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# THE THERMAL DECOMPOSITION OF METAL COMPLEXES—IV\*

## THE PREPARATION AND THERMAL DECOMPOSITION OF SOME PYRIDINE AND SUBSTITUTED-PYRIDINE COMPLEXES OF NICKEL (II) HALIDES

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Abstract—Complexes have been prepared between pyridine,  $\alpha$ -,  $\beta$ - and  $\gamma$ -picoline, 2,6-lutidine, and s-collidine and nickel (II) chloride, bromide, and iodide. The thermal decomposition of these complexes has been studied. Diffuse reflectance spectra have been measured for all complexes and have been used to determine the environment about the nickel atoms.

THE COMPLEXES formed by pyridine, quinoline, and substituted pyridine derivatives with cobalt (II) halides have been previously studied<sup>(1,2)</sup> and their modes of thermal decomposition recorded. The present paper describes a similar study of the complexes formed by nickel (II) halides with  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines, 2,6-lutidine, and *s*-collidine and gives some new data on the complexes in the nickel-pyridine-chloride system. Data on the thermal decomposition of tetrakispyridinenickel (II) chloride have been previously reported from these laboratories.<sup>(3)</sup> At the time of the latter work it was considered that tetrakispyridinenickel (II) chloride was the only complex of its type which would undergo decomposition to product successive intermediate phases before decomposing finally to the anhydrous halide; it has now been found that most complexes of this type undergo thermal decomposition by loss of successive molecules of ligand and that intermediate phases are produced before the anhydrous halides are finally reached.

#### EXPERIMENTAL

Two methods were used to prepare the complexes studied. The first (A) involved heating the appropriate nickel (II) halide with an excess of the nitrogen base to produce a solution. The solution was cooled and the precipitated complex filtered off, washed with diethyl ether and dried in air. Hydrated halides were used in most preparations but in the preparations of  $bis(\alpha$ -picoline)nickel (II) chloride,  $bis(\alpha$ -picoline)nickel (II) bromide, bis(2,6-lutidine)nickel (II) chloride and bis(2,6-lutidine)nickel (II) bromide it was found necessary to use anhydrous halides and to carry out the preparations in a dry-box. The second method of preparation (B) used for some of the derivatives of nickel (II) iodide, consisted of dissolving the nickel halide in ethanol and adding a solution of the base in ethanol. The precipitated complexes were filtered, washed, and dried as in Method A.

The complexes prepared by these two methods are given in Table 1. References are given to previous preparations: where no reference is given it is believed that these are new compounds.

Thermal decomposition studies were carried out on a Stanton Thermal Balance working at a chart speed of 6 in/hr; all thermal decompositions were carried out in air. The new phases isolated

\* Part (III). J. R. ALLAN, D. H. BROWN, R. H. NUTTALL and D. W. A. SHARP, J. Inorg. Nucl. Chem. 26, 1895 (1964).

<sup>(1)</sup> J. R. ALLAN, D. H. BROWN, R. H. NUTTALL and D. W. A. SHARP, *J. Inorg. Nucl. Chem.* In press. <sup>(2)</sup> D. H. BROWN, R. H. NUTTALL and D. W. A. SHARP, *J. Inorg. Nucl. Chem.* **26**, 1151 (1964).

<sup>(3)</sup> D. H. BROWN, R. H. NUTTALL and D. W. A. SHARP, J. Inorg. Nucl. Chem. 25, 1067 (1963).

