the clear pale yellow solution, 0.5 ml. of styrene was added through a syringe. Minute bubbles of gas were evolved immediately and the solution turned orange. After filtration, the clear orange filtrate was concentrated *in vacuo* to one-third the original volume, whereupon orange crystals started to form. The mixture was diluted with an equal volume of petroleum ether, stirred briefly, and placed on an ice bath. The orange product IV (Z = H) was filtered, washed with petroleum ether, and recrystallized from chloroform.

Analogous ethylene displacements were performed on the various ethylene 4-substituted pyridine N-oxide platinum complexes. The properties of the products isolated corresponded to those of the complexes made directly by the interaction of styreneplatinous chloride with the appropriate pyridine N-oxide derivatives. The complexes are characterized in Table I.

N-Oxide Exchange Reactions.—The following equilibrium was studied independently from each direction

$$\text{IV}\ (Z = NO_2) + C_5H_5NO \leftrightarrows \text{IV}\ (Z = H) + 4\text{-}NO_2C_5H_4NO$$

An approximately 1.3×10^{-3} *M* chloroform solution of each complex was treated with an approximately 6.8×10^{-3} *M* solution of the N-oxide in chloroform. Concentration changes were measured spectrophotometrically but both forward and reverse reactions were slow and after 10 days equilibrium still had not been attained and the solutions were slowly depositing platinum. However, in the forward reaction, some complex IV (Z = H) was isolated, m.p. 139°; infrared spectrum identical with an authentic sample. In the reverse reaction, the mixture was worked up after 4 days at room temperature, whereupon some IV ($Z = NO_2$), m.p. 168°, was isolated; infrared spectrum identical with an authentic sample. From the same reaction mixture it also was possible to isolate some C_5H_5NO as its picrate, m.p. 176–177°, identical with an authentic sample.

Acknowledgments.—The authors wish to thank Professor T. B. Cameron for many helpful comments. The authors also are grateful to Engelhard Industries, Inc., for a generous supply of platinum.

CONTRIBUTION FROM THE INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7, ENGLAND

Mesityl Oxide Complexes of Palladium and Platinum

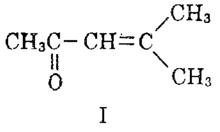
BY G. W. PARSHALL* AND G. WILKINSON

Received March 23, 1962

The long known complex of mesityl oxide and platinum(II) chloride has been shown to be a polymer of platinum(II) chloride units bridged by the olefin and ketone functions of mesityl oxide. The condensation product of mesityl oxide and palladium(II) chloride is a π-allyl complex, $[C_6H_9O{\cdot}PdCl]_2$.

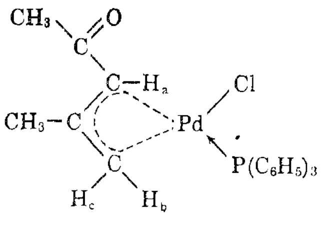
Among the oldest coördination compounds known is a crystalline complex of mesityl oxide (I) and platinum(II) chloride, $[C_6H_{10}O{\cdot}PtCl_2]$.[1] More recently, a different type of complex has been prepared from mesityl oxide and palladium(II) chloride.[2] The structure of these compounds has now been elucidated by proton magnetic resonance and infrared spectral studies.[3]

We have formulated the palladium complex as a π-allylic derivative (II). This yellow crystalline material is insoluble in non-polar organic solvents but dissolves readily in basic solvents which are known to cleave halogen bridges.

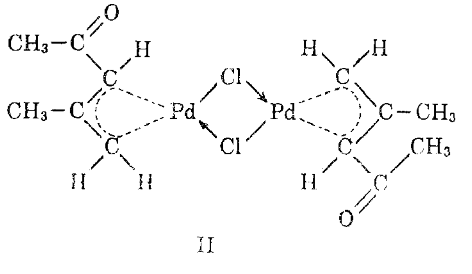


$CH_3C(=O)-CH=C(CH_3)_2$

I



III



II

---

[*] Central Research Department, E. I. du Pont de Nemours and Co., Wilmington 98, Delaware.

