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Complexes with Six-Membered Chelate Rings. III.[1] Factors Influencing the Values of the Platinum–Proton Coupling Constants $^3J_{\text{Pt–N–C–H}}$ and $^4J_{\text{Pt–N–C–CH}_3}$ in Diamine Complexes of Platinum(II) and -(IV)

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The value of $^3J_{\text{Pt–N–C–H}}$ in platinum–diamine complexes depends chiefly on the oxidation state of the platinum ion, the nature of the ligands trans to the chelate ring, and the dihedral angle between the planes PtNC and NCH. The natures of the diamine and of cis ligands (in Pt(IV) complexes) have a smaller effect. For complexes containing the grouping Pt–NH_2–CH–CH_3, values of $^4J_{\text{Pt–N–C–CH}_3}$ have been interpreted in terms of the conformational behavior of the chelate rings. There is a significant solvent effect on the conformational equilibrium of bis(ammine)(butane-1,3-diamine)platinum(II) perchlorate.

Introduction

It has been recently demonstrated[3] that in some amino acid complexes of platinum(II) the coupling constant $^3J_{^{195}\text{Pt–N–C–H}}$ shows a Karplus type dependence on the dihedral angle, ϕ, between the planes PtNC and NCH, *i.e.*, $J_{\text{Pt–N–C–H}} \approx K \cos^2 \phi$, where K is a constant. This relationship is of considerable value in the study of the conformational behavior of platinum complexes by nmr. However, other factors could also influence the coupling constant, and it is desirable that the magnitude of such effects be known. We have studied the spectra of a number of complexes of the types $\text{Pt(diamine)L}_2{}^{2+}$ and *trans'*-$\text{Pt(diamine)(NH}_3)_2\text{Y}'_2{}^{2+}$, where L and Y are neutral and uninegative ligands, respectively, and diamine = en, tn, dan.[4]

In a previous paper,[1] we reported that for some platinum(II) complexes of *meso*-pentane-2,4-diamine there was significant ^{195}Pt–N–C–CH_3 coupling. In the present work, several other platinum complexes of this ligand and of racemic pentane-2,4-diamine, butane-1,3-diamine, and propylenediamine have been studied. These complexes all contain the grouping Pt–NH_2–CH–CH_3, and values of the long-range platinum–methyl coupling constant have been correlated with the conformational behavior of the chelate rings.

Experimental Section

Preparation of Ligands.—Butane-1,3-diamine was prepared by the method of Strack and Fanselow,[5] except that the diamine was isolated from the sodium reduction reaction mixture by steam distillation into hydrochloric acid. The dihydrochloride was purified by recrystallization from 95% ethanol. *Anal.* Calcd for $C_4H_{14}N_2Cl_2$: C, 29.8; H, 8.8; N, 17.4; Cl, 44.0. Found: C, 29.6; H, 8.4; N, 17.5; Cl, 44.3.

Propylenediamine, ethylenediamine, and trimethylenediamine were used as commercially available. Other diamines were prepared as previously described.[6]

Platinum(II) Complexes.—Some of the complexes of the types Pt(diamine)Cl_2 and $\text{Pt(diamine)(NH}_3)_2{}^{2+}$ have been previously described,[6] and the remainder were prepared by the same general methods (complexes listed in Table I). The complexes $[\text{Pt(pn)(NH}_3)_2]\text{Cl}_2$ and $[\text{Pt(bdn)(NH}_3)_2]\text{Cl}_2$, as usual,[6] were not easily characterized (due to partial decomposition and, for the bdn complex, almost instantaneous deliquescence in air), but tetrachloroplatinate salts derived from their solutions were characterized.

Bis(aquo)(diamine)platinum(II) Complexes.—The solution obtained by treating Pt(diamine)Cl_2 with silver perchlorate (molar ratio 1:2) in aqueous solution[6] was filtered and then evaporated on a steam bath. The resultant oil was dissolved in acetone, the solution was filtered, and excess ether was added. An oil separated, from which the ether–acetone was decanted. The oil was washed with ether and then placed in a vacuum desiccator over phosphorus(V) oxide. After several days, a pale yellow solid, presumably the anhydrous perchlorate, was obtained. The solid dissolved readily in water to give a colorless solution containing $[\text{Pt(diamine)(H}_2\text{O)}_2](\text{ClO}_4)_2$. No attempt was made to characterize these compounds, other than by their pmr spectra in D_2O.

Bis(pyridine)(ethylenediamine)platinum(II) Perchlorate.—This complex was prepared from a solution of $[\text{Pt(en)(H}_2\text{O)}_2](\text{ClO}_4)_2$ by a similar procedure to that used for bis(ammine)(diamine) complexes,[6] using pyridine in place of ammonia solution. The yield of the purified product was 56%. *Anal.* Calcd for $\text{PtC}_{12}\text{H}_{18}\text{N}_4\text{Cl}_2\text{O}_8$: C, 23.5; H, 3.0; N, 9.2; Cl, 11.6. Found: C, 23.4; H, 3.0; N, 8.7; Cl, 11.5.

Bis(dimethyl sulfide)(ethylenediamine)platinum(II) Perchlorate.—Several drops of dimethyl sulfide were added to a solution of $[\text{Pt(en)(H}_2\text{O)}_2](\text{ClO}_4)_2$. The solution was evaporated in a vacuum desiccator over phosphorus(V) oxide, to give a colorless oil. This was dissolved in acetone at room temperature, the solution was filtered, and excess ether was added. The ether–acetone was decanted from the resultant oil, which was washed with ether by decantation, and then dried in a vacuum desiccator over phosphorus(V) oxide. A white solid was obtained whose pmr spectrum in D_2O (Table III) was consistent with the formulation $[\text{Pt(en)((CH}_3)_2\text{S)}_2](\text{ClO}_4)_2$. If heat was applied during the preparation, a second, unidentified product tended to form as well. The yield of the purified complex was 65%. *Anal.* Calcd for $\text{PtC}_6\text{H}_{20}\text{N}_2\text{Cl}_2\text{S}_2\text{O}_8$: C, 12.5; H, 3.5; N, 4.8. Found: C, 12.4; H, 3.6; N, 4.9.

Bis(triphenylphosphine)(ethylenediamine)platinum(II) Chloride.—Excess ethylenediamine was allowed to react in aqueous solution with 0.324 g of *cis*-$\text{Pt(P(C}_6\text{H}_5)_3)_2\text{Cl}_2$.[7] The resultant solution was filtered and then concentrated to the point of crystallization (5 ml). The colorless crystals which formed were filtered off, washed with acetone, and dried in a vacuum desiccator (yield 0.20 g or 57% based on $\text{Pt(P(C}_6\text{H}_5)_3)_2\text{Cl}_2$). Further quantities of crude product could be obtained by evaporation of the filtrate. It was only moderately soluble in water at room temperature but was much more soluble in hot water, from which it could be recrystallized. The presence of both P and N coordinated to Pt seems to cause low C values. *Anal.* Calcd

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(1) Part II: T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **9**, 1807 (1970).

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(3) L. E. Erickson, J. W. McDonald, J. K. Howie, and R. P. Clow, *J. Amer. Chem. Soc.*, **90**, 6371 (1968).

(4) Abbreviations: en, ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$; tn, trimethylenediamine (propane-1,3-diamine), $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$; dan, 2,2-dimethylpropane-1,3-diamine, $\text{NH}_2\text{CH}_2\text{C(CH}_3)_2\text{CH}_2\text{NH}_2$; pn, propylenediamine (propane-1,2-diamine), $\text{NH}_2\text{CH(CH}_3)\text{CH}_2\text{NH}_2$; bdn, butane-1,3-diamine, $\text{NH}_2\text{CH(CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2$; dptn, pentane-2,4-diamine, $\text{NH}_2\text{CH(CH}_3)\text{CH}_2\text{CH(CH}_3)\text{NH}_2$; py, pyridine, C_5H_5N.

(5) H. Strack and H. Fanselow, *Hoppe-Seyler's Z. Physiol. Chem.*, **180**, 153 (1929).

(6) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **9**, 1800 (1970).

(7) A. A. Grinberg and Z. A. Razumova, *Zh. Prikl. Khim. (Leningrad)* **27**, 105 (1954).

