acetamido-4-phenyl-1-butene was formed. (An authentic sample was prepared for comparison.)

(11) (a) Shono et al.[11b] reported that hydrolysis of the 3,5-dinitrobenzoate analogous to **1a** (**7**) in 75% aqueous dioxane at 130 °C gave 85–88% **6** and 12–15% 2-phenylcyclopropylcarbinyl alcohol (**8**). Under the same conditions, the 3,5-DNB of **6** gave only **6.** Methanolysis of **7** gave **5a** and a trace of **8.** (b) T. Shono, I. Nishiguchi, and R. Oda, *J. Org. Chem.*, **35,** 42 (1970). (c) Deamination of *trans*-2-phenylcyclopropylcarbinyl amine afforded 82% **6, 14%** *trans*-**8,** 3% phenylcyclopropylcarbinyl alcohol, 1% 4-phenyl-3-buten-1-ol, and <1% *cis*-**8.**[11d] (d) C. Dupin and R. Fraisse-Jullien, *Bull. Soc. Chim. Fr.*, 1993 (1964).

(12) For a discussion, see P. J. Wagner in "Creation and Detection of the Excited State", Vol. 1, A. A. Lamola, Ed., Marcel Dekker, New York, 1971, p 173.

(13) (a) J. K. Kochi in "Free Radicals", Vol. 2, J. K. Kochi, Ed., Wiley-Interscience, New York, 1973, p 698; (b) T. Koenig, ref 13a, Vol. 1, p 113; (c) T. Koenig and H. Fischer, ref 13a, Vol. 1, p 157.

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(15) For example, D could be water. It is very difficult to prepare and maintain absolutely dry acetonitrile.

(16) In yet another experiment a solution of **1a** (0.1 M) and *N,N*-dimethylaniline (0.05 M) in 10 mL of methanol was irradiated through Pyrex with the 300-nm lamps of a Rayonet photochemical reactor. After 32 h there remained 33% *trans*-**1a**, 20% *cis*-**1a**, and a small amount of an unidentified product similar in GC retention time to *trans*-**1a**. No **2a** or **5a** could be detected.

(17) The trifluoroacetate **9** analogous to **1a** had a measured τ_s of 1.5 ns.[18] Photolysis[4] of 1.56 mmol of **9** in acetonitrile for 4 h provided 31% *trans*-**9,** 25% *cis*-**9,** and at least six unidentified higher boiling products. No product analogous to **5** could be detected. (In a previous experiment,[18] it had been found that extended irradiation of **9** resulted only in cis-trans isomerization and little loss of cyclopropane.) Attempts to study the photolysis of **9** in methanol were frustrated by its rapid methanolysis (hydrolysis?) to *trans*-2-phenylcyclopropylcarbinyl alcohol; see R. A. Sneen, K. M. Lewandowski, I. A. I. Taha, and B. R. Smith, *J. Am. Chem. Soc.*, **83,** 4843 (1961).

(18) J. A. Gere, Ph.D. Thesis, University of Massachusetts, 1977.

(19) It is convenient to view the ionization as occurring in two steps, though the "radical-like" singlet postulated may not lie at an energy minimum.

(20) R. S. Becker, L. Edwards, R. Bost, M. Elan, and G. Griffin, *J. Am. Chem. Soc.*, **94,** 6584 (1974).

(21) This mechanism is in many ways similar to that discussed by Walling for the decomposition of diacyl peroxides: C. Walling, H. P. Waits, J. Milanovic, and C. G. Pappiaonnou, *J. Am. Chem. Soc.*, **92,** 4927 (1970).

(22) It is the inductive effect of the $-CF_3$ (and $-CN$) group which is considered to enhance excited-state interaction between the cyclopropane and aromatic rings and thus promote cyclopropane bond weakening. The effect of the aromatic $-CF_3$ group on benzylic radical stability is of lesser importance.

(23) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *J. Am. Chem. Soc.*, **86,** 4628 (1964).

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(25) J. Cornelisse, *Pure Appl. Chem.*, **41,** 433 (1975), and references therein.

