J. Inorg. Nucl. Chem., 1965, Vol. 27, pp. 345 to 351. Pergamon Press Ltd. Printed in Northern Ireland

INTERACTION OF AMINES AND SOME NICKEL (II) SCHIFF-BASE COMPOUNDS—I

AMINE EXCHANGE

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(*Received* 6 *July* 1964)

Abstract—The scope of *in situ* preparations of nickel (II) Schiff-base compounds is considered with respect to nickel (II) ion, substituted salicylaldehydes, and various amines, and the effectiveness of the method is disscussed with respect to preparation of the Schiff-base ligands and nickel (II) Schiff-base compounds. Amine exchange as a method of preparation is discussed and compared with the method of direct amine addition to bis(salicylaldehydo)nickel (II). Some new Schiff-base compounds of nickel (II) are reported and characterized. Several examples of anomalous amine exchange are described which involve dehalogenation of chloroform solvent.

Two kinds of interactions between an amine and a nickel (II)–chelate compound may be expected. First, the amine may co-ordinate to the nickel (II) ion, forming a new compound in which nickel has an expanded co-ordination number. Secondly, reaction with the co-ordinated ligand may occur, such as condensation with a β-diketone to form a β-ketoimine, or in the case of imine coordination, $>C{=}N \rightarrow$ Ni(II), the interaction may result in amine exchange or transamination. The second kind of interaction is of interest because of its preparative significance, and because of the relation to biological processes of transamination and deamination. These processes, with intermediate formation of Schiff-bases, have long been known to occur in biological systems.(1) Previous workers have found that amine exchange occurs readily with bissalicylaldiminocopper(II)compounds,(2,3) and only infrequently with bis(β-ketoimino)copper (II) compounds.(1) The first example of an amine exchange reaction of a nickel (II) β-ketoimine has recently been reported.(4) It seemed desirable to extend the investigation of the scope of amine exchange to other nickel (II) derivatives of Schiff-base compounds. The results of a study of amine exchange are reported in the present communication. A subsequent communication will describe the results of adduct formation.

EXPERIMENTAL

Materials. Unless otherwise noted, the synthesis and properties of the ligands and metal-chelate compounds have been described previously.(1,5,6)

Preparation of nickel (II) derivatives of Schiff-bases. Two methods were used for the preparation of the metal-chelate compounds. *Constituent combination* was effected by mixing an aqueous or

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(3) H. S. VERTER and A. E. FROST, *J. Amer. Chem. Soc.* **82**, 85 (1960).

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ammoniacal solution of the nickel (II) acetate and an ethanolic solution of the aldehyde and amine. The desired product precipitated upon mixing. *Amine exchange* took place upon the addition of a three-fold excess of amine to an ethanolic solution of the nickel (II) Schiff-base chelate compound and subsequent heating at reflux temperature for two hours. The properties of compounds prepared by the two methods are listed in Tables 1 and 2. The synthesis of the following two compounds are typical.

Bis(N-ethylsalicylaldimino)nickel (II) (constituent combination). To a stirred solution of salicylaldehyde (2·44 g., 0·02 mole) and ethylamine (0·9 g, 0·02 mole) was added a solution of nickel (II) acetate tetrahydrate (2·5 g, 9 mmole) in 50 ml of water. A green precipitate began to form. The stirring was continued for 2 hrs. The green precipitate was collected by filtration and was recrystallized from ether.

Bis(N-n-butylsalicylaldimino)nickel (II) (amine exchange). Bis(salicylaldimino)nickel (II) (2·99 g, 0·01 mole) and butylamine (2·3 g, 0·031 mole) were dissolved in 250 ml of chloroform. The solution was refluxed for 8 hr. During this time, a colour change from brown to deep green and some formation of a green precipitate occurred. The solution was evaporated to 50 ml, and the green precipitate was separated by filtration, using a sintered glass filter. The precipitate was recrystallized from ethanol.

Bis(N-phenylsalicylaldimino)nickel (II) (Schiff's method). To 250 ml of ethanol was added 3·36 g (0·01 mole) of bis(salicylaldehydo) nickel (II) dihydrate followed by 1·66 g (0·021 mole) of aniline. The solution was refluxed for 20 hr during which time dark green crystals began to form. The solution was evaporated to 50 ml, and the crystals were collected by filtration.

