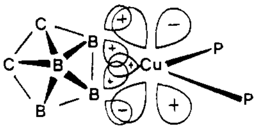
The B–B bond in B_6H_{10} is ~0.22 Å shorter[52] than in the complex $(B_6H_{10})_2PtCl_2$. This can be explained in terms of back-donation of electron density from nonbonding d orbitals on the metal fragment to an antibonding B–B orbital. Theoretical calculations on B_6H_{10} suggest that there is a low-lying empty orbital analogous to the π^* orbital of ethylene.[53] Bonding between the carborane anion cage and L_2Cu in the species I–IV may be described similarly. Donation of a pair of electrons from the B–B bond in the anion into an empty sp^2 type orbital on the Cu may be accomplished by back-bonding from a filled d orbital on the Cu into the antibonding orbital of the B–B bond. Thus the structure shown below assumes the perpendicular mode of attachment, found for similar systems, and may be compared with metal–olefin interactions in organometallic systems:



This back-bonding argument was not mentioned in the theoretical discussion[54] of $(CO)_4FeB_6H_{10}$, and the same workers suggested that the bonding in $(CO)_4FeB_6H_{10}$ is different from that in the hypothetical species[55] $(\mu\text{-}(H_3P)_2Cu)B_5H_8$, which might be expected to resemble the compounds I–IV prepared in this study.

The proposed structures shown in Figure 1 for species I–IV have been drawn purposely to suggest that the Cu lies close to the basal plane of the carborane. This would be expeected if the Cu does interact with a terminal H on an adjacent B atom to form a bridge bond. If this is the case, the L_2Cu fragment becomes a pseudovertex as it does in the species $(CO)_3FeB_5H_8Cu[P(C_6H_5)_3]_2$, where there is a bent Cu–H–B bridge bond.[11] According to the polyhedral skeletal electron pair theory,[13] the L_2Cu moiety contributes two electrons to the cluster, which is thus best described as a nido-hexagonal-pyramidal species. The alternative way to consider this system is assume that the L_2Cu moiety replaces a proton and thus does not contribute to the polyhedral skeletal electron count. X-ray structural determinations for these species would help resolve this question.

Acknowledgment. We acknowledge support from the Weldon Spring Endowment fund of the University of Missouri. Some of the NMR spectra were obtained with the aid of Dr. V. Rutar at the University of Missouri—Columbia. Finally we thank Professor Sheldon G. Shore of The Ohio State University, in whose laboratory the work was initiated by L.B. with support through NSF Grant CHE76-17805 (to S.G.S.).

Registry No. I, 97921-24-9; II, 97921-25-0; III, 97921-26-1; IV, 97921-27-2; $[(C_6H_5)_3P]_2CuBr$, 47814-88-0; (dppe)CuI, 15228-76-9.

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Diastereotopic Exchange in the Square-Planar Platinum(II) Complex (*N*,*N'*-Dimethylethylenediamine)bis(guanosine)platinum(II)[1]

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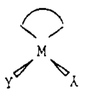
A total of six diastereomeric configurations of the chiral square-planar platinum(II) complex (*N*,*N'*-dimethylethylenediamine)bis(guanosine)platinum(II), $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$, are detected. Three sets of stereoisomers result from the configuration of the two coordinated ethylenediamine nitrogens, and these are designated *RR*, *SS*, and *SR*. In addition, the ribose moieties of the guanosines break all mirror symmetry in and between the stereoisomers, producing pairs of diastereomers possessing different physical and chemical properties. Rotation about the Pt–guanosine bond, which is rapid at 103 °C on the NMR time scale, causes exchange within each pair of diastereomers producing a sharp, four-line, ^1H NMR spectrum in the guanosine H(8) region. A complex set of ^1H NMR resonances is observed at −32 °C due to slow exchange in the *SR* set of diastereomers and in one of the *RR* or *SS* sets of diastereomers while the fast-exchange peak from the remaining set of diastereomers is only approaching coalescence. The concentration-dependent activation free energy for exchange between the *SR* diastereomers is about 65 kJ mol^{-1} while that for the higher energy exchange process between the *RR* or *SS* diastereomers is about 55 kJ mol^{-1}.