DECOMPOSITION PRODUCTS	
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COMPOUNDS /	
BLE 1STARTING	
Τ	

¥	ź	Nipy <sub>4</sub> Cl <sub>2</sub> * 12-9(13-0); Cl, 15-9(16-0)	180°	Nipy <sub>2</sub> Cl <sub>2</sub> Ni, 20·2(20·3); Cl, 24·6(24·6)	Z	NipyCl <sub>a</sub> i. 28·6(28·0): Cl. 34·2(34·1)
					150°	NiCl <sub>8</sub>
		Ni(α-pic) <sub>2</sub> Cl <sub>2</sub> <sup>(5)</sup>		Ni(α-pic)Cl.	z	1, 44·8(45·2); C1, 54·7(54·8) NiCl.
A	ź	18-1(18-5); Cl, 22-1(22-5)	87	Ni, 26.5(26.3); Cl, 31.6(31.9)	Z0.28	i, 44·9(45·2); Cl, 55·0(54·8)
		Ni( $\beta$ -pic) <sub>4</sub> Cl <sub>2</sub>	160°	$Ni(\beta-pic)_2Cl_2$	× 003	$Ni(\beta-pic)Cl_2$
4	ź	11-5(11-7); Cl, 14-0(14-2)		Ni, 19-1(18-5); Cl, 22-0(22-5)	z	i, 25-8(26-3); Cl, 31-2(31-9)
			₹°032	Ni 30.0(30-6)- Cl 36.8(37.1)	320°*	NiCl <sub>2</sub>
		Ni(y-pic) <sub>4</sub> Cl <sub>2</sub>		Ni(y-pic)Cl <sub>2</sub>	A	1, 44.3(4.3'2), CI, JJ'3(34'8) NiCla
A	ź	11-4(11-7); Cl, 14-0(14-2)	3	Ni, 26-1(26-3); Cl, 30-9(31-9)	Z	i, 44-4(45-2); Cl, 55-0(54-8)
		Ni lut <sub>2</sub> Cl <sub>2</sub>	2500	Ni lutCl <sub>2</sub>	A.000	NiCl <sub>2</sub>
A	ī	17-1(17-2); Cl, 20-3(20-5)		Ni, 24-5(24-2); CI, 29-4(29-9)	Z	i, 44 6(45·2); Cl, 54·9(54·8)
		Ni coll <sub>4</sub> Cl <sub>2</sub>	260°↓	Ni collCl <sub>2</sub>	<b>4</b> 0° <b>¥</b>	NiCl <sub>2</sub>
A	ź	9-4(9-6); Cl, 11-5(11-7)		Ni, 23·7(23·5); Cl, 28·0(28·3)	Z	i, 44 6(45·2); Cl, 55 0(54·8)
		Nipy <sub>4</sub> Br <sub>2</sub> <sup>(6)</sup>	140°	Nipy <sub>2</sub> Br <sub>2</sub>	200.	NipyBr <sub>2</sub>
×	ź	10-7(10-9); Br, 29-9(29-9)		Ni, 15·2(15·5); Br, 42·1(42·4)	z	i, 19-3(19-7); Br, 53-4(53-7)
				ļø.	<b>▲</b> .00	NiBr <sub>2</sub>
					Z	i, 26.6(26.9); Br, 72.8(73.1)
		Ni(a-pic) <sub>2</sub> Br <sub>2</sub> <sup>(5)</sup>	350°¥	NiBr <sub>2</sub>		
V	ź	14-1(14-5); Br, 39-2(39-6)		Ni, 26·4(26·9); Br, 73·0(73·1)		
		Ni(ß-pic)4Br2	160°	$Ni(\beta-pic)_2Br_2$	<b>▲</b> 88	$Ni(\beta-pic)Br_2$
V	ź	9-8(9-9); Br, 26-9(27-1)		Ni, 14·2(14·5); Br, 39·1(39·6)	z	i, 18-9(18-8); Br, 51-8(51-3)
			230°	Ni <sub>s</sub> ( $\beta$ -pic) <sub>2</sub> Br <sub>6</sub>	<b>3</b> 00°	NiBr <sub>2</sub>
				Ni, 20-0(20-8); Br, 57-0(57-0)	Z	i, 26.5(26.9); Br, 73.4(73.1)
		Ni( $\gamma$ -pic) <sub>4</sub> Br <sub>2</sub>	190	$Ni(\gamma-pic)Br_2$	400	Nis( $\gamma$ -pic)2Br6
<	ź	9-8(9-9); Br, 27-0(27-1)		Ni, 18·8(18·8); Br, 51·9(51·3)	Z	i, 20-0(20-8); Br, 56-2(57-0)
				ļø	400	NiBr
					Z	i, 26·7(26·9); Br, 73·5(73·1)

