

A PMR Method of Assigning the Absolute Configurations
of Platinum(IV) Propylenediamine Coordination Complexes¹

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The pmr spectra of the diastereomeric pairs: (+)_D and (-)_D-[Pt(S-pn)₃](C₂O₄)₂, (+)_D and (-)_D-[Pt(R-pn)₂(en)]Cl₄, and (+)_D and (-)_D-[Pt(R-pn)(en)₂]Cl₄ were studied. The chemical shift of the methyl signal of the coordinated propylenediamine ligand is different in each diastereomeric pair and can be empirically related to the orientation of the carbon-carbon bond axis of propylenediamine with respect to the C₃ or pseudo C₃ rotation axis of the complex ion. Since the orientation of the coordinated propylenediamine ligand in the diastereomeric pair can be determined from the pmr spectrum, it is possible to use the chemical shift to determine the absolute configuration of the Pt^{IV}-propylenediamine complexes.

Introduction

The absolute configurations of the enantiomers^{2,4} or diastereomers⁵ of several trisdiamine cobalt(III) coordination complexes have been determined using X-ray diffraction techniques. No X-ray diffraction data have been published giving the absolute configuration of a Pt^{IV} coordination complex. However, the absolute configurations of some trisdiamineplatinum(IV) coordination complexes have been assigned using the solubilities of diastereomeric salts,^{6,8} circular dichroism⁹ or optical rotatory dispersion curves,¹⁰ or stereospecific reaction ratios.^{7,8} As a result, the absolute configurations of a number of enantiomeric and diastereomeric trisdiamineplatinum(IV) coordination complexes are known with a high degree of certainty.

The pmr spectra of enantiomeric complexes must be identical, but the pmr spectra of diastereomeric complexes need not be the same.¹¹⁻¹⁵ In this work

the pmr spectra of diastereomeric trisdiamineplatinum(IV) complexes were measured. Each diastereomeric pair of complexes contained at least one diamine ligand which was (R)- or (S)-propylenediamine. The conformation of propylenediamine chelate rings is such that the ligand has different orientations with respect to the C₃ or pseudo C₃ rotation axis of the complex ion in the Δ and Λ absolute configurations of the trisdiamineplatinum(IV) complex.¹⁶⁻¹⁸

The pmr spectra of trisdiamineplatinum(IV) complexes were examined to see if there repeating regularities in the chemical shifts of the methyl resonance signal of coordinated propylenediamine which could be used to assign the absolute configurations of diastereomeric pairs. A pmr method for assigning the absolute configuration of diastereomeric pairs of trisdiamineplatinum(IV) complexes would provide still another check on the assignments made by chemical or spectroscopic methods.

Experimental Section

Compounds. (A) The following complexes were generously provided by the late Professor F. P. Dwyer of the John Curtin School of Medical Research, Australian National University, Canberra City, A. C. T., Australia.

- 1) (+)_DTris(S-propylenediamine)platinum(IV) oxalate
- 2) (-)_DTris(S-propylenediamine)platinum(IV) oxalate
- 3) (+)_DBis(ethylenediamine)R-propylenediamineplatinum(IV) chloride.
- 4) (-)_DBis(ethylenediamine)R-propylenediamineplatinum(IV) chloride.
- 5) (+)_DBis(R-propylenediamine)ethylenediamineplatinum(IV) chloride.
- 5) (-)_DBis(R-propylenediamine)ethylenediamineplatinum(IV) chloride.
- 7) (+)_DBis(S-propylenediamine)R-propylenediamineplatinum(IV) chloride.

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Table I. Stereochemistry and PMR Data on Some tris-Diamine Platinum(IV) Complexes

Complex Ion	Rotation at NaD Line	Absolute Configuration of Complex Ion ^{a, b, c}	Conformation of propylenediamine	Orientation of Carbon-Carbon Bond Axis	PMR Solvent	Chemical Shift in Hz ^d
[Pt(S-pn) ₃] ⁴⁺	(+)	Δ	δ	oblique	1 M D ⁺ -D ₂ O	93.5
	(-)	Λ	δ	parallel	1 M D ⁺ -D ₂ O	95.2
[Pt(R-pn) ₂ (en)] ⁴⁺	(+)	Δ	λ	parallel	D ₂ O	94.8 ^e
	(-)	Λ	λ	oblique	D ₂ O	93.5
[Pt(R-pn)(en) ₂] ⁴⁺	(+)	Δ	λ	parallel	D ₂ O	94.8
	(-)	Λ	λ	oblique	D ₂ O	93.5

^a F. P. Dwyer and A. M. Sargeson, *J. Amer. Chem. Soc.*, **81**, 5272 (1959). ^b F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **81**, 1043 (1959). ^c S. F. Mason, A. M. Sargeson, R. Larson, B. J. Norman, A. J. McCaffrey, and G. H. Searle, *Inorg. Nucl. Chem. Lett.*, **2**, 333 (1966). ^d Chemical shifts are measured in Hz from DDS as an internal reference on a Varian A-60 Spectrometer. ^e Chemical shift is the average of two peaks split by 0.4 Hz.

