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## Complexes between Pyridine-2-aldehyde-2'-pyridylhydrazone and the Platinum Metals. I. Rhodium

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Mono, bis, and tris complexes of rhodium(III) and pyridine-2-aldehyde-2'-pyridylhydrazone have been prepared and studied. In all three, the hydrogen atom of the imino group of the ligand shows marked acidity associated with coordination to a tripositive metal. The ligand is tridentate in the mono and bis complexes but bidentate in the tris complex. Possible geometrical isomers of this are discussed and its probable structure is described.

### Introduction

The complexes between divalent transition metal ions and the ligand 1,3-bis(2'-pyridyl)-1,2-diaza-2-propene (pyridine-2-aldehyde-2'-pyridylhydrazone; PAPHY, I) have been described in a number of recent papers.<sup>1-3</sup>

In these the ligand invariably acts as a tridentate ligand forming mono or bis complexes according to the preferred coordination number of the metal. Apart from the bis complex of cobalt(III),<sup>4</sup> produced when cobalt(II) is oxidized by excess PAPHY, little appears to be known of the complexes between PAPHY and tri- or tetrapositive ions.

As part of a study of the compounds formed between PAPHY and the platinum metals, we describe in this paper results on rhodium(III) complexes. Mono, bis, and tris complexes have been prepared and characterized. The formation of the mono and bis complexes illustrates the behavior of PAPHY as a tridentate ligand, while the existence of a tris complex demonstrates, for the first time, its action as a bidentate ligand.

### Experimental Section

**Materials.**—The ligand was purchased from the Aldrich Chemical Co., Inc., Milwaukee, Wis. Rhodium(III) chloride trihydrate (rhodium content = 39.9%) was supplied by International Nickel Co. Ltd., London. Cellulose phosphate was Chromedia P-11 grade purchased from British Drug Houses Ltd., Poole, Dorset, England. Buffer solutions: universal buffer mixture (containing diethylbarbituric acid) or sodium acetate-perchloric acid mixture was used.

**Thermogravimetric Analyses.**—These were performed on the Stanton TR-01 thermobalance and differential thermal analyses on the "Standata" 6-25, both manufactured by Stanton Instruments, London.

**Visible and Ultraviolet Spectra.**—These were measured on the Optica recording spectrophotometer, CF4-N1, using matched 1-cm silica cells.

**Conductance Measurements.**—These were performed with a Doran conductivity bridge (Derritron Instruments Ltd., Stroud, England) using platinum-coated electrodes of the dip-type on approximately  $10^{-3}$  M solutions in nitrobenzene, nitromethane, and water at 20°.

**Potentiometric Titrations.**—These were performed using the

Vibron pH meter, Model 39A (Electronic Instruments Ltd., Richmond, Surrey, England).

**Infrared Spectra.**—These were recorded on the Grubb-Parsons double-beam grating spectrometer using the potassium bromide disk technique.

**Nmr Spectra.**—All measurements were made on a Varian HA-100 spectrometer.

**Analyses.**—These were performed variously by Drs. Weiler and Strauss, Micro-Analytical Laboratory, Oxford, England, and F. Pascher and E. Pascher, Mikro-analytisches Laboratorium, Bonn, Germany.

**Trichloro[1,3-bis(2'-pyridyl)-1,2-diaza-2-propene]rhodium(III) Monohydrate (II).**—To a solution of 0.258 g (1 mmol) of rhodium(III) chloride trihydrate in 10 ml of ethanol was added 0.198 g (1 mmol) of PAPHY dissolved in 20 ml of ethanol. A brown precipitate was immediately produced and the mixture refluxed for 10 min. After cooling, filtering, and washing successively with water and ethanol, the solid was dried *in vacuo* over phosphorus pentoxide. The solid was insoluble in most solvents; it dissolved to a limited extent in dilute acids and alkalis. It could not be sublimed under vacuum without decomposition. Analyses on products from repeated preparations showed that these were not completely pure. *Anal.* Calcd for  $\text{Rh}(\text{C}_{11}\text{H}_{10}\text{N}_4)\text{Cl}_3 \cdot \text{H}_2\text{O}$ : C, 31.03; H, 2.82; N, 13.17; Cl, 25.00; Rh, 24.2. Found: C, 28.45; H, 2.55; N, 11.9; Cl, 29.45; Rh, 24.6.

