J. Inorg. Nucl. Chem., 1964, Vol. 26, pp. 1577 to 1587. Pergamon Press Ltd. Printed in Northern Ireland

# BASE-CATALYSED CONDENSATIONS OF A METAL-CHELATE TEMPLATE

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(Received 30 December 1963; in revised form 5 February 1964)

Abstract—The synthesis of condensation products of ethylenediamine with  $\beta$ -diketones,  $\beta$ -ketoimines, and with substituted salicylaldehydes and *o*-hydroxyacetophenones is reported. Some physical and chemical properties of the compounds are discussed. The scope of the reaction is considered with respect to catalysts, metal-chelate templates and condensed ligands. The absorption spectra of the compounds are reported. The reaction mechanism is discussed, and ebullioscopic, conductometric and spectroscopic evidence is offered which indicates the stoicheiometry and the stereochemistry of the reaction intermediates.

THE preparation of bisacetylacetone-ethylenediiminonickel (II) and related complexes has been achieved by condensation of an appropriate  $\beta$ -diketone with bisethylene-diaminenickel (II) chloride.<sup>(1)</sup>



It was suggested<sup>(1)</sup> that this was an example of a "template synthesis", i.e. a synthesis in which the coordination sphere of a metal ion or metal-chelate compound acts as a "template" and induces ligand molecules to orient in a manner that is suitable for condensation and complex formation.\* The condensation described in Equation (1) requires the addition of pyridine as a catalyst which is believed to replace the bridging chloride ions in bisethylenediaminenickel (II) thus allowing acetylacetone (or acetylacetonate ion) to co-ordinate to the nickel (II) complex. The co-ordinated acetylacetone molecule would be in the environment of the ethylenediamine molecules and condensation would be facilitated. The present paper offers additional evidence to support and clarify this mechanism, the scope of the reaction is indicated, and the preparation and characterization of a number of new compounds is described.

### Materials

## EXPERIMENTAL

Tetrakisethylenediamine-µ-dichlorodinickel(II) chloride. The compound was prepared using the

\* Other examples of template synthesis have been observed.<sup>(2)</sup>

<sup>&</sup>lt;sup>(1)</sup> E. J. OLSZEWSKI, L. J. BOUCHER, R. W. OEHMKE, J. C. BAILAR, JR. and D. F. MARTIN, *Inorg. Chem.* 2, 661 (1963).

<sup>&</sup>lt;sup>(2)</sup> Reactions of Coordinated Ligands. (Edited by R. F. GOULD and D. H. BUSCH.) Advances in Chemistry Series No. 37 (1963).



AS PREPARED BY A TEMPLATE SYNTHESIS

		m.p.	Yield		Analysis*			
Z	Y	(°Ċ)	(%)	С	Ĥ	N	Colour	
H†	Н	350	94	58.83	4.31	8.62	Brown	
				58-39	4.24	8.64		
5-Cl	н	330	83	48.82	3.07	7.11	Brown	
				49.22	3.41	6.86		
5-Br	Н	330	97	39.82	2.51	5.80	Ochre	
				40.23	2.85	5.49		
3-OCH <sub>3</sub> ,	н	d280	71	39.82	2.95	5.16	Olive	
5-Br				38.71	2.69	5.04		
4-CH <sub>3</sub>	н	320	89	61.30	5.14	7.94	Brown	
				59-53	5.47	7.62		
3-NO <sub>3</sub>	н	360	96	46.34	2.90	13.51	Orange	
				45.92	2.92	13.40	-	
5-NO <sub>3</sub>	Н	350	95	46.34	2.90	13.51	Orange	
				45.47	2.71	12.94	-	
4-OH	Н	350	86	53.88	3.93	7.85	Red-brown	
				53.72	4.25	7.29		
5-OH	н	340	97	53.88	3.93	7.85	Brown	
				53.14	3.68	7.40		
2,4-								
di-OH	CH3	320	54	56.15	4.68	7.28	Red	
				55.33	4.51	7.14		
2,5-								
di-OH	CH3	310	67	56.15	4.68	7.28	Brown	
				55.69	4·70	6.77		
2-OH†	CH <sub>3</sub>	290	81	61.24	5.10	7.94	Tan	
				61.72	5-47	8.27		

\* First line represents calculated percent, second line found.