J. R. ALLAN, D. H. BROWN, R. H. NUTTALL and D. W. A. SHARP

		Ni lut <sub>2</sub> Br <sub>2</sub>	Ni lutBr <sub>2</sub>	NiBr.
<	ī.	13-4(13-6); Br, 37-0(37-2)	Ni, 17·5(17·9); Br, 49·0(49·2)	Ni, 26·4(26·9); Br, 73·0(73·1)
		Ni coll <sub>4</sub> Br <sub>2</sub> 220	Ni collBr₂ 310 <sup>∞</sup>	NiBr <sub>2</sub>
¥	ī	8-3(8-3); Br, 22-3(22-8)	Ni, 17-6(17-2); Br, 47-9(47-2)	Ni, 26-0(26-9); Br, 73-6(73-1)
		Nipys12 100'	√► Nipy₁I₂ 1000►	Nipy <sub>2</sub> 1;
A	ź	7-3(7-4); I, 31-8(32-2)	Ni, 9-1(9-3); I, 40-1(40-4)	Ni, 12·3(12·4); I, 54·1(54·0)
		Nipy <sub>4</sub> 1 <sub>2</sub> <sup>(5)</sup>		
8	ź.	9.1(9.3); I, 40.1(40.4)	As above	
		Ni(α-pic) <sub>2</sub> I <sub>2</sub> I <sub>20</sub>	<b>▲</b>	
в	ī	11-5(11-8); 1, 50-6(50-9)	Nil <sub>s</sub> : NiO	
		$Ni(\beta-pic)_{4}I_{2}$ 150°	- $Ni(x-pic)_2I_2$	
¥	ź	8-3(8-6); I, 37-0(37-1)	Ni, 11-1(11-7); I, 50-6(50-9)	
		Ni(2-pic) <sub>6</sub> 1 <sub>2</sub>	► Ni(γ-pic),I 3	Ni( $\gamma$ -pic),I,
۲	, Z	6-8(6-7); 1, 29-0(29-2)	Ni, 8-7(8-6); I, 37-2(37-1)	Ni, 11-7(11-7); I, 50-6(50-9)
		Ni(2/-pic),12		
æ	ī	8.6(8.6); I, 37.0(37.1)	As Above.	
		Ni lut <sub>4</sub> 1 <sub>2</sub> 1000	Ni lut <sub>2</sub> I <sub>2</sub>	
8	Ż	7·9(7·9); I, 34·2(34·3)	Ni, 11-0(11-1); I, 48-7(48-3)	
		Ni coll <sub>4</sub> I <sub>2</sub>	Ni coll₂I₃	
в	īź	7-3(7-4); I, 31-9(31-9)	Ni, 10-4(10-6); 1, 45-6(45-8)	
2		net nic nicoline(methylawridine)	1100 - Venibirvelytemit/Jenibirti 2,6,101	2.4.6 willidina(trimothylmuridina)
· ( . I		is, pic, prominential promined	, iui, zivriunume (umieninyipyinume), com,	
*	hcse d	ata have alrcady been published.	(3)	

A and B refer to method of preparation, see text. Analytical figures in parentheses are those calculated for given compound.

as a result of thermal decomposition studies are given in Table 1. Diffuse reflectance spectra were taken for all starting materials and all new phases produced by thermal decomposition on a Hilger Uvispek Spectrophotometer; spectra were measured over the range 350–1000 m $\mu$ . All starting materials and solid thermal decomposition products were examined by X-ray powder photography using a 9 cm. camera and Cu K $\alpha$  radiation. Magnetic susceptibility measurements were made by the Gouy method on finely powdered solids.

