for σ_p[32,61] rely on the inverse excitation energies of the molecule, with lower excitation energies resulting in downfield shifts. Adopting a similar formalism for the methoxy ligand, we find that the large overall shift of both the ^1H and ^{19}F resonances to lower field in the $U(OCH_3)_nF_{6-n}$ series with respect to the $W(OCH_3)_nF_{6-n}$[16,26] series is consistent with the lower LMCT excitation energies in $U(OCH_3)_nF_{6-n}$[12,18] vs. $W(OCH_3)_nF_{6-n}$.[62] However, the trends among the individual members of the series will depend largely upon such factors as changes in the excitation energies, changes in the electron density on the atoms in question, and intramolecular electric field effects.[24,35] Detailed calculations of the electronic structures and charge distributions for any of these systems are not available.

Interestingly, for a given member of the $U(OCH_3)_nF_{6-n}$ series, the fluorine resonance of a fluorine atom trans to a methoxy ligand is always downfield of the fluorine resonance for a fluorine atom trans to another fluorine ligand (Figure 3). This same trend is observed in IOF_5,[63] $TiF_5{\cdot}ROH^-$,[64] $Te(OH)_nF_{6-n}$,[27] $Te(OR)F_5$,[56] and $SnL_nF_{6-n}^{2-}$.[24a,b] The opposite trend is observed in WOF_5^-,[47] $ReOF_5$,[63] $OsOF_5$,[63] WCl_nF_{6-n},[25] $W(OCH_3)_nF_{6-n}$,[16,26] $W(OR)F_5$,[55] $SnL_nF_{6-n}^{2-}$,[24a,c] $Ti(OR)F_5^{2-}$,[65] and $U(OTeF_5)_nF_{6-n}$.[28] Shielding of the axial fluorine in $ReOF_5$ and the $W(OR)F_5$ complexes was attributed to $p\pi$–$d\pi$ bonding between the filled fluorine 2p orbitals and unoccupied $(n-1)$d orbitals in Re(VII)[63] and W(VI).[55] The $(n-1)$d orbitals are filled in Sn(IV) and I(VII), and the observed trends are assigned to intramolecular electric field effects.[24,63] The reason for the trend observed in the $U(OCH_3)_nF_{6-n}$ species is not clear since $p\pi$–$d\pi(f\pi)$ bonding is likely to be important in these molecules.

The present study also demonstrates the remarkable sensitivity toward both solvent and temperature that the ^{19}F chemical shifts of U(VI) complexes can display. Charge-transfer interactions between the solvent and solute presently offer the best explanation of these effects. That such large differences in the fluorine chemical shifts can occur with solvent and temperature in U(VI) complexes (and likely other metal complexes as well) should be borne in mind when one interprets or calculates the fluorine NMR spectra of metal complexes.

Acknowledgment. We thank the National Science Foundation (T.J.M.; Grants CHE76-84494 A01 and CHE-8009060), the Electric Power Research Institute (Contract RP506-7), and the Northwestern University Office of Research and Sponsored Projects for support of this research. We are grateful to Professor Eric Weitz for stimulating discussions. We also thank Allied Chemical for a gift of UF_6 and Dr. S. S. Miller for assistance with the mass spectral measurements. T.J.M. is a Camille and Henry Dreyfus Teacher-Scholar.

Registry No. UF_6, 7783-81-5; $U(OCH_3)F_5$, 71186-40-8; *cis*-$U(OCH_3)_2F_4$, 77241-89-5; *trans*-$U(OCH_3)_2F_4$, 77286-40-9; *fac*-$U(OCH_3)_3F_3$, 77255-89-1; *mer*-$U(OCH_3)_3F_3$, 77286-92-1; *cis*-$U(OCH_3)_4F_2$, 77241-90-8; *trans*-$U(OCH_3)_4F_2$, 77286-41-0; $U(OCH_3)_5F$, 77241-91-9; $U(OCH_3)_6$, 69644-82-2; $CH_3Si(OCH_3)_3$, 1185-55-3.

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(61) (a) Ebraheem, K. A. K.; Webb, G. A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 149. (b) Saika, A.; Slichter, C. P. *J. Chem. Phys.* **1954**, *22*, 26.

(62) (a) Bloor, J. E.; Sherrod, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 4333. (b) Rianda, R.; Frueholz, R. P.; Kuppermann, A. *J. Chem. Phys.* **1979**, *70*, 1056. (c) Darling, F. E.; Dahl, J. P. *Chem. Phys.* **1977**, *20*, 129. (d) McDiarmid, R. *J. Chem. Phys.* **1974**, *61*, 3333.

(63) Bartlett, N.; Beaton, S.; Reeves, L. W.; Wells, E. J. *Can. J. Chem.* **1964**, *42*, 2531.

(64) (a) Ragsdale, R. O.; Stewart, B. B. *Inorg. Chem.* **1963**, *2*, 1002. (b) R = Me, Et, and *i*-Pr.

(65) (a) Dean, P. A. W.; Evans, D. F. *J. Chem. Soc. A* **1970**, 2569. (b) R = Me, Et, *n*-Pr, and *n*-Bu.

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Conformations of (1,3-Diamine)platinum(II) Chelates As Studied by ^{13}C and ^1H NMR Spectroscopy

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Received July 8, 1980

The ^{13}C NMR spectra of a series of aqueous solutions of square-planar platinum(II) chelates, Pt(2,2′-bipyridine)(aliphatic 1,3-diamine)$^{2+}$, have been obtained for eight different diamines. The ^{13}C chemical shifts of the bpy carbons resemble quite closely the bpy ^{13}C shifts of the analogous 1,2-diamine chelates which we reported earlier (*Inorg. Chem.* **1975**, *14*, 3007). Only the C_6 carbon exhibits a significant difference in chemical shift between the two series with an $\approx$2 ppm upfield shift in the present series, which is attributable to increased steric crowding around the C_6–H_6 bonds by the coordinated amine substituents in the 1,3-diamine chelates. Evidence is presented that the six-membered chelate ring is in a distorted-chair conformation, flattened in the region between the PtNN and NCCN planes. In the limit of severe flattening, an envelope conformation, as found in the *N,N′*-dimethyl-1,3-propanediamine (*N,N′*-Me_2tn) chelates, results. In such envelope conformations the *N,N′*-methyl groups stereoselectively form meso complexes with the methyl groups pointing inward toward the envelope as determined from analysis of $^3J_{HNCN}$ data. As found earlier, $^3J_{PtNCC}$ data follow a Karplus-like dihedral angle relationship and along with $^3J_{PtNCH}$ and $^3J_{HCCH}$ provide the basis for assigning conformational preferences of methyl substituents. For example, for the 1,3-diaminobutane complex, the equilibrium distribution is estimated to consist of 80% equatorial-methyl group preference in a flattened-chair conformation in solution. In the racemic 2,4-diaminopentane chelate the diequatorial skew boat predominates over the axial–equatorial dimethyl chair conformation in solution. J_{PtC} values involving diamine ring β-carbons provide further evidence for multipath coupling, i.e., algebraic additivity of two or more independent coupling paths that link two nuclei to give the observed J_{PtC}.

Introduction

In earlier papers in this series we used carbon-13 NMR spectra to probe the configuration and conformation of some α-amino acid[2,3] and 1,2-diamine[4] complexes of platinum(II). These works[2-4] and the findings of others[5,6] have shown the

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(1) (a) Fairfield University. (b) Grinnell College. (c) The University of North Carolina.

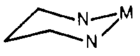
(2) Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1978**, *17*, 1701.

(3) Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1978**, *17*, 1711.

0020-1669/81/1320-2137$01.25/0

considerable value that vicinal coupling of platinum-195 and carbon-13 nuclei can afford in probing the solution structure of diamagnetic platinum(II) and platinum(IV) complexes. This paper concerns the solution conformations of chelated 1,3-diaminopropanes; in conjunction with ^{195}Pt–^{13}C coupling data other vicinal coupling relationships in these complexes, namely, $^3J_{HH}$[7] and $^3J_{PtH}$,[8] can simultaneously provide valuable structural information about the six-membered chelate rings. Coupling in all these vicinal frameworks appears to follow the well-known Karplus-type dihedral angle dependence.[7]

Six-membered chelate rings formed by 1,3-aliphatic diamines generally are found to adopt a chair conformation (**1**)



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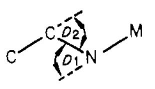
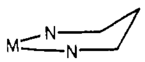


2

with some distortion due to flattening[9] of the ring (best viewed in **2**, the side view of **1**). This flattening is manifested by a decrease of the dihedral angle (D_1) between the NMN and NCCN planes, going from 60° in the ideal chair to commonly 20–40° in these chelates.[10] The dihedral angle (D_2) between the NCCN and CCC planes is found experimentally to be 62 ± 5°, close to the ideal 60°. Jurnak and Raymond[10] have discussed some molecular features that will influence the flattening around the D_1 dihedral angle. They conclude that flattening of the chair conformer is especially pronounced for complexes with longer metal–nitrogen bond lengths and that a direct effect of this flattening is expansion of the M–N–C bond angle to near 120°. In the limit of complete flattening at D_1 (i.e., $D_1 = 0°$) an envelope conformation (**3**) is generated



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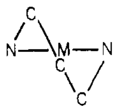

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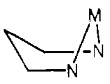

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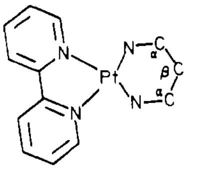
which has previously been invoked[11] as an activated complex in the low-energy pathway for chair–chair ring inversion.