(1) H. Zeise, *J. prakt. Chem.*, **20**, 193 (1840); W. Prandtl and K. A. Hofmann, *Chem. Ber.*, **33**, 2981 (1900).

(2) I. I. Moiseev, E. A. Feodorovskaya, and Ya. K. Syrkin, *Zh. Neorg. Khim.*, **4**, 2641 (1959); *Russ. J. Inorg. Chem.* (English Transl.), **4**, 1218 (1959).

(3) Preliminary note, G. W. Parshall and G. Wilkinson, *Chem. Ind.* (London), 261 (1962).

The dimeric nature of the complex is supported by its reaction with triphenylphosphine to give a readily soluble monomeric derivative, $C_6H_9O \cdot PdCl \cdot P(C_6H_5)_3$ (III). The infrared spectra of both monomeric and dimeric complexes show the carbonyl stretching absorption at approximately the same frequency as in mesityl oxide itself (1685 cm.$^{-1}$). Both complexes react with 2,4-dinitrophenylhydrazine to give yellow-orange 2,4-dinitrophenylhydrazones. Evidently the ketone function is not coördinated to the metal atom. The infrared spectrum of $[C_6H_9O \cdot PdCl]_2$ in the KBr region shows bands at 410 (w) and 357 (m, broad) cm.$^{-1}$ assignable to palladium–carbon valence and palladium–chlorine bridge absorption by analogy with the spectrum of π-methallylpalladium chloride.[4]

The proton magnetic resonance spectra of monomeric derivatives of the palladium complex provide more definitive evidence for its structure. The proton resonance spectrum of mesityl oxide itself (Fig. 1) contains a low field septuplet (340 c.p.s., not shown) assignable to the lone olefinic proton and a higher field singlet (113 c.p.s.) due to the methyl group adjacent to the carbonyl function. The olefinic methyl group resonances appear as doublets (J = 1.4 c.p.s.) at 92 and 123 c.p.s from tetramethylsilane as an internal reference (*cf.* Jackman, ref. 5).

The proton resonance spectrum (Fig. 1) of the triphenylphosphine derivative (III) shows a peak of intensity one at 219.6 c.p.s. from tetramethylsilane which has been assigned to the olefinic proton adjacent to the carbonyl group (Table I). The peculiar structure of this peak, like that of the highest field peak assigned to the methyl group attached to the olefin, is attributed to the presence of two isomers of the complex. In the isomer in which the methyl group and the acetyl group are in a *cis* relationship, splitting of the methyl resonance into a doublet and the olefinic resonance into a quadruplet would be expected. In the sterically favored *trans* relationship, little spin–spin coupling of these protons would be expected. The line structures and relative intensities of the components of these two resonances seem to support this hypothesis. Further support is supplied by the fact the shapes (but not the total intensities) of these two lines vary from sample to sample. A similar situation in the case of 1-methyl-π-allylcobalt tricarbonyl has been noted by McClellan, *et al.*[6]