Bis(3-butylimino-1,3-diphenylpropane-1-ono)nickel (II). Bis(3-phenylimino-1,3-diphenylpropane-1-ono)nickel (II) (1·5 g, 2 mmole) was dissolved in 100 ml of butylamine and refluxed for 24 hr. The solution was then evaporated to 10 ml and the green solid which formed was separated by filtration and dried *in vacuo*. (Found, C, 72·63, H, 6·74, N, 4·56; Calc. for $NiC_{38}H_{40}N_2O_2$; C, 72·48, H, 6·51, N, 4·56% m.p. 208°C., yield, 0·48 g or 38%).

The same product was obtained in lower yields (21 per cent) by refluxing bis(3-phenylimino-1,3-diphenylpropane-1-ono)nickel (II) with a five-fold excess of butylamine in an ethanol solvent.

N-(2-thiohydroxyphenyl)salicylaldiminonickel (II). This compound was prepared by constituent combination. A brown precipitate formed which was collected and washed several times with ether, and recrystallized from methanol. The compound was characterized by microanalysis and by infrared spectra, using KBr pellets. A significant feature of the spectra was the absence of a band at 2600 cm^{-1} which is usually attributed to the S—H stretch. The following bands (in cm^{-1}) were observed; 3055 *m*, 3010 *m*, 1604 *s*, 1588 *s*, 1570 *s*, 1528 *s*, 1460 *s*, 1440 *s*, 1371 *s*, 1335 *s*, 1270 *m*, 1250 *s*, 1232 *m*, 1180 *s*, 1148 *s*, 1128 *m*, 1060 *w*, 1039 *m*, 1023 *m*, 972 *w*, 950 *w*, 930 *m*, 860 *w*, 845 *w*, 806 *w*, 748 *s*, 715 *m*, 608 *w*, 555 *s*, 470 *m*, 388 *w*. Band strengths are represented as: *s*, strong; *m*, medium; *w*, weak.

Attempted synthesis of β-ketoimino-nickel (II) compounds by amine exchange. When a solution of 1·3 g (0·002 mole) of bis(3-phenylimino-1,3-diphenylpropane-1-ono)nickel(II) in 100 ml of cyclohexylamine was refluxed for 8 hr, no amine exchange was observed. Only decomposition of the starting nickel salt took place.

The same procedure when used with 2·54 g (0·01 mole) of bis(4-iminopentane-2-ono)nickel (II) in 150 ml of aniline gave only unreacted starting material. (Found, C, 47·53, H, 6·00, N, 10·82, Calc. for $NiC_{10}H_{16}N_2O_2$; C, 47·10, H, 6·20, N, 10·90% m.p. 246°C).

When 150 ml. of butylamine was used, only unreacted starting material was recovered. (Found, C, 48·85, H, 6·87, N, 10·61, Calc. for $NiC_{10}H_{16}N_2O_2$; C, 47·10, H, 6·20, N, 10·90%).

When 150 ml of ethylamine was used decomposition was observed, and the only product, a green precipitate, could not be identified. Nickel (II) ion is known to be soluble in ethylamine, and this was probably a factor in the decomposition of the original nickel–chelate compound.

Bis(N-2-picolylsalicylaldimino)nickel (II): dehalogenation of chloroform. Bis(*N-n*-butylsalicylaldimino)nickel (II) (2 g, 0·005 mole) and 2-aminomethylpyridine (2 g, 0·02 mole) were dissolved in 300 ml of chloroform. Upon standing at room temperature, the green solution turned brown during a 40 min period. To ensure completion of reaction, the solution was refluxed for 48 hr. Upon filtration, a violet precipitate was deposited from the brown solution. The precipitate was washed with n-pentane and was dried *in vacuo*. To the brown solution was added 200 ml of petroleum ether and 50 ml of water. A brown precipitate which formed was collected by filtration, washed with n-pentane, and dried *in vacuo*.