### RESULTS

A list of the starting materials is given in Table 1. Where there have been previous studies of these systems the complexes prepared in the present work are generally in agreement with those reported previously. The compound  $Ni_2py_3Cl_4$  reported to result,<sup>(4)</sup> from the evaporation of what would now be formulated as pyridinium tetrachloronickelate (II) was not found in the system pyridine–nickel–chloride but the exact conditions used in the preparation of this compound were not duplicated. Complexes between 2,6-lutidine and nickel (II) chloride, bromide, and iodide were readily isolated. Previous workers<sup>(7)</sup> have found mixtures of two blue forms for the bromide and a mixture of a yellow and blue form for the chloride but such isomerism was not observed in the present work. No analysis was reported in the previous work for the complex of the type  $L_2NiX_2$  (where L is a substituted pyridine and X is a halogen) exist in two forms as does bisquinolinenickel (II) chloride<sup>(9)</sup> but such polymorphism was not observed in the present work. However, no special

(a) NiL <sub>4</sub> X <sub>2</sub> type—distorted octahedral environment about nickel.								
Complex	Colour	<sup>3</sup> T <sub>2</sub> g(F)	<sup>3</sup> T <sub>1</sub> g(F)	<sup>1</sup> Eg(D)	${}^{1}T_{2}g(D)$	<sup>3</sup> T <sub>1</sub> g(P)		
Nipy₄Cl₃*	light blue	920	620	770	510	390		
Ni(β-pic) <sub>4</sub> Cl <sub>2</sub>	light blue	900	630	800	_	390		
$Ni(\gamma - pic)_4Cl_2$	light blue	890	620	780	480	390		
Ni coll <sub>4</sub> Cl <sub>2</sub>	light blue	920	630	750	_	400		
Ni py <sub>4</sub> Br <sub>2</sub>	light blue	950	650	800	_	400		
$Ni(\beta - pic)_{4}Br_{2}$	light blue	930	640	810	500	400		
Ni( $\gamma$ -pic) <sub>4</sub> Br <sub>2</sub>	light blue	900	640	800	500	390		
Ni coll <sub>4</sub> Br <sub>2</sub>	light blue	920	650	780	_	400		
Ni py <sub>4</sub> I <sub>2</sub>	light blue		630	810	_	400		
$Ni(\beta-pic)_{4}I_{2}$	light blue	_	590	850	_	380		
Ni(7-pic) <sub>4</sub> I <sub>2</sub>	light green	_	630	850		400		
Ni lut <sub>4</sub> I <sub>2</sub>	light green	_	660	_	_	400		
Ni coll <sub>4</sub> $I_2$	light green		660	—	—	390		
(b) NiL <sub>2</sub> X <sub>2</sub> ty	pe-distorted	octahedra	al enviror	nment ab	out nicke	I.		
Nipy <sub>2</sub> Cl <sub>2</sub> *	yellow		710	770	440	410		
$Ni(\dot{\beta}-pic)_2Cl_2$	yellow		720	800	_	420		
Nipy <sub>2</sub> Br <sub>2</sub>	yellow		740			430		
$Ni(\dot{\beta}-pic)_2Br_2$	yellow		740		-	420		

TABLE 2.—Spectra (all figures in  $m\mu$ )

<sup>(4)</sup> R. REIZENSTEIN, Z. anorg. Chem. 11, 254 (1896); 15, 192 (1897); 18, 253 (1898); Annalen 282, 267 (1894).

<sup>(5)</sup> M. D. GLONEK, C. CURRAN and J. V. QUAGLIANO, J. Amer. Chem. Soc. 84, 2014 (1962).

<sup>(6)</sup> R. VARET, C.R. Acad. Sci., Paris 124, 1156 (1897).

<sup>(7)</sup> S. BUFFAGNI, L. M. VALLARINO and J. V. QUAGLIANO, Inorg. Chem. 3, 480 (1964).

- (8) A. W. DOWNS and P. A. ONGLEY, Chem. & Industr. 493 (1963).
- <sup>(9)</sup> D. M. L. GOODGAME and M. GOODGAME, J. Chem. Soc. 207 (1963).