† Compounds previously reported, cf. Reference (10).

procedure of STATE.<sup>(4)</sup> (Found: C, 19·47; H, 6·51; N, 22·21. m.p., 270°C, yield 82%. Calc. for  $C_8H_{32}N_8Cl_4Ni_2$ ; C, 19·23; H, 6·46; N, 22·43%).

Tetrakispropylenediamine- $\mu$ -dichlorodinickel (II) chloride. This was prepared by the same method except that precipitation of the blue compound required 550 ml of acetone rather than 100 ml. The product precipitated as a blue oil, which was made to crystallize by repeated washings with *n*-pentane. (Found: C, 23.28; H, 7.94; N, 17.45. m.p., 65–6°C; yield 78%. Calc. for C<sub>12</sub>H<sub>40</sub>N<sub>8</sub>Cl<sub>4</sub>Ni<sub>2</sub>.2H<sub>2</sub>O: C, 22.96; H, 7.65; N, 17.86%).

Bisethylenediaminecopper (II) chloride. This compound was prepared by addition of 12 g (0.2 mole) of ethylenediamine in 10 ml of water to 16.9 g (0.1 mole) of cupric chloride dihydrate dissolved in 50 ml of water. The deep blue solution was evaporated almost to dryness. Two drops of ethylenediamine was added, and the oil was cooled in an ice-bath. After repeated washings of the oil with acetone and n-pentane, a blue powder was obtained. (Found: C, 18.70; H, 6.11; N, 21.84. m.p., 218–20°C; yield 88%. Calc. for C<sub>4</sub>H<sub>18</sub>N<sub>4</sub>Cl<sub>2</sub>Cu: C, 18.87; H, 6.29; N, 22.02%).

*Tris*-(2-aminomethylpyridine)nickel (II) chloride. To a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (2·38 g, 0·01 mole) in 10 ml of water was added a solution of 2-aminomethylpyridine (3·5 g, 0·032 mole) in 40 ml of methanol. The purple solution was filtered and the filtrate evaporated to dryness on a steam bath. The violet precipitate was washed successively with ether, acetone, and n-pentane and was dried *in vacuo*. (Found: C, 44·01; H, 5·73; N, 16·74. m.p. 174–6°C, yield 89%. Calc. for  $C_{18}N_{24}N_6Cl_2Ni\cdot2H_2O$ ; C, 44·21; H, 5·73; N, 17·19).

Bisethylenediamine-2-aminomethylpyridinenickel (II) chloride. To a solution of tetrakisethylenediamine- $\mu$ -dichlorodinickel (II) chloride (0.5067 g, 0.001 mole) in 40 ml of methanol was added 2-aminomethylpyridine (0.200 g, 0.0019 mole). A change in colour of the solution from blue to violet was observed. The solvent was evaporated to dryness by heating gently on a steam bath. The violet precipitate was washed successively with ether, acetone and n-pentane. The product was very hygroscopic, and care had to be taken to insure dryness. (Found: C, 31.43; H, 6.91; N, 21.43; yield 91 %. Calc. for C<sub>10</sub>H<sub>24</sub>N<sub>6</sub>Cl<sub>2</sub>Ni-2H<sub>2</sub>O; C, 30.56; H, 7.13; N, 21.39%).

The complex was run through a column of alumina with a methanol solvent to check whether the compound obtained was not instead a mixture of trisethylenediaminenickel (II) chloride and tris-2-(aminomethyl)pyridinenickel (II) chloride as a result of disproportionation. Only a single violet band was observed.

### Ligands

All salicylaldehydes, *o*-hydroxyacetophenones and  $\beta$ -diketones used were either commercial samples or student preparations. The synthesis and properties of the  $\beta$ -ketoimines are described elsewhere.<sup>(4)</sup>

#### Amine catalysed condensations

The condensation of salicylaldehydes, *o*-hydroxyacetophenones, or  $\beta$ -ketoimines with nickel (II) diamine compounds was effected using the following procedure; the products are described in Tables 1 and 2.

The appropriate keto compound (0.02 mole) dissolved in 20 ml of methanol was added to a mixture of tetrakisethylenediamine- $\mu$ -dichlorodinickel (II) chloride (0.005 mole or 2.49 g) and pyridine (four drops) dissolved in 60 ml methanol. The material was allowed to reflux for 2 hr. As the reaction proceeded, the solution changed in colour from blue-green to brown and the product precipitated from solution. The precipitate was collected in a sintered glass funnel and washed twice with 50 ml portions each of water, methanol and ether respectively.