TABLE I

PLATINUM(II) COMPLEXES

Complex	Color	% yield[a]	Analyses, %									
			Pt		C		H		N		Cl	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Pt((\pm)pn)Cl_2$[b]	Yellow	83[c]	57.4	57.8	10.6	10.6	3.0	2.9	8.2	8.3	20.8	20.7
$Pt((\pm)bdn)Cl_2$	Yellow	71[d]	55.1	55.0	13.6	13.4	3.4	3.5	7.9	7.6	20.0	20.1
$[Pt((\pm)pn)(NH_3)_2][PtCl_4]$	Violet	100			5.6	5.7	2.5	2.4	8.8	8.7	22.2	21.8
$[Pt((\pm)bdn)(NH_3)_2](ClO_4)_2$	White	70			9.3	9.1	3.5	3.2	10.9	10.6	13.7	14.2
$[Pt((\pm)bdn)(NH_3)_2][PtCl_4]$	Violet	100	59.7	59.2	7.3	7.4	2.8	2.8	8.6	8.1		

[a] Based on methods described in ref 6. [b] Previously prepared: L. A. Tschugaeff and W. Sokolov, *Ber.*, **40,** 3461 (1907). [c] Using free base in preparation. [d] Preparation at pH 10, using dihydrochloride.

TABLE II

PLATINUM(IV) COMPLEXES

Complex[a]	Color	% yield[b]	Analyses, %										Ref[c]
			Pt		C		H		N		Cl		
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$[Pt(en)_2Cl_2]Cl_2 \cdot H_2O$	Pale yellow	81			10.1	9.8	3.8	4.0	11.8	12.2			9
$[Pt(en)(NH_3)_2Cl_2]Cl_2$	Pale yellow	62			5.6	5.3	3.3	3.2	13.0	12.5			
$[Pt(en)(NH_3)_2(OH)_2](ClO_4)_2$	White	79			4.6	5.0	3.1	3.1	10.7	10.3			
$[Pt((\pm)pn)(NH_3)_2Cl_2]Cl_2$	White	44			8.1	8.0	3.6	3.9	12.6	12.1			
$[Pt(tn)_2Cl_2]Cl_2 \cdot 2H_2O$	Pale yellow	79	37.4	36.9	13.8	13.8	4.6	4.7	10.8	10.7	27.2	26.9	8
$[Pt(tn)(NH_3)_2Cl_2]Cl_2$	Very pale yellow	48	43.8	44.2	8.1	8.1	3.6	3.5	12.6	12.4			
$[Pt(tn)_2(OH)_2](NO_3)_2$	Colorless crystals	82			14.4	14.0	4.4	4.4	16.8	17.3			
$[Pt(tn)_2(OH)_2](ClO_4)_2$	Colorless crystals	70			12.5	12.6	3.9	4.0	9.7	9.9	12.3	12.5	
$[Pt(\textit{meso}\text{-}dptn)(NH_3)_2Cl_2]Cl_2 \cdot H_2O$	Pale yellow	41	39.7	39.6	12.2	12.2	4.5	4.5	11.4	11.0	28.9	28.5	
$[Pt(\textit{meso}\text{-}dptn)(NH_3)_2Br_2]Cl_2$	Yellow	80	34.7	35.2	10.7	10.8	3.6	3.9	10.0	9.8			
$[Pt(\textit{meso}\text{-}dptn)(NH_3)_2(OH)_2](ClO_4)_2$	White	64			10.6	11.1	3.9	3.9	9.9	10.1			
$[Pt((\pm)dptn)(NH_3)_2Cl_2]Cl_2$	Yellow	29			12.7	12.5	4.3	4.0	11.8	11.2			
$[Pt((\pm)dptn)(NH_3)_2(OH)_2](ClO_4)_2$	White	48			10.6	10.8	3.9	3.8	9.9	9.8			
$[Pt((\pm)bdn)(NH_3)_2Cl_2]Cl_2$	White	74	42.5	42.0	10.5	10.5	4.0	3.9	12.2	11.9	30.9	30.7	
$[Pt((\pm)bdn)(NH_3)_2(OH)_2](ClO_4)_2$	White	65			8.7	8.9	3.7	3.7	10.2	10.2	12.9	13.1	

[a] For all complexes the four N atoms are coplanar. [b] Based on $Pt(diamine)Cl_2$ for $[Pt(diamine)(NH_3)_2X_2]Cl_2$ (X = Cl, Br), on $[Pt(diamine)_2](anion)_2$ for $[Pt(diamine)_2Y_2](anion)_2$ (Y = Cl, OH), and on $[Pt(diamine)(NH_3)_2](ClO_4)_2$ for $[Pt(diamine)(NH_3)_2(OH)_2](ClO_4)_2$. [c] Where previously prepared.

for $PtC_{38}H_{38}N_2Cl_2P_2$: C, 53.7; H, 4.5; N, 3.3; Cl, 8.3. Found: C, 48.9; H, 5.1; N, 3.6; Cl, 7.7.

Platinum(IV) Complexes. ***trans*-Dichlorobis(diamine)platinum(IV) Complexes.**—Complexes *trans*-$[Pt(diamine)_2Cl_2]Cl_2 \cdot xH_2O$ were prepared by the action of hydrogen peroxide solution (30%) on a heated solution of $[Pt(diamine)_2]Cl_2$ in hydrochloric acid.[8,9] They separated from concentrated solutions as well-formed crystals, sometimes quite large. Water of crystallization was lost on standing for a few hours in an oven at 110°. They were only moderately soluble in water at room temperature ($[Pt(en)_2Cl_2]Cl_2$ more so than $[Pt(tn)_2Cl_2]Cl_2$) and could be recrystallized from hot water. Analyses are given in Table II.

***trans*-Dihalo-*cis*-bis(ammine)(diamine)platinum(IV) Chlorides.**—Chlorine gas was slowly bubbled through an aqueous solution of $[Pt(diamine)(NH_3)_2]Cl_2$ (the reaction mixture from Pt(diamine)Cl_2 and aqueous ammonia could be used directly, after warming to remove excess ammonia). The colorless solution turned yellow. After a few minutes the chlorine flow was stopped, the solution was allowed to stand for a time, and then air was blown through to remove excess chlorine. The solution was filtered and then evaporated nearly to dryness. Addition of excess acetone caused precipitation of *trans'*-$[Pt(diamine)(NH_3)_2Cl'_2]Cl_2$, white or pale yellow in color. These complexes are readily characterized and are sufficiently soluble in water for good pmr spectra to be obtained (unlike most complexes of of the type *trans*-$[Pt(diamine)_2Cl_2]Cl_2$). These complexes are listed in Table II.

The dibromo complexes, *trans'*-$[Pt(diamine)(NH_3)_2Br'_2]Br_2$, could be prepared by the action of bromine on aqueous solutions of $[Pt(diamine)(NH_3)_2]Br_2$ but were insufficiently soluble for pmr spectra to be obtained in D_2O. Attempts were made to prepare $[Pt(diamine)(NH_3)_2Br_2]Cl_2$ complexes by treating aqueous solutions of $[Pt(diamine)(NH_3)_2]Cl_2$ with a few drops of liquid bromine, blowing off excess bromine, passing the solution down an anion-exchange column in the chloride form, and evaporating to dryness in a vacuum desiccator. However, analytical results and pmr spectra showed that some exchange between coordinated bromide and the chloride anions occurred in most cases, although at least one complex of this type, $[Pt(\textit{meso}\text{-}dptn)(NH_3)_2Br_2]Cl_2$, appeared to be obtained pure.

***trans*-Dihydroxo Complexes.**—Some complexes of the type *trans*-$[Pt(diamine)_2(OH)_2]Cl_2$ were prepared by the method of Basolo, *et al.*,[9] but they were generally quite deliquescent and thus not easily characterized. As well, there appeared to be some tendency for chloride ions to displace coordinated hydroxide. On the other hand, complexes $[Pt(diamine)_2(OH)_2](NO_3)_2$ and $[Pt(diamine)_2(OH)_2](ClO_4)_2$ (prepared by hydrogen peroxide oxidation of the appropriate salts of $Pt(diamine)_2^{2+}$) had low solubilities in water. Complexes *trans'*-$[Pt(diamine)(NH_3)_2$-

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[8] H. D. K. Drew and H. J. Tress, *J. Chem. Soc.*, 1335 (1933).