The other ideal conformations, which are generally found to be at higher energy than the chair, are the skew boat (or twist), **4**, and the boat, **5**; both possess more eclipsing and unfavorable steric interactions than the chair conformation.[12] Examples of a preference for skew-boat conformations[10] have been found in some chelates of racemic 2,4-diaminopentane, which adopt a diequatorially substituted skew-boat structure[13-15] rather than a chair conformation with one axial methyl group. However, recently the chelate bis((*R*,*R*)-2,4-diaminopentane)platinum(II) has been shown to adopt a chair conformation with each ring having one axial and one equatorial methyl group.[16]

Previous experimental measurements of the solution conformation preferences of methyl-substituted 1,3-diamine chelates have been performed by ^{1}H NMR for square-planar platinum(II) complexes[17] and for octahedral nickel(II) complexes,[14] the latter of course having the added steric influence of two out-of-plane donor groups. The earlier platinum(II) studies[17] concentrated on bis(diamine)complexes or bis(amine)(1,3-diaminopropane)platinum(II) complexes. The present studies are concerned with mixed bipyridine–1,3-diamine complexes of type **6** where a variety of methyl-substituted diamines were employed.[18]



6

Part of the purpose of this study was to evaluate what interligand influence on diamine ring conformation was exerted by the bpy ligand in these complexes (**6**). A study of molecular models reveals that the bipyridine ligand possesses two protruding protons (H_6 and H_6'), which will be oriented in direct steric juxtaposition with the equatorial amine substituent in the normal chair conformation in these platinum chelates, and hence some conformational adjustment might be expected relative to the complexes that Appleton and Hall have studied previously.[18]

A second interest of this study was to provide further foundation for understanding ^{195}Pt–^{13}C coupling in small-membered rings. Earlier in our ^{13}C NMR studies of (1,2-diamine)platinum chelates we observed evidence[4] for the operation of an apparent algebraic additivity of individual two- and three-bond coupling paths that simultaneously link the metal ion and some ring carbons in these systems. Further evidence of this multipath coupling should be available in the 1,3-diamine chelates where the β-carbon is coupled to the platinum-195 nucleus by two distinct vicinal coupling paths (**6**). Other workers have recently reported similar phenomena of additive multiple-path coupling contributions in ^{13}C–^{13}C[19] and ^{13}C–^{14}N[20] coupling in small-ring systems.

Experimental Section

Diamines. Some of the diamines were obtained commercially from Aldrich Chemical Co. or Ames Laboratories, Inc. 1,3-Diaminocyclohexane was prepared by a method described in the literature,[21] and the cis isomer was separated from the trans isomer by using a method previously described.[22] The preparation of other diamines was described in a previous paper.[14]

Complexes. All complexes were prepared from Pt(bpy)Cl_2 as described earlier.[4]

NMR Spectra. Conditions under which ^{13}C spectra were obtained are the same as described earlier.[4] The 270-MHz ^{1}H NMR spectra

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(4) Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1975**, *14*, 3007.

(5) Bagger, S. *Acta Chem. Scand., Ser. A* **1974**, *A28*, 467.

(6) Yano, S.; Tukada, T.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1978**, *17*, 2520.

(7) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11.

(8) Erickson, L. E.; McDonald, J. W.; Howie, J. K.; Clow, R. P. *J. Am. Chem. Soc.* **1968**, *90*, 6371.

(9) Geue, R. J.; Snow, M. R. *J. Chem. Soc. A* **1971**, 2981.

(10) Jurnak, F. A.; Raymond, K. N. *Inorg. Chem.* **1974**, *13*, 2387.

(11) Gollogly, J. R.; Hawkins, C. J. *Inorg. Chem.* **1972**, *11*, 156.

(12) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; p 204.

(13) Kobayashi, A.; Marumo, R.; Saito, Y. *Acta Crystallogr., Sect. B* **1972**, *B28*, 3591; **1973**, *B29*, 2443.

(14) Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1974**, *13*, 977.

(15) Ohba, S.; Miyamae, H.; Sato, S.; Saito, Y. *Acta Crystallogr., Sect. B* **1979**, *B35*, 321.

(16) Nakayama, Y.; Ooi, S.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 914.

(17) (a) Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1972**, *11*, 124. (b) *Ibid.* **1970**, *9*, 1807. (c) *Ibid.* **1971**, *10*, 1717.

(18) The ligands and their abbreviations used in this paper: bipyridine, bpy; 1,3-diaminobutane, 1-Metn; *meso-* and *rac*-2,4-diaminopentane, 1,3-Me$_2$tn; *N*,*N'*-dimethyl-1,3-diaminopropane, *N*,*N'*-Me$_2$tn; *N*,*N'*,2-trimethyl-1,3-diaminopropane, *N*,*N'*-2-Me$_3$tn; *cis*-1,3-diaminocyclohexane, dach. Abbreviation labeling is based on substituting the parent tn ligand (**6**). Also, the notation α for the ring C_1 and C_3 and their substituents and β for C_2 and its substituents will be employed throughout the paper.

(19) Marshall, J. L.; Faehl, L. G.; Katner, R. *Org. Magn. Reson.* **1979**, *12*, 163.

(20) Valckz, L. A.; Borremans, F. A. M.; Becu, C. E.; DeWaele, R. H. K.; Anteunis, M. J. O. *Org. Magn. Reson.* **1979**, *12*, 302.

(21) Stetter, H.; Theisen, D.; Steffens, G. J. *Chem. Ber.* **1970**, *103*, 200.

(22) Neilsen, A. T. *J. Org. Chem.* **1962**, *27*, 1998.

were obtained with the use of the Southern New England High Field NMR Facility at Yale University. Ambient temperature for these spectra was 20 ± 2 °C.

Results

Proton and carbon-13 NMR spectral parameters are summarized in Table I. All data are consistent with the formulated 1:1 mixed-complex structure (**6**) with both the diamine and bipyridine ligands being bound as bidentate chelates.

^{13}C Spectra. The general features of the carbon NMR parameters for these complexes resemble closely those reported[4] for the $Pt(bipyridine)(1,2\text{-diamine})^{2+}$ chelates; a typical spectrum has been published in ref 4. Proton-noise-decoupled ^{13}C resonances in these platinum complexes consist of a main peak flanked by two satellites in a relative intensity of 1:4:1. This pattern results because the only platinum isotope with a nonzero nuclear spin is ^{195}Pt ($I = {}^1/_2$, natural abundance $\approx$ 33%). J_{PtC} is the spacing measured in hertz between the outer peaks of the multiplet.

Bipyridine chemical shifts and platinum–carbon coupling constants (J_{PtC}) for the various bpy ring carbons show little variation across the series in Table I and are very close to those observed earlier in the 1,2-diamine chelate series[4] (see last entry in Table I for a typical example of the latter). Only the C_6 chemical shifts, which are in the range 149.0 ± 0.6 ppm in the present series, differ substantially from those in the 1,2-diamine complexes where the identical bpy carbon showed a shift range of 151 ± 1 ppm.

Chemical shifts for the coordinated aliphatic diamine skeletal carbons in the 1,3-diamine series in Table I give a consistent pattern of substituent effects that parallel effects of *N*- and *C*-methyl substitution in the related 1,2-diamine complexes. Relative to the unsubstituted tn chelate (**7**, in Table I) α-methyl substitution (to give **10**) introduces a 5–8 ppm downfield shift at the substituted ring α-carbon resonance and a 6–7 ppm downfield shift at the β-carbon; *N*-methyl substitution generates a downfield shift of 10–11 ppm in the chemical shift of the α-carbon adjacent to the substituted nitrogen and an $\approx$4 ppm upfield shift in the β-carbon resonance. In molecules like **8** and **12** multiple methyl substitution appears to have an additive influence on the ring β-carbon chemical shifts; relative to the β-carbon in **7**, the β-carbon in the $N,N'\text{-}Me_2tn$ complex (**12**) shows a 7.6 ppm upfield shift while in the *meso*-1,3-Me_2tn complex (**8**) a 14.7 ppm downfield shift is seen for the β carbon vs. **7**. Such trends are also evident in the earlier 1,2-diamine data.[4]

For every compound reported in Table I substantial platinum–carbon coupling is detected for all carbons of the aliphatic diamine ligands. $^2J_{PtC}$ for α-carbons is consistently found to be 20–25 Hz; this behavior contrasts with very small Pt–C coupling that was seen for α-carbons in coordinated 1,2-diamine complexes (generally <10 Hz; in many cases no coupling was detectable at all). β-Carbons of the chelated 1,3-diamines generally show a 30–40 Hz coupling to the platinum-195 nucleus. Notably the β-carbon of the *rac*-1,3-Me_2tn complex (**9**) shows a J_{PtC} of only 20 Hz. ^{13}C spectra of **9** and **10** were also run at 90 °C, and the J_{PtC} values found were not significantly different from those obtained from the ambient-temperature spectra (35 °C).