TABLE 1. PREPARATION OF COMPOUNDS OF THE TYPE $Ni(o\text{-}OC_6H_4CR{=}NR')_2$

R	R′	Method*	m.p.(°C)	Analysis†		
				C	H	N
H	C_6H_5	A	48–49	79·18	5·58	7·11‡
				78·67	5·57	7·28
H	C_6H_5	B	>330	56·25	4·02	9·38§
				56·19	4·04	9·27
H	C_4H_9	A	139	64·29	6·82	6·82
				64·23	7·01	7·00
H	C_4H_9	B	>330	56·25	4·02	9·38§
				57·48	4·49	9·24
H	C_2H_5	A	172–3	60·90	5·64	7·89
				60·91	5·58	7·65
H	C_2H_5	B	>330	56·25	4·02	9·38§
				56·54	4·28	9·15
H	$C_6H_5CH_2$	A	207	70·20	5·02	5·85
				70·64	5·27	6·06
H	$C_6H_5CH_2$	B	207	70·20	5·02	5·85
				70·16	5·21	6·14
H	$p\text{-}NO_2C_6H_4$	A	152–3	64·46	4·13	11·57‡
				63·55	4·20	11·68
H	$p\text{-}NO_2C_6H_4$	B	>330	56·25	4·02	9·38§
				55·67	4·27	9·46
H	CH_3	A	202–4	49·90	4·16	—††
				49·50	4·30	—
H	CH_3	B	>330	56·25	4·02	9·38§
				55·84	4·03	9·38
CH_3	C_6H_5	A	—	Decomposition		
CH_3	C_6H_5	B	>340	58·78	4·90	8·57
				58·77	5·04	8·06
CH_3	C_4H_9	A	—	Decomposition		
CH_3	C_4H_9	B	>340	58·78	4·90	8·57§
				58·88	5·06	8·59
H	C_6H_{11}	A	191	67·43	6·92	6·05
				67·29	6·73	5·79
H	C_6H_{11}	B	193	67·43	6·92	6·05
				66·69	6·90	5·88
			>340	56·25	4·02	9·38§
				55·33	4·00	9·53
H	$o\text{-}C_5H_4NCH_2$	A	d246–9	64·93	4·58	11·65
				64·21	5·49	10·97
H	$o\text{-}C_5H_4NCH_2$	B	d245–7	64·93	4·58	11·65
				63·91	5·22	11·21
H	$(CH_2CH_2)_{1/2}$	A	330–3	59·13	4·31	8·61
				58·95	4·17	8·51
H	$(CH_2CH_2)_{1/2}$	B	331	59·13	4·31	8·61
				58·75	4·08	8·34
H	$(o\text{-}C_6H_4S)_{1/2}$	A	d190	54·60	3·15	4·90
				53·90	3·61	5·01
H	$(o\text{-}C_6H_4S)_{1/2}$	B	d188	51·53	3·97	9·25
				50·24	3·12	8·44
H	C_4H_9	C	>330	56·25	4·02	9·38
				55·85	3·93	8·88
H	C_6H_5	C	>330	56·25	4·02	9·38
				55·81	3·79	8·97

* Constituent combination; A, aqueous nickel ion; B, ammoniacal nickel ion; C, hexaammine-nickel (II) bromide.

† First line, calculated; second line, found.

‡ Ligand only.

§ Calculated for amine.

†† Analysis for bis(salicylaldehydo)nickel (II) dihydrate.

The violet material was water soluble and gave a white precipitate upon addition of silver nitrate. A positive Bielstein test indicated the presence of chloride ion. Microanalytical data correspond to those expected for bis(2-aminomethylpyridine)nickel (II) chloride dihyrate. (Found, C, 37·59, H, 5·33, N, 14·30, Calc. for $NiC_{12}H_{16}N_4Cl_2{\cdot}2H_2O$; C, 37·83, H, 5·25, N, 14·71% Yield, 0·8 g., 59%). The properties of this material were the same as a sample prepared by an unambiguous method.(4)

The brown material was bis(N-2-picolylsalicylaldimino)nickel (II). (Found, C, 64·21, H, 5·49, N, 10·97, Calc. for $NiC_{26}H_{22}N_4O_2$; C, 64·93, H, 4·58, N, 11·65% Yield, 0·48 g, 20%.)