Thermogravimetric analysis showed a weight loss below 140° corresponding with one molecule of water. Rapid decomposition occurs above 350° to yield rhodium(III) oxide.

**Bis[1,3-(2'-pyridyl)-1,2-diaza-2-propenato]rhodium(III) Chloride Dihydrate (III).**—An aqueous solution of rhodium(III) chloride, containing 0.258 g (1 mmol) of the trihydrate in 5 ml of water and buffered at pH 6, was added slowly with stirring to a solution of 0.396 g (2 mmol) of PAPHY in 15 ml of ethanol. The red solid which precipitated immediately was filtered off and purified by an ion-exchange chromatographic procedure. An aqueous solution of the product was transferred to the top of a column of cellulose phosphate, pretreated with sodium chloride solution, and washed well with water until free from chloride ion. Elution with 0.05 M sodium chloride produced one broad band, orange-red and evidently containing the bulk of the reaction product and several smaller, less strongly colored bands. The eluate containing the main band was evaporated to low bulk. On cooling, dark green crystalline platelets were formed, mp 270°. The finely divided solid is deep red. The same compound results from the reaction between a suspension of rhodium(III) hydroxide (1 mol) and PAPHY (2 mol). Dehydration was effected by heating and elemental analysis carried out on the anhydrous material. *Anal.* Calcd for  $\text{Rh}(\text{C}_{11}\text{H}_9\text{N}_4)_2\text{Cl}$ : C, 49.3; H, 3.39; N, 21.0; Cl, 6.63. Found: C, 49.3; H, 4.05; N, 21.28; Cl, 6.63.

The presence of two water molecules in the reaction product was shown by thermogravimetric analysis. Decomposition of the complex begins at 250° and is complete at 450°. Total loss on heating is 77% of the weight taken initially corresponding with conversion to  $\text{Rh}_2\text{O}_3$ .

(1) J. F. Geldard and F. Lions, *Inorg. Chem.*, **2**, 270 (1963).

(2) R. W. Green, P. S. Hallman, and F. Lions, *ibid.*, **3**, 376 (1964).

(3) R. W. Green, P. S. Hallman, and F. Lions, *ibid.*, **3**, 1541 (1964).

(4) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

Differential thermal analysis showed a broad endothermic peak between 20 and 150° corresponding with loss of water, a small exothermic peak at 270°, the melting point, and a large exothermic peak with a maximum at 425° which is associated with loss of two PAPHY molecules.

**Tris[1,3-bis(2'-pyridyl)-1,2-diaza-2-propene]rhodium(III) Chloride Tetrahydrate (IV).**—A solution of 1 g (4 mmol) of rhodium(III) chloride trihydrate in 50 ml of water and 25 ml of ethanol was refluxed for 1 hr with 5 g (25 mmol) of PAPHY. The mixture was cooled and filtered to remove unreacted PAPHY, and the filtrate was treated with sodium perchlorate to precipitate the complex perchlorate. The perchlorate was converted to the chloride using Deacidite FF resin in the chloride form. Evaporation of the aqueous solution of the chloride gave green crystals. The finely divided solid is reddish brown. *Anal.* Calcd for  $\text{Rh}(\text{C}_{11}\text{H}_{10}\text{N}_4)_3\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ : C, 45.26; H, 4.34; N, 19.2; Cl, 12.15; Rh, 11.76. Found: C, 47.15; H, 5.00; N, 19.2; Cl, 12.3; Rh, 11.70.

Thermogravimetry showed the loss of four molecules of water was completed by 200°, followed by the formation of an intermediate decomposition product at 270°. Prolonged heating of IV at 200° converted it completely to this product which was identified with the anhydrous bis complex by analysis. Total weight loss on heating IV to 600° was 84% of the initial weight, leaving  $\text{Rh}_2\text{O}_3$ .

Differential thermal analysis showed a broad, flat endothermic peak between 20 and 150° (loss of water), an exothermic peak with a maximum at 270° corresponding to partial conversion to the anhydrous bis complex, and a large broad exothermic peak with a maximum at 490° caused by decomposition to the final product,  $\text{Rh}_2\text{O}_3$ .

