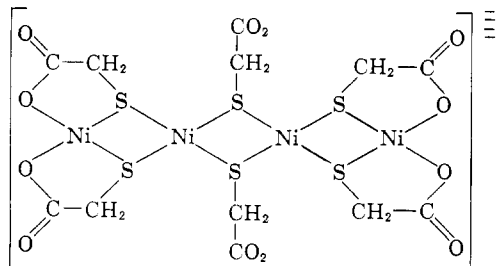


The third member can be formed from the second by the displacement of two adjacent carboxylate groups to give

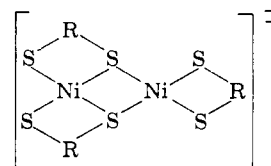


This is plausible because of the relatively weak complexing of the carboxylate group with the divalent transition metals compared to that of the mercaptide group (see refs. 4 and 7). The carboxylate groups which are coordinated to nickel must certainly be hydrated in aqueous solution. This may be the source of the extra heat (and stability) noted above for  $\text{Ni}_4(\text{RS})_6^{-4}$ .<sup>15</sup>

(15) Referee I points out that there are 3(Ni-S) and 1(Ni-O) bonds per nickel in the tetramer but 2(Ni-S) and 2(Ni-O) bonds in the monomer and that higher bond energy of Ni-S relative to Ni-O would account for the observation. However, a comparison of the Ni-S bonding between the tetramer and monomer is obscured by the fact that in the tetramer the sulfur is multiply bonded to metal ions, whereas,

Higher complexes can be built up by a repetition of the last process. But then uncoordinated carboxylate groups appear adjacent to each other in the polymer and charge repulsion must bring about a decrease in stability.

On this basis it is also possible to explain the fact that with the dithiols only dimeric complexes are observed. The structure of these can be pictured as



where all the square-planar positions on the nickel(II) ions are occupied by sulfur atoms, and therefore a further increase in chain length is not feasible.

The sulfur atoms in the polymeric complexes would tend to develop a positive charge because of the multiple bonding to the nickel ions. This positive charge may be relieved by the back donation of electrons from the metal ions to the sulfur through  $\pi$  bonding.<sup>16</sup> In this may lie the reason for the pronounced spectral differences between the polymeric and monomeric complexes. The bonding appears to be predominantly  $\sigma$  in these latter.<sup>4</sup>

in the monomer it is only singly bonded. A clear-cut distinction between the relative importance of the NiS bonding and the hydration of the carboxylate groups toward the heat of formation of the tetramer therefore cannot be made. Both factors should be considered then. We wish to thank Referee I for suggesting this additional possibility.

(16) A similar  $\text{MS}_2\text{M}$  ring system has been reported to be formed with either Pd(II) or Pt(II). The S-Pt-S-Pt ring is claimed to be

"aromatic" in character (J. Chatt and F. A. Hart, *J. Chem. Soc.*, 2363 (1953)).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

## The Complexes of Nickel(II), Palladium(II) and Platinum(II) with 2-Pyridinaldoxime<sup>1</sup>

BY RONALD A. KRAUSE AND DARYLE H. BUSCH

RECEIVED FEBRUARY 3, 1960

Several complexes of nickel(II), palladium(II) and platinum(II) with 2-pyridinaldoxime (HPOX) have been prepared, characterized, and compared with the complexes formed by the similar ligands dimethylglyoxime, 2,2'-bipyridine and 2-methyl-2-amino-3-butanone oxime. Nickel(II) has been observed to form a number of complexes, the most typical of which are  $[\text{Ni}(\text{HPOX})_3]_2$ ,  $[\text{Ni}(\text{HPOX})_2\text{Cl}_2]$ ,  $[\text{Ni}(\text{HPOX})(\text{POX})]_2$  and  $[\text{Ni}(\text{POX})_2]$ . All of the nickel(II) complexes are paramagnetic, with magnetic moments which indicate the presence of two unpaired electrons. The magnetic moment of the uncharged nickel(II) complex  $[\text{Ni}(\text{POX})_2]$  is associated with an unusually high Weiss constant. Palladium(II) forms the typical square planar complexes  $[\text{Pd}(\text{HPOX})(\text{POX})]\text{Cl}$  and  $[\text{Pd}(\text{POX})_2]$ , while platinum(II) forms  $[\text{Pt}(\text{POX})_2]$ .