The following bands were observed in the infra-red spectra of the nickel compound taken by means of KBr pellets: 3080 *m*, 3050 *m*, 3020 *m*, 2900 *m*, 2800 *m*, 1640 *s*, 1630 *s*, 1600 *s*, 1575 *s*, 1531 *s*, 1488 *s*, 1470 *s*, 1452 *s*, 1420 *s*, 1405 *s*, 1350 *s*, 1288 *s*, 1251 *w*, 1220 *w*, 1190 *s*, 1155 *s*, 1131 *s*, 1110 *w*, 1068 *m*, 1052 *s*; 1036 *m*, 1021 *m*, 1003 *w*, 913 *s*, 849 *m*, 758 *s*, 739 *s*, 660 *m*, 627 *w*, 580 *m*, 537 *m*, 493 *m*, 472 *m*, 425 *m*. The bands are in cm^{-1}, with band strengths represented as: *s*, strong; *m*, medium; *w*, weak.

TABLE 2.—PREPARATION OF COMPOUNDS OF THE TYPE, $Ni(o\text{-}OC_6H_4CH{=}NR)_2$*

R	m.p.(°C)	Yield (%)	Analysis†		
			C	H	N
C_6H_5	269–71	88	69·22	4·44	6·21
			69·18	4·53	6·28
CH_3	204–6	67	58·78	4·90	8·57
			56·97	4·81	8·54
C_4H_9	139	94	64·29	6·82	6·82
			64·02	6·87	7·01
C_6H_{11}	191	89	67·43	6·92	6·05
			67·32	6·75	5·84
$o\text{-}C_5H_4NCH_2$	210	91	64·93	4·58	11·65
			64·27	4·02	10·91
$o\text{-}C_6H_4SH$	—		Decomposition		

* Co-ordinated carbonyl condensation;

$$Ni(o\text{-}C_6H_4CHO)_2 + 2\,RNH_2 \rightarrow Ni(o\text{-}OC_6H_4CH{=}NR)_2 + 2H_2O.$$

† First line, calculated; second line, found.

Amine exchange under forcing conditions; formation of trisethylenediaminenickel (II) carbonate. Bis(4-iminopentane-2-ono)nickel (II) (2·54 g, 0·01 mole) was dissolved in 100 ml of ethylenediamine and allowed to reflux for 48 hr. A pink product was formed which was separated by filtration and washed with ether. The material was water soluble, and the solution gave a white precipitate upon addition of silver nitrate. Microanalysis corresponded to that for trisethylenediaminenickel (II) carbonate. (Found, C, 30·78, H, 7·97, N, 28·21, Calc. for $NiC_7H_{24}N_6O_3$; C, 28·14, H, 8·03, N, 28·14% m.p. (decomp.) 240°C, yield, 0·72 g, 24%).

The same reaction in propylenediamine gave an analogous pink material as product having similar properties. This was found to be trispropylenediaminenickel (II) carbonate. (Found, C, 37·55, H, 8·74, N, 23·61, Calc. for $NiC_{10}H_{30}N_6O_3$; C, 34·59, H, 8·65, N, 24·21. M.p. (decomp.) 280°C, yield, 0·71 g, 21%).

When a 2:1 excess of ethylenediamine or propylenediamine was added to bis(4-iminopentane-2-ono)nickel (II) and the solution refluxed for 2 hr, only the unreacted nickel (II)–chelate compound was obtained.

DISCUSSION

Direct combination reactions. Because of the current interest in nickel Schiff-base compounds, it seems appropriate to comment on some methods of preparation (other than chelate exchange(5) or template synthesis(4,7)). N-Substituted salicylaldimine-nickel (II) compounds, used in this study, were prepared by several methods, one of

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(7) E. J. OLSZEWSKI, L. J. BOUCHER, R. W. OEHMKE, J. C. BAILAR, Jr. and D. F. MARTIN, *Inorg. Chem.*, **2**, 661 (1963).

which was constituent combination. This consisted of the reaction of salicylaldehyde, amine, and nickel (II) ion. Depending upon the basicity of the amine that was present, one of three reactions was observed:

(1) Ligand Condensation:

$$o\text{-HOC}_6\text{H}_4\text{CHO} + \text{RNH}_2 \xrightarrow{\text{Ni}^{2+}} o\text{-HOC}_6\text{H}_4\text{CH}{=}\text{NR} + \text{H}_2\text{O} \qquad (1)$$

(2) Condensation and Chelation:

$$o\text{-HOC}_6\text{H}_4\text{CHO} + \text{RNH}_2 \xrightarrow{\text{Ni}^{2+}} (o\text{-OC}_6\text{H}_4\text{CH}{=}\text{NR})_2\text{Ni} \qquad (2)$$