(c) NiL <sub>2</sub> X <sub>2</sub> type—tetrahedral environment about nickel								
Complex	Colour	<sup>3</sup> A <sub>2</sub> ()	F)	۱D		T <sub>1</sub> (P)		
$Ni(\alpha - pic)_{2}Cl_{2}$	dark blue	~10	00			580		
Ni lut <sub>2</sub> Cl <sub>2</sub>	dark blue			800(sh)		610		
$Ni(\alpha - pic)_2Br_2$	dark blue	$\sim 10$	00	_		580		
Ni lut <sub>2</sub> Br <sub>2</sub>	dark blue			_		610		
Nipy <sub>2</sub> I <sub>2</sub>	dark green			800(sh)		660		
Ni(α-pic) <sub>2</sub> I <sub>2</sub>	dark green			850(sh)		650		
$Ni(\beta-pic)_2I_2$	dark green					650		
$Ni(\gamma - pic)_2 I_2$	dark green			850(sh)		660		
Ni $lut_2I_2$	dark green			750(sh)	)	670		
Ni $coll_2 I_2$	brown			7 <b>60(</b> sh)		660		
(d) NiLX <sub>2</sub> typ	e- octahedra	l environr	nent abou	it nickel.				
Complex	Colour	<sup>3</sup> T <sub>2</sub> g(F)	<sup>3</sup> T <sub>1</sub> g(F)	<sup>1</sup> Eg(D)	${}^{1}T_{2}g(D)$	<sup>3</sup> T <sub>1</sub> g(P)		
NipyCl <sub>2</sub> *	yellow		750			440		
Ni(α-pic)Cl <sub>2</sub>	light blue		760			450		
Ni(β-pic)Cl₂	yellow		750	850		440		
$Ni(\gamma-pic)Cl_2$	yellow		760	800	_	440		
Ni lut Cl <sub>2</sub>	light blue	_	700		530	420		
Ni collCl <sub>2</sub>	yellow	—	750	880		440		
Ni pyBr <sub>2</sub>	orange	_	800		550	470		
$Ni(\beta-pic)Br_2$	red		830	950	570	480		
Ni(7-pic)Br <sub>2</sub>	orange		780	•	540	450		
Ni lutBr <sub>2</sub>	light blue		700	- •	• •			
Ni collBr <sub>2</sub>	red		850	950		480		
(e) Ni <sub>3</sub> L <sub>2</sub> X <sub>6</sub> typeoctahedral environment about nickel.								
Ni <sub>3</sub> ( $\beta$ -pic) <sub>2</sub> Cl <sub>6</sub>	yellow	_	770	850	540	450		
$Ni_3(\beta-pic)_2Br_6$	orange	· -	830	950		480		
$Ni_3(\gamma-pic)_2Br_6$	orange		810	·	—	470		
(f) NiL <sub>6</sub> X <sub>2</sub> type—octahedral.								
Nipy <sub>6</sub> I <sub>2</sub>	pale blue	880	610			400		
$Ni(\gamma - pic)_{s}I_{2}$	pale blue	880	600		—	410		

TABLE 2 (Cont'd)

\* These data already have been published.<sup>(3)</sup>

precautions were taken with a view to isolating unstable species from solution. Trispyridinenickel (II) iodide has been reported previously<sup>(10)</sup> in the pyridine-nickel-iodide system but was not found in the present work.

The results of thermal decomposition studies are given in Table 2 which also includes the previously published<sup>(3)</sup> data on tetrakispyridinenickel (II) chloride for comparison. The temperatures quoted are those of the maximum rate of decomposition under the conditions used. In all cases X-ray powder photography showed the presence of distinct new phases for these thermal decomposition products. Phases with a ratio of three nickel atoms to two ligand molecules could only be isolated in a relatively small number of cases but the thermal decomposition curves of tetrakispyridinenickel (II) chloride and tetrakis( $\gamma$ -picoline)nickel (II) chloride

<sup>(10)</sup> F. Ephraim and R. LINN, Chem. Ber. 46, 3754 (1913).

showed inflections at the points corresponding to these phases. Distinct complexes  $Ni_3py_6Cl_6$  and  $Ni_3(\gamma-pic)_2Cl_6$  could not, however, be isolated. The nickel iodide complexes do not give pure nickel iodide after thermal decomposition as there is partial oxidation to give a mixture of nickel (II) oxide and nickel (II) iodide.