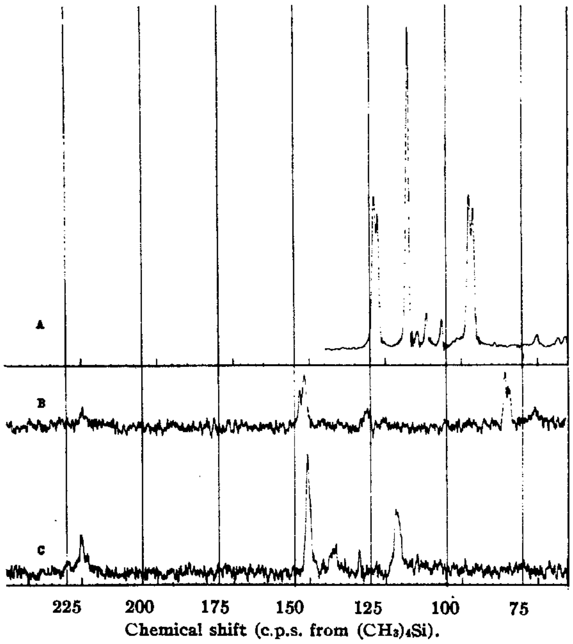


Fig. 1.—Proton magnetic resonance spectra at 60 Mc./sec.: A, mesityl oxide (20% in benzene); B, $C_6H_9O \cdot PdCl \cdot P(C_6H_5)_3$ (4% in benzene); C, $C_6H_9O \cdot PdCl \cdot P(C_6H_5)_3$ (10% in $CDCl_3$).

The reaction of the palladium complex (II) with α-picoline (2-methylpyridine) gives a monomeric compound similar to that obtained from triphenylphosphine. The aliphatic region of the spectrum is similar to that of the triphenylphosphine derivative and similar line assignments have been made (Table I).

Proton resonance studies of $C_6H_{10}O \cdot PtCl_2$ were handicapped by the low solubility of this material in organic solvents with which it does not react. The spectrum of the platinum complex in concentrated sulfuric acid in which it is readily soluble (Fig. 2) is relatively simple and unresolved. The lone olefinic proton resonance appears at +371 c.p.s. from the H_2SO_4 line, much higher than that (+273 c.p.s.) of mesityl oxide itself. The methyl resonances (two coinciding at +486 c.p.s., one at +522 c.p.s.) appear in the same region as those of mesityl oxide but in the absence of fine structure no exact assignments can be made. An allylic structure analogous to that of the palladium complex is excluded by this spectrum as well as by the stoichiometry of the platinum complex.

The infrared spectrum and chemical reactions of $C_6H_{10}O \cdot PtCl_2$ suggest a polymeric structure

---

(4) H. P. Fritz, *Chem. Ber.*, **94**, 1217 (1961).

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, 1959, pp. 83–84.

(6) H. C. Dehm and J. C. S. Chien, *J. Am. Chem. Soc.*, **82**, 4429 (1960); W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *ibid.*, **83**, 1601 (1961).

TABLE I

PROTON MAGNETIC RESONANCE SPECTRA OF $C_6H_9O{\cdot}PdCl{\cdot}P(C_6H_5)_3$ AND $C_6H_9O{\cdot}PdCl{\cdot}(\alpha$-PICOLINE)

		Chemical shift			
Compound	Proton assignment	c.p.s. from $(CH_3)_4Si$ (60 Mc./sec.)	c.p.s. from $(CH_3)_4Si$ (40 Mc./sec.)	τ[a]	Relative intensity
$C_6H_9O{\cdot}PdCl{\cdot}P(C_6H_5)_3$ (4% in C_6H_6)	H_a	219.6	149.3	6.30	1.2
	H_b	148.2	96.5	7.54	1.3
	H_c	126.0	85.9	7.86	1.3
	$O{=}C{-}CH_3$	146.9	100.4	7.51	3.0
	$C{=}C{-}CH_3$	81.0	55.1	8.62	2.7
$C_6H_9O{\cdot}PdCl{\cdot}P(C_6H_5)_3$ (10% in $CDCl_3$)	H_a	220	...	6.34	...
	H_b	146	...	7.57	...
	H_c	132	...	7.80	...
	$O{=}C{-}CH_3$	146	...	7.57	...
	$C{=}C{-}CH_3$	117	...	8.05	...
$C_6H_9O{\cdot}PdCl{\cdot}NC_6H_7$ (10% in $CHCl_3$)	H_a	230.1 at 56.4 Mc./sec.	...	5.92	0.9
	H_b	136.3	...	7.59	1.5
	H_c	128.1	...	7.74	0.9
	$O{=}C{-}CH_3$	153.3	...	7.28	6.0[b]
	$C{=}C{-}CH_3$	117.7	...	7.91	3.3

[a] $\tau = 10 - \Delta((CH_3)_4Si)$/oscillator frequency (Mc./sec.); G. V. D. Tiers, *J. Phys. Chem.*, **62**, 115 (1958). [b] The resonance of the ketonic methyl coincides with that of the methyl group of α-picoline.