Stephen S. Hixson,* Jeffrey A. Gere, Lothar A. Franke
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01003

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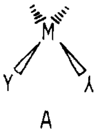
Evidence for Diastereomers of the [Platinum (N,N,N',N'-tetramethylethylenediamine)(guanosine)$_2$]$^{2+}$ Cation[1]

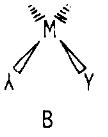
Sir:

In the course of our investigation of the square-planar platinum(II) complex *cis*-$[Pt(NH_3)_2(guanosine)_2]^{2+}$,[1] I, it occurred to us that, as a result of the arrangement of the guanosine ligands, the platinum center of this compound was chiral (Figure 1).

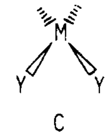
A square-planar metal complex, with two ligands of C_s local symmetry in cis positions, can exist in three possible configurations: A–C. Isomers A and B are nonsuperimposible mirror images and are therefore enantiomers in which the metal atom is the chiral center. Isomer C, corresponding to the meso form, contains an improper symmetry operation and the metal center is not chiral.



A



B



C

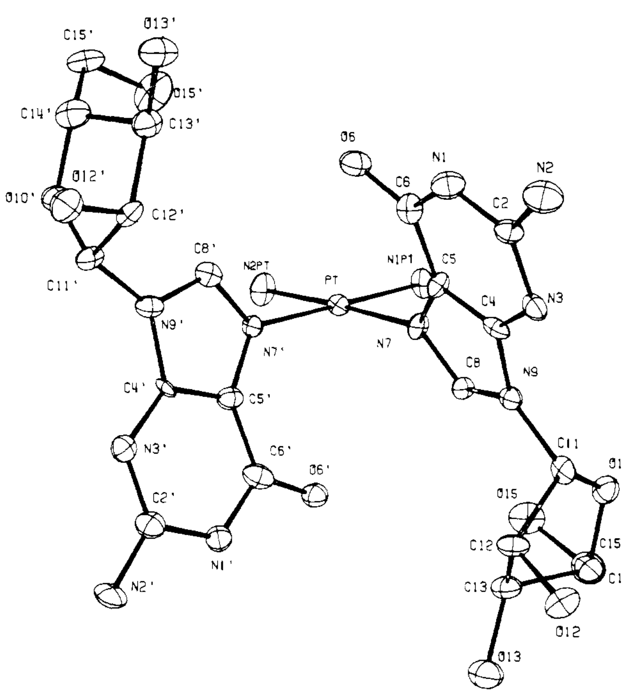


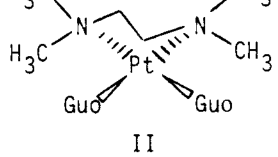
Figure 1. A view of the *cis*-$[Pt(NH_3)_2(guanosine)_2]^{+2}$ cation.

In the case of compound I, the ribose moiety of the guanosine ligands is a source of additional chirality. Since the absolute configuration of the ribose moiety in both guanosine ligands is the same, the mirror symmetry between the enantiomers A and B is broken and these isomers become diastereomers. Since diastereomers are chemically nonequivalent they may be differentiated by various physical techniques in a nonchiral medium.

The crystal structure of compound I shows the presence of only one of the possible diastereomers.[2] However, investigation disclosed only those optical effects due to the guanosines. The ^1H and ^{13}C NMR showed only resonances due to a single isomer, or a mixture of isomers rapidly exchanging on the NMR time scale (Figure 2). We propose that interconversion between the diastereomers occurs and is rapid on the NMR time scale.

A dissociative mechanism for the interconversion of the isomers of I which is rapid enough to be fast on the NMR time scale can be ruled out because platinum(II) is substitution inert. However, rapid exchange of these isomers can occur by simple rotation of both guanosines about the platinum guanosine bond. The bulk of the purine rings will provide some barrier to rotation about this bond, but rotation of a guanosine past an ammonia is easy. However, replacement of the ammonia ligands of I with bulky ligands could sterically inhibit this rotation. We therefore prepared the analogue of I in which the ammonia ligands have been replaced by N,N,N',N'-tetramethylethylenediamine.

