

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
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## Nuclear Magnetic Resonance Studies in Some Dichloro(pyridine 1-oxide)ethyleneplatinum(II) Complexes

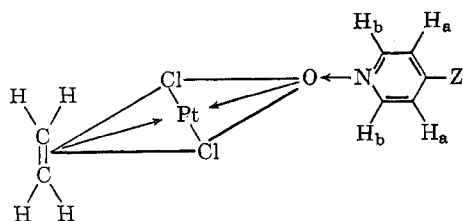
BY PHYLLIS D. KAPLAN AND MILTON ORCHIN

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The chemical shifts and coupling constants of protons in a series of dichloro(4-substituted-pyridine 1-oxide)ethyleneplatinum(II) complexes (I) were determined. The coupling constant between platinum and the protons of ethylene as well as the chemical shift of the protons is influenced by the nature of the substituent on the *trans* N-oxide. As the electron-withdrawing character of the substituent increases, the chemical shift, as expected, moves downfield; however, the coupling constant increases. The chemical shifts of the protons *ortho* to the substituent on the N-oxide move upfield as the electron-donating power of the substituent is increased while the *meta* protons are influenced in the same way but to a much lesser extent.

### Introduction

Previous effort in this laboratory has been directed toward the investigation of bonding in the ethylenic platinum(II) complexes.<sup>1</sup> Variations of infrared stretching frequencies caused by a change in the substituent, Z, of the pyridine N-oxide ligand in dichloro(4-Z-pyridine 1-oxide)ethyleneplatinum(II) complexes (I) have been demonstrated.



I, Z = CH<sub>3</sub>O, CH<sub>3</sub>, H, Cl, COOCH<sub>3</sub>, NO<sub>2</sub>

The present study was undertaken in order to ascertain whether effects on bonding by variation of Z would be discernible in the nuclear magnetic resonance (n.m.r.) spectra. Chemical shifts of ethylenic and aromatic protons in the complexes, as well as the Pt<sup>195</sup>-H<sup>1</sup> coupling constant, were determined. Chemical shifts of uncomplexed N-oxides and the protonated N-oxides were measured; the effect of protonation was expected to parallel the effect of coordination to platinum in the complex.

### Results and Discussion

Table I lists chemical shifts and Pt<sup>195</sup>-H<sup>1</sup> coupling constants of the ethylenic protons in the complexes. Also included in this table are data for Zeise's salt, K<sup>+</sup>[C<sub>2</sub>H<sub>4</sub>PtCl<sub>3</sub>]<sup>-</sup>, in methanol and in deuterium oxide. The chemical shift data will be discussed first.

The chemical shift of free ethylene occurs at  $\delta$  5.41 in CDCl<sub>3</sub>; on complexing with a metal, an upfield shift is to be expected because the diamagnetic anisotropy of the carbon-carbon double bond is perturbed, shifting the magnetic dipole somewhat toward the

TABLE I  
N.M.R. DATA OF ETHYLENIC PROTONS IN DICHLORO-(4-Z-PYRIDINE 1-OXIDE)ETHYLENEPLATINUM(II) COMPLEXES

Z	Chemical shift of ethylenic proton in I, <sup>a</sup> $\delta$	$J_{Pt^{195}-H^1}$ , c.p.s.	Solvent
NO <sub>2</sub>	4.656 <sup>b</sup>	...	CDCl <sub>3</sub>
COOCH <sub>3</sub>	4.438	71.0	CHCl <sub>3</sub>
Cl	4.383		CHCl <sub>3</sub>
H	4.383	68.8	CDCl <sub>3</sub>
CH <sub>3</sub>	4.323	69.0	CDCl <sub>3</sub>
OCH <sub>3</sub>	4.350	67.5	CDCl <sub>3</sub>
OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	4.296	67.1	CDCl <sub>3</sub>
[(C <sub>2</sub> H <sub>4</sub> )PtCl <sub>3</sub> ] <sup>-</sup> K <sup>+</sup>	4.408	66.0	CH <sub>3</sub> OH
	4.408	66.0	4% w./v. HCl in CH <sub>3</sub> OH
	4.678	65.2	D <sub>2</sub> O