**Pyridine-2-aldehyde-2'-pyridylhydrazone Dihydroperchlorate.**—PAPHY in ethanol solution was treated with cold aqueous perchloric acid (71% w/w). The dihydroperchlorate precipitated immediately as a pale yellow solid.

**Conversion of IV to III.**—Attempted chromatographic separation of the two possible isomers of IV using a column of cellulose phosphate failed due to the conversion of IV to III during the time required for elution.

In aqueous solution of pH 4 IV is completely converted to III when exposed to sunlight for 4 hr. The rate of decomposition followed by spectrophotometry at 485 m $\mu$  obeyed a first-order law with an approximate rate constant of  $3.8 \times 10^{-4} \text{ sec}^{-1}$  (25°).

**Absorption Spectra.**—A stock solution of II was prepared by dissolving 0.0104 g in a small volume (1 ml) of 3 M sodium hydroxide and then diluting to 100 ml with water. Aliquots of 2 ml were diluted to 25 ml with appropriate buffers and the spectra of the diluted solutions were recorded.

A stock solution of III was prepared by dissolving 0.0407 g in 100 ml of water. Aliquots of 2 ml were diluted to 10 ml with buffers and the spectra were recorded.

A stock solution of IV was prepared by dissolving 0.03626 g in 100 ml of water. Aliquots of 1 ml were diluted to 25 ml with buffers and the spectra of the diluted solutions were recorded.

**Potentiometry.**—Substance III ( $0.25 \times 10^{-3}$  mol) was dissolved in 10 ml of water and titrated with 0.1 M hydrochloric acid. The titration curve was smooth, showing no inflection points.

Substance IV ( $10^{-4}$  mol) was dissolved in 10 ml of water and the solution was titrated with 0.02 M perchloric acid. No inflection points were found. This compound ( $10^{-4}$  mol) in 25 ml of water was titrated with  $10^{-4}$  M sodium hydroxide. A sigmoid-shaped curve was obtained showing that two protons per mole of complex were titrated and that titration was complete by pH 11. No evidence was found for the loss of a third proton.

**Conductance.**—Molar conductances, in reciprocal ohms, were in water, nitromethane, and nitrobenzene, respectively:  $\text{Rh}(\text{C}_{11}\text{H}_9\text{N}_4)_2\text{Cl} \cdot 2\text{H}_2\text{O}$ , 139.2, 59.2, 14.4;  $\text{Rh}(\text{C}_{11}\text{H}_{10}\text{N}_4)_3\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ , 303, 107.2, 18.5.

The bis complex in water has the conductance expected for a 1:1 electrolyte. In nitromethane, the value is somewhat lower than the range reported<sup>5</sup> for this electrolyte type ( $\sim 70$ – $90 \text{ ohm}^{-1}$

$\text{cm}^2$ ). In nitrobenzene the value is about half that found for other 1:1 electrolytes.<sup>6</sup>

In water, the tris complex shows a conductance between the normal values for a 1:2 and a 1:3 electrolyte. The values in nitromethane and nitrobenzene are much lower than expected for a 1:3 electrolyte ( $\sim 260$  and  $\sim 90 \text{ ohm}^{-1} \text{ cm}^2$ , respectively).<sup>5</sup>

Abnormally low conductances are usually attributed to ion-pair formation resulting from Coulombic interaction. An important additional factor in the case of IV is the hydrogen bonding likely to occur, particularly in solvents of dielectric constant markedly lower than that of water, between the anions and the imino groups of the coordinated PAPHY molecules in the cation. It has been suggested<sup>7</sup> that this kind of interaction accounts for the unusually low conductances found for substituted ammonium picrates in nitrobenzene solution whenever the cation contains a hydrogen atom bound directly to the central nitrogen atom.

**Infrared Spectra.**—Results over the range 1700–600  $\text{cm}^{-1}$  for I, II, and III are summarized in Table I. The spectrum of IV is not given because it was found to be almost identical with that of III. The only significant differences were shoulders present at 1084 and 990  $\text{cm}^{-1}$  in IV but absent in III. Spectra of III and IV as Nujol mulls were also extremely similar.