^1H Spectra. In general, complex interproton coupling was observed for the aliphatic diamine backbone proton resonances, and, in some cases, full spectral analysis was not attempted. Where possible $^{195}Pt\text{–}^1H$ coupling constants were determined and are tabulated in Table I. In the *rac*-1,3-Me_2tn complex, platinum satellites around the α-proton resonance overlapped severely with the complex "sextet" resonance that this proton exhibits. $^3J_{PtH}$ of 31 Hz was found for this proton at ambient temperatures while at 90 °C this value is 32 Hz. In the *cis*-1,3-diaminocyclohexane complex the α-proton is the farthest downfield aliphatic resonance and exhibits platinum satellites of 66 Hz separation. Their origin was confirmed by obtaining the spectrum at 60 and 100 MHz. This value of $^3J_{PtH}$ is quite close to that found by Saito and Kidani[23] for the bis complex of this ligand with platinum(II).

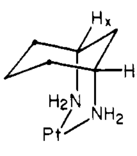
The ^{13}C and 100-MHz ^1H NMR spectra for the $N,N'\text{-}Me_2tn$ complex at pH 7 showed evidence for the presence of one species; earlier, the analogous *N*,*N'*-dimethyl-ethylenediamine system was shown[4] to consist of a nearly 2:1 equilibrium mixture of two isomers that arise because the coordinated secondary amine nitrogen atoms in these complexes are asymmetric centers. Hence meso (*R*,*S*) and racemic (*R*,*R* and *S*,*S*) isomers are possible. Even at 270 MHz the proton NMR spectrum of the $N,N'\text{-}Me_2tn$ complex gives evidence of only one type of methyl resonance. Conceivably, a second isomer could be present at levels lower than 5% of the major isomer but would be difficult to identify in the proton spectra. Three minor resonances in the aliphatic region of the ^{13}C spectrum of this complex are visible with an intensity of 4 ± 2% relative to the major peaks cited in Table I: at 47.50 ppm ($\alpha\text{-}CH_2$), 40.85 ppm (NCH_3), and 18.71 ppm ($\beta\text{-}CH_2$), the last being half the intensity of the first two. These peaks may be due to the other isomer, but their low intensities precluded observation of their platinum satellites. In any event one isomer predominates in the $N,N'\text{-}Me_2tn$ complex by at least a factor of 20 to 1.

For several complexes 270-MHz ^1H NMR spectra were obtained in order to more completely characterize the $^3J_{HH}$ values of the aliphatic diamine chelate ring. Data presented in Table II for **10**, **12**, and **13** were derived from first-order analysis of such spectra.

Discussion

Conformations of the 1,3-Diamine Chelate Rings. The combined use of $^3J_{HH}$, $^3J_{PtH}$, and $^3J_{PtC}$ data for compounds **8–14** permits an assessment of the preferred conformer adopted by the chelated diamine rings. The various chelates will be discussed individually.

$Pt(bpy)(dach)^{2+}$. The most structurally rigid complex in this series is that derived from *cis*-1,3-diaminocyclohexane (dach). Ideally two structures can be envisioned for the dach chelate ring, one having a chair chelate ring (**16**) and one with a boat chelate ring (**17**). In the former $^3J_{PtH_x}$ would occur across a dihedral angle of $\approx$180° while in the latter the vicinal network linking Pt and H_x would be near 135°. The large $^3J_{PtH_x}$ of 66 Hz is consistent with structure **16**. $^3J_{PtC}$ for the two carbons that are effectively axial substituents on the chelate ring in **16** is very small (<6 Hz) because their dihedral angle with platinum is near 90°. These conclusions deduced from the NMR data agree reasonably well with the X-ray structure[24] for the $Pt(bpy)(dach)^{2+}$ complex, which shows a highly flattened chair structure for the 1,3-diamine chelate ring that is perhaps better described as being in an envelope conformation (**3**). This distortion of the chelate ring is best seen from a side-on view, **2**, in which D_1 is 2.3° and D_2 66.9° in **16**. The severe flattening of the ideal chair structure of the chelated diaxial diaminocyclohexane ring results in part from



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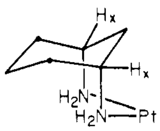

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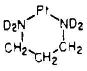
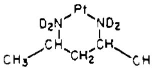
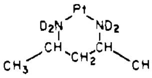
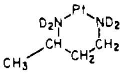
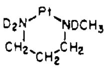
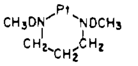
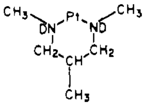
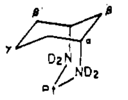
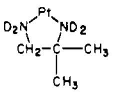
(23) Saito, R.; Kidani, Y. *Chem. Lett.* **1977**, 1141.

(24) Sarneski, J. E.; McPhail, A. T.; Onan, K. D.; Erickson, L. E.; Reilley, C. N. *J. Am. Chem. Soc.* **1977**, *99*, 7376.

Table I. Proton and Carbon NMR Chemical Shifts[a,b] and Coupling Constants (^{195}Pt-^{13}C) for Pt(bpy)(1,3-diamine)$^{2+}$ Complexes

		carbon-13 resonances								
		bpy					diamine chelate ring			
compd	diamine structure	C_2	C_6	C_4	C_5	C_3	α^c	β^c	*C*-CH_3	*N*-CH_3
Pt(bpy)(tn)$^{2+}$	 7	157.09 (34)[d]	148.92 (30)	143.17 (~6)	129.04 (33)	125.35 (27)	42.69 (25)	28.37 (40)		
Pt(bpy)(*meso*-1,3-Me_2tn)$^{2+}$	 8	157.89 (*e*)	148.68 (29)	142.97 (~6)	128.64 (32)	125.35 (28)	50.51 (20)	43.09 (33)	23.01 (38)	
Pt(bpy)(*rac*-1,3-Me_2tn)$^{2+}$	 9	157.10 (33)	149.48 (32)	143.13 (7)	129.00 (33)	125.31 (27)	47.65 (22)	40.55 (20)	22.33 (34)	
	at 90 °C	157.43 (*e*)	149.39 (33)	143.22 (7)	129.00 (34)	125.31 (27)	47.69 (23)	40.85 (21)	22.22 (33)	
	at 10 °C	157.11	149.56	143.28	129.09	125.43	47.69 (~20)	40.50 (~20)	22.33 (34)	
Pt(bpy)(1-Metn)$^{2+}$	 10	157.33 (33)	149.12 (31) 148.96 (31)	143.09 (6)	128.96 (33)	125.35 (27)	49.75 (CH) (23) 41.62 (CH_2) (23)	35.11 (35)	22.37 (32)	
	at 90 °C	157.50 (*e*)	148.97 (31)	143.09 (6)	128.85 (33)	125.32 (27)	49.63 (CH) (23) 41.45 (CH_2) (24)	35.00 (34)	22.19 (31)	
Pt(bpy)(*N*-Metn)$^{2+}$	 11		149.36 (32)		129.40 (32)	125.47 (26)	52.89 (NH) (19)	24.52 (32)		42.69 (22)
		157.06 (34)	148.80 (30)	143.40 (~6)	129.08 (32)	125.43 (26)	43.56 (NH_2) (25)			
Pt(bpy)(*N,N'*-Me_2tn)$^{2+}$	 12	157.37 (33)	148.44 (32)	143.60 (7)	129.24 (33)	125.63 (27)	53.84 (22)	20.79 (34)		42.73 (20)
Pt(bpy)(*N,N'*-2-Me_3tn)$^{2+}$	 13	157.73 (35)	148.46 (29)	143.54 (*e*)	129.14 (32)	125.67 (27)	60.35 (17)	25.33 (27)	17.43 (*e*)	43.25 (25)
Pt(bpy)(dach)$^{2+}$	 14	157.57 (34)	148.36 (27)	143.05 (6)	128.68 (32)	125.35 (28)	44.24 (24)	35.11 (52)	29.40 (β') (*e*) 14.60 (γ') (*e*)	
Pt(bpy)(*C,C*-Me_2en)$^{2+}$	 15	157.29[m] (*e*)	151.74 (32) 151.02 (32)	142.85 (6)	129.28 (35)	125.15 (27)	61.77 (C) (*e*) 56.86 (CH_2) (8)		24.83 (22)	