Introduction

It has been recognized for over 20 years that sufficiently bulky ligands can block rotation about the metal–ligand bond in square-planar complexes.[2,3] Observation of isomers, which can result from such restricted rotation, has been reported for complexes such as $[Pt(L)(olefin)Cl_2]^4$ and *trans*-$[Pd(hydrazone)_2Cl_2]$,[5,6] but such isomers have not been widely studied.

Square-planar complexes having two cis ligands with C_s local symmetry can exist in three stereoisomeric configurations, A–C, where Y represents the bulky ligand and the remaining coordination positions are occupied, for example, by a chelate. The



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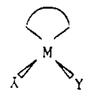

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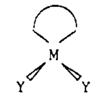

C

head to tail, H–T, isomers A and B are nonsuperimposable mirror

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images and thus enantiomers. Isomer C contains a mirror plane, an improper symmetry element, and therefore is not chiral. Thus, if ligand Y contains no chiral elements, isomers A and B will have identical physical and chemical properties, different from those of C. A mixture of such isomers would produce two sets of NMR signals of generally unequal intensity, similar to that observed for the *trans*-$[Pd(hydrazone)_2Cl_2]$ complexes.[5,6]

Introduction of a chiral element into the Y ligands breaks the mirror symmetry between A and B, which become diastereomers with different physical and chemical properties such as NMR spectra. Thus, for ligands containing the optically pure ribose moiety, such as guanosine, one expects to find all three isomers A, B, and C. In the solid state only a single H–T isomer is found for *cis*-$[Pt(NH_3)_2(Guo)_2]^{2+}$.[7,8] In solution, the NMR spectra of *cis*-$[Pt(NH_3)_2(Guo)_2]^{2+}$ and $[Pt(en)(Guo)_2]^{2+}$ each exhibit only a single H(8) resonance, consistent with the presence of only a single isomer or with fast exchange between isomers. However, for $[Pt(Me_4en)(Guo)_2]^{2+}$, where Me_4en is *N*,*N*,*N*,',*N*'-tetramethylethylenediamine, doubling of the guanosine H(8) resonance is observed.[9] This is consistent with (1) the presence of both H–T diastereomers A and B and the absence of C or (2) the presence of A, B, and C, where A and B have indistinguishable chemical shifts. Due to increased steric interaction in the H–H isomer, we interpreted the NMR of $[Pt(Me_4en)(Guo)_2]^{2+}$ in terms of case 1. Tobias[10] observed doubling of the NMR-signals of $[Pt(en)(Cyd)_2]^{2+}$, where en is ethylenediamine and Cyd is cytidine, which he attributed to both H–H and H–T isomers, i.e. case 2. More recently, Marzilli and Kistenmacher[11] have argued that Tobias' observation was a result of diastereomeric H–T isomers, i.e. case 1.

In order to establish whether case 1 or case 2 pertains, Reedijk[12] synthesized and studied $[Pt(bpe)(9\text{-}MeMeHX)_2]^{2+}$, where bpe is 1,2-bis(pyridin-2-yl)ethane and 9-MeHX is 9-methylhypoxanthine. In this complex the rigid seven-membered Pt–bpe chelate ring creates different environments above and below the platinum coordination plane. An H–T arrangement of the achiral 9-MeHX ligand would thus produce two H(8) resonances, but only a single resonance for a H–H isomer. An X-ray crystal structure revealed a H–T arrangement of the 9-MeHX ligands, and the H^1 NMR exhibited dynamic behavior with two H(8) signals observed at low temperature. This observation confirms that the H–T isomers are present in solution, a conclusion that we have also substantiated by other evidence.[13]

In this paper we report NMR studies of the complex $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$. While exchange between diastereomers A and B is rapid on the NMR time scale for *cis*-$[Pt(NH_3)_2(Guo)_2]^{2+}$ and $[Pt(en)(Guo)_2]^{2+}$, and is slow for $[Pt(Me_4en)(Guo)_2]^{2+}$, it is intermediate for $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$, so that temperature-dependent, dynamical NMR spectra can be observed, confirming that some dynamic molecular process, presumably rotation about the Pt–purine bond, takes place.

