the zigzag (Pt1-Pt2-Pt2' angle = 164.5°) tetranuclear chain is 2.25.[14] Two weakly bonded nitrate ions cap the two ends of this chain. Further elongation of the structure through additional Pt-Pt bonding is prohibited by the steric bulk of the α-pyridonate rings and the unavailability of additional hydrogen bonding groups at the chain ends.[15] This situation may be contrasted with that of the platinum pyrimidine blues, which can exist as oligomeric mixtures with up to 15 or more platinum atoms in the chain,[7b,16] and perhaps accounts for the crystallinity of *cis*-diammineplatinum α-pyridone blue.

The structure may be compared with those of $K_2[Pt_2(SO_4)_4(H_2O)_2]$, in which two platinum(III) atoms are bridged by four bidentate sulfate ligands and capped by two water molecules,[17] and of $Pt_2(NH_3)_4P_2O_7$, where two *cis*-diammineplatinum(II) coordination spheres are doubly bridged by the tetradentate $P_2O_7^{4-}$ ion.[18] In the latter structure, the molecules are further associated in the crystal lattice through metal-metal and hydrogen bonding interactions that are strikingly similar to those observed for *cis*-diammineplatinum

α-pyridone blue. The metal–metal distances in the sulfate (2.446 Å), α-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 α-pyridone blue is unstable in neutral or alkaline solutions, judging by the diminution with time of the broad visible absorption band (λ_{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 α-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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(8) This ligand was suggested by Professor C. R. Cantor of our department.
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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 λ_{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, α = 106.29 (2)°, β = 93.95 (3)°, γ = 73.64 (3)°, V = 1011.4 Å^3, M = 400.8, ρ_{obsd} = 2.62 (2) g/cm^3, ρ_{calcd} = 2.631 g/cm^3 for Z = 4 formula units. Using 3548 unique observed reflections collected with Mo Kα (λ 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 α-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 α-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.
(16) R. D. Macfarlane and D. F. Torgerson, *Science*, **191**, 920 (1976).
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(19) A. H. Reis, Jr., and S. W. Peterson, *Inorg. Chem.*, **15**, 3186 (1976), and references cited therein.
(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.
(23) D. Cahen, results quoted in J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 113 (1976).
(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] α-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-