TABLE I  
INFRARED DATA FOR PAPHY AND ITS RHODIUM COMPLEXES

PAPHY <sup>a</sup>	Rh- (C <sub>11</sub> H <sub>10</sub> N <sub>4</sub> ) <sub>3</sub> - Cl <sub>3</sub> ·H <sub>2</sub> O <sup>b</sup>	Rh- (C <sub>11</sub> H <sub>9</sub> N <sub>4</sub> ) <sub>2</sub> - Cl·2H <sub>2</sub> O <sup>c</sup>	Assignment
1620 s	1620 s	1653 s	Combination band
1613 vs	1603 s	1620 vs	
1587 s		1607 vs	Pyridine I
1569 sh	1562 w	1569 sh	Pyridine II
1550 m	1521 m	1538 sh	C=N?
		1521 s	
		1515 sh	
	1504 sh	1504 sh	
1478 s	1476 w	1476 m	Pyridine III
1449 s	1457 s	1449 m	Pyridine IV
1439 vs	1429 m	1426 vs	Pyridine IV
1351 m	1347 w	1370 m	
1311 m	1303 sh		
1290 s	1280 m	1307 s	$\beta(\text{C-H})$
		1278 m	
	1242 m	1241 m	
	1221 m		
1163 m	1166 sh	1156 sh	
1149 m	1146 m	1133 s	$\beta(\text{C-H})$
1136 sh, w	1136 sh	1116 s	
1087 m	1111 w	1095 sh	$\beta(\text{C-H})$
1049 w	1036 w	1049 w	$\beta(\text{C-H})$
995 s	1004 w	1025 s	Breathing mode
909 m			
769 s	775 m	766 s	$\gamma(\text{C-H})$
745 m	746 w	735 m	$\gamma(\text{C-H})$
	699 m		
627 m			$\gamma(\text{C-C})$

<sup>a</sup> Additional weak bands at 1510, 1462, 1262, 1235, 860, and 800  $\text{cm}^{-1}$ . <sup>b</sup> Additional weak bands at 1512, 1266, 907, 852, 840, and 785  $\text{cm}^{-1}$ . <sup>c</sup> Additional weak bands at 978 and 844  $\text{cm}^{-1}$ .

Protonated PAPHY is present in its dihydroperchlorate and this can be distinguished from PAPHY itself by several new bands at 1648 (s), 1633 (sh, w), 1527 (m), 1399 (br, w), 1378 (sh), 1365 (m), 1250 (sh), 1216 (w), and 1033 (sh, w)  $\text{cm}^{-1}$ .

Band assignments in Table I have been made as far as possible based on the work of Katritzky<sup>8</sup> and comparisons with the spectra, not reported here, of PAPHY complexes with other transition metals.

(5) N. S. Gill and R. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(6) C. M. Harris and R. Nyholm, *ibid.*, 4377 (1956).

(7) (a) E. G. Taylor and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1731 (1947); (b) C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

(8) A. R. Katritzky, "Physical Methods in Heterocyclic Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1963, pp 274–283.

## Results

**Absorption Spectra.**—Representative absorption spectra of aqueous solutions of II–IV are shown in Figures 1–3.

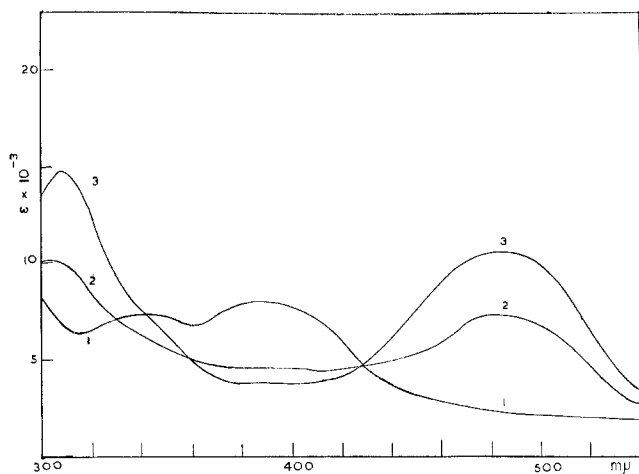


Figure 1.—Spectra of  $\text{Rh}(\text{C}_{11}\text{H}_{10}\text{N}_4)\text{Cl}_3 \cdot \text{H}_2\text{O}$  in aqueous solutions of different pH: 1, pH 1.15; 2, pH 3.45; 3, pH 6.9.