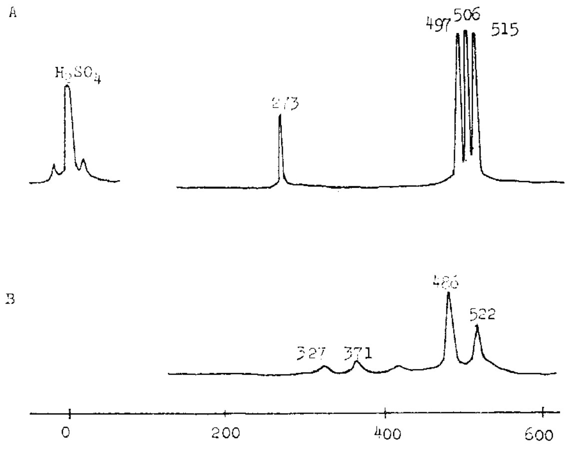
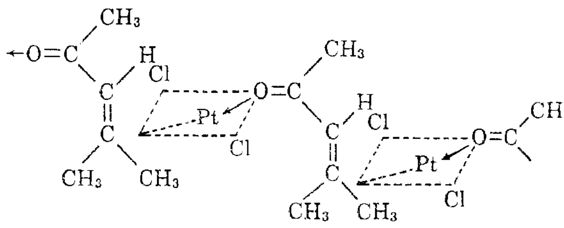


Fig. 2.—Proton resonance spectra at 56.4 Mc./sec.: A, mesityl oxide (10% in concentrated H_2SO_4); B, $C_6H_{10}O{\cdot}PtCl_2$ (10% in concentrated H_2SO_4).

(IV) of $PtCl_2$ units bridged by the olefin and ketone functions of mesityl oxide. The infrared spectrum indicates involvement of both the ketone and olefin functions of mesityl oxide because the 1685 and 1619 cm.$^{-1}$ bands are replaced by a single intense absorption at 1600 cm.$^{-1}$ in the complex. Since the C=C stretching frequencies of coördinated olefins are known to be quite weak, this band probably is due to the coördinated keto group; similar frequency depressions for coördinated ketones are known elsewhere.[7]



IV

The spectrum in the cesium bromide region shows absorption assignable to non-bridging platinum–chlorine bonds in contrast to those in platinum(II) chloride.[8] The complex is insoluble in most inert organic solvents, but the molecular weight in boiling acetone corresponds to a trimer and Prandtl and Hofmann[1] reported it to be monomeric in phenol. This behavior is consistent with displacement of the ketone function from the platinum by these basic solvents. Stronger bases such as pyridine, triphenylphosphine, and dimethyl. sulfoxide completely displace mesityl oxide from the complex giving normal platinous complexes L_2PtCl_2. In concentrated sulfuric acid, the polymeric structure probably is broken by protonation of the ketone function and coördination of a bisulfate ion to the vacant position in the square planar zwitterion complex. On dilution, the polymer is re-formed with little decomposition.

Experimental

Mesityl Oxide–Palladous Chloride Complex.—The complex $[C_6H_9O{\cdot}PdCl]_2$ was prepared by the reaction of palladous chloride with mesityl oxide as described by

---

[7] B. Mori, *et al.*, *Helv. Chim. Acta*, **45**, 77 (1962); D. Cassimati and B. P. Susz, *ibid.*, **43**, 852 (1960).

[8] D. M. Adams, *Proc. Chem. Soc.*, 335 (1961).