<sup>a</sup> The internal reference is tetramethylsilane or 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt. <sup>b</sup> We are indebted to Dr. T. Flaut for obtaining this spectrum at 100 Mc. using a Varian C-1024 time averaging computer. <sup>c</sup>  $J_{Pt-H}$  appears to be 71.7 c.p.s. after 23 scans; however, after 100 scans all peaks broaden and the satellite peaks are indefinite, while after 491 scans they are no longer present and the ethylene peak is broad. This may be a consequence of a time-averaged phenomenon initiated by a catalyst.

metal atom.<sup>2</sup> The bonding between ethylene and a metal is now well understood in terms of the  $\sigma$  bond from the ethylene to the metal and the back bonding from the metal to the ethylene. Electron-releasing substituents *trans* to ethylene would be expected to promote backbonding and strengthen the ethylene-metal interaction; strong electron-withdrawing substituents should have the opposite effect. The chemical shifts in Table I are consistent with this concept; the chemical shift of the 4-NO<sub>2</sub> compound is closest to free ethylene, and the largest chemical shift is obtained with electron-releasing substituents.

The coupling constants are difficult to explain in terms of the preceding simple concepts. Three major factors contribute to the magnitude of this constant: the size of the atoms involved, the hybridization of the

(1) S. I. Shupack and M. Orchin, *J. Am. Chem. Soc.*, **85**, 902 (1963); S. I. Shupack and M. Orchin, *Inorg. Chem.*, **3**, 374 (1964).

(2) M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).

TABLE II  
 N.M.R. OF PYRIDINE N-OXIDES, FREE AND COMPLEXED


Z		Chemical shift, $\delta$				Separation between H <sub>a</sub> and H <sub>b</sub> , p.p.m.																																																																																																																															
		10% w./w. solution		CHCl <sub>3</sub> or CDCl <sub>3</sub>		D <sub>2</sub> O		CHCl <sub>3</sub> or CDCl <sub>3</sub>																																																																																																																													
		D <sub>2</sub> O	D <sub>2</sub> O-HCl	Uncomp.	Comp.	D <sub>2</sub> O	D <sub>2</sub> O-HCl	Uncomp.	Comp.																																																																																																																												
NO <sub>2</sub>	H <sub>a</sub>	8.326 <sup>b</sup>	8.715	8.102 <sup>b</sup>	8.30 <sup>a</sup>	0.20	0.308	0.236	0.305																																																																																																																												
	H <sub>b</sub>	8.526 <sup>b</sup>	9.023	8.338 <sup>b</sup>	8.605 <sup>a</sup>					COOCH <sub>3</sub>	H <sub>a</sub>	8.050	8.520	7.912	8.250	0.375	0.505	0.350	0.516	H <sub>b</sub>	8.425	9.025	8.266	8.766	CH <sub>3</sub>	4.015	4.078	3.963	4.050	Cl	H <sub>a</sub>	7.70	8.168	7.315	7.50 <sup>d</sup>	0.638	0.712	0.875	0.975	H <sub>b</sub>	8.338	8.88	8.190	8.475	H	H <sub>a</sub>	7.692 <sup>c</sup>	8.065 <sup>c</sup>	7.383 <sup>c</sup>	7.695 <sup>e</sup>	0.692	0.85 (H <sub>a</sub> -H <sub>b</sub> )	0.915	0.940 (H <sub>a</sub> -H <sub>b</sub> )	H <sub>b</sub>	8.383	8.915	8.298	8.635	0.446 (H <sub>a</sub> -H <sub>c</sub> )	0.240 (H <sub>a</sub> -H <sub>c</sub> )	H <sub>c</sub>	7.691 <sup>c</sup>	8.512 <sup>c</sup>	7.383 <sup>c</sup>	79.3 <sup>e</sup>	0.403 (H <sub>b</sub> -H <sub>c</sub> )	0.70 (H <sub>b</sub> -H <sub>c</sub> )	CH <sub>3</sub>	H <sub>a</sub>	7.408	7.896	7.178	7.413	0.756	0.816	0.983	1.03	H <sub>b</sub>	8.165	8.713	8.162	8.443	CH <sub>3</sub>	2.445	2.696	2.36	2.515	OCH <sub>3</sub>	H <sub>a</sub>	7.13	7.48	6.865	7.050	1.076	1.20	1.318	1.392	H <sub>b</sub>	8.206	8.681	8.183	8.442	CH <sub>3</sub>	3.95	4.13	3.883	4.016	OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H <sub>a</sub>	7.05	7.433			1.153	1.236			H <sub>b</sub>	8.203	8.67			CH <sub>2</sub>	5.116	5.353		5.20		C <sub>6</sub> H <sub>5</sub>	7.383	7.47	
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<sup>a</sup> Tetramethylsilane is the internal reference in CHCl<sub>3</sub> and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt in D<sub>2</sub>O. <sup>b</sup> The spectrum is composed of a quartet and the chemical shifts for H<sub>a</sub> and H<sub>b</sub> are estimated as the midpoints of each side. <sup>c</sup> In the neutral molecule, H<sub>a</sub> and H<sub>b</sub> appear together as a quartet, whereas in the charged species H<sub>a</sub> moves downfield from H<sub>b</sub> and the chemical shifts for each are estimated. <sup>d</sup> The spectrum is partially obscured by solvent peaks. <sup>e</sup> We are indebted to Dr. T. Flaut at Procter and Gamble Co. for having obtained this spectrum at 100 Mc. using a Varian C-1024 time averaging computer.