### Introduction

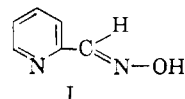
No detailed study has yet been reported on the nickel(II), palladium(II) and platinum(II) complexes of an aromatic amine-oxime. Tschugaeff<sup>2</sup> first prepared palladium(II) and platinum(II) complexes of phenyl- $\alpha$ -pyridyl ketoxime, and Emmert and Diehl<sup>3</sup> later reported on the reaction

(1) Abstracted from the Ph.D. dissertation of R. A. Krause, The Ohio State University, 1959. Portions of this work were presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., 1959.

(2) L. Tschugaeff, *Chem. Ber.*, **39**, 3382 (1906).

(3) B. Emmert and K. Diehl, *ibid.*, **62B**, 1738 (1929).

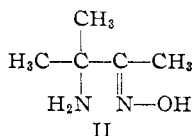
of methyl- $\alpha$ -pyridyl ketoxime with nickel(II). Both studies, however, were of a cursory nature. The present investigation is concerned with the nickel(II), palladium(II) and platinum(II) complexes of a similar aromatic amine-oxime, 2-pyridinaldoxime (HPOX) (I).



It can be seen readily that HPOX shows structural features of two well known ligands, 2,2'-

bipyridine (bipy) and dimethylglyoxime (HDMG) (*i.e.*, HPOX contains an oxime function and  $\alpha$ -pyridyl group).

The aliphatic amine-oxime, 2-methyl-2-amino-3-butanone oxime (AOH) (II), which was studied by Murmann,<sup>4,5</sup> is also similar to 2-pyridinaldoxime.



One would expect these structural similarities to be reflected in chemical similarities, and the complexes of HDMG and bipy should serve as limiting examples of the behavior to be found with HPOX.

### Experimental

**2-Pyridinaldoxime.**—2-Pyridinaldehyde obtained from Aldrich Chemical Co. was dissolved in ethanol and treated with hydroxylamine hydrochloride, maintaining the temperature between 0 and 30° by means of an ice-bath. The acid salt was neutralized with sodium hydroxide, and water and Dry Ice were added to the solution. After cooling for 1 hr., the mixture was filtered and the yellow solid was recrystallized from water containing 10% ethanol using decolorizing charcoal. The resulting white needles melt at 108°; sublimation begins at a somewhat lower temperature; literature value for the melting point, 113.5°. A sample of the oxime purchased from Aldrich Chemical Company also melts at 108°.

*Anal.* Calcd. for  $\text{C}_6\text{H}_8\text{N}_2\text{O}$ : C, 59.00; H, 4.95; N, 22.94. Found: C, 58.95; H, 5.66; N, 22.82.

**Nickel Compounds. Tris-(2-pyridinaldoxime)-nickel(II) Iodide 2-Hydrate.**—6.42 g. of nickel chloride 6-hydrate (0.027 mole) was dissolved in 20 ml. of water. Ten g. of 2-pyridinaldoxime (0.082 mole) was added and the solution was stirred until all dissolved. A solution containing 20 g. of potassium iodide in 20 ml. of water was added and the resulting solution was warmed to 50°. At this temperature, any oil which had formed redissolved. After several minutes at 50°, a tan solid precipitated and the mixture was allowed to cool to room temperature. After 4 hr. the solid was separated by filtration, washed with two small portions of water and dried *in vacuo* over  $\text{P}_2\text{O}_5$ ; yield, 14.55 g. (75.2%).

*Anal.* Calcd. for  $[\text{Ni}(\text{C}_6\text{H}_8\text{N}_2\text{O})_3]_2 \cdot 2\text{H}_2\text{O}$ : C, 30.23; H, 3.10; N, 11.76. Found: C, 30.17; H, 3.00; N, 11.93.

**Dichloro-bis-(2-pyridinaldoxime)-nickel(II).**—16.67 g. of nickel chloride 6-hydrate (0.070 mole) was dissolved in 350 ml. of boiling absolute ethanol; 17.11 g. of 2-pyridinaldoxime (0.140 mole) was added; crystallization started immediately. The solution was boiled for 10 minutes and then allowed to stand overnight. The green crystalline solid was removed by filtration, washed twice with absolute ethanol and dried *in vacuo* over  $\text{P}_2\text{O}_5$ ; yield, 23.4 g. (89.7%).

*Anal.* Calcd. for  $[\text{Ni}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{Cl}_2]$ : C, 38.55; H, 3.24; N, 14.99; Cl, 18.97. Found: C, 38.58, 38.56; H, 3.48, 3.41; N, 14.96, 14.74; Cl, 18.76.