Experimental Section

(*N*,*N*'-Dimethylethylenediamine)bis(guanosine)platinum(II), $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$. $[Pt(N,N'\text{-}Me_2en)Cl_2]$ was synthesized by the appropriate modification of the previously reported synthesis for $[Pt(en)Cl_2]$.[14] Reaction of $[Pt(N,N'\text{-}Me_2en)Cl_2]$ with the stoichiometric amount of $AgClO_4$, and filtering to remove the precipitate of AgCl, produced $[Pt(N,N'\text{-}Me_2en)(H_2O)_2]^{2+}$. This was combined with the stoichiometric amount of guanosine and stirred overnight, analogous to the method reported by Theophanides et al.,[15] to give $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$. The product was isolated by lyophilization.

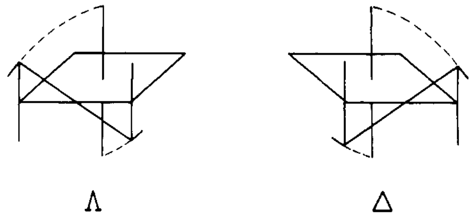

Figure 1. Illustration of the convention used to designate molecular configuration using two skew lines. One line is chosen perpendicular to the square coordination plane, and the second line chosen connects the six-membered rings of the purine ligands.

The material used to prepare NMR samples was dissolved in D_2O and lyophilized. This process was repeated three times in order to replace the labile protons with deuterons. Samples were dissolved in 100.0% isotopically pure D_2O or D_2O/CD_3OD mixtures. The pH of the solutions was approximately 5.5. Samples were prepared for NMR in a glovebag purged with dry nitrogen gas and by using predried glassware.

Proton NMR spectra were obtained in the Fourier transform mode with a Varian XL-100-15 NMR spectrometer equipped with Digilab Fourier transform accessories. Spectra were obtained at 100.1 MHz with a bandwidth of 2000 Hz and a 16K transform. The pulse width was 9 μs, corresponding to a tip angle of 36°. A delay of 1 s was provided between pulses. Proton NMR chemical shifts were measured relative to DSS as an internal standard.

The proton NMR spectrum of $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$ can be divided into four regions. The H(8) resonance of guanosine occurs around 8.4 ppm. The H(1') resonance of the ribose occurs around 5.9 ppm, while the remaining ribose resonances occur in several groups in the range 3.4–4.8 ppm. The *N*-methyl resonances of *N*,*N*'-Me_2en occur around 2.4–2.5 ppm, overlapping, but quite distinct from, the methylene resonances.

Theory

As noted earlier,[9] the H–T orientation of the guanosines produces a chiral center at the platinum. There is no convention for the designation of absolute configuration for chirality of this sort. We propose the absolute configuration be determined in the manner described for assigning the helicity of two skew lines.[16] As the two lines we chose one perpendicular to the coordination plane and the other joining a common reference point on the two ligands (see Figure 1). We have chosen the carbonyl O(6) end of the guanosine molecule as the reference point here; thus, the solid state structure *cis*-$[Pt(NH_3)_2(Guo)_2]^{2+}$ has the Δ configuration.[7,8]

Only one configuration is available for the chiral ribose moiety. This is denoted as + due to the positive rotation of the plane-polarized light at the sodium D line. Rapid conformational inversion occurs in solution between the δ and λ conformers of the 5-membered Me_2en ring, and this source of isomerism need not be considered here.

The coordinated ethylenediamine nitrogens are also chiral, having either an *R* or *S* configuration. Interconversion between *R* and *S* nitrogen configurations requires breaking of the Pt–N bond or abstraction of the amino hydrogen atom. Both of these processes are slow for $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$ at the pH of the solutions used in the NMR study, and interconversion between *R* and *S* nitrogen configurations does not occur on the NMR time scale.[17-20] In the absence of interconversion between nitrogen configurations, three noninterconverting sets of diastereomers with unique nitrogen configurations are possible. Both nitrogens can have the *R* configuration, and we label that set *RR*, or both can have the *S* configuration, labeled *SS*. Finally one nitrogen can be *S* and the other *R*, which we call *SR*. Since inversion of the configuration at an uncoordinated nitrogen is rapid, an equal