PMR Measurements. Solutions for pmr work were prepared by dissolving 0.050 g of the sample in 0.5 ml of deuterium oxide (samples A3 through A7), or 0.050 g of the sample in 0.5 ml of 0.5 M di-deuterio-sulfuric acid in deuterium oxide (Sample A-1 and A-2). Spectra were obtained using a Varian A-60 Analytical Spectrometer. The spectra were taken at 35 ± 3°C, the normal internal temperature of the probe. Sodium (3-trimethylsilyl)propanesulfonate (purchased from Brinkman Instruments, Inc., Westbury, N. Y.), also known as sodium 2,2-dimethyl-2-silapentane-5-sulfonate and abbreviated DSS, was used as an internal reference.

Results and Discussion

(A) Stereochemistry of the Diastereomeric Forms.

The absolute configurations of the diastereomeric pairs: (+)_D and (-)_D-[Pt(S-pn)₃](C₂O₄)₂; (+)_D and (-)_D-[Pt(R-pn)₂(en)]Cl₄; and (+)_D and (-)_D-[Pt(R-pn)(en)₂]Cl₄ are given in Table I. The assignments are based on the work of Dwyer *et al.*^{7,8} and Larson *et al.*⁹ Table I sums up the conformational structure of coordinated propylenediamine in the diastereomeric forms. The conformational assignments are based on the assumption that S-pn will always coordinate in the δ conformation, whereas R-pn will always coordinate in the λ conformation.^{16,19} This requires that the carbon-carbon bond axis of the coordinated S-pn be parallel to the C₃ rotation axis of [Pt(S-pn)₃]⁴⁺ in the Λ absolute configuration and that it be oblique to the C₃ rotation axis in the Δ absolute configuration of the complex ion.¹⁶ In (+)_D and (-)_D-[Pt(R-pn)₂(en)]Cl₄ and in (+)_D and (-)_D-[Pt(R-pn)(en)₂]Cl₄, R-pn is coordinated in the λ conformation. This conformation requires that the carbon-carbon bond axis of the R-pn chelate ring be parallel to the pseudo C₃ rotation axis of the complex ion in the Δ absolute configuration of the complex ion.

(B) Proton Magnetic Resonance Spectra. The pmr spectrum of the free ligand, R-pn, is an ABCX₃ type spectrum. When coordinated to a Pt^{IV} metal ion,

coupling of the methylene and methine protons of R-pn with the Pt¹⁹⁵ isotope (Isotopic abundance ca. 33%) occurs, and the resulting pmr spectrum is complicated.¹⁹ For this reason no attempt was made to analyze the pmr spectra for the ν_i' and J_{ij} of the coordinated propylenediamine ligand. An analysis of the spectrum of coordinated R-propylenediamine has been accomplished aided by using the double resonance technique and the J_{ij} are reported in the literature.¹⁹ The pmr signal of the methyl group of pn can be seen quite clearly in the spectra of the complexes, it appears as a doublet, being split by the methine proton of the ligand. No first order splitting of the methyl signal by the Pt¹⁹⁵ isotope was evident. Our attention was focused on the chemical shift value of the methyl group relative to the internal standard DSS. The methyl pmr signal appeared as a single strong doublet in the spectrum of all the isomeric forms except for (+)_D-[Pt(R-pn)₂(en)]Cl₄ where it appeared as a set of doublets with equal intensity. This spectrum will be discussed later. Table I gives the chemical shift values of the methyl signal in the diastereomeric forms. An examination of Table I shows that the chemical shift of the methyl signal is slightly different (ca. 1.5 Hz) in each pair of diastereomeric complexes. The chemical shift sequence observed in trisdiamineplatinum(IV) complexes can be summarized as follows. The chemical shift of the methyl signal is greater in the diastereomer which has the propylenediamine coordinated such that the carbon-carbon bond axis of the chelate ring is parallel to the C₃ or pseudo C₃ axis of the complex ion. The chemical shift rule does not depend on which isomeric form of propylenediamine is coordinated but depends only on the orientation of the coordinated propylenediamine with respect to the C₃ or pseudo C₃ rotation axis of the complex ion.

If one has the pmr spectra of a Pt^{IV}-propylenediamine diastereomeric pair, one can use the chemical shift rule to get the orientation of the coordinated propylenediamine in the diastereomers, and hence one can assign the absolute configuration of the diastereomers. In the case of a complex such as (+)_D-[Pt(R-pn)(S-pn)₂]Cl₄, one can get the absolute configuration from the pmr spectrum of a single diastereomer. The pmr spectrum of (+)_D-[Pt(R-pn)(S-pn)₂]Cl₄ shows a methyl signal shifted 94.0 Hz from

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DSS of relative intensity 1 and a second methyl signal at 93.1 Hz from DSS with relative intensity 2. This corresponds to one mole of R-pn coordinated parallel to the pseudo C_3 axis and two moles of S-pn coordinated obliquely to the pseudo C_3 axis of the complex ion. This corresponds to R-pn and S-pn coordinated in the Δ absolute configuration of the complex ion. On the basis of the chemical shift rule derived in this work, it is possible to assign the absolute configurations of all Pt^{IV}-propylenediamine complexes using pmr spectroscopy alone.