**Diacetato-bis-(2-pyridinaldoxime)-nickel(II).**—16.67 g. of nickel chloride 6-hydrate (0.070 mole) was dissolved in 85 ml. of hot water, and 17.11 g. of 2-pyridinaldoxime (0.140 mole) was added and dissolved. Twenty-one g. of potassium acetate was added with stirring; the mixture was kept on the hot water-bath for 30 minutes and then allowed to stand overnight. The gray crystalline solid was removed by filtration, washed with one portion of water and dried *in vacuo* over  $\text{P}_2\text{O}_5$ ; yield, 27.7 g. (94%).

*Anal.* Calcd. for  $[\text{Ni}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2(\text{CH}_3\text{COO})_2]$ : C, 45.64; H, 4.31; N, 13.31. Found: C, 45.31; H, 3.51; N, 13.32.

**Acetato-aquo-bis-(2-pyridinaldoxime)-nickel(II).**—Twelve g. of diacetato-bis-(2-pyridinaldoxime)-nickel(II) (0.028 mole) was mixed with 270 ml. of absolute ethanol and 30 ml. of water, heated on the water-bath for twenty minutes and filtered. This solution was poured into 1600 ml. of ether, filtered after 2 hr., washed with ether and dried in the air. The tan solid was recrystallized by dissolving it in 90% ethanol, filtering and pouring the solution into ether as above.

*Anal.* Calcd. for  $[\text{Ni}(\text{C}_6\text{H}_8\text{N}_2\text{O})(\text{C}_6\text{H}_5\text{N}_2\text{O})(\text{CH}_3\text{COO})(\text{H}_2\text{O})]$ : C, 44.36; H, 4.26; N, 14.79. Found: C, 44.20; H, 4.55; N, 14.06.

**Bis-(pyridine)-bis-(2-pyridinaldoxime)-nickel(II) Monoiodide.**—Five g. of dichloro-bis-(2-pyridinaldoxime)-nickel(II) (0.013 mole) was dissolved in 15 ml. of warm water and filtered; 2.50 g. of potassium iodide (0.015 mole) was dissolved in 7 ml. of warm water and added; 4.4 ml. of pyridine (0.055 mole) was added with stirring to the above solution. After standing 1 hr. the orange crystalline solid was removed by filtration, washed three times with water and dried *in vacuo* over  $\text{P}_2\text{O}_5$  at 78°; yield, 6.88 g. (90.3%).

*Anal.* Calcd. for  $[\text{Ni}(\text{C}_6\text{H}_8\text{N}_2\text{O})(\text{C}_6\text{H}_5\text{N}_2\text{O})(\text{C}_5\text{H}_5\text{N})_2]\text{I}$ : C, 45.01; H, 3.61; N, 14.32; I, 21.62. Found: C, 44.83, 44.66; H, 3.73, 3.69; N, 14.01, 14.07; I, 21.93, 21.58, 21.97.

**Bis-(2-pyridinaldoxime)-nickel(II) Monoiodide.**—Bis-(pyridine)-bis-(2-pyridinaldoxime)-nickel(II) monoiodide was placed in a drying pistol over refluxing benzyl alcohol (202°), allowed to stand at atmospheric pressure for 1 hr., and then the pistol was evacuated. After standing over  $\text{P}_2\text{O}_5$  *in vacuo* at this temperature overnight the sample consisted of dark brown crystals.

*Anal.* Calcd. for  $[\text{Ni}(\text{C}_6\text{H}_8\text{N}_2\text{O})(\text{C}_6\text{H}_5\text{N}_2\text{O})]\text{I}$ : C, 33.68; H, 2.59; N, 13.10; I, 29.66. Found: C, 33.58; H, 2.53; N, 12.93; I, 30.03.

**Bis-(pyridine)-bis-(2-pyridinaldoxime)-nickel(II).**—Ten g. of dichloro-bis-(2-pyridinaldoxime)-nickel(II) (0.027 mole) was mixed with 100 ml. of pyridine and heated to boiling with thorough stirring. Ten g. of anhydrous potassium carbonate was added, the mixture again was heated to boiling, 15–20 g. of sodium hydroxide pellets was added and the mixture was boiled with stirring for 45 seconds. It was immediately filtered through a large sintered glass funnel. The filtrate was allowed to cool for 30 minutes, and the purple crystals were collected by filtration, washed twice with pyridine and dried *in vacuo* over  $\text{P}_2\text{O}_5$ ; yield, 7.8 g. (63.6%).

This solid contained some sodium chloride and was recrystallized by dissolving in chloroform, filtering to remove insoluble material and pouring into a volume of pyridine equal to 5 times the volume of chloroform used. The solution was allowed to stand in a stoppered flask overnight before collecting the product by filtration and washing with pyridine. This recrystallization was performed twice; yield on recrystallization, 77%.