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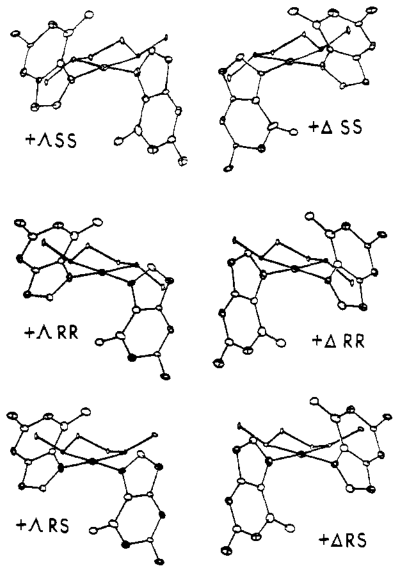

Figure 2. Significantly populated diastereomers for [Pt(*N*,*N'*-Me$_2$en)(Guo)$_2$]$^{2+}$. The + indicates the chirality of the ribose, Δ and Λ indicate the molecular chirality as illustrated in Figure 1, and *R* and *S* refer to the configuration of the coordinated amine nitrogens. The ribose has been omitted from these drawings for clarity.

number of *R* and *S* nitrogens are present in the free ligand, and all three sets of diastereomers are formed upon complexation. Exchange of Δ and Λ configurations by rotation about the Pt–purine bond occurs only between the A and B diastereomers within each set. The significantly populated diastereomers for each of the three noninterconverting sets are illustrated schematically in Figure 2.

In the presence of three chiral centers, two coordinated nitrogens, and the platinum center, there are in principle $2^3 = 8$ isomers. The presence of only + ribose does not introduce additional isomers but rather serves to break any mirror symmetry between enantiomers, thus forming diastereomers. Since the ΔRS isomer is identical with the ΔSR isomer and the ΛRS isomer is identical with the ΛSR isomer, the number of isomers reduces to the six shown in Figure 2. Four more H–H isomers are possible in which the platinum center is not chiral. The first two can be labeled H–H-*RR* and H–H-*SS*, and there are two nonequivalent H–H-SR isomers. These H–H isomers are intermediates in the interconversion processes between the H–T isomers within each set. We have seen no direct evidence for the existence of these H–H isomers, presumably because they are more sterically crowded.

The H(8) protons of the guanosines provide separate, well-resolved proton NMR peaks, very well suited for the study of the dynamical behavior of these molecules. Analysis of the NMR spectra expected in the fast-exchange and slow-exchange regions facilitates an understanding of the experimentally obtained spectra. Since exchange occurs only between diastereomers within each noninterconverting set, each set will be discussed separately.

Under conditions of slow exchange on the NMR time scale, the two populated diastereomers in the *RR* set are expected to exhibit different NMR spectra. Each diastereomer contains a 2-fold axis, which bisects the guanosine N(7)–Pt–guanosine N(7) bond angle, producing magnetically equivalent guanosines. Thus in the slow-exchange limit one signal will be observed for the ΔRR isomer, and another signal will be seen for the ΛRR isomer. Exchange will occur in the *RR* set between the ΔRR and ΛRR diastereomers. This has the effect of averaging the guanosines of both diastereomers so that a single exchange-averaged H(8) resonance will be obtained for the *RR* set of diastereomers in the fast-exchange limit.

Similarly, the *SS* set of diastereomers will produce one H(8) resonance for each of the two populated diastereomers, ΔSS and ΛSS, in the slow-exchange limit, and a single exchange-averaged H(8) resonance for the *SS* set of diastereomers in the fast-exchange limit.