[a] Carbon-13 shifts in ppm from external Me_4Si; measured vs. internal dioxane, which is 67.73 ppm downfield from external Me_4Si; at 32 °C unless stated otherwise. [b] Hydrogen-1 shifts in ppm vs. DSS. [c] α and β designations in the chelate ring are given in structure 6. [d] Coupling constants (Pt-H and Pt-C) are found in parentheses; in Hz. [e] Platinum satellites not observed. [f] Labels A-F refer to substituent position in preferred chair conformation; based on structure in Table II. [g] Vicinal proton couplings: $J_{AB} = J_{EF} = 6.5$ Hz, $J_{CD} = 15.0$ Hz, $J_{AC} = J_{EC} =$

the need to move the amine nitrogens far enough apart to accommodate the chelate ring bite. Other workers[25] who determined the X-ray structure of the analogous bis complex Pd(dach)$_2^{2+}$ found D_1 to be 11.1° and D_2 to be 65.1°, and invoked this explanation for the severe ring flattening in this complex and felt that interligand influences were minimal. The further, more severe chelate ring flattening in Pt(bpy)(dach)$^{2+}$ appears to arise in an attempt to minimize the steric interaction of the amine group equatorial protons with H_6 on the bipyridine rings. In fact when hydrogen positions are calculated in the X-ray structure[24], each bpy H_6 is nearly equidistant from both amino protons of the adjacent NH_2 groups on the flattened dach ligand; this ring deformation is such that the normal axial–equatorial distinction for the NH protons (in a chair ring) has been nearly removed in the flattening process, leaving the NH protons equally placed above and below the nearly planar PtNN'$C_\alpha C_\alpha'$ moiety. Another example of this envelope conformation has recently been reported for a (2,2-dimethyl-1,3-diaminopropane)platinum(II) chelate.[26]

The ^{1}H NMR spectrum of Pt(dach)$_2^{2+}$ has been reported[23] with $^3J_{PtH_3}$ being 74 Hz. The larger value of $^3J_{PtH_3}$ relative to Pt(bpy)(dach)$^{2+}$ is consistent with a less flattening distortion

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(25) Kamisawa, K.; Matsumoto, K.; Ooi, S.; Kuroya, H.; Saito, R.; Kidani, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2330.

(26) van Kralingen, C. G.; Reedijk, J.; Spek, A. L. *Inorg. Chem.* **1980**, *19*, 1481.

proton resonances							
bpy protons				diamine ring protons			
$H_{3,3'}$	$H_{4,4'}$	$H_{5,5'}$	$H_{6,6'}$	α-H[c]	β-H[c]	C-CH_3	N-CH_3
8.42	8.35	7.88	8.62 (32)[d]	3.00 (42)	2.11		
8.50	8.46	7.88	8.64 (32)	3.28 (A,E)[f,g]	1.62 (C)[f,g] 2.04 (D)[f,g]	1.48 (B,F)[f,g]	
8.46	8.50	7.90	8.78 (32)	3.55 (A,F) (31)	2.07 (C,D)	1.56 (B,E)	
8.50	8.53	8.05	8.78 (33)	3.49 (A,F)[h] (32)	2.08 (C,D)[h]	1.57 (B,E)[h]	
8.48	8.52	7.92	8.74 (30) 8.68 (e)[i]	3.39 (E)[f,j] 3.17 (B)[f,j] 3.06 (A)[f,j]	2.28 (D)[f,j] 1.91 (C)[f,j]	1.54 (F)[f]	
8.52	8.46	8.08	8.61 (28) 8.84 (30)	3.2[k]	2.4[k]		3.20 (37)
8.52	8.52	8.00	8.72 (31)	3.33 (A,E)[f,j] 2.98 (B,F)[f,j]	2.57 (C)[f,j] 2.22 (D)[f,j]		3.18 (35)
8.43	8.52	8.02	8.72 (32)	2.96 (A,E)[f,j] 2.75 (B,F)[f,j]	2.3 (C)[f,j]	1.15 (D)[f]	3.16 (34)
8.46	8.46	7.88	8.56 (32)	3.22 (66)	[l]		
8.43	8.43	7.85	8.60 (33)	2.92 (43)		1.58 (<2)	

10.6 Hz, $J_{AD} = J_{ED} = 3.0$ Hz. [h] Because of fast ring inversion between equally populated conformers ν_F, $\nu_B = \nu_E$, and $\nu_C = \nu_D$; $J_{AB} = J_{EF} = 6.6$ Hz and $J_{AC} = J_{AD} = J_{CF} = J_{DF} = 5.9$ Hz. [i] Platinum satellites not resolved from nearby resonances. [j] For complete spectral analysis with coupling constants see Table II. [k] Unresolved multiplet resonances at 100 MHz. [l] Other cyclohexane ring protons in complex multiplet near 2.0 ppm at 100 MHz. [m] Data taken from ref 4.

in the former species. An inspection of molecular models reveals that a flattening of the chair chelate ring toward an envelope (3) conformation decreases the Pt–N–C–H_x dihedral angle from its maximum of very nearly 180° in the undistorted chair conformation; thus $Pt(dach)_2^{2+}$ should have the larger $^3J_{PtH_x}$ on the basis of the X-ray data for D_1 in the two complexes ($Pt(dach)_2Cl_2$ and $Pd(dach)_2Cl_2$ are isomorphous[25]).

An observation having bearing on the question of bpy influence on diamine ring conformation has been made by Hall[27] in studying platinum(II) chelates of the ligand 2-*tert*-butyl-1,3-diaminopropane (2-*t*-Butn) which "locks" the chelate ring into a chair conformation with the bulky *tert*-butyl group being equatorially oriented. In the bis complex $Pt(2\text{-}t\text{-}Butn)_2^{2+}$, α protons show a $^3J_{PtH}$ of 62.0 and 22.0 Hz for equatorial and axial protons, respectively. In the mixed complex Pt(bpy)(2-*t*-Butn)$^{2+}$ the coupling constants are found[27] to be 54.4 and 30.5 Hz. These data can be rationalized by a flattening of the chair 1,3-diamine chelate ring in the bpy complex and a reduced vicinal dihedral angle between Pt and the equatorial α proton as seen in the dach complexes discussed above. It is noteworthy that in these two 2-*t*-Butn complexes $^3J_{HH}$ data for the diamine ring protons are essentially the same, indicating that changes in the geometry of the chelate ring are confined to the region around D_1 (2) with D_2 remaining more or less fixed.

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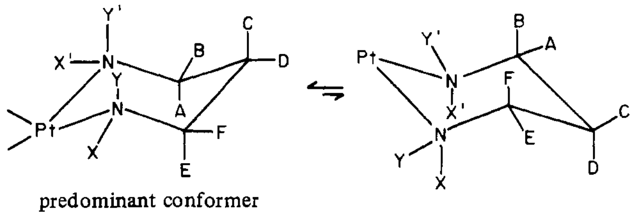
(27) Cullen, W. R.; Hall, L. D.; Price, J. T.; Spendijan, G. *Can. J. Chem.* **1975**, *53*, 336.

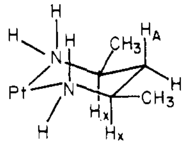
Table II. NMR Data for Diamine Ring Protons from 270-MHz ^{1}H Spectrum[a]



compd	ring proton chemical shifts[b]						ring proton coupling constants, Hz										
	H_A	H_B	H_C	H_D	H_E	H_F	J_{AB}	J_{CD}	J_{EF}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CE}	J_{DE}	J_{CF}	J_{DF}
$Pt(bpy)(1\text{-Metn})^{2+}$	3.06	3.17	1.91	2.28	3.39	*c*	13.3	15.5	*d*	9.4	3.3	3.5	6.3	9.2	3.3	*d*	*d*
$Pt(bpy)(N,N'\text{-Me}_2\text{tn})^{2+}$ [e]	3.33	2.98	2.57	2.22	3.33[f]	2.98[f]	14	15	14[f]	12	3	3	3	12[f]	3[f]	3[f]	3[f]
$Pt(bpy)(N,N'\text{-2-Me}_3\text{tn})^{2+}$	2.96	2.75	2.3	*g*	2.96[f]	2.75[f]	12.5	*d*	12.5[f]	12.5	*d*	~2	*d*	12.5[f]	*d*	~2[f]	*d*
$Pt(bpy)(2\text{-tButn})^{2+}$ [h]	3.17	3.54	2.23	*i*	3.17	3.54	12.8	*d*	12.8	10.9	*d*	3.5	*d*	10.9	*d*	3.5	*d*

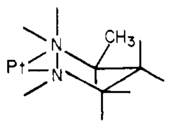
[a] Letter designations refer to conformers depicted here. [b] In ppm. [c] Methyl group present rather than a proton in position F; also X = X' = Y = Y' = H. [d] A coupling constant was not applicable because there was a methyl group present in one position. [e] X = X' = CH_3; Y = Y' = H. [f] Because of symmetry $H_E = H_A$ and $H_B = H_F$; also some coupling constants are equivalent, e.g., $J_{AB} = J_{EF}$ and $J_{CE} = J_{AC}$. [g] Methyl group occupies D position. [h] 2-*t*-Butn = 2-*tert*-butyl-1,3-diaminopropane; data taken from ref 27. [i] *tert*-Butyl group occupies position D.