*Anal.* Calcd. for  $[\text{Ni}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2(\text{C}_5\text{H}_5\text{N})_2]$ : C, 57.55; H, 4.39; N, 18.31; Cl, 0.0. Found: C, 57.22; H, 4.51; N, 18.86; Cl, 0.71.

**Bis-2-pyridinaldoxime)-nickel(II).**—Bis-(pyridine)-bis-(2-pyridinaldoxime)-nickel(II) was placed in a drying pistol at 100° *in vacuo* over  $\text{P}_2\text{O}_5$  for 16 hr. The drying pistol was opened in a dry box under nitrogen. Before removing the sample from the dry box the magnetic susceptibility tube was filled and capped, and an ampoule for analysis was filled and protected with a magnesium perchlorate tube prior to sealing. The product consisted of brown crystals.

*Anal.* Calcd. for  $[\text{Ni}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2]$ : C, 47.89; H, 3.35; N, 18.62; Cl, none. Found: C, 47.54, 47.29; H, 4.27, 4.10; N, 17.75, 17.64; Cl, 0.73.

**Palladium and Platinum Compounds. Bis-(2-pyridinaldoxime)-palladium(II) Monochloride.**—Two g. of potassium tetrachloropalladate (0.0061 mole) was dissolved in 70 ml. of water, 1.50 g. of 2-pyridinaldoxime (0.012 mole) was added, and the mixture was heated to boiling, filtered and allowed to cool. The solid product was removed by filtration and washed with water. Crude material was recrystallized by dissolving in 7 ml. of hot water, filtering, then adding 3 drops of concentrated hydrochloric acid and allowing the solution to cool. After standing overnight

(4) R. K. Murmann, *THIS JOURNAL*, **79**, 521 (1957).

(5) R. K. Murmann, *ibid.*, **80**, 4174 (1958).

the orange crystals were removed by filtration, washed with water and dried *in vacuo* over  $P_2O_5$ ; yield, 1.51 g. (64.0%).

*Anal.* Calcd. for  $[Pd(C_5H_5N_2O)(C_5H_5N_2O)]Cl$ : C, 37.39; H, 2.88; N, 14.53; Cl, 9.20. Found: C, 37.38; H, 3.07; N, 14.31; Cl, 9.04.

**Bis-(2-pyridinaldoxime)-palladium (II).**—Three g. of potassium tetrachloropalladate (0.00916 mole) was dissolved in 200 ml. of water and 2.24 g. of 2-pyridinaldoxime (0.0183 mole) was added. The solution was heated to boiling, digested until the solid dissolved and then filtered. One g. of sodium hydroxide (0.025 mole) dissolved in 20 ml. of water was added to the hot filtrate with stirring. When the addition was complete a mass of yellow needles was present; the solution was allowed to cool and filtered. The solid was washed with water and dried *in vacuo* over  $P_2O_5$ .

The solid was recrystallized by dissolving in boiling chloroform (100 ml. of solvent per gram of material), evaporating the solvent to half its original volume and cooling. The purified product was collected by filtration, washed with chloroform and dried *in vacuo* over  $P_2O_5$ ; yield, 3.20 g.

*Anal.* Calcd. for  $[Pd(C_5H_5N_2O)_2]$ : C, 41.30; H, 2.89; N, 16.06; Pd, 30.58. Found: C, 41.39; H, 3.00; N, 16.02; Pd, 30.52.

**Bis-(2-pyridinaldoxime)-platinum (II).**—Two g. of potassium tetrachloroplatinate (0.00482 mole) was dissolved in 90 ml. of hot water, and a solution of 1.18 g. of 2-pyridinaldoxime (0.00966 mole) in 50 ml. of hot water was added. Within a few seconds, a fine, light colored solid precipitated. Immediately 0.4 g. of sodium hydroxide (0.010 mole) in 20 ml. of water was added. The precipitate dissolved leaving a clear brown solution; within one minute fine brown needles began to precipitate. After standing overnight the solid was collected by filtration, washed with several portions of water and dried *in vacuo* over  $P_2O_5$ ; yield, 1.87 g.

This material was impure and was recrystallized by dissolving in boiling chloroform (50 ml. per g. of solid), filtering to remove a light tan solid and allowing the filtrate to stand overnight. The brown needles were collected by filtration, washed with chloroform and dried *in vacuo* over  $P_2O_5$ ; yield on recrystallization, 53.8%.