[9] F. Basolo, J. C. Bailar, Jr., and B. R. Tarr, *J. Amer. Chem. Soc.*, **72,** 2433 (1950).

TABLE III

PMR SPECTRA OF COMPLEXES OF ETHYLENEDIAMINE, TRIMETHYLENEDIAMINE, AND 2,2-DIMETHYLPROPANE-1,3-DIAMINE IN D_2O

Complex[a]	τ'_{CH_2}	$^3J_{Pt-H}$,[b] Hz	Other aspects of spectra
$[Pt(en)(H_2O)_2](ClO_4)_2$	7.47	52.5	Slow N-deuteration
$[Pt(en)(py)_2](ClO_4)_2$	7.17	42.5	$^3J_{Pt-N-C-H}(py) = 39$ Hz
$[Pt(en)((CH_3)_2S)_2](ClO_4)_2$	7.13	41.0	$^3J_{Pt-S-C-H} = 45$ Hz, τ'_{S-CH_3} 7.48
$[Pt(en)(NH_3)_2](ClO_4)_2$	7.34	41.5	Ref 1
$[Pt(en)_2]Cl_2$	7.34	41.0	Ref 1
$[Pt(en)(P(C_6H_5)_3)_2]Cl_2$	7.29	32.0[c]	At 92°, to increase solubility
$[Pt(en)(NH_3)_2Cl_2]Cl_2$	6.94	26.0	
$[Pt(en)_2Cl_2]Cl_2$	6.97	26.0	
$[Pt(en)(NH_3)_2(OH)_2](ClO_4)_2$	7.07	26.5	
$[Pt(en)(NH_3)_2(H_2O)_2](ClO_4)_4$	6.93	24.5	$[Pt(en)(NH_3)_2(OH)_2](ClO_4)_2 + HClO_4$
$[Pt(tn)(NH_3)_2]Cl_2$	7.23	43.0	τ'_{C-CH_2-C} 8.27; $J_{CH_2-CH_2} =$ 5.5 Hz; ref 1
$[Pt(tn)(NH_3)_2Cl_2]Cl_2$	7.19	27.0	τ'_{C-CH_2-C} 7.98; $J_{CH_2-CH_2} =$ 5.0 Hz
$[Pt(dan)(NH_3)_2]Cl_2$	7.54	40.5	Ref 1

[a] For all complexes, the four N atoms are coplanar. [b] Unless otherwise indicated, values are accurate to ±0.5 Hz. [c] Deviation ±1 Hz.[2]

TABLE IV

PMR SPECTRA OF PENTANE-2,4-DIAMINE COMPLEXES IN D_2O

Complex	$^4J_{Pt-H}$	τ'_{CH_2}		τ'_{H_X}	τ'_{CH_3}	J_{AB}	J_{AX}	J_{BX}	$J_{CH_X-CH_3}$	Ref[a]
		H_A	H_B							
$[Pt(\textit{meso}\text{-dptn})(NH_3)_2]Cl_2$	6.5	8.15	8.78	6.98	8.83	15.0	2.3	11.0	6.5	1
$[Pt(\textit{meso}\text{-dptn})(H_2O)_2](ClO_4)_2$	9.5	*b*	*b*	*b*	*b*	*b*	*b*	*b*	6.5	
$[Pt(\textit{meso}\text{-dptn})(NH_3)_2Cl_2]Cl_2$	5.0	7.99	8.33	6.50	8.63	15.5	2.5	10.5	6.5	
$[Pt(\textit{meso}\text{-dptn})(NH_3)_2Br_2]Cl_2$	5.0	7.90	8.44	6.49	8.64	15.5	2.0	11.0	6.5	
$[Pt(\textit{meso}\text{-dptn})(NH_3)_2(OH)_2](ClO_4)_2$	6.5	7.89	8.43	6.74	8.64	15.5	2.5	11.0	6.5	
$[Pt(\textit{meso}\text{-dptn})(NH_3)_2(H_2O)_2](ClO_4)_4$[c]	6.5	7.75	8.39	6.75	8.61	15.5	2.3	11.0	6.5	
$[Pt((\pm)dptn)(NH_3)_2]Cl_2$	2	8.28	...	6.89	8.68	...	5.5	...	6.5	1
$[Pt((\pm)dptn)(H_2O)_2](ClO_4)_2$	2	8.34	...	7.04	8.64	...	5.3	...	6.5	
$[Pt((\pm)dptn)(NH_3)_2Cl_2]Cl_2$	2.5	8.00	...	6.43	8.63	...	7.0	...	6.5	
$[Pt((\pm)dptn)(NH_3)_2(OH)_2](ClO_4)_2$	3.8	8.01	...	6.65	8.63	...	7.5	...	6.5	
$[Pt((\pm)dptn)(NH_3)_2(H_2O)_2](ClO_4)_4$[c]	4.0	7.95	...	6.57	8.60	...	7.5	...	6.5	

[a] Where previously described. [b] Not measured. [c] $[Pt(diamine)(NH_3)_2(OH)_2](ClO_4)_2 + HClO_4$.

$(OH)'_2](ClO_4)_2$ were easily characterized and quite water soluble. They were prepared by the action of a small volume (0.5 ml) of 30% hydrogen peroxide solution on an aqueous solution containing about 0.1 g of $[Pt(diamine)(NH_3)_2](ClO_4)_2$. The solution was heated and then evaporated to dryness on a steam bath. The resultant white, crystalline solid was washed with acetone (unlike the Pt(II) starting materials, these complexes are insoluble in this solvent), collected on a filter, and dried over phosphorus(V) oxide in a vacuum desiccator. These complexes are listed in Table II.

Instrumentation.—Pmr spectra (60 MHz) were run on a Varian A-60 spectrometer. *tert*-Butyl alcohol was used as an internal reference, and chemical shifts are reported on a τ' scale (relative to DSS, 2,2-dimethylsilapentane-5-sulfonate), using τ' 8.77 for *tert*-C_4H_9OH. Proton–proton spin–spin decoupling spectra were run on a Varian HA-100 spectrometer by Dr. S. R. Johns, of the Division of Applied Chemistry, CSIRO, Melbourne, Australia.

Results

Proton Magnetic Resonance Spectra. Ethylenediamine Complexes.—The methylene groups of all complexes in D_2O gave sharp resonances with "satellites" due to coupling with ^{195}Pt (34% abundance, $I = {}^1/_2$), with the exception of $[Pt(en)(H_2O)_2](ClO_4)_2$. The solution of this complex was slightly acidic, due to dissociation of H (or D) atoms from the coordinated water molecules, which caused N-deuteration (catalyzed by OH^-) to be extremely slow. Thus, the methylene resonance was broadened by coupling with the amino protons. For some complexes, the other ligands coordinated to the platinum ion would be expected to give characteristic peaks in the pmr spectrum; these peaks occurred for all such cases. For example, the spectrum of $[Pt(en)\{(CH_3)_2S\}_2](ClO_4)_2$ in D_2O (after standing for sufficient time to allow complete N-deuteration) consisted of two 1:4:1 triplets, of relative intensities 1:3, corresponding to the four protons from the ethylenediamine and twelve protons from the dimethyl sulfide groups, each coupling to ^{195}Pt. Details of the spectra are given in Table III (some previously obtained results are included for comparison).

Trimethylenediamine Complexes.—*trans'*-$[Pt(tn)(NH_3)_2Cl'_2]Cl_2$ gave a spectrum in D_2O qualitatively similar to those of Pt(II) complexes,[1] the outer methylene groups giving a "triplet" with "satellite" triplets from coupling with ^{195}Pt and the inner methylene group giving a complex multiplet.

***meso*-Pentane-2,4-diamine Complexes.**—Details of these spectra are given in Table IV, with labeling as shown in Figure 1, together with some previously obtained results for comparison. Proton–proton coupling constants are very similar to those in the Pt(II) complexes previously described.[1] All these complexes

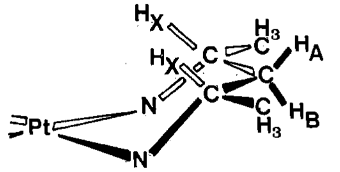


Figure 1.—The *meso*-pentane-2,4-diamine chelate ring in the preferred conformation.

show significant long-range platinum–methyl coupling, **which** in general results in a doublet symmetrically **about** each of the peaks of the main methyl doublet **(Figure** 2).