$Pt(bpy)(meso\text{-}1,3\text{-}Me_2tn)^{2+}$. The *meso*-1,3-$Me_2$tn chelate can adopt a chair conformation in which both methyl groups are equatorially oriented (**18**). Vicinal proton couplings between H_A, H_B, and H_X are in agreement with this conformation and are very similar to those reported by Appleton and Hall for other Pt^{II} and Pt^{IV} complexes of this ligand.[17b] As in their complexes the methyl proton resonance exhibits a $^4J_{PtH}$ of 6 Hz. Coupling of the platinum-195 nucleus with the methyl carbon in this structure would be expected to be very favorable, as is observed with a $^3J_{PtC}$ of 38 Hz. An idealized chair structure would place these methyl carbons in **18** at very close to a 180° dihedral angle with the platinum atom. From studies of 1,2-diamine chelates such trans coupling should maximally yield a $^3J_{PtC}$ of ≈52 Hz. The diminished equatorial methyl carbon–platinum coupling is probably due to a flattening of the chair chelate ring, as seen in the X-ray structure of $Pt(bpy)(dach)^{2+}$, to relieve interaction of the equatorial amino protons with the bipyridine H_6's. A study of models reveals that a flattening of the chelate ring to $D_1 \approx$ 20–30° would decrease the Pt-C vicinal dihedral angle and a value of 150–160° for the latter could account for the somewhat lower value observed for $^3J_{PtC}$.



18

$Pt(bpy)(1\text{-}Metn)^{2+}$. The 1,3-butanediamine (1-Metn) complex, contains a single methyl substituent, and two chair conformers, **19** and **20**, exist, related by ring inversion. Population of the axial conformer (**20**) in this case is potentially more favorable than in the above *meso*-1,3-Me_2tn complex, which would require two bulky methyl groups to occupy axial positions simultaneously. In the 1-Metn complex the only vicinal ^{195}Pt–^{13}C coupling interaction that is directly indicative of methyl group orientation is $^3J_{PtC}$ for the methyl carbon. The value of 32 Hz found for this coupling at 35 °C indicates a methyl equatorial preference although this $^3J_{PtC}$ is lower than that observed in the *meso*-1,3-Me_2tn complex. At 90 °C this $^3J_{PtC}$ is 31 Hz; the slightly diminished magnitude (vs. 35 °C) may indicate a slightly greater population of the less favorable axial conformer **20** at the higher temperature. Assuming $^3J_{PtC}$ for the equatorial methyl carbon in **19** is 38 Hz (as seen for **18**) and $^3J_{PtC}$ is 0–4 Hz for the corresponding axial methyl group in **20**, one calculates 83 ± 1% equatorial conformer at 35 °C and 80 ± 1% at 90 °C for the equilibrium **19** $\rightleftarrows$ **20**. This corresponds to a ΔG of 1.0 ± 0.1 kcal/mol at 35 °C for the conformational inversion **19** $\rightarrow$ **20**. ΔG for the similar axial–equatorial methyl group chair conformer inversion in the octahedral nickel complex $Ni(1\text{-}Metn)(H_2O)_4^{2+}$ was found[14] to be 1.8 ± 0.1 kcal/mol. Of course the octahedral complex has the unfavorable interaction of the axial methyl group and one of the coordinated water molecules.



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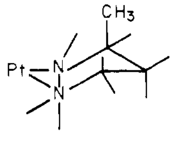
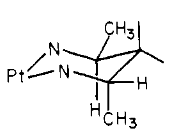


20

The 270-MHz ^{1}H NMR spectra of this complex show five separate multiplets for the five different ring protons. First-order analysis of these multiplets gives $^3J_{HH}$ values (see Table II) that are in agreement with the predominance of the methyl equatorial chair conformer, **19**.

$Pt(bpy)(rac\text{-}1,3\text{-}Me_2tn)^{2+}$. The *rac*-2,4-diaminopentane complex provides a situation in which either chair conformation (**21**, **22**) for the diamine ring places one methyl group in axial orientation and the other in an equatorial orientation. By analogy to the $Pt(bpy)(1\text{-}Metn)^{2+}$ data (vide supra) this axial methyl group should cost about 1.0 kcal/mol of free energy (ΔG), relative to the diequatorial methyl chair conformer of the *meso*-1,3-Me_2 tn complex. However, the $Pt(bpy)(rac\text{-}1,3\text{-}Me_2tn)^{2+}$ complex also has available the alternative diequatorial skew-boat conformation (**23**), which avoids the unfavorable axial placement of the methyl group. In octahedral nickel(II) complexes the chair–skew-boat free energy difference has been found[14] to be 1.4 kcal/mol so that skew-boat conformers may be found in situations where the available chair conformations are destabilized by axial substituents.



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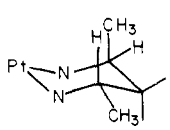

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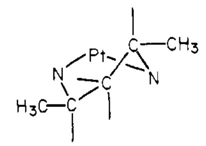


23

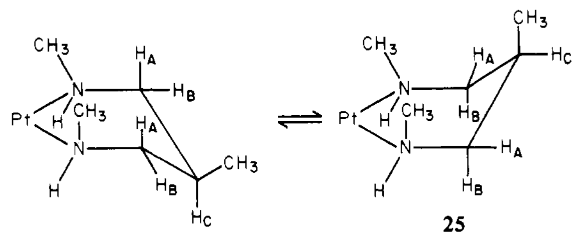
The most direct probe of conformation in this molecule is the vicinal coupling of the platinum-195 nucleus with the methyl carbon-13 nucleus, which is found to be 34 Hz at 35 °C and 33 Hz at 90 °C. If the chair conformation were the only (or predominant) structure for this complex, the chair conformers (**21**, **22**) would be present in equal abundance and be rapidly interconverting. This would give rise to a $^3J_{PtC}$ of $\approx$20 Hz, which is the average of $^3J_{PtC}$ for an equatorial methyl (38 Hz in the *meso*-1,3-Me$_2$tn complex, **18**) and $^3J_{PtC}$ for an axial methyl (<4 Hz for the axial C in the dach complex, **16**). That the observed $^3J_{PtC}$ for the methyl carbon is much greater than 20 Hz is an indication that the skew-boat conformer (**23**) is playing an important role in the conformer distribution in solution. If one assumes that the diequatorial skew boat gives $^3J_{PtC} \approx 40$ Hz for the methyl carbon (a reasonable estimate based on dihedral angles from models and X-ray data[13,15] and $^3J_{PtC}$(trans) = 52 Hz), one calculates a 70:30 conformer distribution with the skew boat form predominating. The fact that there is little change in $^3J_{PtC}$ for the methyl group across the temperature range 10°–90 °C also agrees with the fairly large free energy difference between skew-boat (**23**) and chair (**21**) conformers; from the above data ΔG is $\approx$1 kcal/mol at 308 K.

The observed $^3J_{PtH}$ coupling of 32 Hz to the α-H is also compatible with the predominance of the skew-boat conformer. This α-H would be in an axial orientation in **23**; from the dihedral angle near 45° (estimated from models) across the Pt–N–C–H network and $^3J_{PtH}$(trans) $\simeq$ 79 Hz (see ref 28) one would calculate $^3J_{PtH}$ to be 39 Hz in reasonable agreement with the value of 32 Hz found experimentally. Further evidence for the predominance of the skew boat comes from the ^{195}Pt coupling to the diamine ring β-carbon but discussion of this will be postponed until a later section.

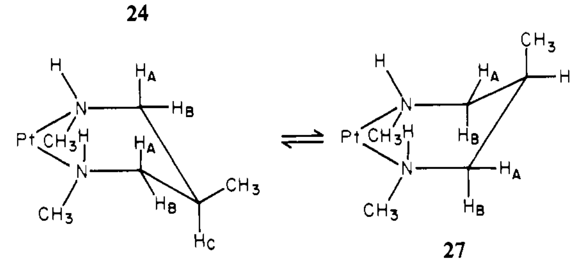
Other workers have reported the ^{13}C spectra for some platinum(II) complexes involving racemic 1,3-diamine ligands. In Pt(*S*,*S*-1,3-Me$_2$tn)(NH$_3$)$_2^{2+}$ the J_{PtC} data[16] are as follows: CH$_3$, 31 Hz; β-CH$_2$, 21 Hz; α-CH, 25 Hz. By analogy with Pt(*S*,*S*-1,3-Me$_2$tn)$_2$Cl$_2$ whose X-ray structure[16] showed a chair conformation for the chelate rings, a chair conformation was inferred for Pt(*S*,*S*-1,3-Me$_2$tn)(NH$_3$)$_2^{2+}$. Also, the complex Pt((*R*,*R*)-1,3-Ph$_2$tn)(NH$_3$)$_2^{2+}$ was prepared and its ^{13}C spectrum investigated (1,3-Ph$_2$tn = 1,3-diphenyl-1,3-diaminopropane).[29] The J_{PtC} data obtained were: α-CH, 22 Hz; β-CH$_2$, 22 Hz; phenyl C$_1$, 25.6 Hz. The latter is a $^3J_{PtC}$ value which was interpreted to correspond to the average between an axial and equatorial environment with the complex existing in a chair conformation.