*Anal.* Calcd. for  $[Pt(C_5H_5N_2O)_2]$ : C, 32.94; H, 2.30; N, 12.81. Found: C, 32.88; H, 3.03; N, 12.80.

**Physical Measurements. Conductivity.**—All conductivity measurements were made with a conductivity bridge, model RC-16B, manufactured by Industrial Instruments, Incorporated.

**pH Titrations.**—pH titrations were carried out using a Beckman model G pH meter with a saturated calomel electrode and a glass electrode.

**Magnetic Moments.**—Magnetic moments were determined using a Gouy type balance and solid samples; ferrous ammonium sulfate 6-hydrate and water were used as standards. The reported values are corrected for ligand and anions.

Temperature dependence studies of the magnetic moment were conducted using the apparatus described by Stoufer.<sup>6</sup>

**Analyses.**—Analyses were performed by Galbraith Micro-analytical Laboratories and also by Schwarzkopf Micro-analytical Laboratories.

## Discussion

**Nickel(II) Complexes.**—The complexes formed by 2-pyridinaldoxime with nickel(II), palladium(II) and platinum(II) are summarized in Table I, where magnetic moments and molar conductances also are reported. Three classes of nickel(II) compounds are contained in this tabulation: those which contain only neutral ligand molecules, those containing one mole of ionized ligand and those containing two moles of ionized ligand. The discussion below follows this classification.

A stable complex,  $[Ni(HPOX)_3]^{++}$ , readily is precipitated from aqueous solution as the tan, crystalline iodide salt, which has a magnetic

(6) R. C. Stoufer, Ph.D. dissertation, The Ohio State University, 1958.

TABLE I  
MAGNETIC MOMENTS AND CONDUCTIVITIES OF COMPLEXES  
OF 2-PYRIDINALDOXIME

Compound	$\mu_{eff}$ (B. M.)	$\Lambda_M$ (in MeOH) ( $\Omega^{-1}$ at 25°)
$Ni(HPOX)_3I_2 \cdot 2H_2O$	3.12	181.2
$Ni(HPOX)_2Cl_2$	3.16	111.4
$Ni(HPOX)_2Ac_2$	3.12	33.9
$Ni(POX)(HPOX)(Ac)(H_2O)$	3.08	32.0
$Ni(POX)(HPOX)(py)_2I$	3.18	89.7
$Ni(POX)(HPOX)I$	3.01	88.8
$Ni(POX)_2(py)_2$	2.83	13.4
$Ni(POX)_2$	3.56 <sup>a</sup>	...
	2.74 <sup>b</sup>	
$Pd(POX)(HPOX)Cl$	...	86.5
$Pd(POX)_2$	...	2.6
$Pt(POX)_2$	...	3.7

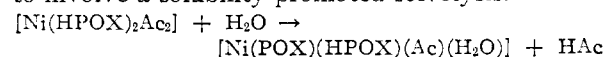
<sup>a</sup> Solid sample, moment calculated using the experimentally determined Weiss constant,  $\theta$ , with a value of 226.3°. <sup>b</sup> Solution in chloroform, moment calculated assuming  $\theta = 0$ .

moment of 3.12 Bohr Magnetons. In methanol the compound displays a molar conductivity of 181.2 ohms<sup>-1</sup> which approximates the value expected of a di-univalent electrolyte.<sup>6</sup> This compound appears to have the octahedral configuration and to be completely similar to  $[Ni(bipy)_3]^{++}$ .

Dichloro-bis-(2-pyridinaldoxime)-nickel(II),  $[Ni(HPOX)_2Cl_2]$ , is precipitated from a solution of nickel chloride 6-hydrate in ethanol by the addition of 2-pyridinaldoxime. This complex consists of fine, green crystals. It has a magnetic moment of 3.16 Bohr Magnetons and shows a molar conductivity in methanol of 111.4 ohms<sup>-1</sup>. Stoufer<sup>6</sup> has observed similar values of the conductivity for closely related substances and has postulated that some of the chlorides, which originally were coordinated, have been displaced by solvent molecules.  $[Ni(HPOX)_2Cl_2]$  appears to have an octahedral configuration and in its physical properties, preparation method and probable configuration, it bears a very close resemblance to  $[Ni(bipy)_2Cl_2]$  and  $[Ni(HDMG)_2Cl_2]$ . However, there is a principal point of contrast. When  $[Ni(HPOX)_2Cl_2]$  is dissolved in water there is no apparent reaction, and the solution retains its green color, while the similar bipy and HDMG complexes revert to more stable forms,  $[Ni(bipy)_3]^{++}$  and  $[Ni(DMG)_2]$ , respectively. In fact, the closely related compounds  $[Ni(HPOX)_2(C_2H_3O_2)]$  and  $[Ni(HPOX)_2I_2]$  may be prepared in aqueous solution.