(3) Amine Exchange:

$$o\text{-HOC}_6\text{H}_4\text{CHO} + \text{RNH}_2 \xrightarrow[\text{NH}_3]{\text{Ni}^{2+}} (o\text{-OC}_6\text{H}_4\text{CH}{=}\text{NH})_2\text{Ni} + \text{RNH}_2 \qquad (3)$$

Ligand condensation (Equation 1) occurred when a relatively weak base (aniline, *p*-nitroaniline) was used, though generally condensation and coordination (Equation 2) was observed. In an effort to effect condensation, an ammoniacal solution of nickel ion was used, but amine exchange (Equation 3) was observed in several cases (methyl-, ethyl-, and butyl-amine, aniline and *p*-nitroaniline). In one instance (cyclohexylamine), both complex formation and amine exchange occurred.

Constituent combination reactions with 2-aminobenzenethiol or 2-aminomethylpyridine gave (N-2-thiohydroxyphenyl)salicylaldiminonickel (II) and bis (N-2-picolylsalicylaldimino)nickel (II) respectively. The 2-aminobenzenethiol derivative indicated the formation of a three-coordinate nickel compound, on the basis of analytical data and the absence of the SH stretch band in the infrared absorption spectrum. It is probable that the material is dimeric containing bridging sulphur atoms; however, the poor solubility of the compound in most common organic solvents precluded the determination of its molecular weight.

Constituent combination was studied with compounds related to salicylaldehyde. When *o*-hydroxyacetophenone and aniline or butylamine were condensed in the presence of nickel ion either decomposition or amine exchange occurred, depending upon whether an aqueous or an ammoniacal solution was used. When β-diketones (acetylacetone, benzoylacetone, dibenzoylmethane) were used, decomposition was observed in most cases, or formation of the bis(β-diketono)nickel (II) compound (dibenzoylmethane and benzoylacetone with aniline or butylamine). Ammoniacal nickel solutions often gave nickel (II) hydroxide.

Constituent combination offered the advantages of being rapid and of giving nearly quantitative yields. The products were not obtained as oils, which was a contrast to the experience of other workers, and the products were obtained in a good state of purity. It should be noted that the procedure used in this study did not involve the use of large excess of ligand or amine, and non-volatile base (sodium hydroxide or sodium acetate) was not used.

Co-ordinated carbonyl condensation. A variation of the constituent combination procedure permitted the scope of the reaction to be extended to the preparation of compounds derived from weakly basic amines. The first variation consisted in adding a primary amine to an ethanolic slurry of bis(salicylaldehydo)nickel (II) dihydrate.

$$(o\text{-OC}_6\text{H}_4\text{CHO})_2\text{Ni} + 2\text{RNH}_2 \rightarrow (o\text{-OC}_6\text{H}_4\text{CH}{:}\text{NR})_2\text{Ni} + 2\text{H}_2\text{O} \qquad (4)$$

Generally, stoichiometric amounts of amine were used to avoid contamination of the product with excess amine, a difficulty which other workers have described.(8) A slight excess of amine was used in order to avoid contamination by unreacted starting material. The slight disadvantage in this method, the synthesis of bis(salicylaldehyde)-nickel (II), was not serious.

TABLE 3.—AMINE EXCHANGE REACTIONS*

			Product analysis†	
R	R'NH$_2$	C	H	N
C_6H_5	NH_3	56·25	4·02	9·38
		56·43	4·18	9·41
H	*n*-$C_4H_9NH_2$	64·29	6·82	6·82
		63·88	6·84	7·10
C_4H_9	$C_6H_5NH_2$	No reaction		
C_4H_9	NH_3	No reaction		
C_4H_9	$NH_2CH_2CH_2NH_2$	59·13	4·31	8·62
		60·73	4·61	9·21
C_4H_9	*o*-$C_5H_4NCH_2NH_2$	64·93	4·58	11·65
		64·70	5·35	10·72
H	$C_6H_{11}NH_2$	No reaction		
H	*o*-$HSC_6H_4NH_2$	46·95	3·91	9·13‡
		46·62	4·06	9·41
H	$C_6H_5NH_2$	No reaction		

* Ni(*o*-$OC_6H_4CH{=}NR)_2$ + 2 R'NH_2 → Ni(*o*-$OC_6H_4CH{=}NR')_2$ + 2 RNH_2.