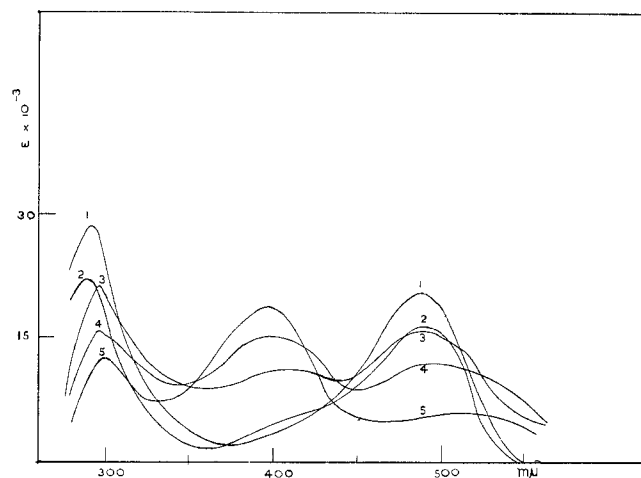


Figure 2.—Spectra of  $\text{Rh}(\text{C}_{11}\text{H}_9\text{N}_4)_2 \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$  in aqueous solutions of different pH: 1, pH 5.05; 2, pH 2.62; 3, pH 2.05; 4, pH 1.49; 5, pH 0.65.

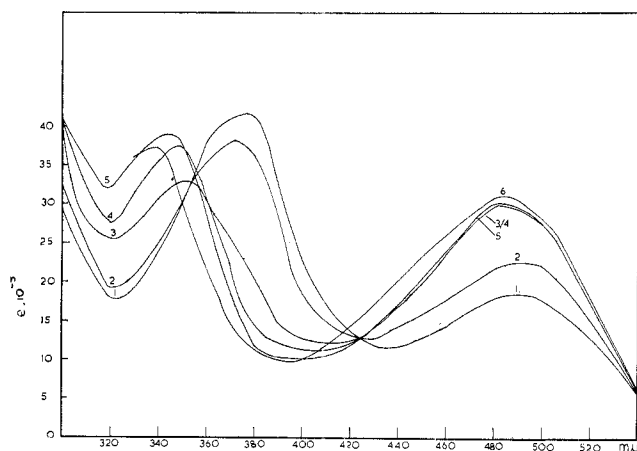


Figure 3.—Spectra of  $\text{Rh}(\text{C}_{11}\text{H}_{10}\text{N}_4)_3\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  in aqueous solutions of different pH: 1, pH 1.72; 2, pH 2.27; 3, pH 3.38; 4, pH 4.28; 5, pH 5.72; 6, pH 9.55.

Spectra of solutions of II are substantially identical when pH is  $>6.9$ , with  $\lambda_{\text{max}}$  at 480  $\text{m}\mu$ .  $\epsilon_{\text{max}}$  is 10,600 at pH 6.9. Below pH 6.9, the spectra are characterized by decreased absorbance at 480  $\text{m}\mu$  and the appearance of a new band with  $\lambda_{\text{max}}$  at 390  $\text{m}\mu$ . An isosbestic point is found at 427  $\text{m}\mu$ . These observations are consistent with the preponderance at low and high pH values, respectively, of neutral and deprotonated forms of the complex. Deprotonation on the addition of alkali is confirmed by the formation of an intensely colored species which is strongly retained by an anion-exchange resin. The proton in question is the imino hydrogen of the PAPHY molecule. From the spectra, the pK value was calculated to be 3.3.

Solutions of III at pH  $>3.18$  have identical spectra and are characterized by a broad absorption band with  $\lambda_{\text{max}}$  of 485  $\text{m}\mu$  and  $\epsilon_{\text{max}}$  of 20,900. Below this, a new absorption band appears ( $\lambda_{\text{max}} \sim 400 \text{ m}\mu$ ) and the absorbance at 485  $\text{m}\mu$  decreases. The species at higher pH values is the fully deprotonated complex ion,  $\text{Rh}(\text{C}_{11}\text{H}_9\text{N}_4)_2^+$ ; in acid solution protonation occurs to give  $\text{Rh}(\text{C}_{11}\text{H}_{10}\text{N}_4)(\text{C}_{11}\text{H}_9\text{N}_4)^{2+}$  and  $\text{Rh}(\text{C}_{11}\text{H}_{10}\text{N}_4)_2^{3+}$ . The isosbestic point observed at 350  $\text{m}\mu$  for solutions between pH 2.65 and 0.65 probably relates to equilibrium mixtures of these two latter ions. It therefore appears that the imino hydrogen atoms in both coordinated PAPHY molecules are markedly acidic and ionization of these is complete above pH 3.18.