Moiseev, *et al.*[2] However, better yields were obtained by boiling a solution of 0.8 g. of sodium chloropalladite in 15 ml. of freshly distilled mesityl oxide for 15 min. When the brown solution was cooled, it became almost solid. The crude mixture was pressed down on a filter and was washed with mesityl oxide, water, and acetone, successively, to give fine yellow crystals. Recrystallization from tetrahydrofuran gave 0.7 g. of the complex, $[C_6H_9O\cdot PdCl]_2$. The infrared spectrum and the decomposition point (210°) were the same as that of a sample obtained from palladous chloride. The complex was very slightly soluble in benzene and ethanol and was insoluble in petroleum ether, chloroform, methylene chloride, acetone, and carbon disulfide.

Reactions of $[C_6H_9O\cdot PdCl]_2$. Triphenylphosphine.—A solution of 185 mg. of triphenylphosphine in 10 ml. of tetrahydrofuran was added to a solution of 170 mg. of $[C_6H_9O\cdot PdCl]_2$ in 75 ml. of warm tetrahydrofuran. The clear yellow solution was allowed to stand at room temperature for 30 min. and then was evaporated under reduced pressure to give a yellow oil. The oil was crystallized from a mixture of benzene and petrol. Two recrystallizations gave $C_6H_9O\cdot PdCl\cdot(C_6H_5)_3P$ as clusters of light yellow crystals (decomposition point 175°).

Anal. Calcd. for $C_{24}H_{24}ClOPPd$: C, 57.6; H, 4.83; Cl, 7.09; P, 6.18; mol. wt., 501.3. Found: C, 57.61; H, 4.90; Cl, 6.63; P, 6.29; mol. wt., 491 (ebullioscopic, benzene).

α-Picoline.—A solution of 93 mg. of $[C_6H_9O\cdot PdCl]_2$ in 50 ml. of tetrahydrofuran was treated with 0.40 ml. of α-picoline at room temperature. Evaporation of the clear yellow solution gave an oil which was recrystallized from a benzene–petroleum ether mixture. Recrystallization from a chloroform–petroleum ether mixture gave coarse yellow needles of $C_6H_9O\cdot PdCl\cdot C_6H_7N$.

Anal. Calcd. for $C_{12}H_{16}ClNOPd$: C, 43.2; H, 4.84; N, 4.21; Pd, 31.9. Found: C, 43.21; H, 4.74; N, 4.21; Pd, 31.36.

2,4-Dinitrophenylhydrazine.—A 2,4-dinitrophenylhydrazine test solution reacted with $[C_6H_9O\cdot PdCl]_2$ to give yellow-orange crystals of a 2,4-dinitrophenylhydrazone which melted without apparent decomposition at 210°. (The parent complex decomposes without melting at 210°.) (The 2,4-dinitrophenylhydrazone of mesityl oxide is a crimson solid, m.p. 201–203°.) The infrared spectrum did not contain the ketone stretching function at 1690 cm.$^{-1}$ but did contain bands at 1594 and 1615 cm.$^{-1}$ associated with a 2,4-dinitrophenylhydrazone.

Other Reagents.—$[C_6H_9O\cdot PdCl]_2$ is instantly reduced to palladium by sodium borohydride or sodium amalgam in ethanol. Addition of water to a solution of the complex in dimethyl sulfoxide instantly precipitated yellow crystals whose infrared spectrum was identical with that of the original complex.

$[C_6H_9O\cdot PdCl]_2$ reacted with sodium cyclopentadienide in tetrahydrofuran to give a deep red, air-sensitive solid. The solid did not sublime at 100° at 1 μ pressure and could not be obtained pure by recrystallization although it was soluble in tetrahydrofuran, chloroform, and methylene chloride.

Mesityl Oxide–Platinum Chloride Complex from Na_2PtCl_4.—A mixture of 1.1 g. of sodium chloroplatinite and 10 ml. of mesityl oxide was boiled under reflux for 2 min. and was filtered immediately. On cooling, 670 mg. of fine yellow needles separated from the brown reaction mixture. The product was washed with water and tetrahydrofuran and was recrystallized from tetrahydrofuran. The infrared spectrum was identical to that of a sample of the complex prepared by the method of Zeise.[1]

Anal. Calcd. for $[C_6H_{10}O\cdot PtCl_2]_3$: C, 19.8; H, 2.77; O, 4.39; Cl, 19.5; mol. wt., 1092. Found: C, 19.70; H, 2.98; O, 4.04; Cl, 19.35; mol. wt., 1125.