The process of thermal decomposition was studied for most complexes on a melting point apparatus. It appeared that a liquid phase was generally present at the phase change but owing to the comparatively deep colours of the complexes it was not possible to make precise measurements of the melting points.

Spectroscopic data for the various complexes prepared in the present study are given in Tables 2(a-f). Spectra of the complexes in the pyridine-nickel-chloride system are again given for comparison. The spectra of the complexes of type NiL<sub>1</sub>X<sub>2</sub>, are all consistent with a distorted octahedral environment around the nickel atom. The complexes are light green in colour. For a  $d^8$  ion in a regular octahedral field the ground state is  ${}^{3}A_{\circ}g(F)$  and the bands observed are assigned to electronic transitions on the basis of a regular octahedral field around the nickel atom. All of the spectra are very similar to those of tetrakispyridinenickel (II) chloride<sup>(11)</sup> or nickel chloride<sup>(12)</sup> where assignments have been made previously. Using the  ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(F)$  transition as a criterion there is a weakening of the ligand field on going from chlorides to bromides but this weakening is not maintained when going to the iodide. The change from chloride to iodide is as expected from the spectrochemical series but the change from bromide to iodide is unexpected and can only be explained by extra distortion in the iodides in which case the direction of the change on going from chloride to iodide may well be fortuitous. It is not possible to draw conclusions as to the relative ligand fields produced by the various nitrogen-bases from the present spectra.

The complexes of type  $NiL_2X_2$  gave rise to two types of spectra. Some of the complexes were yellow in colour and the spectra are typical of nickel (II) complexes in a distorted octahedral environment. As with the complexes of type  $NiL_4X_2$  there is a weakening of the ligand field on going from chlorides to bromides. The remaining specimens of this stoichiometry had a more intense colour and the spectra are those characteristic of nickel (II) in a tetrahedral environment. The ground state is  ${}^{3}T_{1}(F)$ and the transitions corresponding to the two intense bands are  ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$  and  ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}(F)$ . The weak band, or shoulder, at about 800 m $\mu$  is assigned to a spin-forbidden transition to an upper state arising from the <sup>1</sup>D state of the free ion.<sup>(7,9,13)</sup> The spectra recorded for bispyridinenickel (II) iodide and  $bis(\beta$ -picoline)nickel (II) iodide are somewhat different from those measured previously<sup>(5)</sup> but the previous measurements were made in benzene solution and are not strictly comparable with those made in the present work. Previous studies were taken to indicate that bis( $\alpha$ -picoline)nickel (II) chloride and bis( $\beta$ -picoline)nickel (II) chloride and bromide have a tetrahedral environment about the metal atoms. However, the complexes prepared in the present work are yellow in colour and the nickel atoms are definitely in octahedral environments. All the complexes of types NiLX<sub>2</sub>, Ni<sub>3</sub>L<sub>2</sub>X<sub>6</sub>, and NiL<sub>6</sub>X<sub>2</sub> gave rise to spectra characteristic of nickel (II) in a distorted octahedral environment. The positions of absorption maxima are recorded in Tables 2(d-f).

<sup>(11)</sup> O. BOSTRUP and C. K. JØRGENSEN, Acta Chem. Scand. 11, 1223 (1957).

<sup>&</sup>lt;sup>(12)</sup> R. W. ASMUSSEN and O. BOSTRUP, Acta Chem. Scand. 11, 745 (1957).