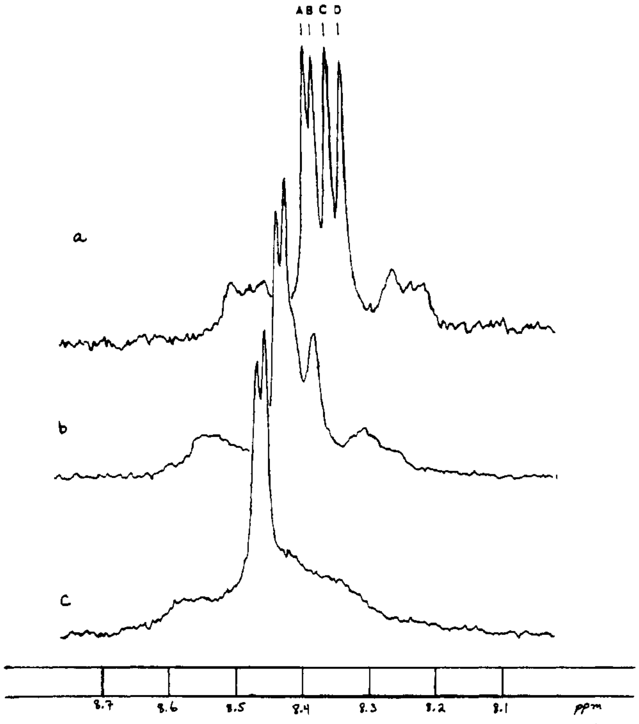

Figure 3. H(8) region of the ^{1}H NMR spectrum of [Pt(*N*,*N'*-Me$_2$en)(Guo)$_2$]$^{2+}$, 0.05 M in D$_2$O: (a) 103 °C; (b) 64 °C; (c) 36 °C.

There is no 2-fold axis or mirror plane in the *SR* diastereomers due to the presence of one *R* and one *S* nitrogen, and therefore the guanosines of the *SR* diastereomers are not magnetically equivalent. In particular the *SR* diastereomers have one guanosine cis to an *S* nitrogen while the other guanosine is cis to an *R* nitrogen. Thus, each guanosine in the ΔSR and ΛSR diastereomers will produce a single H(8) resonance for a total of four H(8) resonances from the *SR* set in the slow-exchange limit. Since nitrogen configurations do not exchange and exchange occurs only by rotation about the Pt–guanosine bond, the guanosine cis to the *R* nitrogen in the ΛSR isomer will exchange with the guanosine cis to the *R* nitrogen in the ΔSR isomer. It does not, however, exchange with the guanosine cis to the *S* nitrogen. At fast exchange, the four H(8) peaks due to the *SR* set of isomers will merge to form two peaks, one due to the guanosines cis to the *S* nitrogens and one due to the guanosines cis to the *R* nitrogens.

The analysis for the *N*-methyl groups of the substituted ethylenediamine is analogous to that for H(8) resonances. Thus, in the slow-exchange limit, the diastereomers in each of the *RR* and *SS* sets will produce two methyl proton resonances while the *SR* set of diastereomers will produce four methyl proton resonances, for a total of eight. In the fast-exchange limit, four methyl proton peaks are expected, one for each of the *RR* and *SS* sets of diastereomers and two for the *SR* set of diastereomers.

In general it is expected that the rotational barrier that separates the ΔRR and ΛRR isomers will be different from that between the ΔSS and ΛSS isomers. Thus, the slow-exchange signals from the *RR* set should undergo coalescence at a different temperature than those from the *SS* set of isomers. Each of the guanosines in the *SR* set of isomers is unique and may be expected to have different rotational barriers. However, the H–H-SR isomers, which are intermediates in the exchange process, are nonequivalent. In one H–H isomer both guanosines have the O(6) oxygens directed toward the same side of the platinum coordination plane as the two amine methyl groups. This produces a much more sterically crowded, and hence higher energy, intermediate than the other isomer in which both guanosines have the O(6) oxygens directed toward the opposite side of the platinum coordination plane as the amine methyl groups. The higher energy intermediate is thus inaccessible, and exchange between the ΔSR and ΛSR diastereomers becomes a concerted process limited to a single pathway. In this case, when the rotation of one of the guanosines