For certain of the ligands, viz., 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, and 3-methoxy-5-bromosalicylaldehyde, precipitation occurred immediately upon addition of reactants, and refluxing was continued only for 2 hr to ensure completion of reaction. For other ligands, such as 4-hydroxysalicylaldehyde and 2,4-dihydroxyacetophenone, refluxing was continued for 72 hr.

Condensations of  $\beta$ -ketoimines gave the same condensation products as the analogous  $\beta$ -diketones. The products are described in Table 3. The procedures are as follows: Bisacetylacetoneethylenediiminonickel (II). To 0.2496 g (0.0005 mole) of tetrakisethylenediamine-

Bisacetylacetoneethylenediiminonickel (II). To 0.2496 g (0.0005 mole) of tetrakisethylenediamine-  $\mu$ -dichlorodinickel (II) chloride was added five drops of pyridine. To this moist mixture was added enough methanol to make a thick paste. Finely ground acetylacetoneimide (0.210 g, 0.00212 mole) was then added and mixed intimately with the paste. The mixture was then heated gently in a testtube over an open flame. Formation of dark brown crystals indicated condensation. The residue was washed (and filtered) twice each with 40 ml portions of water, methanol and ether respectively.

Bisbenzoylacetoneethylenediiminonickel (II). A mixture of tetrakisethylenediamine- $\mu$ -dichlorodinickel (II) chloride (0·2496 g, 0·0005 mole) and five drops of pyridine was dissolved in 50 ml of hot methanol. To this was added 1-phenyl-(3-imino)-1-butanone (0·322 g, 0·002 mole) or 1-phenyl-(3-phenylimino)-1-butanone (0·454 g, 0·002 mole) dissolved in 20 ml of hot methanol. The solution was allowed to reflux for 48 hr. During this time, formation of dark brown crystals of bisbenzoylacetoneethylenediiminonickel (II) occurred. The reaction mixture was filtered through a sintered glass funnel and washed successively with 40 ml portions of water, methanol and ether and dried *in vacuo*.

<sup>(3)</sup> H. M. STATE, Inorganic Syntheses VI, 198 (1960).

(4) T. M. HSEU, D. F. MARTIN and T. MOELLER, Inorg. Chem. 2, 587 (1963).



	Yield		Analysis*				
Z	(%)	С	Ĥ	Ν	Colour		
5-Cl†	84	50.16	3.44	6.88	Brown		
		49.47	3.98	6.93			
5-Br	90	41.09	2.82	5.64	Brown		
		40.81	3.11	5.53			
3-OCH₃,	81	38.31	3.38	5.26	Brown		
5-Br		38.95	3.89	4.77			
4-CH <sub>3</sub>	85	62·17	5.45	7.64	Tan		
		61.80	5.67	7.28			
3-NO <sub>2</sub>	88	47.59	3.27	13.07	Orange		
		47.11	3.43	13.13	U		
5-NO <sub>2</sub>	92	47.59	3.27	13.07	Orange		
		46.97	3.21	12.82	U		
4-OH	76	55-11	4.32	7.58	Brown-red		
		54.30	4.12	7.01			
5-OH	49	55.11	4.32	7.58	Dark brown		
		54.76	4.69	7.46			

AS PREPARED BY TEMPLATE SYNTHESIS

\* First line represents calculated percent, second line found.

<sup>†</sup> None of the compounds were found to melt up to 330°C.

	m.p.	Yield	Analysis†			
Ligand*	(°Ċ)	(%)	С	Ĥ	N	
Acetylacetoneimide	201	12	51.25	6.41	9.97	
-			51.41	6.63	9.58	
1-Phenyl(-3-phenyl-						
imino)-1-butanone	290	69	65.23	5.44	6.92	
			64.62	5.54	7.00	
1-Phenyl(-3-imino)-						
1-butanone	289	28	65.23	5.44	6.92	
			65.44	5.02	6.67	

Table 3.—Compounds of the type  $Ni[RCOCHCR'=NCH_2]_2$  prepared by a template synthesis

\*  $\beta$ -Ketoimine used as starting material.

† First line represents calculated per cent, second line found.