Pt(bpy)(*N*,*N*′,2-Me$_3$tn)$^{2+}$. This complex can potentially exist in three different geometrical isomers (interconvertible only by a bond-breaking process), each with two conformational forms (related by simple ring inversion) as shown in **24**–**29**. The pair **28** ⇄ **29** represents the two conformers of the racemic isomer, in which the two asymmetric coordinated nitrogen atoms have the same chirality (*R* or *S*); of course, two other nonsuperimposable mirror-image isomers of these conformers exist, but they are not depicted here. For the racemic isomer the two conformers (**28** and **29**) related by ring inversion are not expected to be equienergetic (as is the case in the *N*,*N*′-Me$_2$tn complex; vide infra) because ring inversion exchanges the methyl group at the 2-position between axial and equatorial environments.

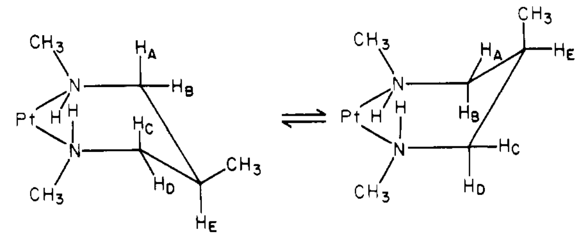
The other four species (**24**–**27**) although different have one feature in common, that is, the two asymmetric nitrogen atoms in each structure have different configurations (one *R*, one *S*); thus they are meso isomers. The β-carbon in these isomers is not asymmetric in the typical sense but has two substituents (–CH$_2$NH(CH$_3$)Pt) attached to it, which are equivalent except for the chirality of the nitrogen atom, one being *R* and the other being *S*.



24 **25**



26 **27**



28 **29**

The depiction of the conformations of these complexes (**24**–**29**) is in the envelope rather than the usual chair conformation for reasons discussed earlier in the structure description of the dach complex[24] and Hall's NMR observations[27] for the 2-*t*-Butn ligand coordinated trans to bpy. Further, a consideration of molecular models for the available chair structure supports a ring flattening which, in the extreme, gives the envelope conformation. In the *meso*-*N*,*N*′-Me$_2$tn complexes (**24**–**27**) the diequatorial methyl orientation normally favored by 1,3-substituents in the stereochemistry of chair six-membered ring systems presents severe steric interaction between equatorial methyl groups on the amine nitrogen and the bipyridine 6- and 6′-protons. The alternative diaxial methyl orientation leads to significant 1,3-interaction of axial groups on the tn ring; ring flattening is seen to reduce such unfavorable steric crowding by moving the groups apart. A flattening of the chelate ring as is commonly found in six-membered tn chelate rings[10] reorients the normal equatorial and axial substituents on the coordinated amine nitrogens, making the equatorial group more axial and the axial one more equatorial. In the limit of total ring flattening between the PtNN and NCCN planes the coordinated amine nitrogen's substituents are identically oriented with respect to the plane of the flattened ring, hence losing the axial–equatorial character of such substituents in the chair conformation. However, the positions of the two amine substituents are not identical in the envelope conformation. One substituent on each nitrogen atom (e.g., the CH$_3$ groups in **26**) points toward the inside of the envelope, i.e., toward the flap of the envelope; this *N*-methyl group originates from an axial substituent in the related chair conformer. The other nitrogen substituent points away from the envelope flap and can be considered as being derived from the corresponding equatorial amine substituent in the chair analogue in the flattening process. This distinction of amine substituents (easily described as pointing *in* and *out*, respectively) makes it easy to describe the dif-

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(28) Erickson, L. E.; Erickson, M. D.; Smith, B. L. *Inorg. Chem.* **1973**, *12*, 412.

(29) Noji, M.; Okamoto, K.; Kidani, Y. *Chem. Lett.* **1979**, 741.

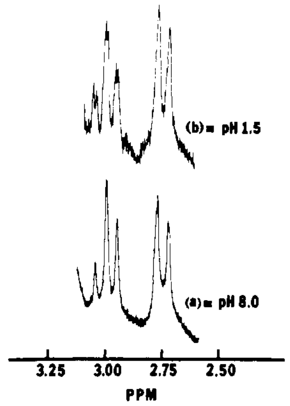


Figure 1. The 270-MHz ^{1}H NMR spectrum of the α-CH resonances of Pt(bpy)(*N*,*N'*-2-Me$_3$tn)$^{2+}$: (a) in D_2O at pH 8 (the *N*-methyl singlet at 3.16 ppm is not shown); (b) in H_2O at pH 1.5 (methyl group at 3.16 ppm (not shown) is a doublet due to 6.0 Hz $^3J_{HNCH}$ coupling).

ference between the envelope conformers; **26** and **24** both have an equatorial 2-methyl group, but in **24** the *N*-methyls point out while in **26** they point in. These in and out isomers are only interconvertible by a bond-breaking process with formation of the opposite chiral configuration at the coordinated nitrogen donor atoms. If the envelope conformers are bent back into the usual chair structure, **24** would then have two equatorial *N*-methyl groups while **26** would have two axial *N*-methyl groups and both would retain equatorial 2-methyl groups.

Molecular models suggest that the steric environments of the nitrogen substituents in the envelope conformation are quite different. The out substituent is staggered with respect to the two substituents on the adjacent α-carbon while the in group is trans to one and gauche to the other. Also the out *N*-methyl groups reside on the same side of the ring as two adjacent axial α substituents; the in *N*-methyls have only one β axial substituent in close proximity.

Of the three different possible isomers that could result for the Pt(bpy)(*N*,*N'*,2-Me$_3$tn)$^{2+}$ complex, the 270-MHz proton NMR spectrum gives evidence of only one species in solution at any significant concentration level at pH 8. The presence of less than 2% of other isomers could go undetected in the experiment. This isomer preference detected by NMR must be thermodynamic in origin because at pH 8 amine proton exchange and subsequent nitrogen inversion would be sufficiently rapid to produce an equilibrium isomer[30] distribution rather than some kinetically preferred species in the initial synthesis.

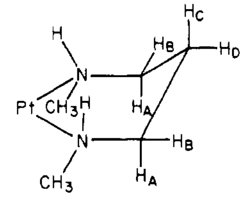
The 270-MHz ^{1}H NMR spectrum shows one type of methyl group and a splitting pattern of the diamine backbone protons consistent with an (AB)$_2$CM$_3$ spectrum (data are given in Table II; A, B, and C spectral designations refer to structures **24**–**29**). The substantial difference in chemical shift of the α protons (A and B), 0.2 ppm shown in Figure 1(a), and the distinct difference in their vicinal coupling constants with the β proton (C), J_{AC} = 12.5 Hz and J_{BC} = 2 Hz, imply the dominant presence of a conformer with the 2-methyl group in an equatorial orientation in solution. The large vicinal coupling of H_A and H_C indicates a largely trans time-averaged orientation of these protons and resembles quite closely the corresponding value found for chelated 2-*tert*-butyl-1,3-propanediamine in which Hall[27] showed that the *tert*-butyl group was locked into an equatorial environment. The vicinal interproton coupling constants are consistent with the predominance of one of three conformers having an equatorial 2-methyl group, **24**, **26**, or **28**.

To decide which of these three conformer structures is the predominant species in solution, we must introduce further NMR evidence. Only one type of methyl resonance is observed in the 270-MHz ^{1}H spectrum, an observation which cannot account for structure **28** unless accidental degeneracy of the resonances for the two different kinds of *N*-methyl groups (in and out) has occurred. Such accidental degeneracy at high field is considered unlikely; also the ^{13}C spectrum shows but one kind of *N*-methyl group. Hence **24** or **26** must represent the appropriate species predominating in the solution distribution.

The choice between **24** and **26** can be made on the basis of a further experiment in which the ^{1}H NMR spectrum is measured in H_2O solvent under conditions of a slow exchange[30] of the amine hydrogen, permitting the measurement of the three-bond spin–spin coupling of the amine proton to the three different α protons (H_A, H_B, and CH_3). With use of Karplus-type vicinal coupling arguments the coupling across the H–N–C–H bonds can be used to identify approximate dihedral angles in this framework. The ^{1}H spectrum of the α-proton resonances in H_2O at pH 1.5 is seen in Figure 1(b) and shows that the axial α proton (H_A) couples to the amine hydrogen with a ^3J of ≈4 Hz; the equatorial α proton (H_B) shows essentially no coupling to the amine hydrogen while the *N*-methyl protons show a typical $^3J_{HNCH}$ of 6.0 Hz. Earlier studies[8] of such coupling in platinum complexes have shown $^3J_{HNCH}$ in the trans orientation to be 11–12 Hz. In the *N*-methyl out envelope conformation (**24**) the dihedral angle of the H–N–C–H network is ≈60° for the equatorial H_B and ≈160° for the axial H_A. In the *N*-methyl in conformation, **26**, the dihedral angle is ≈70–80° for the equatorial H_B and ≈45–50° for the axial H_A. In the latter structure the axial α-H should show significant coupling to the amine proton, ($^3J_{HH}$(trans))($\cos^2 \phi$) $\simeq$ 4–5 Hz, while the equatorial α proton should show coupling of 1 Hz, as is observed. In the *N*-methyl out structure (**24**) H_A should show a very large $^3J_{HH}$ (near 10–11 Hz) and the equatorial H_B a coupling of 3–4 Hz.