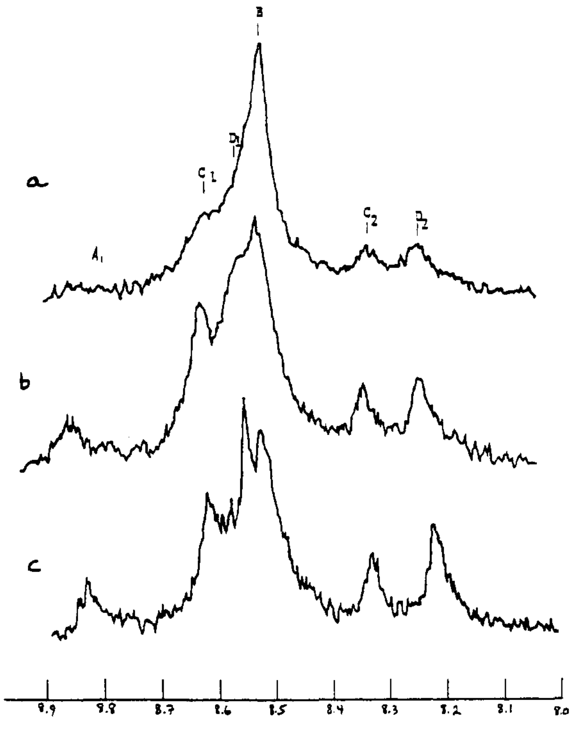

Figure 4. H(8) region of the ^{1}H NMR spectrum of $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$ in D_2O/CD_3OD: (a) 0.025 M, −4 °C; (b) 0.025 M, −14 °C; (c) 0.0125 M, −24 °C.

becomes slow, rotation of the other guanosine necessarily becomes slow as well. Thus, the H(8) peaks from both guanosines must obtain coalescence simultaneously.

Results and Discussion

Proton NMR spectra of $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$ expanded to show the H(8) proton region over the temperature range 103 to −24 °C are shown in Figures 3 and 4. The spectrum at 103 °C (Figure 3a) exhibits four sharp lines consistent with a mixture of each of the three noninterconverting sets of diastereomers in the fast-exchange region. On the basis of the coalescence behavior of the slow-exchange peaks, the peaks labeled A and B can be assigned to the *RR* and *SS* sets of diastereomers and the peaks labeled C and D can be assigned to the *RS* set. As the temperature is lowered, the C and D peaks become exchange broadened simultaneously, (Figure 3b) and pass through coalescence. At 36 °C (Figure 3c) the C and D peaks have obtained the slow-exchange region and have reappeared as two broad humps slightly high field and low field from their original positions. Peak A is slightly exchange broadened while peak B is unaffected. Figure 3 also illustrates the temperature dependence of the chemical shifts, presumably due to intermolecular associations in solution similar to the base-stacking and hydrogen-bonding interactions found in the solid state for $[Pt(NH_3)_2(Guo)_2]^{2+}$.[7,8]

Spectra obtained below 0 °C, of solutions diluted with methanol-d_4, show two of the exchange processes reaching the slow-exchange region (Figure 4). The spectrum at −4 °C (Figure 4a) shows peaks C and D reappearing in the slow-exchange region as four peaks labeled C_1, D_1, C_2, and D_2. Peak A is not visible at this temperature, being near coalescence, while peak B is still sharply resolved in the fast-exchange region. The spectrum at −14 °C (Figure 4b) now has one component of peak A reappearing as the lowest field peak labeled. The second member of the pair of slow-exchange A peaks overlaps peak D_2. Finally, at −24 °C (Figure 4c) peak B is beginning to show effects of exchange broadening. Lowering the temperature further results in peak B broadening to an unresolved shoulder on the high-field side of peak D_1 at −32 °C. Thus, at −24 °C, the *RS* set of diastereomers is in the slow-exchange region on the NMR time scale. In addition, either the *RR* or *SS* set of diastereomers has also reached the slow-exchange region while exchange within the remaining set of *SS* or *RR* diastereomers is only beginning to slow.

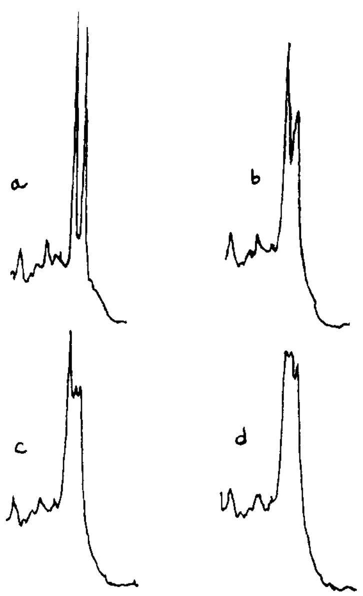

Figure 5. Methyl region of the ^{1}H NMR spectrum of $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$, 0.025 M in D_2O/CD_3OD: (a) 26 °C; (b) 4 °C; (c) −4 °C; (d) −14 °C.