orbitals involved, and the distance between the atoms.<sup>3</sup> In our complexes the hybridization and the distance need be considered. According to present theory, internuclear coupling through the Fermi contact term can occur only when the orbitals involved possess some s character. The  $J_{\text{Pt}^{195}\text{-H}^1}$  for hydrogen bonded to carbon bonded directly to platinum through an sp<sup>3</sup> orbital, as in the methyl-platinum complexes,<sup>4,5</sup> is always larger than that observed for any of the ethylene complexes, as one would expect in a  $\sigma$ -bonded system with good orbital overlap between the metal and the carbon. Thus, for example, the methyl-platinum complexes such as  $[(\text{CH}_3)_3\text{PtL}]_n$  where L = I, NO<sub>3</sub>, [CH(COR)<sub>2</sub>] and n = 1, 2, and 4, or  $[(\text{CH}_3)_2\text{PtC}_6\text{H}_{12}]$ , have coupling constants which vary from 71.6 to 86 c.p.s. In the case of the ethylene complexes, the relatively large coupling constant must be due to more than the  $\sigma$  bond, as this involves only the p orbitals of ethylene overlapping with the dsp<sup>2</sup> orbital of the platinum. The next largest olefin-platinum coupling occurs in the  $\pi$ -allyl complex  $[\text{Pt}(\text{C}_3\text{H}_5)(\text{C}_6\text{H}_5)]$  (54 c.p.s. for the *anti* protons and 29 c.p.s. for the *syn* protons)<sup>6</sup>; next in decreasing order are those observed

for the 1,5-cyclooctadiene complex (40 c.p.s.)<sup>5</sup> and the cyclopentadienyl complex (10-13 c.p.s.).<sup>6,7</sup> The Pt<sup>195</sup>-H<sup>1</sup> coupling constants of the ethylene protons in our compounds are all close to the value of 64 c.p.s. reported by Cramer<sup>8</sup> for *cis*-[*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)-PtCl<sub>2</sub>]. A previously reported<sup>9</sup> coupling constant for Zeise's salt is half the value observed here. In our series of complexes it would be anticipated that when electron-releasing substituents are *trans* to ethylene, occupation of the  $\pi^*$  orbitals of ethylene would increase the s character of the carbon orbitals. However, the results show that electron-releasing substituents have the smallest effect. This anomaly leads us to consider the distance between the ethylene and the platinum. Although no clear explanation is available to justify an assumption of a greater ethylene-platinum distance in the case of electron-releasing substituents, one may invoke the possibility of a simple crystal field type of repulsion which increases this distance, since the major part of ligand-metal bonding is probably due to the  $\sigma$  bond interaction.

Table II illustrates the similarity between complexing the N-oxide with platinum and protonating the oxygen atom by dissolving the N-oxide in an acidic medium.<sup>10</sup>

(3) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 184-188.

(4) J. S. S. Smith, *J. Chem. Soc.*, 4736 (1962).