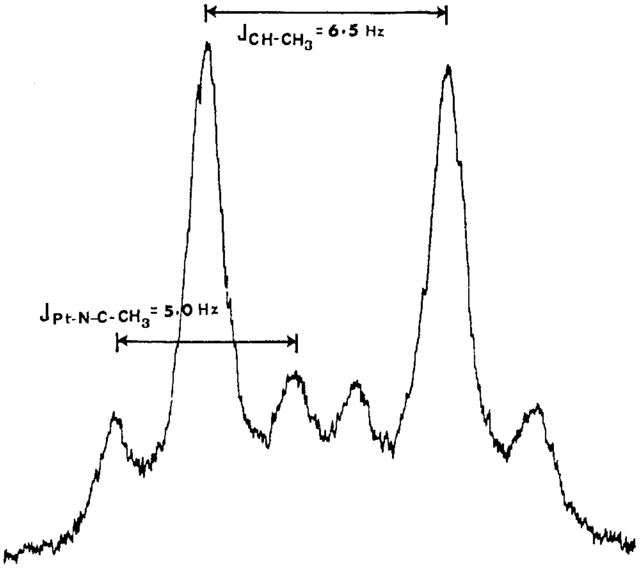


Figure 2.—The methyl region of the pmr spectrum of [Pt(*meso*-dptn)$(NH_3)_2Cl_2]Cl_2$.

An attempt was made to determine the values of $^3J_{Pt-N-C-H_x}$ for [Pt(*meso*-dptn)$_2]Cl_2$ and *trans'*-[Pt(*meso*-dptn)$(NH_3)_2Cl'_2]Cl_2$ by simplifying the H_x resonance through proton–proton spin decoupling. When the methyl resonance of the former complex was strongly irradiated, the H_x protons gave a doublet (splitting 10.5 Hz) from coupling with H_B, as well as peaks attributable to platinum–proton coupling, $^3J_{Pt-N-C-H_x}$ = 15 Hz. There is a further splitting of the peaks (~2 Hz) from coupling with H_A. With the less soluble Pt(IV) complex, good-quality decoupled spectra could not be obtained, and the platinum–proton coupling constant could not be measured.

***rac*-Pentane-2,4-diamine Complexes.**—Details of these spectra are given in Table IV. They are qualitatively similar to those of the Pt(II) complexes previously described.[1] However, values of $J_{CH_x-CH_3}$ are generally higher for Pt(IV) complexes than for Pt(II), and the Pt(IV) complexes, unlike those of Pt(II) do show significant Pt–N–C–CH_3 coupling.

An attempt was made to determine the values of $^3J_{Pt-N-C-H_x}$ for [Pt((±)dptn)$_2]Cl_2$ and *trans'*-[Pt((±)-dptn)$(NH_3)_2Cl'_2]Cl_2$ using proton–proton decoupling. When the methyl resonance of the Pt(II) complex was strongly irradiated, the methine protons gave a triplet (from coupling with the methylene protons) with a triplet on each side of the main peaks (from coupling with ^{195}Pt). Simultaneous irradiation of the methylene resonance gave almost complete decoupling of the methine protons from other protons (low-intensity peaks from coupling with methylene protons could not be completely removed) and the pattern approached that of a singlet with "satellites," $J_{Pt-N-C-H_x}$ = 38.5 Hz. With less soluble [Pt((±)dptn)$(NH_3)_2Cl_2]Cl_2$, good-quality decoupled spectra could not be obtained.

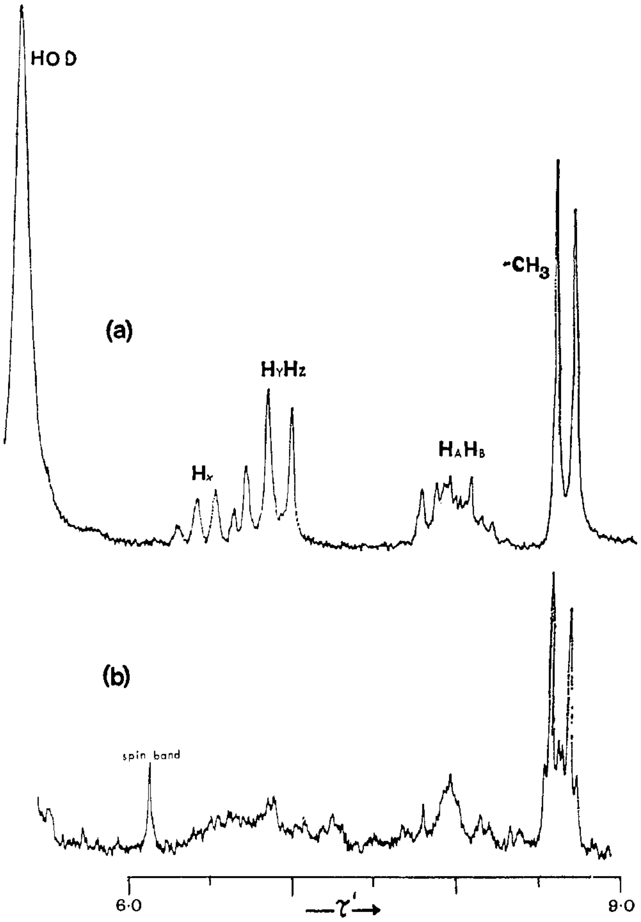
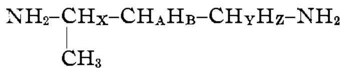


Figure 3.—The 60-MHz pmr spectra of butane-1,3-diamine compounds in D_2O: (a) bdn$(HCl)_2$; (b) [Pt(bdn)$(NH_3)_2Cl_2]Cl_2$.

Butane-1,3-diamine Compounds.—The spectrum of ((±)bdn)$(HCl)_2$ is reproduced in Figure 3a. With the ligand protons labeled as



$$NH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H_X\text{-}CH_AH_B\text{-}CH_YH_Z\text{-}NH_2$$

H_X gives a sextet centered at τ' 6.45 (spacing 6.5 Hz), H_YH_Z gives a triplet at τ' 6.84 (spacing 8.5 Hz, partially overlapping the H_X signal), H_AH_B gives a complicated pattern at τ' 7.95, and the methyl protons give a doublet at τ' 8.64 ($J_{CH_x-CH_3}$ = 6.5 Hz).

In the spectrum of [Pt((±)bdn)$(NH_3)_2](ClO_4)_2$ in D_2O, the signals from H_X, H_Y, and H_Z overlap to give a complex pattern from τ' 6.7 to 7.6, and the H_AH_B protons give another complex pattern centered about τ' 8.2. The methyl protons give a doublet ($J_{CH_x-CH_3}$ = 6.5 Hz) at τ' 8.71, with additional peaks from coupling with ^{195}Pt, $^4J_{Pt-N-C-CH_3}$ = 3.5 Hz. In different solvents at 30°, the value of this coupling constant varies significantly (Table V). On heating to 90° in D_2O, the coupling constant decreases to 3.0 Hz.

Table V
Solvent Effect on Value of $^4J_{Pt-N-C-CH_3}$ for [Pt((±)bdn)$(NH_3)_2](ClO_4)_2$ at 30°

Solvent[a]	$^4J_{Pt-N-C-CH_3}$, Hz (±0.2 Hz)	Solvent[a]	$^4J_{Pt-N-C-CH_3}$, Hz (±0.2 Hz)
$(CH_3)_2S{=}O$	3.0	CH_3CN	3.8
H_2O	3.5	$(CH_3)_2C{=}O$	4.3
$H_2O + OH^-$	3.5	CH_3OH	4.7
$H_2O + H^+$	3.7		

[a] Or deuterated solvent.

The spectrum of *trans'*-$[Pt((\pm)bdn)(NH_3)_2Cl'_2]Cl_2$ in D_2O is reproduced in Figure 3b. The methyl resonance is centered at τ' 8.62 ($J_{CH_x-CH_3}$ = 6.5 Hz; $^4J_{Pt-N-C-CH_3}$ = 5.2 Hz). For *trans'*-$[Pt((\pm)bdn)(NH_3)_2(OH')_2](ClO_4)_2$, the methyl resonance occurs at τ' 8.61 ($J_{CH_x-CH_3} = J_{Pt-N-C-CH_3}$ = 6.5 Hz).