Table I. Kinetic and Thermodynamic Quantities for Exchange Processes

concn, M	peak	T_c, K	$\Delta\nu_o$, s^{-1}	k_R, s^{-1}	$\Delta G^\ddagger$, kJ mol^{-1}
	$[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$				
0.05	C (*RS*)	308	25.3	56.2	65.2
0.05	D (*RS*)	308	26.6	59.1	65.1
0.025	C (*RS*)	303	27.5	61.9	63.9
0.025	D (*RS*)	303	30.8	68.4	63.6
0.025	A (*RR*, *SS*)	273	32.0	71.1	57.0
	$[Pt(N,N,N',N'\text{-}Me_4en)(Guo)_2]^{2+}$				
0.05	H(1′)	373	3.2	7.1	86.0[a]

[a] Lower limit, ref 9.

The environments of the ethylenediamine methyl groups are analogous to the H(8) environments. The methyl resonances appear as two well-resolved peaks in the fast-exchange region at 26 °C, (Figure 5a). Four peaks are expected in the fast-exchange region, as observed for the H(8) resonances; however, chemical shift differences are apparently not large enough to resolve all four peaks, and they appear as two overlapping sets of two peaks. On the basis of the corresponding temperature dependence of the H(8) resonances, the low-field peak is assigned to the *RR* and *SS* sets of diastereomers and the high-field peak is assigned to the *RS* set of diastereomers. The high-field peak due to the *RS* set of diastereomers is exchange broadened at 4 °C (Figure 5b) and at −4 °C (Figure 5c) has gone through coalescence and reappeared in the slow-exchange region as two peaks. Four peaks are expected for the *RS* set of diastereomers in the slow-exchange region, analogous to the H(8) resonances; however, again chemical shift difference is insufficient for their resolution. The two peaks resolved are probably due to methyl groups on the same side and/or opposite sides of the coordination plane from the guanosine carbonyl groups, with the diastereotopic peaks unresolved. When the temperature is lowered further, the peak assigned to the *RR* and *SS* sets of diastereomers also goes through coalescence (Figure 5d). However, the spectrum is not resolved well enough to be interpreted.

The NMR data show that exchange between the diastereomers within the three noninterconverting sets of diastereomers occurs as three separate processes. This is expected since diastereomers have different physical and chemical properties. Thus, there is a significant difference in the rate of exchange between the diastereomers in the *RR* and *SS* sets, although we do not know which is *RR* and which is *SS*. The rate of exchange and the activation energy for the two higher energy processes can be calculated from the coalescence temperature and the chemical shift differences at the slow-exchange limit.[21,22] These data are summarized in Table I. The rate of exchange is observed to depend inversely on the concentration of the sample. This is due to intermolecular interactions in solution similar to the base-stacking and hydrogen-bonding interactions found in the solid state for $[Pt(NH_3)_2(Guo)_2]^{2+}$.[7,8] The activation free energy for the exchange between the RS set of diastereomers in a 0.025 M solution is 63.8 kJ mol^{-1} while the activation free energy for the higher energy exchange process between the *RR* or *SS* set of diastereomers is 57.0 kJ mol^{-1}. The activation free energy for the lower energy exchange process between the *SS* or *RR* set of diastereomers cannot be determined, as this process does not obtain the slow-exchange limit in the available temperature range.

The rotational barriers reported here for $[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$ complexes are similar to those reported for platinum–olefin complexes, which range from about 42 to 67 kJ mol^{-1} [23-26] although the structure and bonding in the two types of compounds would seem to be quite different. The barriers are also similar to those reported for the *trans*-$[Pt(hydrazone)_2Cl_2]$ complexes, 68 kJ mol^{-1}.[27]

The rotational barriers observed in this work are similar to the 50 kJ mol^{-1} reported by Reedijk for the compound $[Pt(bpe)(9\text{-}MeHX)_2]^{2-}$, which has a seven-membered chelate ring.[12] Reedijk has also studied complexes of the type $[Pt(tren)(Puo)_2]^{2+}$ where tren = triethylenediamine and Puo = Guo, or 9-MeHX, which have six-membered chelate rings.[28] His results parallel ours for the five-membered chelate ring system; namely, (1) with no methyl groups on the coordinated tren nitrogens, fast exchange is observed, (2) with two methyl groups on each nitrogen, slow rotation of the purine results, and (3) with one methyl group on each nitrogen, dynamic NMR is observed. However with the six-membered chelate ring, the rotational barrier seems lower than those for the five-membered chelate rings.