The removal of one ligand proton and the replacement or removal of the coordinated chlorides from the compound just discussed,  $[Ni(HPOX)_2Cl_2]$ , produces these species:  $[Ni(POX)(HPOX)(C_2H_3O_2)(H_2O)]$ ,  $[Ni(POX)(HPOX)(py)_2]I$  and  $[Ni(POX)(HPOX)]I$ . These compounds are analogous to Murmann's complex,  $[Ni(AO)(AOH)]^+$ , in their distribution of ligand protons and similar properties might be expected.

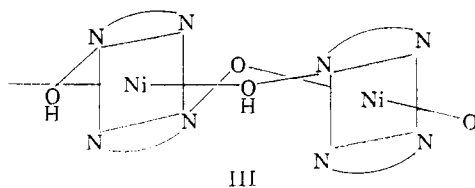
The monoacetato complex  $[Ni(POX)(HPOX)(C_2H_3O_2)(H_2O)]$ , is prepared by dissolving the gray diacetato complex  $[Ni(HPOX)_2Ac_2]$ , in 90% ethanol, and adding ether. The process appears to involve a solubility promoted solvolysis.



The product has a magnetic moment of 3.08 Bohr Magnetons, and there is little doubt of its displaying the octahedral configuration. The molar conductivity in methanol for  $[\text{Ni}(\text{POX})(\text{HPOX})(\text{C}_2\text{H}_3\text{O}_2)(\text{H}_2\text{O})]$  of  $32.0 \text{ ohms}^{-1}$  indicates that the substance does not undergo extensive solvolysis.

The second compound of this class,  $[\text{Ni}(\text{POX})(\text{HPOX})(\text{py})_2]\text{I}$ , is precipitated as orange crystals from an aqueous solution of  $[\text{Ni}(\text{HPOX})_2\text{Cl}_2]$  and potassium iodide by the addition of three equivalents of pyridine. One equivalent of pyridine is utilized apparently in the neutralization of an oxime proton, the other two equivalents coordinating to the nickel(II) atom. The conclusion that the nickel(II) is octahedrally coordinated is supported by the observed magnetic moment of 3.18 Bohr Magnetons. This compound displays a molar conductivity (in methanol) of  $89.7 \text{ ohms}^{-1}$  which may well serve as a standard for complexes which are uni-univalent electrolytes in methanol.

Removal of the coordinated pyridine from  $[\text{Ni}(\text{POX})(\text{HPOX})(\text{py})_2]\text{I}$  at  $200^\circ$  *in vacuo* produces  $[\text{Ni}(\text{POX})(\text{HPOX})]\text{I}$ , which is also a uni-univalent electrolyte (methanol). In view of the electrolyte type, it is most interesting to observe that the compound is paramagnetic, with a magnetic moment of 3.01 Bohr Magnetons. From the observed stoichiometry and molar conductance, a planar structure and the associated diamagnetism would have seemed quite probable. Indeed, the diamagnetism of the analogous compound of 2-methyl-2-amino-3-butanone oxime,  $[\text{Ni}(\text{AO})(\text{AOH})](\text{ClO}_4)$ , indicates a square planar configuration in that case.<sup>4</sup> There are two possible explanations for the apparent coordination number of six. Although the iodide is ionic in solution, it might well be coordinated in the solid state and shared between nickel atoms. Such a sharing of iodide ions between molecules would produce chains of octahedra linked at corners. The other possibility requires that the oxime oxygens act as donors. Again the octahedra would not be discrete but linked in one of several possible ways (structure III). In view of the behavior observed among the uncharged complexes (below), this latter suggestion seems plausible.



The class of complexes which remains to be discussed is that which is derived from  $[\text{Ni}(\text{HPOX})_2\text{Cl}_2]$  by the removal of two oxime protons from the ligands and the removal of the chlorides to give an uncharged compound of the type  $[\text{Ni}(\text{POX})_2]$ . From the behavior of similar ligands, it would seem likely that such a species should precipitate from water as a red or orange diamagnetic solid containing a square planar four-coordinate nickel(II) complex. Such a compound is not readily obtained by the reaction of nickel(II) salts with 2-pyridinaldoxime, the second oxime proton being relatively difficult to remove. As mentioned above,