(5) C. Kistner, J. Hutchinson, J. Doyle, and J. Storlie, *Inorg. Chem.*, **2**, 1255 (1963).

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(7) H. P. Fritz and C. G. Kreiter, *Chem. Ber.*, **96**, 2008 (1963).

(8) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

(9) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960).

(10) A. R. Katritzky and J. M. Lagowski, *ibid.*, 43 (1961).

In all cases protonation and "metalation" cause downfield shifts of each ring proton as would be expected. The 2,6 protons are further downfield than the 3,4 protons. Greater differences in the chemical shifts of  $H_a$  and  $H_b$  occur upon protonation than upon metalation because of stronger bonding between oxygen and proton than between oxygen and platinum.

### Experimental

The preparation and properties of the olefin complexes<sup>11</sup> and of the uncomplexed 4-substituted pyridine N-oxides<sup>12</sup> have been reported previously.

- (11) L. Garcia, S. I. Shupack, and M. Orchin, *Inorg. Chem.*, **1**, 893 (1962).  
 (12) E. Ochai, *J. Org. Chem.*, **18**, 534 (1953).

**N.m.r. Spectra.**—Spectra of solutions containing an internal standard were obtained on a Varian Associates A-60 spectrometer at 34–35°. The audiooscillation side-band technique was used for calibration. In addition, spectra of the olefin complexes were obtained in the absence of internal standard because prolonged contact with the standard caused decomposition of the complexes.

**Acknowledgment.**—The authors wish to acknowledge the support of this research by the donors of the Petroleum Research Fund, which is administered by the American Chemical Society, and to thank Dr. F. Kaplan for many helpful discussions. We also wish to thank Engelhard Industries, Inc., for a generous supply of platinum.

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## Stereochemistry of Complexes of Multidentate Ligands. I. Isomers of the Dichloro-2,9-diamino-4,7-diazadecanecobalt(III) Ion

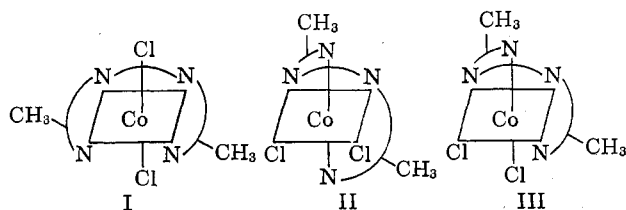
BY ROBERT G. ASPERGER AND CHUI FAN LIU

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The preparation of the ligand 2,9-diamino-4,7-diazadecane (to be referred to as *l,l'-α,α'*-dimethyltriethylenetetramine) is reported. The cobalt(III) complex ion dichloro-*l,l'-α,α'*-dimethyltriethylenetetraminecobalt(III) can exist in three possible geometric isomers. All three were prepared. The configurations of these isomers were assigned on the basis of n.m.r. data.

### Introduction

A cobalt(III) complex of triethylenetetramine was first prepared by Basolo.<sup>1</sup> The stereochemistry of the dichlorotriethylenetetraminecobalt(III) ion has been further studied by other investigators.<sup>2</sup> Most recently Sargeson and Searle<sup>3</sup> reported the separation of the two *cis* isomers of the dichlorotriethylenetetraminecobalt(III) ion. No complexes of other straight-chain tetramines have been reported in the literature. The present investigation is concerned with the cobalt(III) complex of an analogous ligand, *l,l'-α,α'*-dimethyltriethylenetetramine. Like the corresponding triethylenetetramine complex the dichlorodimethyltriethylenetetraminecobalt(III) ion has three possible geometric isomers.



In addition there are optical isomers resulting from asymmetry of the *cis* complexes and asymmetry of the

- (1) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).  
 (2) (a) B. Das Sarma and J. C. Bailar, Jr., *ibid.*, **77**, 5480 (1955); (b) J. Selbin and J. C. Bailar, Jr., *ibid.*, **82**, 1524 (1960).  
 (3) (a) A. M. Sargeson and G. A. Searle, *Nature*, **200**, 356 (1963); (b) A. M. Sargeson and G. A. Searle, *Inorg. Chem.*, **4**, 45 (1965).

ligand. It is the purpose of this investigation to obtain the three possible geometric isomers and assign their configurations. In this study the ligand with con-