From Zeise's Salt.—A solution of 0.5 g. of $Na_2PtCl_3\cdot C_2H_4$ in 12 ml. of mesityl oxide was allowed to stand at room temperature for 1 hr. The solid which separated was washed with water and with tetrahydrofuran to give 0.3 g. of fine yellow needles of $C_6H_{10}O\cdot PtCl_2$. The infrared spectrum was identical with that of the product obtained above.

From Diacetone Alcohol.—A clear red solution of 0.5 g. of sodium chloroplatinite in 8 ml. of diacetone alcohol was warmed to about 150°. A vigorous exothermic reaction occurred and a white crystalline solid separated. The mixture was filtered and the filtrate was diluted with benzene. The red oil which separated deposited yellow needles of $C_6H_{10}O\cdot PtCl_2$ when it was repeatedly washed with benzene.

Reactions of $C_6H_{10}O\cdot PtCl_2$. Triphenylphosphine.—Addition of a solution of 150 mg. of triphenylphosphine in a minimum of acetone to a solution of 40 mg. of $C_6H_{10}O\cdot PtCl_2$ in 4 ml. of acetone led to immediate precipitation of fine white needles of *trans*-bis-(triphenylphosphine)-platinum dichloride, m.p. 298–305° dec. (lit.[9] 310°). The same result was obtained when the amount of $C_6H_{10}O\cdot PtCl_2$ was in excess of the theoretical quantity for this reaction.

2,4-Dinitrophenylhydrazine.—A dilute solution of $C_6H_{10}O\cdot PtCl_2$ in methanol reacted with 2,4-dinitrophenylhydrazine to give yellow-orange needles which decomposed at 250°. The infrared spectrum no longer contained the characteristic 1600 cm.$^{-1}$ band of $C_6H_{10}O\cdot PtCl_2$ but did contain bands at 1594 and 1616 cm.$^{-1}$ assignable to 2,4-dinitrophenylhydrazine.

Other Reagents.—$C_6H_{10}O\cdot PtCl_2$ was instantly reduced to the metal by sodium borohydride in ethanol. No platinum-containing derivative was obtained by treatment with phenylisocyanate in acetone or pyridine. A solution of $C_6H_{10}O\cdot PtCl_2$ in dimethyl sulfoxide deposited white crystals on standing at room temperature. The crystals, perhaps $[(CH_3)_2SO]_2PtCl_2$, melted to a red liquid at 222°.

$C_6H_{10}O\cdot PtCl_2$ was recovered largely unchanged from sulfuric acid solution by dilution with water.

Infrared Spectra. $C_6H_{10}O\cdot PtCl_2$ (Nujol Mull).—1600 vs, 1405 w, 1389 m, 1374 s, 1349 m, 1262 w, 1186 m, 1044 w, 1021 w, 1008 m, 954 w, 882 w, 846 w, 798 w, 718 w, 662 m, 517 w, 492 m; (CsBr wafer) 363 m, 355 sh, 324 m.

$[C_6H_9O\cdot PdCl]_2$ (Nujol Mull).—1690 vs, 1420 m, 1355 m, 1342 m, 1280 m, 1173 s, 1028 m, 960 m (broad), 863 m, 718 m, 688 w, 631 m, 410 w, 357 m (broad).

The spectra in pyridine and in dimethyl sulfoxide solutions were similar but the C=O stretching frequency was shifted to 1670 and 1655 cm.$^{-1}$, respectively.

$C_6H_9O\cdot PdCl\cdot P(C_6H_5)_3$ (Nujol Mull).—1682 vs, 1479 m, 1429 m, 1374 m, 1345 m, 1279 m, 1172 s, 1093 m, 1025 w, 992 w, 963 w (broad), 834 w, 750 m, 743 m, 700 m, 688 s.