Propylenediamine Complexes.—The spectrum of $[Pt((-)pn)_2]Cl_2$ has been recently described.[10] Although no Pt–N–C–CH_3 coupling was reported, it could be possible for a small coupling to remain undetected by workers who were not expecting it. Consequently, we ran the spectra of $[Pt((\pm)pn)(NH_3)_2]Cl_2$ and *trans'*-$[Pt((\pm)pn)(NH_3)_2Cl'_2]Cl_2$ in D_2O. Sharp methyl doublets ($J_{CH_x-CH_3}$ = 6.5 Hz) were obtained at τ' 8.71 and 8.54, respectively. In neither case was coupling between ^{195}Pt and the methyl group observed.

Discussion

Factors Influencing $^3J_{Pt-N-C-H}$.—For none of the complexes listed in Table III is there a single preferred conformation (*i.e.*, there is no preferred orientation of the Pt–N–C–H bonds). The spectra of these complexes illustrate the effect of the following factors on $^3J_{Pt-N-C-H}$: (i) the oxidation state of the platinum ion, (ii) the nature of the coordinated diamine, (iii) the nature of ligands trans to the diamine (for Pt(II) complexes), and (iv) the nature of the ligands cis to the diamine (for Pt(IV) complexes). These factors will be considered in turn.

(i) As would be expected, the oxidation state has a marked effect on the coupling constant. For example, the coupling constant decreases from 41.5 to 26 Hz when $Pt(en)(NH_3)_2^{2+}$ is oxidized to $Pt(en)(NH_3)_2Cl_2^{2+}$.

(ii) Comparison of coupling constants for the complexes $Pt(diamine)(NH_3)_2^{2+}$, where diamine = en, tn, dan, and $Pt(diamine)(NH_3)_2Cl_2^{2+}$, where diamine = en, tn, shows that the value of the coupling constant does not depend markedly on the structure of the diamine (at least for these simple aliphatic diamines), provided that, as here, there is no single preferred conformation. The small effect that does exist may be due, in part at least, to the varying strengths of the Pt–N bonding. Thus, trimethylenediamine, which is a stronger base than ethylenediamine,[11] might be expected to form stronger Pt–N bonds, giving slightly higher coupling constants. The effect may also be due to the Karplus type angular dependence of the coupling constant.[3] Figure 4 shows a chelate ring viewed down one of the N–C bonds. $J_{Pt-N-C-H_{eq}}$ will be expected to be greater than $J_{Pt-N-C-H_{ax}}$, since ϕ_{eq} is in the vicinity of 180° and ϕ_{ax} is in the vicinity of 60°. Since any one methylene proton spends equal time as an axial and as an equatorial proton, the observed coupling constant will be the average of $J_{Pt-N-C-H_{eq}}$ and $J_{Pt-N-C-H_{ax}}$ (assuming that the time required for conformational inversion is short compared with the conformational lifetime). The exact values of ϕ_{eq} and ϕ_{ax} and thus of these coupling constants will depend on details of the chelate ring conformation and in this way may vary slightly from compound to compound.

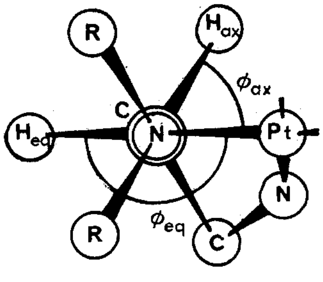


Figure 4.—The chelate ring viewed down an N–C bond.

(iii) The coupling constants for the complexes $Pt(en)L_2^{2+}$ show that the trans ligand, L, can have a marked effect. For the complexes studied, $J_{Pt-N-C-H}$ decreases in the order $H_2O > py \sim NH_3 \sim en \sim (CH_3)_2S > P(C_6H_5)_3$, *i.e.*, in the order of increasing trans influence (*cf.* behavior of J_{Pt-CH_3} in trimethylplatinum(IV) complexes[12]).

(iv) For the Pt(IV) complexes studied, the cis ligands have only a small effect on the coupling constant. The small variations observed could arise from a direct electronic effect in the Pt–N bonds or from changes in the chelate ring conformations resulting from steric interactions or perhaps H bonding with these "axial" groups. Possibly there is a combination of these effects.

There is little correlation between the chemical shifts of the methylene protons and the coupling constants with ^{195}Pt, but this is not unexpected when some of the trans ligands contain aromatic groups. All of the methylene resonances for the ethylenediamine complexes studied occur upfield from that of $(en)(HCl)_2$ (τ' 6.57[1]) and those for Pt(II) complexes are upfield from those of Pt(IV) complexes. This is expected since the electron-accepting tendency decreases in the order $H^+ > Pt(IV) > Pt(II)$.

Conformations of Pentane-2,4-diamine Chelate Rings.—The proton–proton coupling constants for the Pt(IV) complexes of *meso*-pentane-2,4-diamine indicate that, as for the Pt(II) complexes previously discussed,[1] the chelate ring takes up the expected chair-type conformation with both methyl groups equatorial (Figure 1). In this preferred conformation, there is now a preferred orientation of the Pt–N–C–H angles, since the methine protons are axial, with $\phi_{ax} \approx 60°$. Thus a comparison of $^3J_{Pt-N-C-H}$ between the complexes $[Pt(en)_2]Cl_2$ and $[Pt(meso\text{-}dptn)_2]Cl_2$, for which oxidation states and trans ligand atoms are similar, should illustrate the effect of the dihedral angle on this coupling constant. The low value of $^3J_{Pt-N-C-H}$ for the *meso*-dptn complex (15 Hz) compared with that for the ethylenediamine complex (41 Hz) confirms the Karplus type angular dependence of the three-bond coupling constant. If the coupling constant for the *meso*-dptn complex is regarded as that for a typical axial proton in a Pt(II) complex with nitrogen ligands trans to the chelate ring, the coupling to a typical equatorial proton, which has not been directly observed, may be calculated

$$^1/_2(J_{Pt-N-C-H_{eq}} + J_{Pt-N-C-H_{ax}}) \simeq 40 \text{ Hz}$$

$$J_{Pt-N-C-H_{eq}} \simeq 65 \text{ Hz}$$

The preferred conformation of the chelate ring in complexes of Pt(II) with $(\pm)$dptn cannot be unequivocally determined from proton–proton coupling con-

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[10] S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 3184 (1969).

[11] D. D. Perrin, *Aust. J. Chem.*, **17**, 484 (1964).

[12] D. E. Clegg and J. R. Hall, *ibid.*, **20**, 2025 (1967).

TABLE VI

$^3J_{\text{Pt-N-C-H}}$ FOR ETHYLENEDIAMINE COMPLEXES AND $^4J_{\text{Pt-N-C-CH}_3}$ FOR *meso*-PENTANE-2,4-DIAMINE, (±)-PENTANE-2,4-DIAMINE, BUTANE-1,3-DIAMINE, AND PROPYLENEDIAMINE COMPLEXES IN D_2O AT 30°[a]

Complex	$^3J_{\text{Pt-H}}$ (±0.5) en	$^4J_{\text{Pt-H}}$ (±0.2) *meso*-dptn	$^4J_{\text{Pt-H}}$ (±0.2) (±)bdn	$^4J_{\text{Pt-H}}$ (±)dptn	$^4J_{\text{Pt-H}}$ (±)pn
$Pt(N-N)(H_2O)_2^{2+}$	52.5	9.5	4.3	<2	
$Pt(N-N)(NH_3)_2^{2+}$	41.5	6.5	3.5	<2	<2
$Pt(N-N)(NH_3)_2Cl_2^{2+}$	26.0 (41.5)[a]	5.0 (8.0)	5.2 (8.3)	2.5 (4.0)	<2
$Pt(N-N)(NH_3)_2(OH)_2^{2+}$	26.5 (42.3)	6.5 (10.4)	6.5 (10.4)	3.8 (6.1)	
$Pt(N-N)(NH_3)_2(OH)_2 + HClO_4$	24.5 (39.2)	6.5 (10.4)	6.5 (10.4)	4.0 (6.4)	

[a] Coupling constants are in hertz. Figures in parentheses are "compensated" for the increase in Pt oxidation state from II to IV by multiplying the observed coupling constant by the factor 41.5/26.0.

stants.[1] However, using the Karplus type angular dependence of $^3J_{\text{Pt-N-C-H}}$ illustrated above, a conformational assignment can be made from the value of 38.5 Hz obtained for this coupling constant with $[Pt((\pm)dptn)_2]Cl_2$. This value is consistent with a rapid equilibrium between two equivalent chair conformations, in each of which one methine proton is axial and one equatorial, rather than a skew-boat conformation with both methine protons axial.