Spectra of solutions of IV over the range pH 1.56–10.03 show one broad band with  $\lambda_{\text{max}}$  varying from 485 to 489  $\text{m}\mu$  which becomes more intense at higher pH values ( $\epsilon_{\text{max}}$  is 30,200 at pH 9.55). As for II and III, this behavior may be attributed to the deprotonation of coordinated PAPHY molecules.

At pH 3.38 and above, a second absorption band is found with  $\lambda_{\text{max}}$  varying from 338  $\text{m}\mu$  (pH 7.61) to 355  $\text{m}\mu$  (pH 3.38). At low pH values, the spectra are characterized by a peak at longer wavelengths ( $\lambda_{\text{max}}$  is 372  $\text{m}\mu$  at pH 2.27 and 376  $\text{m}\mu$  at pH 1.72). PAPHY itself in aqueous solutions of low pH shows a similar broad band ( $\lambda_{\text{max}}$  is 372  $\text{m}\mu$  at pH 2.1) due to the protonation of nitrogen atoms in the pyridine rings. We conclude that uncoordinated pyridine nitrogens must also be present in acidic solutions of IV. These do not arise from the decomposition of the tris to the bis complex in solution, thereby releasing free PAPHY, because the absorption band ( $\lambda_{\text{max}} \sim 400 \text{ m}\mu$ ) characteristic of the bis complex at low pH is not observed. Moreover, the isosbestic point at 424  $\text{m}\mu$  suggests two colored species only predominate. Therefore, we conclude PAPHY is acting as a bidentate ligand in IV. There are three pyridine nitrogen atoms in this complex which could be protonated and three imino groups capable of losing protons: it therefore becomes impossible to assign spectra to individual ions and to calculate pK values.

**Potentiometry.**—The behavior of III is typical of the titration of a weak base by a strong acid and is in accordance with spectrophotometric evidence that protonation only occurs at low pH values.

The titration of IV with acid indicates protonation of the pyridine nitrogen atoms but this does not take place in well-defined steps. Titration with alkali shows two protons are lost forming  $\text{Rh}(\text{C}_{11}\text{H}_{10}\text{N}_4)(\text{C}_{11}\text{H}_9\text{N}_4)_2^+$  from  $\text{Rh}(\text{C}_{11}\text{H}_{10}\text{N}_4)_3^{3+}$ . To determine  $\text{p}K$  values, it is necessary to assume the uncoordinated pyridine nitrogens are not protonated at the start of the titration. Approximate values for the dissociation constants were then calculated to be  $\text{p}K_1 = 5.5$  and  $\text{p}K_2 = 7.5$ .

**Infrared Spectra.**—The spectra of PAPHY and its metal complexes are complicated by the presence in the ligand molecule of two pyridine rings in different environments. This is particularly evident in the frequency range  $1400\text{--}1650\text{ cm}^{-1}$  where the pyridine ring vibrations occur and so the assignments in Table I must be regarded as tentative.

The pyridine ring frequencies show little change on coordination, except for pyridine I which is raised by  $20\text{ cm}^{-1}$  in compound III.

The  $\text{C}=\text{N}$  stretch frequency is assigned on the expectation that coordination should result in the increased importance of charged structures.<sup>9</sup> When the coordinated ligand is deprotonated, the possible resonance forms are further increased in number. Whether or not the proton remains on the coordinated ligand, we would still expect the  $\text{C}=\text{N}$  bond to have more single-bond character than in the free ligand and hence to absorb at a lower frequency.

We cannot assign with certainty the N-H deformation band although this may be the very weak band observed at  $1510\text{ cm}^{-1}$  in PAPHY.