(Dichloro)(N,N,N',N'-tetramethylethylenediamine)platinum(II) was prepared by the method of Mann and Watson[3]



II

by the addition of a threefold excess of free amine to an aqueous solution of H_2PtCl_6. The colorless diaquo complex was

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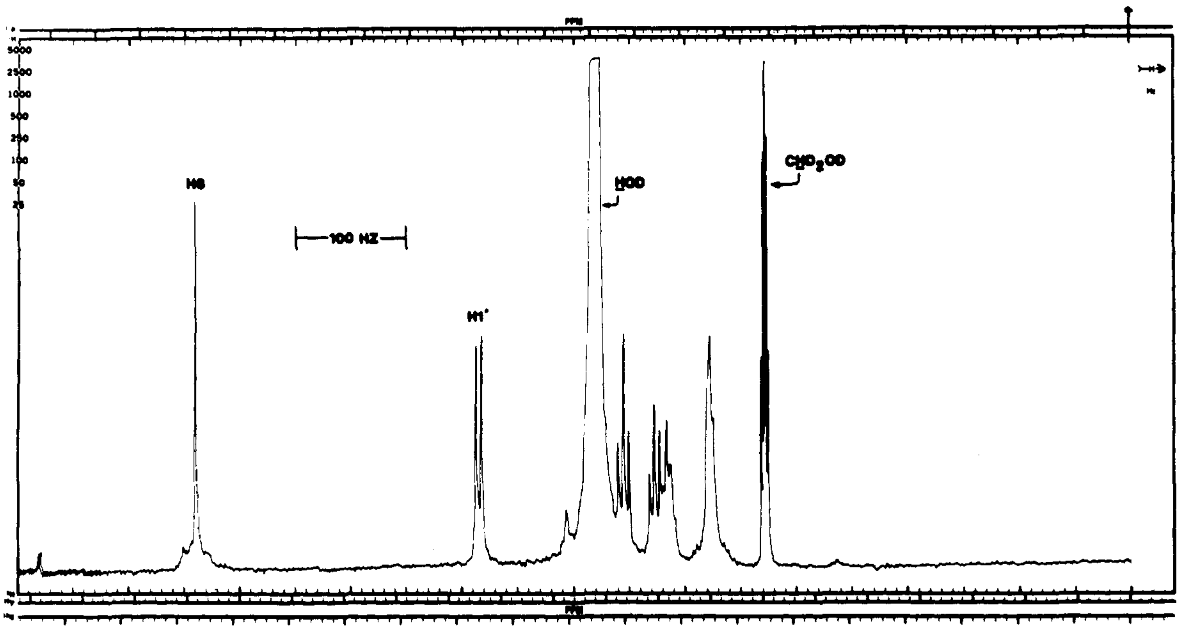

Figure 2. 100-MHz FT ^{1}H NMR spectrum of *cis*-[Pt(NH$_3$)$_2$(guanosine)$_2$]$^{+2}$ in D$_2$O/CD$_3$OD. The resonances between HOD and CHD$_2$OD are those of the ribose protons.