The nonavailability of a value of $^3J_{\text{Pt-N-C-H}}$ for Pt(IV) complexes of (±)dptn prevents a similar unambiguous assignment of the ring conformation based on the angular dependence of this coupling constant. However, it is important for the discussion of four-bond couplings to establish the conformational behavior of the chelate ring in these complexes. In a Pt(IV) complex there are coordinated "axial" substituents, and the axial methyl group in a chair-type conformation would experience a severe steric interaction (Figure 5a). In a skew-boat conformation, both methyl groups could be equatorial, and there would be no such severe interactions (Figure 5b); this conformation is probably favored for Pt(IV) complexes. The increase in J_{AX} in going from Pt(II) to Pt(IV) complexes (∼2 Hz) is consistent with a change from chair to skew-boat conformation. In a skew-boat conformation (SB), with labeling as in Figure 5, $J_{A''X'}$ would have a value corresponding to $\phi \approx 180°$ (J_{180}) and $J_{A''X''}$ a value corresponding to $\phi \approx 60°$ (J_{60}). Then, if an averaged coupling is experienced by $H_{A''}$, the averaged coupling constant for a skew-boat conformation is

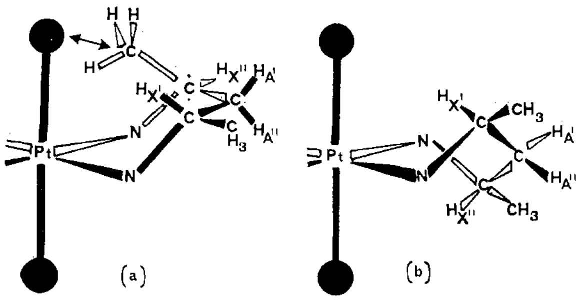

Figure 5.—Conformations of the *rac*-pentane-2,4-diamine chelate ring in a Pt(IV) complex: (a) chair; (b) skew boat.

$$J_{AX(AV-SB)} \approx \frac{1}{2}(J_{180} + J_{60})$$

since $H_{A'}$ is equivalent to $H_{A''}$. In each chair conformation (Ch), $H_{A'}$ and $H_{A''}$ are nonequivalent. In the chair conformation shown in Figure 5a, $J_{A''X'}$ will have a value corresponding to $\phi \approx 180°$, and $J_{A''X''}$ will correspond to $\phi \approx 60°$. However, in the other, equivalent chair conformation, $J_{A''X'}$ and $J_{A''X''}$ will both correspond to $\phi \approx 60°$. Then, if all the couplings are averaged

$$J_{AX(AV-Ch)} \approx \frac{1}{4}(J_{180} + 3J_{60})$$

Then

$$J_{AX(AV-SB)} - J_{AX(AV-Ch)} \approx \frac{1}{4}(J_{180} - J_{60})$$

From the Karplus equation,[13] $J_{180} > J_{60}$, so that

$$J_{AX(AV-SB)} > J_{AX(AV-Ch)}$$

A typical value of $(J_{180} - J_{60})$ might be ∼8 Hz. This would give an increase in J_{AX} in changing from chair to skew-boat conformation of the order of 2 Hz, the increase observed in going from Pt(II) to Pt(IV) (*cf.* the corresponding trimethylenediamine complexes where $J_{CH_2-CH_2}$ decreases slightly). The above argument is, of course, semiquantitative only, as J_{180} and J_{60} will not be identical for all the sets of couplings considered, but it is valid provided that they are of the same order.

Factors Influencing the Value of $J_{\text{Pt-N-C-CH}_3}$.—In our previous publication,[1] we reported long-range platinum–proton coupling in Pt(II) complexes of *meso*-pentane-2,4-diamine and suggested that it occurred here because a planar-W configuration of the Pt–N–C–C–H bonds was possible when the methyl groups were equatorial, as in the preferred conformation of these chelate rings. To rationalize the long-range coupling constants found in this work, it is further proposed that, after allowing for the effects of oxidation state of the platinum ion and the trans influence of ligands trans to the diamine (the factors having greatest effect on $^3J_{\text{Pt-N-C-H}}$), the value of the four-bond coupling constant depends predominantly on the degree of preference for the conformation with the methyl group equatorial (expressed as the percentage of molecules in this conformation at any instant, n_{eq}). Table VI lists the values of these four-bond coupling constants for the complexes studied, together with values of $^3J_{\text{Pt-N-C-H}}$ for corresponding ethylenediamine complexes, for comparison. For the Pt(IV) complexes, an attempt has been made to compensate for the effect of increased oxidation state on the coupling constants by multiplying by the factor 41.5/26 (*i.e.*, the ratio of platinum–methylene coupling constants $J(Pt(en)(NH_3)_2^{2+})/J(Pt(en)(NH_3)_2Cl_2^{2+})$). These "compensated" values are given in parentheses in Table VI.

The effect of the trans ligands on $^4J_{\text{Pt-N-C-CH}_3}$ is illustrated by the coupling constants for $Pt(\textit{meso}\text{-dptn})(H_2O)_2^{2+}$ and $Pt((\pm)bdn)(H_2O)_2^{2+}$, which are greater than those for the corresponding bis-ammine complexes. The ring conformations would be expected to be almost

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

unaffected by the trans ligands, so this change in coupling constants is due to electronic modification of the bonds, reflecting the lower trans influence of H_2O compared with that of NH_3. It is not clear why the relative change for the *meso*-dptn complexes (47%) should be greater than that for the bdn complexes (23%) or for $^3J_{\text{Pt-N-C-H}}$ in the corresponding ethylenediamine complexes (28%).

The "compensated" coupling constants may be listed in the following order: Pt(IV)-(*meso*-dptn) ~ Pt(IV)-(bdn) > Pt(II)-(*meso*-dptn) > Pt(IV)-((±)dptn) ~ Pt(II)-(bdn) > Pt(IV)-(pn) ~ Pt(II)-(pn) ~ Pt(II)-((±)dptn).

If the above hypothesis is correct, that these coupling constants depend chiefly on n_{eq}, this list should represent a decreasing order of n_{eq}. The conformational behavior of the chelate rings is known only semiquantitatively, but this does correspond to the expected order of preference for the conformation with the methyl group equatorial. The conformational equilibria involved are represented in Figure 6.

In a Pt(IV) complex of *meso*-dptn or bdn the "axial" ligand attached to the metal ion would interact so severely with an axial methyl group that the equatorial conformation would be almost exclusively preferred ($n_{\text{eq}} \approx 100\%$). In Pt(II) complexes there is no such "axial" ligand, so that the preference for the equatorial conformer, while still high, is less than for the Pt(IV) complexes. Further, for bdn complexes there is only one methyl group which must be either equatorial or axial, while for *meso*-dptn there are two such methyl groups, so that the preference for the equatorial conformation would be less for Pt(II)-(bdn) than for Pt(II)-(*meso*-dptn). Thus the order of n_{eq} for these complexes is Pt(IV)-(*meso*-dptn) ~ Pt(IV)-(bdn) > Pt(II)-(*meso*-dptn) > Pt(II)-(bdn), in agreement with the order of coupling constants. As discussed earlier, a skew-boat conformation with both methyl groups equatorial is probably preferred for Pt(IV) complexes of (±)dptn, and n_{eq} for these complexes could well be similar to that for Pt(II)-(*meso*-dptn).