---

(9) K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 237 (1936).

The spectrum in pyridine solution was similar but the C=O stretching frequency appeared at 1673 cm.$^{-1}$.

Nuclear magnetic resonance spectra were carried out on Varian high resolution spectrometers at 40, 56.4, and 60 Mc./sec. Spectra in organic solvents are calibrated with respect to tetramethylsilane as an internal reference.

Acknowledgment.—One of the authors is indebted to E. I. du Pont de Nemours and Company for a fellowship and leave of absence to work on this and related problems.

Contribution from the Department of Chemistry,
University of Michigan, Ann Arbor, Michigan

The Thermodynamics of Complexes Formed with 2,2′-Bipyridine and Transition Metal Ions

By GORDON ATKINSON[1] AND JOHN E. BAUMAN, JR.[2]

Received November 24, 1961

The thermodynamic quantities of formation have been measured for the Mn(II), Ni(II), Cu(II), and Zn(II) complexes formed with 2,2′-bipyridine. The Bjerrum potentiometric titration technique was used to measure ΔF. ΔH was measured using an adiabatic calorimeter and a titration method analogous to the ΔF determination. The sequential decrease of ΔF during stepwise complex formation is shown to be primarily an entropy effect within experimental error. The stability of the Cu(II) complexes is lower than those of ethylenediamine. A correlation between the thermodynamic and spectroscopic stabilization energies is made for the Ni(II) complex.

Introduction

The ability of 2,2′-bipyridine to complex with transition metals has been known for many years. The work prior to 1954 has been reviewed by Brandt, *et al.*[3] The similarity of bipyridine to other biologically important heterocyclic nitrogen ligands such as the porphyrins and purines has promoted an interest in the study of the bonding in metal complexes.[4-6]

Recent work in the thermodynamics of bipyridine complexes has been reported by various workers.[7-11] Due to the lack of comparable data obtained by a single method under identical conditions of temperature and ionic strength, a comparison of the thermodynamics for a group of transition metal ions has really not been possible. In order to better understand the bonding a study of a series of related metals similar to that reported for ethylenediamine is desirable. Irving[11] has used a partition method to obtain the formation curves for several of the transition metal ions with bipyridine.

Both the free energies and heats of formation of a series of transition metal ions with bipyridine were determined at 25° in a 1 M $NaClO_4$ solution. By keeping the concentrations of reacting species below 0.01 M and maintaining a constant ionic strength the activities of the ions may be considered to be proportional to the concentrations. The concentrations of all of the reacting species were determined by measuring $[H^+]$ and calculating the stoichiometry of the reaction.

The enthalpies of formation were measured by direct calorimetry rather than by a temperature dependency study in the potentiometric determination of the equilibrium constants.

Experimental

Reagents.—2,2′-Bipyridine and the metal perchlorates were obtained from the G. F. Smith Company. The bipyridine was purified by recrystallizing from petroleum ether to a melting point of 69.0–70.0°. Its base strength was checked by titration against standard $HClO_4$ in

---

[1] Department of Chemistry, University of Maryland, College Park, Maryland.

[2] Department of Chemistry, University of Missouri, Columbia, Missouri. Taken in part from the Ph.D. Thesis of J. E. Bauman, University of Michigan, 1961.

[3] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

[4] D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, **78**, 1137 (1956).

[5] H. Irving and R. J. P. Williams, *Analyst*, **77**, 813 (1952).

[6] S. Herzog, *J. Inorg. Nucl. Chem.*, **8**, 556 (1958).

[7] R. L. Gustafson and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 525 (1959).

[8] S. Cabani and E. Scrocco, *J. Inorg. Nucl. Chem.*, **8**, 332 (1958).

[9] K. Yamasaki and M. Yasuda, *J. Am. Chem. Soc.*, **78**, 1324 (1956).

[10] R. R. Miller and W. W. Brandt, *ibid.*, **77**, 1384 (1955).

[11] H. Irving, Proceedings of the 1959 International Coördination Conference, London.