† First line, calculated; second line, found.

‡ Analysis is for bis(2-aminobenzenethiolo)nickel (II).

Amine exchange. A second variation, amine exchange or transamination, was studied more extensively. The procedure consisted of the interaction of an amine and a nickel-salicylaldimine compound (Equation 5).

$$(o\text{-}OC_6H_4CH{:}NR)_2 + 2R'NH_2 \rightarrow (o\text{-}OC_6H_4CH{:}NR')_2Ni + 2RNH_2 \qquad (5)$$

While other workers have used the amine R'NH_2 as solvent,(2,9) it was found in this study that a three-fold excess of amine in a neutral solvent, e.g., chloroform, was effective. The yields were nearly quantitative if R'NH_2 was significantly more basic than RNH_2, but the yields were poor (10–20 per cent) if R'NH_2 and RNH_2 had nearly the same basicities. As other workers have found, the reactions did not proceed to completion (even in amine solvents(9)), and it was difficult to determine the rate of exchange spectrophotometrically. The solutions did not always follow Beer's Law, presumably because of solute-solute interactions.(10)

A qualitative order of exchange was obtained by maintaining constant reaction conditions. The order was: R = CH_2—(en) ∼ *o*-$NC_5H_4CH_2$— > $(CH_2)_3CH_3$— > H— > C_6H_5—. A qualitative order of stability may also be inferred from these data. The fact that bis(N-phenylsalicylaldimino)nickel (II) underwent exchange with

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(9) Y. MUTO, *Bull. Chem. Soc., Japan* **33**, 1242 (1960).

(10) R. H. HOLM, *Advances in the Chemistry of the Co-ordination Compounds* (Edited by S. KIRSCHNER) p. 341. Macmillan, New York (1961).

butylamine, although bis-(N-n-butylsalicylaldimino)nickel (II) did not undergo exchange with aniline, might indicate that the stability of the N-n-butyl derivative is greater than that of the N-phenyl derivative.

In contrast to salicylaldimine complexes, β-ketoimine compounds underwent decomposition under amine exchange conditions, especially when forcing conditions were used. Only one example of amine exchange was observed: bis(3-butylimino-1,3-diphenylpropane-1-ono)nickel (II) was prepared by refluxing the phenylimino derivative in butylamine. On the other hand, when bis(4-iminopentane-2-ono)-nickel (II) was heated in ethylenediamine, trisethylenediaminenickel (II) carbonate was obtained; using propylenediamine, trispropylenediaminenickel (II) carbonate was obtained; using chloroform as a solvent, trisethylenediaminenickel (II) chloride was isolated (a 4:1 ratio of ethylenediamine to nickel was used).

Amine exchange could not be effected by addition of catalytic amounts of amine hydrochloride or acetic acid to amine-bis(β-ketoimino)nickel (II) solutions. No reaction was observed with small amounts of acid; with large quantities, decomposition took place.

Anamolous amine exchange was also observed with bis(N-butylsalicylaldimino)-nickel (II). When the complex and 2-aminomethylpyridine were heated in methanol, the expected amine-exchange product, a brown solid, was obtained. In chloroform solution, a violet, water-soluble material was obtained. This material contained chloride ion, and it was found to be bis(2-aminomethylpyridine)nickel (II) chloride dihydrate on the basis of analytical data and comparison with an authentic sample. The only way chloride ion could be obtained was by dehalogenation of chloroform, it is likely that a carbene intermediate was involved. The dehalogenation reaction has not been investiagted thoroughly, but certain observations are pertinent. It is probable that the bidentate amine abstracts a proton by chelation from chloroform; since amines are known to effect dehalogenation of chloroform.(11) It could well be that the nickel ion is involved only in the formation of insoluble bis(2-aminomethylpyridine)nickel (II) chloride. The formation of this compound is probably the driving force of the reaction. It should be noted that in an atmosphere of air, the yield of bis(2-aminomethylpyridine)nickel (II) chloride was 80 per cent; in a nitrogen atmosphere, only a 15 per cent yield was obtained. The dehalogenation reaction is being investigated further.

Acknowledgement—This investigation was supported by P.H.S. Research Grant 7873, Division of General Medical Sciences, U.S. Public Health Service.

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