# Molecular weight determinations

Due to the low solubility of the compounds in such common solvents as acetone, chloroform, carbon tetrachloride, benzene and ethanol, it was not possible to obtain molecular weights of the new condensation products listed in Tables 1 and 2.

The molecular weight of tetrakisethylenediamine-µ-dichlorodinickel (II) chloride in absolute

ethanol was determined ebullioscopically by Mr. J. NEMETH. The apparent molecular weight was 213, indicating an actual molecular weight of 639; calculated, 501.04.

### Nuclear magnetic resonance

Spectra were examined at 40°C using a Varian A-60 instrument. Poor solubility of the compounds in suitable solvents tended to complicate their nuclear magnetic resonance spectra. For partially soluble samples such as these, the increase in receiver sensitivity necessary to obtain a measurable signal tended to produce a broad solvent band envelope. The solutions could not be made sufficiently concentrated to give a good signal-to-noise ratio. The solvent peak for dimethyl sulphoxide was discernible at 7.5 p.p.m. with respect to tetramethyl silane (T = 10) although the solvent bands were spread over the area 6.1 to 8.7 T. At higher temperatures, the solubility of a number of the compounds in dimethyl sulfoxide increased considerably. However, at 40°C and with increased amplitude no additional bands were observed. The spectrum was scanned from -2,000 to +500 c/s with respect to tetramethyl silane.

#### Absorption spectra

Ultra-violet and visible absorption spectra of methanol and water solutions were obtained using a Cary Model 14 M spectrophotometer. Job's titrations were made using the Cary Model 14 M, and Beckmann DU spectrophotometers, using one or two centimeter optics. Infra-red absorption spectra were determined using a Perkin-Elmer Model 21 spectrophotometer and using potassium bromide disks.

#### Conductance measurements

Conductance measurements were made using a model RC 16B Conductivity Bridge, with a bridge frequency of 50–60 c/s. A dipping electrode with platinum black plates was used, with a cell constant of k = 1.05184 cm<sup>-1</sup>. Into an air-tight beaker containing a magnetic stirring bar was added 200 ml of dry methanol (resistance,  $1.06 \times 10^7 \Omega$ ). This was titrated with  $6.5 \times 10^{-2}$  M pyridine. A second run was made in which 25 ml of tetrakisethylenediamine- $\mu$ -dichlorodinickel (II) chloride ( $6.5 \times 10^{-2}$  in Ni(II) ion) was added to 175 ml of methanol and likewise titrated with pyridine of the same concentration.

#### RESULTS

### Infra-red spectra

The spectra for the nickel (II) complexes of bisacetylacetoneethylenediamine, bisbenzoylacetoneethylenediamine, bisacetylacetonepropylenediamine, and bisbenzoylacetonepropylenediamine are identical to those reported elsewhere,<sup>(5)</sup> and are not included in this paper. Although the spectra for bis-salicyladehyde-ethylenediamine appears in the literature,<sup>(6)</sup> it is included here as the parent compound of the series, and also to indicate digressions from some of the band assignments previously made. Significant band assignments are indicated in Tables 4 and 5 and are consistent with previous assignments.<sup>(5-10)</sup>

### Ultra-violet absorption spectra

The spectra of methanolic or aqueous pyridine solutions has a triplet at 250, 256 and 263 m $\mu$  ( $\epsilon = 25,207, 28,896$  and 19,059) respectively. There is no change in the position or intensity of the triplet when bisethylenediaminenickel (II) chloride is added to the solution; the intensity of the triplet is directly related to the pyridine

- <sup>(6)</sup> K. UENO and A. E. MARTELL, J. Phys. Chem. 60, 1270 (1956).
- <sup>(7)</sup> L. J. BELLAMY, The Infra-red Spectra of Complex Molecules, Methuen, London (1960).
- <sup>(8)</sup> B. DAS SARMA and J. C. BAILAR, JR. J. Amer. Chem. Soc. 77, 5476 (1955).
- <sup>(9)</sup> L. A. KAZITSYNA, N. B. KUPLETSKAYA and YU. A. KOLESNIK, Zh. Obshch. Khim. 32, 1586 (1962)
- <sup>(10)</sup> R. L. BELFORD, A. E. MARTELL and M. CALVIN, J. Inorg. Nucl. Chem. 2, 11 (1956).