The pyridine breathing frequency increases on coordination (from  $995\text{ cm}^{-1}$  in I to  $1025\text{ cm}^{-1}$  in III as found by Gill, *et al.*<sup>10</sup>). As well as the band at  $1025\text{ cm}^{-1}$  in IV, a shoulder is found at  $990\text{ cm}^{-1}$ . This could be due to the presence of uncoordinated pyridine rings in this complex and hence supporting evidence for PAPHY acting in a bidentate fashion.

A comparison of the infrared spectra of III and IV with that of  $\text{Co}(\text{C}_{11}\text{H}_9\text{N}_4)_2\text{ClO}_4$  shows very close correlations between all three. As the cobalt(III) complex is known to contain deprotonated ligands, we must conclude the ligands are also in this form in the two rhodium complexes. There is conflict here with the analytical evidence which points to the presence of acidic hydrogens in IV but not in III. These may not necessarily be located on the imino nitrogen atom but a search in the infrared spectra for other possible protonated species which could be present, such as protonated pyridine groups or oxonium ions, has failed to show any indication of these.

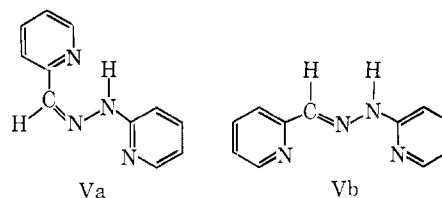
**Nmr Spectra**—Solutions of PAPHY in DMSO and  $\text{CDCl}_3$  show a low-field peak separate from the resonance due to aromatic protons and the aldehydic hydrogen. Deuterium exchange removes this peak and so it is attributed to the  $>\text{N}-\text{H}$  proton, which may form an inter- or intramolecular hydrogen bond.<sup>11</sup> In  $\text{CDCl}_3$ ,

the bond is intermolecular because the peak position varies with concentration. There is no indication of the presence of the azo tautomer<sup>12</sup> and the ligand is therefore in the hydrazone form in these solvents.

In DMSO solutions of III resonance of the pyridine ring protons is observed between 640 and 836 cps (compared with 672 and 856 cps for PAPHY). The spectrum of IV is similar to that of III but with extra peaks at 817, 858, 864, 870, and 882 cps due to the imino group protons (identified by deuterium exchange). This confirms our formulations of IV and III as containing, respectively, PAPHY and deprotonated PAPHY.

## Discussion

**Configuration of the Ligand.**—The PAPHY molecule can theoretically show the geometrical isomerism represented by structures Va and Vb (*syn* and *anti* forms, respectively). Karabatsos and co-workers<sup>11</sup> have concluded that the *syn* isomer of a hydrazone is



thermodynamically favored over the *anti* isomer and it is well known that many hydrazones exist almost exclusively in the *syn* form.<sup>13</sup> Our work shows that PAPHY in  $\text{CDCl}_3$  solution undergoes intermolecular hydrogen bonding. The configuration Va favors intramolecular whereas Vb favors intermolecular hydrogen bonding. We propose therefore that PAPHY in  $\text{CDCl}_3$  exists as the *anti* isomer.

When coordinating as a tridentate ligand, PAPHY is in the *anti* configuration but it can chelate as a bidentate ligand in either the *syn* or the *anti* form. Molecular models show that, in the case of a tris complex, it is sterically impossible for three PAPHY molecules in the *anti* form to coordinate to a single metal ion and we conclude that in complex IV, the PAPHY molecules have the *syn* configuration. In this form, only the ring nitrogen in the pyridylhydrazone residue can participate in chelation: it is not possible for the other pyridine ring to be involved.

In the mono-PAPHY complex of rhodium, the organic molecule acts as a tridentate ligand in the same way as in other mono complexes.<sup>14</sup> Only one configuration of the coordinating atoms round the metal is possible due to the planar nature of the ligand. The marked acidity of the imino hydrogen is in accord with coordination of the ligand to tripositive rhodium, which has powerful electron-withdrawal properties.

In the bis complex, the hydrogens of the two imino groups are much more acidic than those in the bis-

(9) G. J. Karabatsos, B. L. Shapiro, F. M. Vane, J. S. Fleming, and J. S. Ratka, *J. Am. Chem. Soc.*, **85**, 2784 (1963).

(12) G. J. Karabatsos and R. A. Taller, *ibid.*, **85**, 3624 (1963).