aqueous pyridine suffices to remove the first proton. In water, the second proton may be removed in a highly concentrated caustic solution; however, this treatment causes an oil of uncertain composition to separate. It is necessary to abandon water as a solvent and employ anhydrous pyridine in order to obtain the neutral nickel complexes of pyridinaldoxime. By treating a pyridine solution of  $[\text{Ni}(\text{HPOX})_2\text{Cl}_2]$  with solid sodium hydroxide an uncharged complex,  $[\text{Ni}(\text{POX})_2(\text{py})_2]$ , may be obtained. This compound forms as gleaming, purple crystals. Its conductivity in methanol ( $13.4 \text{ ohms}^{-1}$ ) verifies its nonionic nature, and the magnetic moment of the solid (2.83 Bohr Magnetons) suggests an octahedral configuration, as is also implied by the presence of six donor groups. The pyridine in this complex is retained tenaciously; drying *in vacuo* over  $\text{P}_2\text{O}_5$  causes no apparent loss.

Bis-(2-pyridinaldoxime)-nickel(II),  $[\text{Ni}(\text{POX})_2]$ , is prepared by heating the dipyridinate,  $[\text{Ni}(\text{POX})_2(\text{py})_2]$ , *in vacuo* at  $100^\circ$ . This material is not only unusual with respect to the method required for its synthesis but also in a number of other respects. Of all the compounds of nickel(II) with 2-pyridinaldoxime this compound,  $[\text{Ni}(\text{POX})_2]$ , has the greatest likelihood of showing the planar configuration.  $[\text{Ni}(\text{POX})_2]$  is, however, paramagnetic with a magnetic moment which appears to have the value of 2.6 Bohr Magnetons (calculated using the equation

$$\mu_{\text{eff}} = 2.83\sqrt{\chi_A\tau} \quad (1)$$

This value is lower than that expected for two unpaired electrons (theoretical, 2.83 B.M. with no orbital contribution).

There are two possible explanations for the small value of the observed moment. The Curie-Weiss law

$$\mu_{\text{eff}} = 2.83\sqrt{\chi_A(T + \theta)} \quad (2)$$

may be required for the calculation of the magnetic moment, or an equilibrium may exist between two electronic spin states, spin-paired and spin-free in this case. Stouffer<sup>6</sup> has discussed this possibility for some cobalt(II) complexes which exhibit unusual magnetic moments. If such a situation exists, the Curie-Weiss law will not be obeyed.

From measurements over the range from 180 to  $373^\circ\text{K}$ ., it appears that the magnetic susceptibility of  $[\text{Ni}(\text{POX})_2]$  follows a Curie-Weiss dependence on temperature; consequently, the second explanation (that of spin state equilibria) need be considered no further. From these results,  $\theta$  is found to have the value of  $226.3^\circ$ . Using this value for  $\theta$  in the calculation of the magnetic moment, a value of  $3.56 \pm 0.02$  Bohr Magnetons is obtained. With such an unusually high value for  $\theta$  the validity of the calculated magnetic moment is questionable.

From the standpoint of the familiar valence bond theory, it must be concluded that the uncharged complex,  $[\text{Ni}(\text{POX})_2]$ , is non-planar. Since this material was not exposed to moisture but was handled only in a dry box, it is concluded that the substance does not exist as a hydrated species such as  $[\text{Ni}(\text{POX})_2(\text{H}_2\text{O})_2]$ . Consequently, a structure is tentatively proposed similar to that suggested for  $[\text{Ni}(\text{POX})(\text{HPOX})]\text{I}$  (structure III), in which

the oxime oxygens are assumed to act as donors. This is similar to the structure proposed by Stratton<sup>7</sup> for paramagnetic bis-(salicylaldehyde)-nickel(II), in which uncoordinated hydrazone  $-NH_2$  groups are assumed to act as donors to nickel atoms of adjacent molecules, resulting in an octahedral configuration about nickel. The apparent aversion for a planar configuration shown by these compounds is considered to be most unusual.

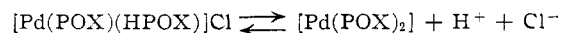
**Palladium(II) and Platinum(II) Complexes.**—Palladium(II) and platinum(II) behave exactly as one might expect in their coordination with 2-pyridinaldoxime. They readily precipitate the complexes of the relationship  $[M^{II}(\text{POX})_2]$  from aqueous solutions containing two equivalents of base, in sharp contrast to the corresponding nickel(II) system.

The bis-(2-pyridinaldoxime)-palladium(II) complex is a strong dibasic acid. The titration of a mixture containing two moles of ligand and one mole of palladium(II) with sodium hydroxide proceeds to a sharp break in  $pH$  at two equivalents of base with no perceptible inflection in the curve at one equivalent. The shape of the curve is typical of a strong acid-strong base titration.