Although there is a wealth of evidence that the propylenediamine chelate ring prefers the puckered conformation with the methyl group equatorial, including results from a pmr study of $[Pt((-)pn)_2]Cl_2$ in D_2O solution,[10] n_{eq} would be less for pn complexes than for the corresponding bdn complexes. As illustrated in Figure 7, the interactions of an axial methyl group with other atoms in the chelate ring are considerably less for propylenediamine (Figure 7c and d) than for butane-1,3-diamine (Figure 7a and b). Also, an axial methyl group does not approach an "axial" ligand coordinated to Pt(IV) as closely for pn as for bdn, especially since the steric interaction for the pn complex may be further reduced by distortion of the five-membered chelate ring from a symmetrical gauche conformation.[14] Although flattening of M-N-C angles has been observed in all six-coordinate trimethylenediamine complexes studied by X-ray crystallography,[15-17] very severe flattening of these angles in the bdn ring would be necessary to relieve greatly the steric interactions. Thus the order of n_{eq}, Pt(II)-(bdn) > Pt(IV)-(pn) > Pt(II)-(pn), is reasonable.

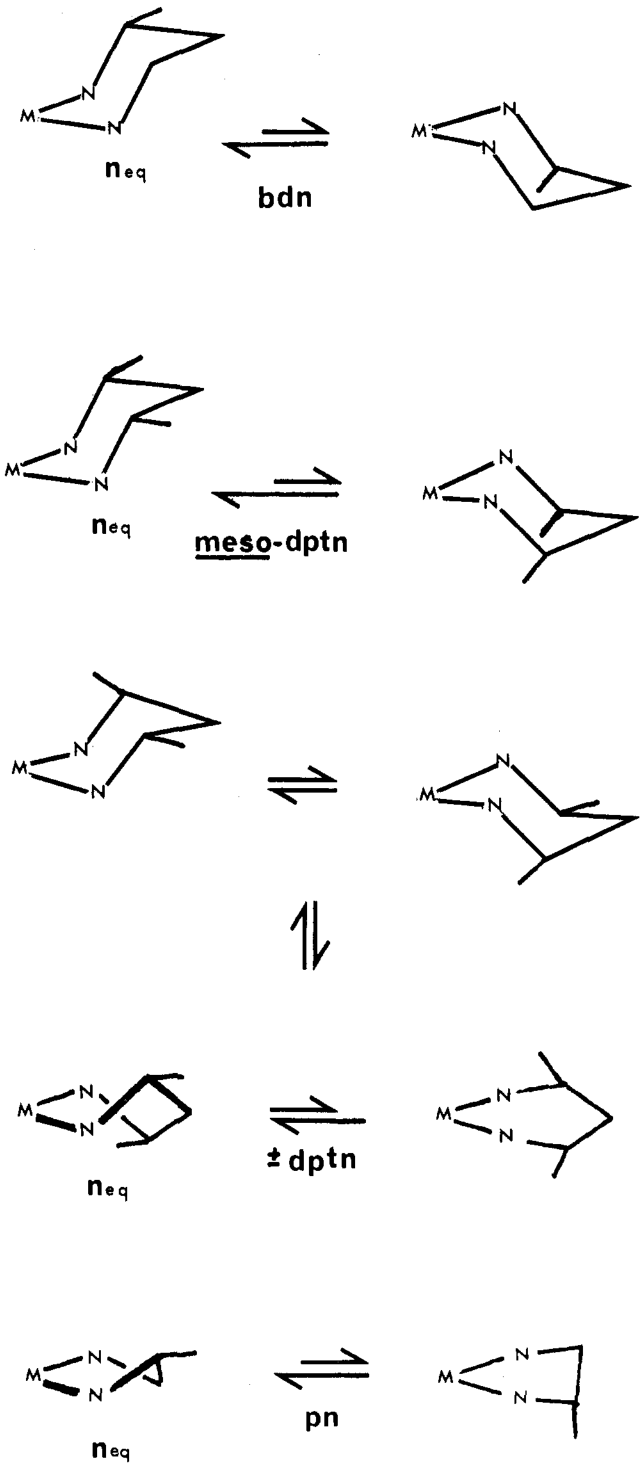

Figure 6.—Conformational equilibria of chelate rings.

As shown by $^3J_{\text{Pt-N-C-H}}$ for Pt(II) complexes of *rac*-pentane-2,4-diamine, there is rapid interconversion between two equivalent chair conformations, in each of which one methyl group is equatorial and the other axial. Thus, each methyl group is equatorial for 50% of the time, and $n_{\text{eq}} = 50\%$, the lowest value of n_{eq} for all the complexes studied.

This correlation between the long-range coupling constants and n_{eq} provides empirical support for the proposal that the "compensated" four-bond coupling constants depend mainly on the degree of preference for

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(14) J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969).

(15) Y. Saito, T. Nomura, and F. Marumo, *Bull. Chem. Soc. Jap.*, **42**, 1016 (1969).

(16) A. Pajunen, *Suom. Kemistilehti B*, **41**, 232 (1968).

(17) A. Pajunen, *ibid.*, *B*, **42**, 15 (1969).

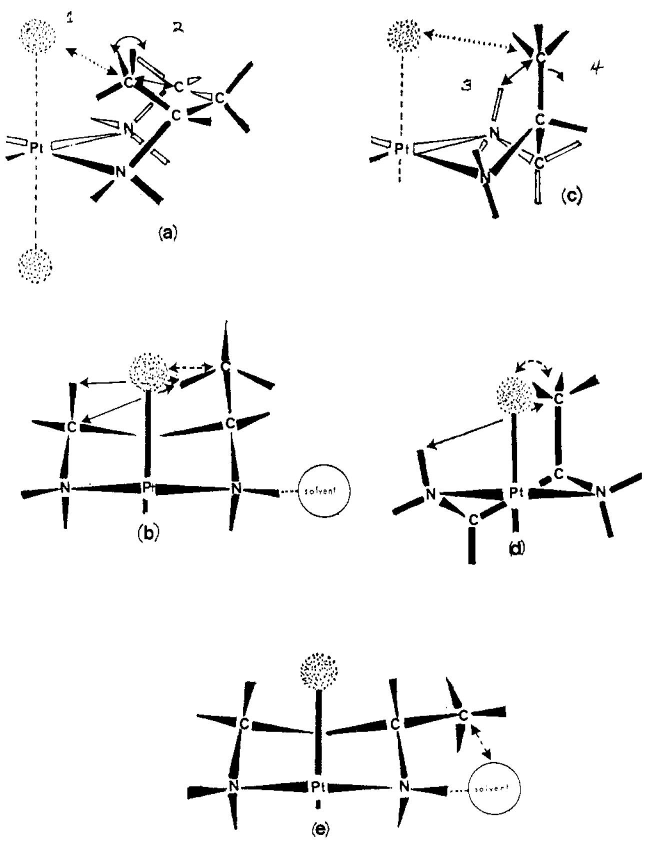

Figure 7.—Conformations of propylenediamine and butane-1,3-diamine chelate rings: (a), (b) bdn axial; (c), (d) pn axial; (e) bdn equatorial; 1, severe interaction for Pt(IV); 2, significant interactions across ring; 3, little interaction across ring; 4, moderate interaction for Pt(IV) partially relieved by angle bending.

the conformation with the methyl group equatorial. Further, it will be noticed that the coupling constant is very sensitive to the degree of conformational preference and is only observed when n_{eq} is quite high. No measurable coupling is observed for complexes with n_{eq} less than for Pt(II)–(bdn) (*i.e.*, for pn complexes and Pt(II)–(($\pm$)dptn)). A simple averaging law would predict that the coupling in Pt(II) complexes of ($\pm$)dptn would be the average of $J_{\text{Pt-N-C-CH}_3\text{(eq)}}$ ($\geqslant 6.5$ Hz) and $J_{\text{Pt-N-C-CH}_3\text{(ax)}}$ ($\geqslant 0$) (*i.e.*, at least 3 Hz) and larger values for pn complexes. The difference between the coupling constants for $\text{Pt}(\textit{meso}\text{-dptn})(\text{NH}_3)_2^{2+}$ and $\text{Pt(bdn)(NH}_3)_2^{2+}$ is also greater than would be expected from a simple averaging law. It is not clear why a simple averaging law is not followed. Factors such as the comparatively long lifetime or greater rigidity associated with a very highly preferred conformation may be responsible.