<sup>&</sup>lt;sup>(5)</sup> K. UENO and A. E. MARTELL, J. Phys. Chem. 59, 998 (1955).



x	Y	Phenyl C—H stretch <sup>(7)</sup>	Symmet- rical and anti- symmet- rical C—H <sup>(7)</sup>	C=N stretch <sup>(8)</sup>	Conju- gated ring inter- action <sup>(7)</sup>	aromatic C=C stretch <sup>(8,9)</sup>	CH <sub>2</sub> defor- mation modes <sup>(5,10)</sup>	C—O stretch <sup>(8)</sup>	C—N stretch <sup>(8)</sup>	NO <sub>2</sub> <sup>(7)</sup>
н	н	3030 m*	2930 m 2860 sh	1628 sh	1600 s	1530 s	1465 sh	1313 s	1204 s	
Н	CH3	3040 m	2960 m 2920 m	1608 s	1580 s	1 <b>528</b> s	1465 sh 1444 s	1309 sh	1 <b>24</b> 6 s	
3NO <sub>2</sub>	Н	3040 m	2930 m 2870 m	1638 sh	1600 s	1550 sh 1530 sh	1465 sh 1442 s	1290 s	1220 sh 1198 sh	1498 s 1335 s
5-NO <sub>2</sub>	н	3080 m	2930 m 2855 sh	1627 sh	1600 s	1547 s	1467 s 1449 sh	1300 s	1208 s	1492 s 1335 s
5-Br, 3-OCH <sub>3</sub>	Н	3080 m	2940 m 2860 sh	1624 s	1600 sh	1537 m	1464 s 1445 sh	1315 s	1220 sh 1195 sh	
5-Br	н	3040 m	2920 m 2860 sh	1628 sh	.1610 sh	1520 s	1450 s 1425 s	1310 s	1202 m	
5-Cl	н	3060 m	2920 m 2860 m	1630 sh	1605 s	1524 s	1450 s 1425 s	1310 s	1205 s	
4-CH <sub>3</sub>	н	3010 m	2910 s 2860 s	1630 sh	1610 s	1545 sh 1530 s	1463 s 1430 sh	1310 s	1225 s 1207 sh	
5-OH	CH3	3080 w	2980 w 2910 sh	1620 w	1575 s	1520 s	1460 s 1425 sh	1315 sh 1295 sh	1225 s	
4-OH	н	3020 m	2980 m 2940 m	1630 s	1595 s	1535 s	1450 s	1285 m	1210 s	
4-OH	CH <sub>3</sub>	3020 m	2980 m 2940 m	1610 s	1590 s	1551 sh 1534 s	1450 s	1285 s	1205 sh	
5-OH	н	3020 m	2980 m 2940 m	1630 s	1611 s	1565 sh 1545 s	1450 s	1300 s	1225 s 1200 sh	

\* s = strong, m = medium, w = weak, sh = shoulder.

concentration. As would be expected, the addition of acid causes significant changes in the spectrum of aqueous pyridine. The addition of hydrochloric acid (molar ratio pyridine:hydrochloric acid = ca. 1:6) results in a broad singlet centred at 255 m $\mu$ ( $\epsilon = 51,000$ ). Similarly, upon the addition of acetic acid (molar ratio pyridine:acetic acid = ca. 1:9) a broad singlet, centred at 256 m $\mu$  ( $\epsilon = 36,300$ ), is observed. However, the presence of acetylacetone (1:1 molar ratio) causes no discernible changes in the spectrum of methanolic pyridine or acetylacetone.

The spectrum of methanolic 2-(aminomethyl)pyridine is characterized by a broad band centered at 260 m $\mu$  ( $\epsilon = 32,500$ ); the spectrum is not altered by the addition of bisethylenediaminenickel (II) chloride.