Reedijk[28] has also reported slow rotation about the Pt–2–Pic bonds in *cis*-$[Pt(2\text{-}Pic)_2(Puo)_2]^{2+}$ where 2-Pic = 2-methylpyridine and Puo = Guo or 9-MeHX. Slow rotation about the Pt–purine bond was found for $[Pt(bpy)(Puo)_2]^{2+}$, where bpy is 2,2′-bipyridine.[28] Thus the steric bulk of a bpy ligand is sufficient to cause slow exchange between atropisomers of square-planar compounds.

Pasini[29] has reported two H(8)–Guo NMR signals for the compounds $[Pt(R\text{-}pn)(Guo)_2]^{2+}$ and $[Pt(S\text{-}pn)(Guo)_2]^{2+}$, where pn is the unsymmetrical 1,2-diaminopropane chelate, as one would expect for these molecules, which have no symmetry elements. He reports that these H(8) signals collapse to a single resonance at 80 °C for the *R*-pn compound and 97 °C for the *S*-pn chelate. Surprisingly he attributes this to fast rotation about the Pt–purine bonds, although it is not clear how this would render the two H(8) environments equivalent. In view of our results and Reedijk's[28] it is likely that fast rotation occurs at all temperatures in Pasini's compounds. It is known that the chemical shifts of these systems are concentration and temperature dependent.[9,28] The collapse of the two H(8) signals of $[Pt(Me_4en)(Guo)_2]^{2+}$ at high temperature has been attributed to accidental chemical shift degeneracy due to the temperature dependence of the chemical shifts.[9] A similar collapse of resonances has been observed for $[Pt(tmdap)(Guo)_2]^{2+}$, where tmpad is *N,N,N′,N′*-tetramethyl-1,3-diaminopropane, and again it was attributed to temperature dependence of the chemical shifts, not rapid rotation about the Pt–purine bond.[28] It is therefore likely that the result reported by Pasini[29] is also due to temperature-dependent chemical shifts and not slow Pt–purine rotation.

Although fast rotation about the Pt–purine bond occurs for $[Pt(en)(Guo)_2]^{2+}$, slow rotation is observed for $[M(en)(Cyd)_2]^{2+}$, (M = $Pt^{10,11}$ and Pd^{30}). This has been attributed to interligand–intracomplex hydrogen bonds. Thus while steric bulk seems to provide the rotational barrier in $[Pt(Me_4en)(Guo)_2]^{2+}$, a different source for this barrier is proposed for $[Pt(en)(Cyd)_2]^{2+}$.[30]

In a previous communication[9] we suggested that square-planar platinum(II) complexes having two asymmetric ligands occupying relative cis positions can have a chiral metal center. If the ligands are not too bulky, exchange between the diastereomers will be rapid on the NMR time scale as has been observed for the compound $[Pt(NH_3)_2(Guo)_2]^{2+}$.[9] We have shown that by increasing the steric bulk of the ligands adjacent to the guanosines a substantial barrier can be produced between the A, B, and C diastereomers. Thus, exchange between these diastereomers is slow on the NMR time scale for $[Pt(N,N,N',N'\text{-}Me_4en)(Guo)_2]^{2+}$.[9] We have now demonstrated that we can tune the steric bulk of the ligands adjacent to the guanosines to produce a barrier to exchange between the diastereomers that is intermediate on the NMR time scale, resulting in the observation of dynamical NMR spectra. These results can be extended to other systems of square-planar metal complexes, and we are currently pursuing a course along this line.

Registry No. (*R,R*)-$[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$, 97905-46-9; (*S,S*)-$[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$, 97905-47-0; (*R,S*)-$[Pt(N,N'\text{-}Me_2en)(Guo)_2]^{2+}$, 97826-28-3.

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