(13) G. J. Karabatsos and K. L. Krumel, *Tetrahedron*, **23**, 1097 (1967).

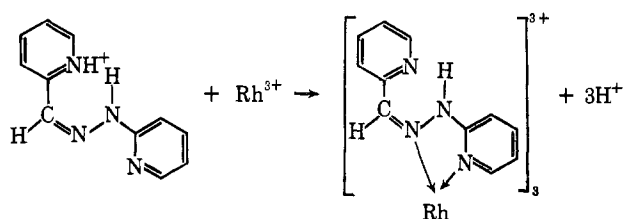
(14) I. G. Dance, J. Lewis, and F. Lions, *J. Chem. Soc., Sect. A*, 565 (1967).

(9) M. A. Robinson and D. H. Busch, *Inorg. Chem.*, **2**, 1171 (1963).

(10) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

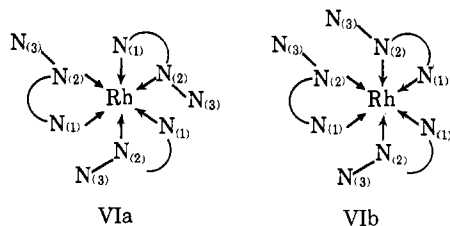
PAPHY complexes of divalent metals ( $pK_1 = 1.16$  and  $pK_2 = 2.56$  compared with  $pK_1 = 5.68$  and  $pK_2 = 6.57$ , for  $Fe^{2+}$ )<sup>2</sup> to such an extent that preparation in neutral solutions gives rise directly to the fully deprotonated bis complex.

The tris complex can only be made in acid solution. Lions<sup>3</sup> suggests that, when PAPHY solutions are acidified, protonation of the pyridine nitrogen of the aldehyde residue occurs first. On chelation with rhodium, the basicity of the pyridine nitrogen will be reduced and the proton lost. Assuming that PAPHY reacts in the *syn* configuration, the formation of the tris complex may be represented as



Comparison of the possible resonance structures that arise if bidentate PAPHY coordinates through the pyridine ring nitrogen of its aldehyde or hydrazine residue confirms that the latter mode of attachment leads to a more stable complex. Hydrogen bonding of the same kind as in PAPHY itself should be possible but to a greater extent because of the enhanced acidity of the imino-group hydrogen. Indeed, the infrared spectra of the tris complex can only be interpreted satisfactorily on the assumption that this hydrogen is fully ionized.

Two geometrical isomers are possible for the tris complex, arising from the unsymmetrical nature of the ligand. These are represented by VIa and b (the ligand is here designated by N(1)-N(2)-N(3) where N(3) is the ring nitrogen of the aldehyde residue), the first being the *cis* isomer with a threefold rotation axis and the second being the *trans* isomer with lower symmetry.



Attempts to find evidence for the existence of these using ion-exchange chromatography failed because

conversion of the tris to the bis complex occurred under the experimental conditions. Therefore, our interpretation of the properties of the tris complex has been made on the assumption that one only of the possible isomers was present.

It has been established<sup>15</sup> that tris complexes capable of showing this kind of isomerism show differences in their proton resonance spectra which can be used as aids to identification. The spectrum of the *trans* isomer is of greater complexity with fine structure or broadening because all three chelate rings are in different environments: that of the *cis* isomer is simpler because the rings are in identical environments. The spectra of III (which has some elements of symmetry) and IV are very similar except for the extra bands in the latter due to the protons of the imino groups. Hence we conclude that IV should be formulated as the *cis* isomer, VIa.

Our attempts to prepare an analogous tris complex with cobalt(III) have not been successful. Toward this and all other metal ions so far studied except rhodium, PAPHY behaves as a tridentate ligand. Scaled molecular models show that, even with a small metal ion, some strain is developed in the organic molecule when it is tridentate. As the size of the ion is increased, *e.g.*, on going from cobalt(III) (octahedral radius = 1.22 Å) to rhodium(III) (1.32 Å),<sup>16</sup> the cumulative ring strain is accentuated<sup>17</sup> and tridentate coordination becomes less easy. This is, however, still the preferred coordination to Rh(III) unless additional factors, in particular the competitive protonation of the pyridine nitrogens which occurs in solutions of low pH, favor the bidentate ligand action of PAPHY.

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