(C) *Geometric Isomerism.* Diastereomeric complexes of Pt^{IV} containing two or three R- or S-propylenediamine ligands can exist as geometric isomers. The nitrogen atoms alpha to the asymmetric carbon atoms of propylenediamine are used as the reference atoms for naming the geometric isomers. Figure 1

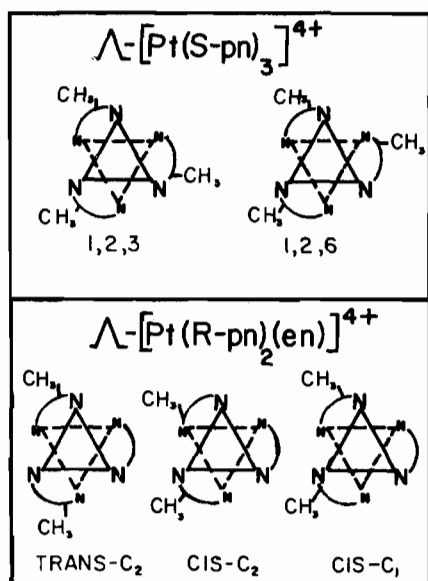


Figure 1. Possible Geometric Isomers for $[\text{Pt(S-pn)}_3]^{4+}$ and $[\text{Pt(R-pn)}_2\text{(en)}]^{4+}$.

shows the geometric isomers possible for $\Lambda\text{-[Pt(S-pn)}_3\text{]}^{4+}$ and $\Lambda\text{-[Pt(R-pn)}_2\text{(en)}]^{4+}$. For $\Lambda\text{-[Pt(S-pn)}_3\text{]}^{4+}$, two geometric isomers are possible which are called the 1, 2, 3 isomer and the 1, 2, 6 isomer. The 1, 2, 3 isomeric form has C_3 symmetry and the 1, 2, 6 isomer has C_1 symmetry. The $\Lambda\text{-[Pt(R-pn)}_2\text{(en)}]^{4+}$

$(\text{en})]^{4+}$ complex ion can exist in three geometric isomers which are called $\Lambda\text{-cis-C}_2$, $\Lambda\text{-cis-C}_1$, and $\Lambda\text{-trans-C}_2$.

Mac Dermott²⁰ has obtained a partial separation of the geometric isomers of $[\text{Co(R-pn)}_3]^{3+}$ and $[\text{Co(R-pn)}_2(\text{en})]^{3+}$. There is no reason to presume that the $[\text{Pt(S-pn)}_3]^{4+}$ and $[\text{Pt(R-pn)}_2(\text{en})]^{4+}$ systems do not form geometric isomers. The methyl pmr signal of $\Lambda\text{-(-)}_D\text{-[Pt(R-pn)}_2(\text{en})]\text{Cl}_4$ is a sharp doublet but the methyl pmr signal of $\Delta\text{-(+)}_D\text{-[Pt(R-pn)}_2(\text{en})]\text{Cl}_4$ appears as two doublets of equal intensity split by 0.4 Hz. Spees *et al.*¹³ have observed a methyl doublet for $\Delta\text{-(-)}_D\text{-[Co(R-pn)}_2(\text{en})]^{3+}$ and a singlet for $\Lambda\text{-(+)}_D\text{-[Co(R-pn)}_2(\text{en})]^{3+}$, a direct analogy to the Pt^{IV} case studied here. Hence there is pmr evidence for the presence of geometric isomers for the $\Delta\text{-[M(R-pn)}_2\text{en}]^{m+}$ system. It is impossible to say which geometric isomers are present in the $\Delta\text{-(+)}_D\text{-[Pt(R-pn)}_2(\text{en})]^{4+}$ system from the pmr data alone. The *cis-C*₁ isomers would give doublet methyl signal but an equimolar mixture of the *cis-C*₂ and *trans-C*₂ isomer or an equimolar mixture of the *cis-C*₂, *trans-C*₂ and *cis-C*₁ isomer might also give the same spectrum. There is no evidence of geometric isomerism in the pmr spectra of $(+)_D$ and $(-)_D\text{-[Pt(S-pn)}_3]^{4+}$ and $(+)_D\text{-[Pt(R-pn)}_2(\text{en})]^{4+}$. This cannot be taken to mean that geometric isomers are not formed in the reaction mixture. Mac Dermott's work was done on a freshly prepared reaction mixture whereas the pmr spectrum was taken on a product that had been subjected to a numerous fractional recrystallizations. Diastereomeric forms are known to separate on fractional recrystallization²⁰ and hence in the samples used for pmr work some fractional separation of the isomers may have occurred. The methyl pmr signal is rather insensitive to the presence of small amounts of one geometric isomer. If one geometric isomer is present in small amounts, its methyl pmr signal will very likely merge with the pmr line due to the other isomer. Hence in a 60 Mc spectrometer the resolution will not be great enough to permit the detection of both isomeric forms.

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