### Visible absorption spectra

The spectrum of methanolic bisethylenediaminenickel (II) chloride has a broad band centered at 570 m $\mu$  ( $\epsilon = 6.49$ ). The addition of butylamine or pyridine does

TABLE 5.—INFRA-RED SPECTRA OF COMPOUNDS OF THE TYPE



x	Phenyl C—H stretch <sup>(7)</sup>	Symmet- rical and anti- symmet- rical C—H stretch <sup>(7)</sup>	C=N stretch <sup>(8)</sup>	Conju- gated ring inter- action <sup>(6)</sup>	Aromatic C=C stretch <sup>(8,9)</sup>	CH <sub>2</sub> defor- mation modes <sup>(5,10)</sup>	C—O stretch <sup>(8)</sup>	CN stretch <sup>(8)</sup>	—NO <sub>2</sub> <sup>(7)</sup>
3-NO <sub>2</sub>	3070 m*	2930 m	1638 sh	1600 s	1550 s	1463 sh	1290 s	1197 m	1501 s
5-NO <sub>2</sub>	3080 m	2880 sh 2980 m 2920 m	1629 s	1597 s	1530 sh 1550 s	1445 s 1470 s 1446 sh	1300 s	1208 s	1335 s 1495 s 1335 s
5-Br 3-OCH <sub>3</sub>	3080 sh	2940 m 2840 sh	1620 s	1600 sh	1540 m	1463 s 1445 s	1317 s	1220 m 1197 sh	
5-Br	3080 sh	2990 w	1625 s	1590 m	1529 s	1462 s	1310 s	1205 m	
5-Cl	3060 m	2900 sh 2980 m 2920 m	1630 sh	1600 sh	1530 s	1425 m 1465 s 1426 s	1315 s	1205 s	
4-CH <sub>3</sub>	3020 m	2920 m 2860 m	1630 sh	1610 s	1547 sh 1535 s	1470 s 1425 sh	1315 s	1225 s 1207 sh	
4-OH	3020 m	2980 m	1625 s	1600 s	1535 s	1440 s	1285 s	1217 s	
5-OH	3040 m	2940 m 2960 m 2920 m	1630 s	1610 s	1545 s	1445 s	1300 s	1220 s 1195 sh	

\* s = strong, m = medium, w = weak, sh = shoulder.

not alter the position of the band, but the intensity increases ( $\epsilon = 7.77$  and 6.70 respectively). Upon the addition of acetylacetone, the band was immediately shifted to 560 m $\mu$  ( $\epsilon = 5.59$ ). The spectrum of the condensation product, bisacetylacetone-ethylenediiminonickel (II), in methanol is characterized by a broad band which is centered at 560 m $\mu$  ( $\epsilon = 60.3$ ).

The method of continuous variations<sup>(11)</sup> (Job's method) was applied to methanolic solutions ( $5\cdot8 \times 10^{-2}$  F) of bisethylenediaminenickel (II) chloride and pyridine; the results are presented in Fig. 1. The method was also applied to chloroform solutions of bis(4-methylsalicylaldehyde)-ethylenediiminonickel (II) and pyridine to determine whether the complex could be converted to a six-co-ordinate species. There was no indication that coordination with pyridine occurred.

### DISCUSSION

# Scope of the template synthesis

It will be seen from Tables 1 and 2 that the base-catalysed condensation of carbonyl compounds with tetrakisethylenediamine- $\mu$ -dichlorodinickel (II) chloride <sup>(11)</sup> W. C. VOSBURGH and G. R. COOPER, J. Amer. Chem. Soc. **63**, 437 (1941).

affords a convenient method for the preparation of a variety of nickel (II)-Schiff base compounds. In general, condensations have been effected using  $\beta$ -diketones, substituted salicylaldehydes and substituted *o*-hydroxyacetophenones. However, only unreacted starting material was obtained in attempts to effect the condensation with substituted  $\beta$ -diketones such as 3-phenyl-2,4-pentanedione, 3-methyl-2,4pentanedione and 1,1-dipivaloylethane. Possibly steric restrictions are responsible for some of these failures. It is worth noting that attempts to effect condensation with ethyl acetoacetate were unsuccessful. Perhaps ethyl acetoacetate is a special case inasmuch as condensation with an amine ordinarily results in a  $\beta$ -ketoamide rather than a  $\beta$ -ketoimine or a  $\beta$ -carbethoxyimine.

Condensations were also effected using  $\beta$ -ketoimines. While this is not of great preparative significance, it does serve to indicate the scope of the reaction. Moreover, this appears to be the first instance in which amine exchange has been used to prepare bisacetylacetone-ethylenediiminonickel (II) or bisbenzoylacetone-ethylenediiminonickel (II).