Although the value of n_{eq} may be the main factor in determining the value of the "compensated" coupling constant, other factors may have a significant effect. The comparative rigidity of chair-type conformations may enhance the coupling. The coupling constant may also depend on the detailed geometry of the preferred conformation. As mentioned above, for Pt(IV) complexes at least, there will probably be some flattening of the Pt–N–C angles. The effect of such flattening on the four-bond coupling constant is not known. The geometry of the ring conformation could also be affected by intramolecular hydrogen bonding between the "axial" ligands and the diamine amino protons. Such H bonding could increase the preference for a particular conformation and could make this conformation more rigid. As well, effects arising from electronic modification of Pt–N bonds (including change of oxidation state) may not parallel closely those for three-bond couplings. Some of these factors may contribute to the observed variations in $^4J_{\text{Pt-N-C-CH}_3}$ when the "axial" ligands are changed. Few complexes with bromo groups as "axial" ligands were studied, because of preparative difficulties, but for what appears to be a genuine sample of $[\text{Pt}(\textit{meso}\text{-dptn})(\text{NH}_3)_2\text{Br}_2]\text{Cl}_2$, the value of the platinum–methyl coupling constant (5.0 Hz) is the same as for the dichloro complex. Thus, a mere increase in size of the "axial" groups has little effect on the coupling. However, all the *trans*-dihydroxo complexes have four-bond coupling constants significantly larger (~30%) than the corresponding *trans*-dichloro complexes (*cf.* an increase of ~4% for the three-bond coupling in the corresponding ethylenediamine complexes). Although it is possible that a direct electronic effect could influence the four-bond coupling more than the three-bond coupling, a conformational effect, perhaps involving H bonding, is probably chiefly responsible. This is supported by the fact that addition of perchloric acid (which would convert the coordinated hydroxo groups to coordinated water) has no effect on the four-bond coupling constants (although $^3J_{\text{Pt-N-C-H}_2}$ decreases from 27.0 to 24.5 Hz in the corresponding en complexes). This suggests that the high values of the four-bond coupling constants in these complexes are associated mainly with the presence of O–H bonds in the "axial" ligands.

Solvent and Temperature Effects on $^4J_{\text{Pt-N-C-CH}_3}$.—The value of $^3J_{\text{Pt-N-C-H}}$ in the complexes $[\text{Pt(diamine)(NH}_3)_2](\text{ClO}_4)_2$ that have been studied is virtually unaffected by variation of solvent or temperature (diamine = en, tn, dan).[1] For *meso*-dptn complexes, the presence of two methyl groups which must be either axial or equatorial gives the chelate ring a strong preference for the conformation with both equatorial. This equilibrium would not be expected to be greatly influenced by solvent or temperature changes, and thus the value of $^4J_{\text{Pt-N-C-CH}_3}$, which depends on this preference, would not be expected to be very sensitive to these changes. Indeed, the value of this coupling constant for $[\text{Pt}(\textit{meso}\text{-dptn})(\text{NH}_3)_2](\text{ClO}_4)_2$ remains unchanged in dimethyl sulfoxide up to 167°.[1] For complexes of butane-1,3-diamine, however, there is only one methyl group to be either axial or equatorial, and the preference for the equatorial conformer would be less than for *meso*-dptn complexes and could be solvent and temperature dependent. This would be reflected in the value of the platinum–methyl coupling constant. For $[\text{Pt(bdn)(NH}_3)_2](\text{ClO}_4)_2$, this coupling constant decreases (from 3.5 to 3.0 Hz) on heating to 90°. This is consistent with the expected decrease in n_{eq} as the temperature is raised. As shown by Table V, there is also a significant solvent effect on the coupling constant, which indicates that there is a solvent effect on the conformational equilibrium. Although solvation effects could be quite complex, there are two relatively simple ways in which the solvent could affect the conformational equilibrium. (i) The first is by pseudocoordination above and below the coordination plane. This would tend to favor the equatorial conformer, since an axial methyl group would interact sterically with the pseudocoordinated solvent molecules. (ii) The second is by H bonding with the amino group H atoms. As illustrated in Figure 7, an equatorial methyl group would hinder close approach of a solvent molecule to the adjacent equatorial hydrogen on N. An axial methyl group would cause much less hindrance to such solvent approach. Thus, in a strongly H-bonding solvent, the equatorial conformer would be less favored than in a more weakly H-bonding solvent.

The solvents which would probably pseudocoordinate strongly to Pt(II) (DMSO, water, and acetonitrile) are also those which might be expected to be strongly H bonded to the diamine amino groups. The fact that the coupling is smaller (and thus the preference for the equatorial conformer) is less in these solvents suggests that (ii) is more important than (i) in influencing the conformational equilibrium (very strong pseudocoordination by the solvent could affect the coupling constant directly by altering the electron density in the Pt–N bonds, but no such effect has been observed for complexes of other diamines).

Conclusions

Results reported in this paper indicate that $^3J_{\text{Pt-N-C-H}}$ decreases on oxidation from Pt(II) to Pt(IV) by a fairly constant factor and decreases with increasing trans influence of ligands trans to the chelate ring. When these factors are constant, a Karplus type angular dependence law is followed. Coupling constants in pmr spectra of (±)dptn complexes support assignment of chair conformation to Pt(II) complexes and skew-boat to Pt(IV) complexes.

A correlation between the conformational behavior and the four-bond platinum–methyl coupling constants in complexes containing the grouping Pt–NH$_2$–CH–CH$_3$ supports the hypothesis that, after allowing for effects of oxidation state and trans influence, the coupling constant increases with increasing preference for the conformation with the methyl group equatorial. Variation of $^4J_{\text{Pt-N-C-CH}_3}$ for [Pt(bdn)(NH$_3$)$_2$](ClO$_4$)$_2$ with different solvents reflects a solvent effect on the conformational equilibrium of the chelate ring.

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Spin–Spin Coupling in the Tetramethylammonium Salt of μ_4-Oxo-hexa-μ-chloro-tetrakis(chlorocuprate(II)), $[(CH_3)_4N]_4[Cu_4OCl_{10}]$

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The magnetic susceptibility of a powdered sample of the tetramethylammonium salt of μ_4-oxo-hexa-μ-chloro-tetrakis(chlorocuprate(II)) was measured in the temperature range 4.2–295°K. The cryomagnetic data exhibit a maximum in the magnetic susceptibility near 29°K and may be described by the Van Vleck equation for a tetrahedral arrangement of copper(II) ions with $J = -16$ cm^{-1}. A comparison of the magnetic properties of $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ and the reported data for the structurally similar $Cu_4OCl_6(TPPO)_4$ (TPPO = triphenylphosphine oxide) is given.

Introduction

X-Ray crystal structure studies have shown μ_4-oxo-hexa-μ-chloro-tetrakis[(triphenylphosphine oxide)copper(II)],[1] $Cu_4OCl_6(TPPO)_4$, and the tetramethylammonium salt of μ_4-oxo-hexa-μ-chloro-tetrakis(chlorocuprate(II)),[2] $[(CH_3)_4N]_4[Cu_4OCl_{10}]$, to have very similar structures. In both complexes, there is a tetrahedral arrangement of copper ions bonded to the single central oxygen atom. Each of the six edges of the Cu$_4$ tetrahedron is occupied by a bridging chloride ion so that each copper ion is linked to each of the other three metal ions through the central oxygen and through three separate chloride bridges. The fifth coordination position of each copper ion, located on the central oxygen–copper axis on the outside of the cluster, is occupied by the oxygen of a TPPO group in the first complex and by a chloride ligand in the second, as is shown in Figure 1. Though there are minor differences in the two structures, both Cu$_4$O units have nearly T_d symmetry and the octahedra of six bridging chlorides have exact or almost exact O_h symmetry. Bond distances and angles are very similar; Cu–Cu distances are 3.11 and 3.18 Å, respectively; Cu–central oxygen distances range from 1.91 to 1.95 Å; Cu–bridging chloride distances are 2.38–2.45 Å; typical bond angles are Cu–O–Cu = 109°, O–Cu–Cl = 85°, and Cu–Cl–Cu = 81°.

Although it had been suggested[1,2] on the basis of room-temperature magnetic susceptibility measurements that no spin interaction existed between the copper ions in either system, more recent studies reported by Martin[3] have demonstrated the presence of very complex interactions in $Cu_4OCl_6(TPPO)_4$. The effective magnetic moment of the compound rises from 1.87 BM at 295°K to 2.12 BM at 54°K and then drops

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