From the observation it might be expected that other palladium(II) complexes could not be isolated. By adding concentrated hydrochloric acid to a solution of ligand and palladium(II), however, a monoprotonated species,  $[\text{Pd}(\text{POX})(\text{HPOX})]\text{Cl}$ , crystallizes. When this compound is dissolved

(7) W. J. Stratton, Ph.D. dissertation, The Ohio State University, 1958.

in methanol, it exhibits the conductivity of a uni-univalent electrolyte ( $86.5 \text{ ohms}^{-1}$ ). Although the ion  $[\text{Pd}(\text{HPOX})_2]^{++}$  is a strong dibasic acid in water, the species in methanol probably is  $[\text{Pd}(\text{POX})(\text{HPOX})]^+\text{Cl}^-$ . This point of view is supported by the realization that ionization of the ligand proton according to the equation



should give rise to a much higher value of the conductivity because of the high conductance of the hydrogen ion.

The only platinum(II) complex which has been isolated in pure form is the uncharged complex,  $[\text{Pt}(\text{POX})_2]$ . Attempts to prepare other species have resulted only in mixtures. The  $pH$  of the solution must be raised to the neutral point in this preparation in order to obtain a reasonably pure product.

On recrystallization of the platinum(II) compound, a light tan material, insoluble in chloroform, is separated from the major product. Analysis of this material suggests it to be the mono-(2-pyridinaldoxime) complex salt  $\text{Na}[\text{Pt}(\text{POX})\text{Cl}_2]$ . This is not surprising considering the tendency of palladium and platinum to form similar species, *i.e.*,  $[\text{Pt}(\text{bipy})\text{Cl}_2]$ . A similar palladium(II) complex,  $[\text{Pd}(\text{POX})\text{Cl}]_2$ , has been obtained but under somewhat different conditions. It will be described in a later paper.

**Acknowledgment.**—These investigations were greatly facilitated by the generous support of the National Institutes of Health.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

## The Complexes of Pyridinaldazine. III. Infrared Spectra and Continued Synthetic Studies

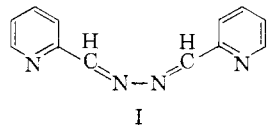
BY WILMER J. STRATTON AND DARYLE H. BUSCH

RECEIVED FEBRUARY 25, 1960

Investigations on the transition metal complexes of pyridinaldazine (PAA) have been extended to cobalt and copper, and these four new compounds are reported:  $[\text{Co}_2(\text{PAA})_3]_2 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Cu}(\text{PAA})\text{Cl}]\text{Cl}$ ,  $[\text{Cu}_2(\text{PAA})\text{Cl}_4]$ ,  $[\text{Cu}_2(\text{PAA})\text{Cl}_2]$ . The new ligand, biacetylhydrazone-azine (BHA) forms bridged dinuclear complexes,  $\text{M}_2(\text{BHA})_3^{+4}$ , with iron (II) and nickel (II), which are similar to those characterized in earlier studies with pyridinaldazine. The infrared spectra of the pyridinaldazine complexes exhibit features which support the rather unusual structures suggested for these interesting compounds. The tridentate chelation of PAA is accompanied by distinct splittings of the high frequency pyridine-ring vibration and of the  $\text{C}=\text{N}$  stretching mode of the azine link, thus distinguishing between these and the bridged dinuclear complexes, in which the PAA is symmetrically coordinated.

### Introduction

It has been shown in earlier investigations<sup>1</sup> that 2-pyridinaldazine forms some unusual and rather



interesting coordination compounds with iron(II) and nickel(II). Upon reaction of 2-pyridinaldazine (abbreviated PAA) with iron(II) or nickel(II)

(1) W. J. Stratton and D. H. Busch, *THIS JOURNAL*, **80**, 1286, 3191 (1958).

salts in aqueous solution at room temperature, compounds of the type  $\text{M}_2(\text{PAA})_3\text{X}_4$  were obtained. Upon heating or prolonged standing in aqueous solution, these substances were converted into compounds of the type  $\text{M}(\text{PAA})_2\text{X}_2$ . The latter compounds contained complex cations of the expected type in which each of the two ligand molecules was assumed to be coordinated in a tridentate manner to a single metal ion (structure II).

The highly unusual  $\text{M}_2(\text{PAA})_3\text{X}_4$  compounds were investigated by means of conductivity, magnetic susceptibility and spectrophotometric (visible region) measurements and, on the basis of these studies, it was concluded that they contained a