It was of interest to learn whether the template synthesis could be extended to include other divalent-metal-chelate compounds and other nickel (II) chelate compounds. Bispropylenediaminenickel (II) chloride was found to condense with acetylacetone under the conditions used for tetrakisethylenediamine- $\mu$ -dichlorodinickel (II) chloride. However, using identical conditions, only bisacetylacetono-copper (II) was obtained (96 per cent yield) from the interaction of bisethylene-diaminecopper (II) chloride and acetylacetone. The same type of reaction with dichlorobisethylenediaminecobalt (III) chloride gave several products, two of which analyzed for bisacetylacetonocobalt (II) and dichlorobisethylenediaminecobalt (II).

A variety of bases can be used to effect the condensation of acetylacetone with tetrakisethylenediamine- $\mu$ -dichlorodinickel (II) chloride. Butylamine, pyridine, 2-methylpyridine and 2,4-dimethylpyridine were used, and no special effect on the yield of the product was noted; dimethylsulphoxide was effective as a catalyst, but the yield of product was poor (8 per cent); aniline, 2,6-dimethylaniline, 2,6-dimethylpyridine, 1:10-phenanthroline, and 2-aminomethylpyridine were ineffective as catalysts.

# Mechanism of the template synthesis

While these results are of preparative significance, they are of greater interest mechanistically. Previous workers<sup>(1)</sup> have suggested that a preliminary step involves replacement of the bridge chlorines in tetrakisethylenediamine- $\mu$ -dichlorodinickel (II) ion by a suitable co-ordinating agent leading to the formation of  $(Nien_2B_2)^{2+}$ . If this is correct, it would imply that to be effective as a catalyst, a reagent, B, must have a co-ordinating tendency greater than that of chloride ion but less than that of the carbonyl compound. Thus, the failure of 2,6-dimethylpyridine as a catalyst is a marked contrast to the effectiveness of 2,4-dimethylpyridine, and, probably, can be attributed to differences in steric hindrance. The apparent catalytic inactivity of 2-aminomethylpyridine requires another explanation. In this case, it seems likely that the bridge chlorines are indeed replaced, but that a stable complex,  $[Nien_2(H_2NCH_2C_5H_5N)]$ -Cl<sub>2</sub>, results and further reaction is precluded. The compound in question was isolated from the reaction mixture, and when prepared directly, it gave no evidence of reacting

with pyridine or acetylacetone. The rationalization of the catalytic ineffectiveness of aniline, 2,6-dimethylaniline and 1:10-phenanthroline is somewhat more difficult. However, it would seem likely that 1:10-phenanthroline would form a too stable complex, while aniline, a weak base, may not be capable of replacing chlorine.

In an attempt to elucidate the mechanism of the template synthesis, the nature of the intermediates was investigated. Previous work<sup>(12)</sup> has shown that what was



FIG. 1.— $(D_{obs} - D_{calc})$  at 580 m $\mu$  as a function of mole fraction [Nien<sub>2</sub>]Cl<sub>2</sub> in methanolic solutions of [Nien<sub>2</sub>]Cl<sub>2</sub> and pyridine; total molarity =  $4.8 \times 10^{-2}$ .

formerly known as bisethylenediaminenickel (II) chloride actually exists in the solid state as a dimer with a pair of bridging chloride ions. The same type of association is found to exist in boiling methanol, as indicated by a molecular weight determination. Potentiometric titration of the nickel (II) complex with silver nitrate at 0°C after the manner of INGOLD,<sup>(13)</sup> shows no difference in the chloride ions thereby indicating that all are equally labile. A Job's titration of the dimer with pyridine in either methanolic (Fig. 1) or aqueous solution indicates the formation of two unique species, one containing a 2:1 ratio of nickel-to-pyridine, the other a 1:2 ratio of nickel to pyridine. Conductivity measurements were also made. The titration of the nickel (II) dimer with pyridine should result in an increase in conductance, according to the following equation in which it is seen that six ions would result from the rupture of the chloride bridges by pyridine:

$$[Ni_2en_4Cl_2]Cl_2 + 2py \rightarrow 2[Nien_2py_2]^{2+} + 4Cl^{-1}$$

Instead, it was discovered (Fig. 2) that conductance actually decreased as pyridine was added to a methanol solution of the dimer, but increased after the pyridine: nickel