These data also can be used to support the envelope nature of the chelate ring rather than the chair structure. In the *N*,*N'*-diequatorial chair that is related to **24** the axial α-H would be trans to the amine proton, leading to a large value for $^3J_{HNCH}$. In the *N*,*N'*-diaxially substituted chair conformer (from **26**) the vicinal H–N–C–H networks should both be near 60°; hence both α protons should show ≈3–4 Hz coupling to the amine proton. Alternative skew-boat conformations have been considered, but none have been found to totally explain the NMR data given above. Although the chelate ring adopts the flattened chair (i.e., envelope) conformation with *N*-methyl groups pointing inside the envelope (**26**), the actual conformation may not be fully flattened but may retain some residual chair character with two pseudoaxial type methyl groups.

Pt(bpy)(*N*,*N'*-Me$_2$tn)$^{2+}$. Like the *N*,*N'*,2-Me$_3$tn complex discussed above the coordinated secondary amines are asymmetric; racemic and meso isomeric complexes are possible. In the meso complex the two methyl groups are symmetrically located; facile ring inversion permits the interconversion of the two distinct meso conformers (**30** ⇄ **31**), which differ in their in and out orientation of the *N*-methyl groups on the envelope.



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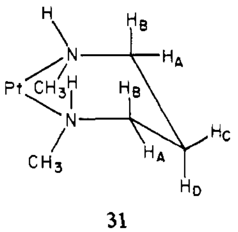

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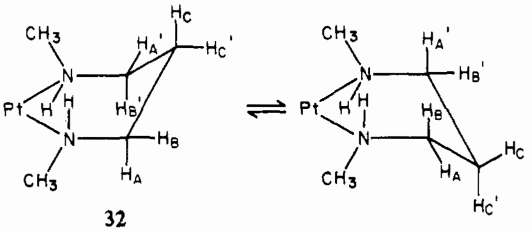
(30) Erickson, L. E. *J. Am. Chem. Soc.* **1969**, *91*, 6284.

The racemic (*R,R* or *S,S*) isomer exists in two equienergetic conformers (**32** ⇌ **33**); with rapid conformational inversion



32 **33**

all six diamine ring protons should exhibit a time-averaged character that is 50% axial and 50% equatorial.

The ^1H and ^{13}C NMR spectra indicate that one isomer predominates by at least a 20:1 majority. The 270-MHz spectrum shows four distinct resonances for the ring protons with vicinal proton–proton coupling constants (Table II) very similar to those observed for the $N,N',2\text{-}Me_3tn$ complex. These observations imply a structure for the latter similar to that for the $N,N'\text{-}Me_2tn$ complex, i.e., a meso complex with the envelope conformation having the methyl groups in (**31**) being the predominant conformer.

It is interesting to compare the isomer distribution of this complex with that of $Pt(N,N'\text{-}Me_2tn)(NH_3)_2^{2+}$ studied earlier by Appleton and Hall.[17a] In contrast, they found a significant quantity of racemic isomer in their equilibrium distribution, the meso to racemic ratio being 2.8 to 1. Their isomer distribution based on the integration of two different kinds of methyl groups was made on the assumption that the diequatorial chair conformer (meso) would be preferred to the racemic species, which is forced to have one axial group. To verify this isomer preference, we prepared the complex $Pt(N,N'\text{-}Me_2tn)(NH_3)_2^{2+}$ and using its 270-MHz NMR spectrum indeed obtained coupling constants (J_{AB} = 12.9 Hz; J_{AC} = 13.2 Hz; J_{CD} = 16.5 Hz; $J_{AD} = J_{BC} = J_{BD}$ = 2.6 Hz) and chemical shifts that are only consistent with the meso isomer predominating. In this complex the NH_3 ligands do not enter into as close a proximity to the amine equatorial chair substituents as the bpy H_6 and H_6' in **12**, and so it may be that less flattening of the chelate ring occurs and the methyl groups still prefer the equatorial environment. Also this preference for an equatorial site is not exclusive since significant racemic isomer is also found. Earlier workers[31] suggested that this might be true because the chelate ring moves the two nitrogen donors apart, lessening 1,3-diaxial steric repulsive forces. Recently an X-ray structure[32] has showed axial *N*-methyl groups in a chair conformation for the complex $Cu(N\text{-}Metn)_2(ONO_2)NO_3$.

Platinum-195–Carbon-13 Coupling Constants and Multipath Coupling. As pointed out in an earlier section, the carbon-13 nuclei in α positions in the 1,3-diamine chelates always show significant coupling of 20–25 Hz to the ^{195}Pt nucleus. By contrast α-carbons in similar (1,2-diamine)platinum complexes[4] show no visible coupling to the platinum nucleus or at best in a few cases 6–8 Hz. One obvious difference between the five- and six-membered ring structure is in the Pt–N–C bond angle, which is nearly 109°[33] in most 1,2-aliphatic diamine chelate rings and close to 120° in the flattened six-membered 1,3-diamine chelate rings.[10] Although bond angle has been suggested[34-36] to influence the magnitude of geminal coupling constants, the fact that in the complex $Pt(bpy)(NH_2CH_3)_2^{2+}$ the methylamine α-carbon shows[4] $^3J_{PtC}$ = 24 Hz seems to indicate that bond angle cannot account for this behavior. In the methylamine complex the Pt–N–C angle should certainly be close to 109°, not 120° as in the strained, flattened-chair six-membered chelate rings. We had earlier ascribed the lack of coupling to α-carbons in the five-membered chelates[4] to a canceling effect due to the operation of simultaneous multiple paths by which the ^{195}Pt and ^{13}C nuclei could couple in these chelates. A two-bond path, normally negative in sign, and a three-bond path through the other nitrogen atom to the same carbon, normally positive in sign, could lead to smaller than expected coupling if such additivity of various paths ($J_{obsd} = {}^2J + {}^3J$) and cancellation occur. The observed sign of a coupling constant reflects the sense of the unpaired s-electron spin density produced at a given nucleus in the coupling process; geminal coupling (^2J) and vicinal coupling (^3J) should produce spin densities of opposite sense to one another at a given nucleus in such multipath situations. Such a cancellation will not be important in the six-membered ring systems because the alternate path to geminal coupling of platinum to the α-carbon is through the other nitrogen and hence involves a four-bond coupling path (**6**), which is known to be quite small in most circumstances.

The six-membered chelate rings provide even further evidence for the operation of such additive simultaneous multiple-path coupling. In five out of the seven tn chelates the β-carbon shows a platinum–carbon coupling constant of 33–40 Hz; only the dach complex with 52 Hz and the *rac*-$1,3\text{-}Me_2tn$ complex with 20 Hz lie outside this range. The 52 Hz coupling to the β-carbon in the 1,3-diaminocyclohexane complex is especially unusual, since from earlier studies a $^3J_{PtC}$ of 52 Hz has been observed for model compounds where the Pt–N–C–C framework was fully trans (ϕ = 180°) and maximally coupled according to Karplus considerations. From the X-ray structure[24] of $Pt(bpy)(dach)^{2+}$ the Pt–N–C–C_β dihedral angle is 31°. Using the usual Karplus-type relationship $^3J_{obsd} = {}^3J_{trans}(\cos^2\phi)$, one would predict a single-path value of 38 Hz. Since it appears improbable that the Pt–N–C–C_β dihedral angle will become 0° because of a large structural change in solution, this large coupling constant may best be explained by remembering that these two nuclei are connected by two identical three-bond paths (**6**). If the individual coupling paths reinforce one another, a Pt–N–C–C dihedral angle of ≈45° would explain the 52 Hz coupling as occurring because of two additive 26 Hz coupling paths. Indeed in the complex $Pd(dach)_2^{2+}$ the $PdNCC_\beta$ dihedral angle is 41°. In our complex, solution conformation mobility may allow a structural change of the needed magnitude simply by movement about the N---N axis of the dach ring without gross structural distortions.

X-ray structures[10] of a variety of 1,3-diamine chelates have shown that the metal–(β-carbon) dihedral angle is usually 55 ± 5°. By use of a similar Karplus-type argument, such an angle would predict a one-path $^3J_{PtC}$ of 13–21 Hz or, because of dual reinforcing paths, 26–42 Hz. Rings with more flattening of the chair conformation, i.e., D_1 (**2**) of 20°, show metal–(β-carbon) dihedral angles of ≈50°, which predicts ≈40-Hz Pt–C_β coupling via multipath coupling. This is, of course, in the appropriate range of J_{PtC} observed for the β-carbons.