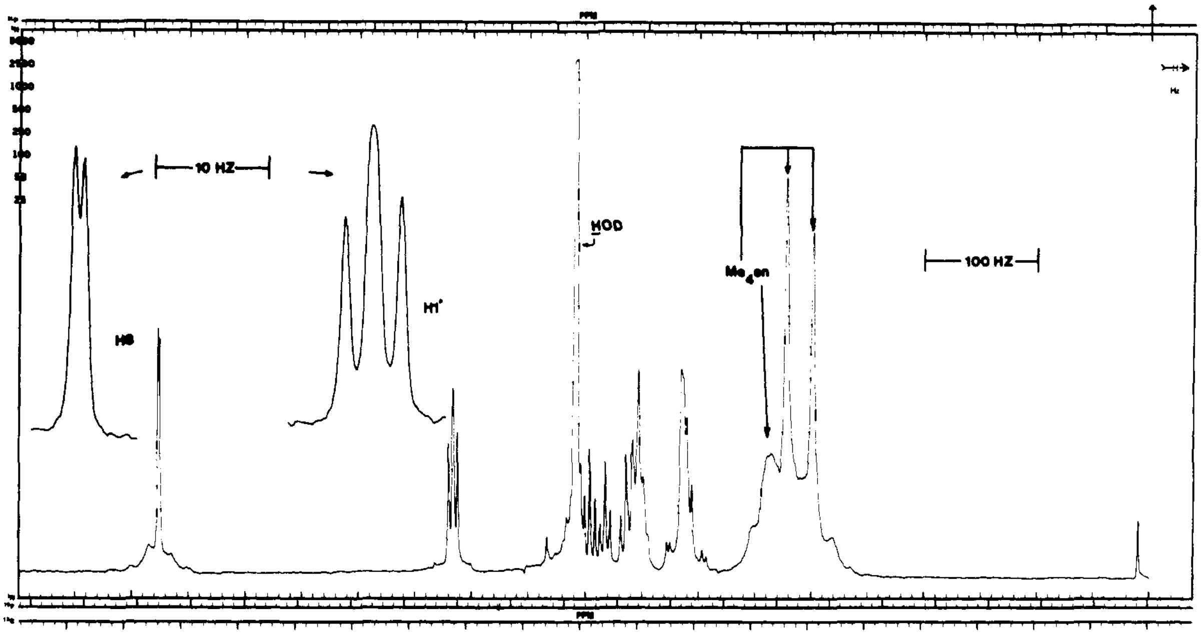

Figure 3. 100-MHz FT ^{1}H NMR spectrum of [Pt(Me$_4$en)(guanosine)$_2$]$^{2+}$ in D$_2$O. The resonances between HOD and Me$_4$en are those of the ribose protons.

prepared from the dichloro complex by removal of the chlorides with silver nitrate. The diaquo complex reacts stoichiometrically with guanosine to produce [platinum(II) (*N,N,N',N'*-tetramethylethylenediamine)(guanosine)$_2$]$^{2+}$, II, for which the same isomers as proposed for compound I are possible. Diastereomer C would be expected to be sterically unfavorable owing to the presence of two *N*-methyl groups and the O(6) carbonyl oxygen of both guanosines on the same side of the platinum coordination plane. Therefore, the presence of only diastereomers A and B is expected.

In each of the diastereomers A and B, the two guanosines are magnetically equivalent owing to the presence of the twofold axis. Hence each diastereomer is expected to exhibit a single resonance for the H(8) protons and a single doublet for the H(1') protons. The four *N*-methyl groups have two different environments. Two of the *N*-methyl groups are on the same side of the platinum coordination plane as the carbonyl O(6) of the cis guanosine and the other two *N*-methyl groups are on the same side of the coordination plane as the ribose group of the cis guanosine. Hence each diastereomer is expected to exhibit two *N*-methyl resonances.

The ^{1}H NMR spectrum of a 0.05 M solution of II in D$_2$O at 26 °C is shown in Figure 3. The presence of two isomers is clearly indicated in the region of H(8) and H(1') absorbance. The diastereotopic *N*-methyl resonances are not resolved and the two resonances observed are due to the *N*-methyl protons in the two different environments for both diastereomers. However, the presence of the diastereotopic *N*-methyl resonances is manifested in the line width (4.5, 5.0 Hz) of each peak. The chemical shifts are listed for several temperatures in Table I. The proton chemical shifts of these molecules are concentration and temperature dependent presumably because

Table I. ^1H NMR Spectral Parameters for $[Pt(N,N,N',N'\text{-}Me_4en)(Guo)_2]^{2+}$, 0.05 M in D_2O

	Chemical Shifts[a]			
T(°C)	H(8)	H(1')	NCH_3	NCH_3
100.3	8.458	5.934 5.902	2.968	2.756
90.1	8.458	5.927 5.892	2.960	2.746
64.7	8.489	5.944 5.911	2.977	2.758
48.0	8.524 8.519	5.962 5.930	2.997	2.775
38.8	8.533 8.527	5.965 5.929	3.001	2.774
26.	8.551 8.539	5.972 5.931	3.007	2.775
0.	8.607 8.583	5.990 5.950	3.039	2.800

[a] Ppm downfield from DSS.

of base-stacking interactions between complexes. As a result of the temperature dependence of the chemical shifts, the two H(8) peaks merge at ~55 °C. However the splitting of the H(1′) peaks is larger and the H(1′) chemical shifts are less dependent on temperature so that two H(1′) doublets remain at 100 °C, confirming slow exchange between the diastereomers at this temperature. A lower limit to $\Delta G^{\ddagger}$ for the interconversion between the diastereomers can be calculated from the chemical-shift difference between the two H(1′) resonances at 100 °C. This difference is 3.2 Hz at 100 °C so that $\Delta G^{\ddagger}$ for the interconversion is >86 KJ mol^{-1}. This value is large enough to allow the possibility of separating the diastereomers, and we are attempting to do so.