 <sup>&</sup>lt;sup>(12)</sup> A. S. ANTSYSHKINA and M. A. PORAI-KOSHITS, *Dokl. Akad. Nauk USSR* 143, 105 (1962).
<sup>(13)</sup> D. D. BROWN and C. K. INGOLD, *J. Chem. Soc.* 2680 (1953).

ratio exceeded 2:1. This decrease in conductance can be attributed to ion-pair formation, which is a common phenomenon in methanol.<sup>(14,15)</sup> The most probable species which exists in solution is Nien<sub>2</sub>Py<sub>2</sub>·2Cl. The increase of conductance after the 2:1 pyridine:nickel ratio has been attained can be attributed to the normal conductivity due to pyridine. Theoretical considerations show<sup>(16)</sup> that for ion-pair formation to occur, the species must have a finite dipole moment. If the species formed upon



FIG. 2.—Conductance of methanol as a function of ml. of  $6\cdot31 \times 10^{-2}$  M pyridine added: Curve A, 200 ml of pure methanol; Curve B, 200 ml of  $0\cdot8 \times 10^{-2}$  F methanolic [Nien<sub>2</sub>]Cl<sub>2</sub>.

pyridine titration were *trans*-Nien<sub>2</sub>-Py<sub>2</sub><sup>2+</sup>, this condition would not be met and ion-pair formation would not be expected. However, the *cis*-configuration has a finite moment, and it would seem logical that inasmuch as the bridging chlorides were originally in the *cis*-position, their replacement by pyridine would likewise result in a *cis*-isomer.

The nature of  $[Nien_2]Cl_2$ -pyridine-acetylacetone interaction in methanol was also investigated by means of a Job's titration (Fig. 3). In these experiments, the pyridinenickel (II) molar ratio was maintained at 2:1, and the mole fraction of acetylacetone was varied. The observed maximum at 0.5 mole fraction of acetylacetone indicates that the stable species contains acetylacetone and bisethylenediaminenickel (II) chloride in equimolar amounts.

Attempts to prepare and isolate *cis*- or *trans*-dipyridinebisethylenediaminenickel (II) chloride were unsuccessful. In pyridine, apparently disproportionation occurs since only trisethylenediaminenickel (II) chloride and nickel (II) chloride were isolated.

<sup>&</sup>lt;sup>(14)</sup> R. FUOSS and C. KRAUS, J. Amer. Chem. Soc. 55, 21, 476, 1019, 2387 (1933).

<sup>(15)</sup> O. T. BENFEY, E. D. HUGHES and C. K. INGOLD, J. Chem. Soc. 2494 (1952).

<sup>&</sup>lt;sup>(16)</sup> F. BASOLO and R. G. PEARSON, *Mechanisms of Inorganic Reactions*, p. 376. J. Wiley, New York (1958).

The evaporation of methanolic solutions of pyridine and bisethylenediaminenickel (II) chloride afforded only trisethylenediaminenickel (II) chloride.

There is a possible alternate mechanism which deserves consideration, viz., an acid-base mechanism. The role of the catalytic base might be to remove a proton from the acidic carbonyl compound, forming, for example, the acetylacetonate anion which would then replace the bridging chlorides. Several observations suggest that



FIG. 3.-- $(D_{obs} - D_{cale})$  at 560 m $\mu$  as a function of mole fraction Nien<sub>2</sub>Cl<sub>2</sub>·2py: acetylacetone in methanol; total molarity = 3.1 × 10<sup>-2</sup>.

this is not a likely mechanism. First, sodium hydroxide and potassium hydroxide do not function as catalysts, and it does not seem reasonable to attribute this to the formation of stable alkali metal-chelate compounds. Secondly, there is no obvious correlation of catalytic activity with base strength as would be expected for an acidbase reaction. Thirdly, the order of addition of reagents is critical. If pyridine is added to the nickel-chelate template after, rather than before, acetylacetone is added, no reaction occurs. This is interpreted as indicating that the catalytic function of pyridine is inhibited by the formation of pyridinium ion. Also, if the bridged chlorides could be replaced by nucleophilic anions, as pictured by the acid-base mechanism, then condensation would be expected with sodium acetylacetonate or thallous benzoylacetonate, and this was not observed. Finally, the fact that 2,6-dimethylpyridine, a stronger base than pyridine, was not successful as a catalyst indicates that perhaps other considerations, such as co-ordination, might be more important.

A study of the kinetics of the template synthesis is in progress.

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