The other unusual value of J_{PtC} for a β-carbon occurs in the *rac*-$1,3\text{-}Me_2tn$ complex where a low value of only 20 Hz is found. This would imply a dihedral angle of 65°, taking account of a dual coupling mechanism. From available X-ray data this would occur if the chair conformation underwent very little flattening, i.e., $D_1 \approx 40°$. Such a chair structure would

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(31) DeHayes, L. J.; Busch, D. H. *Inorg. Chem.* **1973**, *12*, 1505.

(32) Turpeinen, U.; Hämäläinen, R.; Ahlgren, M. *Cryst. Struct. Commun.* **1978**, *7*, 241.

(33) Gollogly, J. R.; Hawkins, C. J. *Inorg. Chem.* **1969**, *8*, 1168.

(34) Pople, J. A.; Bothner-By, A. A. *J. Chem. Phys.* **1965**, *42*, 1339.

(35) Hirao, K.; Nakatusuji, H.; Kato, H. *J. Am. Chem. Soc.* **1972**, *94*, 4078; **1973**, *95*, 31.

(36) Maciel, G. E.; McIver, J. W.; Ostlund, N. S.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4151.

enhance bpy H_6 and $H_{6'}$ and equatorial amine proton steric interaction and leave one methyl group in an axial orientation on the diamine chelate ring. An alternative skew-boat structure could accommodate both methyl groups in equatorial environments and introduce less amine hydrogen–bpy H_6 interaction than the undistorted chair conformation. X-ray data[13,15] for such 1,3-diamine chelate rings found in skew-boat conformations show that the β-carbon has a dihedral angle of 60–70° with the metal atom. This large dihedral angle together with multipath coupling provides a reasonable explanation for the reduced J_{PtC} of 20 Hz in this molecule. This diequatorial skew-boat structure also helps to explain the relatively large platinum coupling to the methyl carbons of 33 Hz as was discussed in the previous section.

Available data for J_{PtC_β} in other 1,3-diamine chelates warrant some discussion: in $\mathrm{Pt(NH_3)_2}$(*S,S*-1,3-$\mathrm{Me_2tn})^{2+}$ $J_{\mathrm{PtC}_\beta} = 21$ Hz[16] while in $\mathrm{Pt(NH_3)_2}$(*R,R*-1,3-$\mathrm{Ph_2tn})^{2+}$ $J_{\mathrm{PtC}_\beta} = 22$ Hz.[28] The former is believed to be in a chair conformation (one methyl axial, one equatorial) as X-ray studies[16] have shown for Pt(*S,S*-1,3-$\mathrm{Me_2tn})_2{}^{2+}$. In this chair structure the dihedral angle (D_1) equals 50°. In such a structure the PtNNC_β dihedral angle will approach 60° and the small J_{PtC_β} can be explained in terms of multipath coupling arguments. It must be kept in mind that such an "idealized" chair configuration is possible when two ammonias fill the platinum coordination sphere but is not feasible in the bpy chelates for reasons already discussed. The *R,R*-1,3-$\mathrm{Ph_2tn}$ complex should exist in a similar chair structure. The workers studying the latter complex also prepared the complex from the meso ligand $\mathrm{Pt(NH_3)_2}$(*meso*-1,3-$\mathrm{Ph_2tn})^{2+}$ and reported the following J_{PtC} data: ${}^2J_{\mathrm{PtC}_\alpha} = 22$ Hz and ${}^3J_{\mathrm{PtC_1(Ph)}} = 42.7$ Hz, but J_{PtC_β} was too small to be observed. The large ${}^3J_{\mathrm{PtC}}$ observed for the phenyl group C_1 indicates that this complex is "locked" into the diequatorially substituted chair structure, analogous to the *meso*-1,3-$\mathrm{Me_2tn}$ chelate (**18**). The latter (**18**) will be very much flattened due to the interligand influence of the bpy moiety while the former should be very much a well-formed chair as in the Pt(*S,S*-1,3-$\mathrm{Me_2tn)(NH_3)_2}{}^{2+}$ chelate. The lack of any significant Pt–C_β coupling seems to imply that the Pt–N–C–C_β dihedral angle is fairly large (>70°?) in the *meso*-1,3-$\mathrm{Ph_2tn}$ complex.

Other Considerations. It had been shown earlier that the ${}^{13}C$ resonances of the C_6 of the bipyridine ring showed about a 1–2 ppm upfield shift in the 1,3-diamine complexes, relative to identical 1,2-diamine chelates. This observation may provide further evidence for the proximity of the 1,3-diamine nitrogen substituents and the bpy H_6. Grant and co-workers[37,38] have shown that relatively close nonbonding interactions produce upfield shifts in the ${}^{13}C$ shifts of the proximate groups.

The 270-MHz proton chemical shift data in Table II reveal that in the 2-*t*-Butn and 1-Metn complexes the axial protons are all upfield from their equatorial counterparts. This is normally the rule for such substituents in chair conformers in aliphatic rings. It must also be noted that in the highly flattened, envelope-type conformers of *N,N'*-$\mathrm{Me_2tn}$ and *N,N'*-2-$\mathrm{Me_2tn}$ chelates the axial–equatorial chemical shift order is reversed, axial protons being more downfield. The reasons for this reversal are not apparent. Examples of other heterocyclic six-membered rings where such a reversal of axial–equatorial chemical shifts has been noted are summarized in the literature.[39]

Acknowledgment. The authors acknowledge the National Institutes of Health, the National Science Foundation, and the Research Corp. (L.E.E. and J.E.S.) for financial support. J.E.S. wishes to thank the Fairfield University Research Committee for making the funds available to obtain the 270-MHz NMR spectra at the Southern New England High Field NMR Facility (Yale University). This latter center was established with the support of the National Institutes of Health Biotechnology Resources Program.

Registry No. $\mathrm{Pt(bpy)(tn)^{2+}}$, 77071-48-8; Pt(bpy)(*meso*-1,3-$\mathrm{Me_2tn})^{2+}$, 77071-49-9; Pt(bpy)(*rac*-1,3-$\mathrm{Me_2tn})^{2+}$, 77121-84-7; $\mathrm{Pt(bpy)(1\text{-}Metn)^{2+}}$, 77071-50-2; Pt(bpy)(*N*-Metn)$^{2+}$, 77071-51-3; Pt(bpy)(*N,N'*-$\mathrm{Me_2tn})^{2+}$, 77071-52-4; Pt(bpy)(*N,N'*-2-$\mathrm{Me_3tn})^{2+}$, 77071-53-5; $\mathrm{Pt(bpy)(dach)^{2+}}$, 77071-54-6.

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(37) Wolfenden, W. R.; Grant, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 1496.
(38) Grant, D. M.; Cheney, B. V. *J. Am. Chem. Soc.* **1967**, *89*, 5315.
(39) Aksnes, D. W.; Bergesen, K.; Strømme, O. *Acta. Chem. Scand., Ser. A* **1979**, *A33*, 413.

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Conformational Behavior of Ligated Tris(dialkylamino)phosphines. X-ray Crystal Structures of $(\mathrm{Me_2N})_3\mathrm{PFe(CO)_4}$ at 21 °C and of $[(\mathrm{Me_2N})_3\mathrm{P}]_2\mathrm{Fe(CO)_3}$ at −35 °C

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Received December 3, 1980

The molecular structures of the tris(dimethylamino)phosphine complexes $(\mathrm{Me_2N})_3\mathrm{PFe(CO)_4}$ (**1**) and $[(\mathrm{Me_2N})_3\mathrm{P}]_2\mathrm{Fe(CO)_3}$ (**2**) have been determined by single-crystal X-ray diffraction methods, the former at room temperature (~21 °C) and the latter at −35 °C. Both molecules crystallize in the monoclinic system, space group $P2_1/c$. For **1** $a = 9.606$ (1) Å, $b = 9.508$ (5) Å, $c = 18.335$ (2) Å, $\beta = 107.87$ (1)°, and $Z = 4$; for **2** $a = 11.177$ (1) Å, $b = 15.778$ (1) Å, $c = 13.270$ (2) Å, $\beta = 90.09$ (1)°, and $Z = 4$. The overall geometries of both **1** and **2** are trigonal bipyramidal at iron, and the $(\mathrm{Me_2N})_3\mathrm{P}$ ligands occupy axial sites. The $(\mathrm{Me_2N})_3\mathrm{P}$ ligand in **1** adopts a roughly C_3 geometry in which two of the $\mathrm{Me_2N}$ groups are nearly trigonal planar and twisted in the same direction (dihedral angle $\phi \approx 90$–100°) and the third such group at $\phi \approx 180°$ is much more pyramidal. One of the $(\mathrm{Me_2N})_3\mathrm{P}$ ligands of **2** has a conformation virtually identical with that of **1**; the other possesses approximately C_s skeletal symmetry. In both compounds the geometries at nitrogen and the N–P bond lengths are dependent on the dihedral angle, along the N–P bond.

Introduction

Aminated phosphorus compounds are assuming an increasingly important role as reagents, solvents, and ligands. In view of these developments, it is perhaps surprising that controversy has surrounded the structure of $(\mathrm{Me_2N})_3\mathrm{P}$, the simplest known tris(amino)phosphine.[1] In 1969 Vilkov and