The chirality demonstrated for the platinum center of II should be a general phenomenon for square-planar complexes. It will occur whenever a pair of large, planar ligands occupy cis positions in the coordination sphere. If these ligands are large enough, steric considerations will prevent their occupying the coordination plane and they will twist above and below it as observed for I. Isomers A, B, and possibly C will result. For exchange to occur among them, the ligands must rotate about the metal bond and in the transition state the ligand plane will lie in the metal coordination plane. This work demonstrates that it is possible, by increasing the steric bulk of the ligands, to destabilize the transition state so that a substantial barrier results between the A, B, and C stereoisomers.

References and Notes

(1) This paper is abstracted from a dissertation submitted to the Graduate Division of the University of Hawaii by P.L.D. in partial fulfillment of the requirements of a PhD. degree in chemistry.
(2) Cramer, R. E.; Dahlstrom, P. L. *J. Clin. Hematol. Oncol.* **1977**, *7*, 330.
(3) Mann, F. G.; Watson, H. R. *J. Chem. Soc.* **1958**, 2772.

Roger E. Cramer,* Phillip L. Dahlstrom
Department of Chemistry, 2545 The Mall
University of Hawaii, Honolulu, Hawaii 96822
Received March 2, 1979

Bis(tetramethylammonium) Tris(sorbitolato)manganate (IV), an EPR-Active Monomeric Complex of Manganese (IV)

Sir:

During recent investigations[1-5] of the redox chemistry for polyhydroxy complexes of manganese, we noted that certain of these ligands stabilize the +4 oxidation state as an apparent high-spin monomeric complex in aqueous alkaline solution. Previous examples of manganese(IV) species appear to be restricted to a series of di-μ-oxo bridged dimers that contain the $[Mn_2{}^{IV}O_2{}^{4+}]$ unit.[6-10] Their low magnetic moments (ca. $\leq 2.5\ \mu_B$) are consistent with considerable antiferromagnetic coupling between the manganese centers.[9] A few unstable halide and pseudohalide monomeric complexes of the type $[MnL_6]^{2-}$ (L = F,[11] Cl,[12] IO_3,[13] or CN[14]) have been reported, but they do not appear to exhibit appreciable distortion from octahedral symmetry and have not been fully characterized. A recent EPR study of a number of dioxygen adducts formed by manganese(II) porphyrins has been interpreted in terms of a manganese(IV)-peroxo formulation.[15] We report here the isolation and characterization of $(Me_4N)_2Mn^{IV}(C_6H_{12}O_6)_3$ ($C_6H_{14}O_6$ = sorbital (D-glucitol)), which we believe to be the first authentic example of a high-spin tris(chelate) monomeric complex of manganese(IV).[16] The complex exhibits an EPR spectrum which is consistent with a ($\frac{1}{2} \rightarrow -\frac{1}{2}$) transition of the spin quartet ground state in an axially distorted octahedral ligand field.

In the formation reaction,[16] the manganese(II)-sorbitol complex appears to reduce triplet-state dioxygen to hydrogen peroxide, with the yield dependent on the equilibrium constants K_1 and K_2.

$$[Mn_2{}^{II}(H_2O)_2(SH_4)_4]^{4-} + {}^3O_2 \xrightleftharpoons{K_1} \underset{(III_A)_2}{[Mn_2{}^{III}(OH)_2(SH_4)_4]^{4-}} + H_2O_2\ (8\%) \quad (1)$$

$$\underset{(III_A)_2}{[Mn_2{}^{III}(OH)_2(SH_4)_4]^{4-}} + {}^3O_2 + 2SH_6 \xrightleftharpoons{K_2} 2[Mn^{IV}(SH_4)_3]^{2-} + H_2O_2\ (60\%) \quad (2)$$

$$SH_6 \equiv C_6H_{14}O_6$$

The yields of hydrogen peroxide have been estimated by means of cyclic voltammetry in aqueous 0.5 M NaOH and 0.5 M sorbitol. The low yield in the (II → III) step is due to a further reaction between manganese(II) and hydrogen peroxide above pH 7.5.[1,5] Such a process yields manganese(III) and may produce ·OH by a process analogous to Fenton's reaction.[18,19] The equilibrium constant (K_2) has been estimated, from the concentration of hydrogen peroxide at 1 atm in 0.5 M NaOH and 0.5 M sorbitol, to be 3.44×10^1 mM atm^{-1} at 298 K.

The infrared spectrum of the solid complex, as a KBr disk, exhibits bands due to the O-H, C-H, and C-O stretching vibrations of sorbitol and a band at 560 cm^{-1}, which is assigned

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