<sup>&</sup>lt;sup>(13)</sup> C. FURLANI and G. MORPURGO, Z. phys. Chem. (Frankfurt) 28, 93 (1961); D. M. L. GOODGAME, M. GOODGAME and F. A. COTTON, J. Amer. Chem. Soc. 83, 4161 (1961).

Magnetic susceptibility measurements showed that all of the complexes studied were paramagnetic. These measurements are consistent with distorted octahedral or tetrahedral environments about the nickel but are not in agreement with a planar environment which would give rise to diamagnetism only.<sup>(9)</sup>

#### DISCUSSION

The complexes found in the present work to result from the action of pyridine and substituted pyridines on nickel (II) halides are shown in Table 1 and the thermal decomposition products of these compounds are listed in Table 2. It is not possible to place too great an emphasis on the absence of particular complexes from these two tables as only a limited number of methods of preparation have been used but, as with the similar cobalt complexes, the presence of methyl groups  $\alpha$  to the nitrogen atom generally results in the formation of complexes with fewer molecules of base for each metal atom. Iodides take on more molecules of base than do chlorides or bromides (see particularly the 2,6-lutadine and s-collidine complexes). A comparison of the complexes formed by cobalt and nickel halides from solution shows very similar complexes to be formed by both metals but, where there are differences, the cobalt complexes invariably contain fewer molecules of ligand than do the nickel complexes. This may be a function of the smaller size and greater polarizing power of nickel (II) as compared with cobalt (II) but, if so, it suggests that steric requirements are of fairly minor importance in determining the type of complex which is formed. A comparison of the phases formed during the thermal decomposition of nickel complexes as compared with those formed during the thermal decomposition of cobalt complexes shows very close similarities between the two metals. The differences appear so random that no significance can be read into them at this stage.

Tetrakispyridinenickel (II) bromide has a *trans* octahedral arrangement of atoms about the central nickel atom; the pyridine molecules are twisted out of the central plane of the octahedron.<sup>(13)</sup> Tetrakispyridinenickel (II) chloride has a similar structure.<sup>(15)</sup> X-ray powder photography<sup>(16)</sup> is taken to show that bispyridinenickel (II) chloride has a structure analogous to that of the violet form of bispyridinecobalt (I) chloride which has an octahedral arrangement of ligands about the central cobalt atom and chloride bridges.<sup>(17)</sup> This structural information is in agreement with the interpretation of the spectroscopic data as given in the section of results.

It is apparent that the factors influencing the stereochemistry adopted by the nickel atom in a particular stoichiometry are complex. The disagreement between the present results for bis( $\alpha$ -picoline)nickel (II) chloride and bis( $\beta$ -picoline) nickel (II) chloride and bromide which are shown in the present work to have distorted octahedral environments about the metal atom whereas they were previously considered<sup>(5)</sup> to have tetrahedral arrangements may well be due to the preparation of different forms of the same complex. The bisquinolinenickel<sup>(11)</sup> halides are octahedral (the yellow form of the chloride), tetrahedral (chloride and bromide), and planar (iodide).<sup>(9)</sup> It appears that the structure adopted is determined by a fine balance between several factors.

<sup>(14)</sup> A. S. ANTSISHKINA and M. A. PORAI-KOSHITS, Kristallografiya 3, 676 (1958).

<sup>(15)</sup> M. A. PORAĬ-KOSHITS, Trudy Inst. Krist., Akad. Nauk. S.S.S.R. 10, 117 (1954).

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In the present work no planar complexes have been identified. Tetrahedral environments are found about the nickel atom for a number of complexes of the type NiL<sub>2</sub>X<sub>2</sub>. For cobalt, where the relative ligand field stabilization energies of a tetrahedral and an octahedral environment favour the tetrahedral form much more than with nickel all the complexes prepared of stoichiometry  $CoL_2X_2$  were tetrahedral except for the violet form of bispyridinecobalt (II) chloride. The fact that several complexes of the type NiL<sub>2</sub>X<sub>2</sub> have a tetrahedral environment about the metal suggests that such an arrangement has considerable stability in the lattice but that this stability is offset by the low ligand field stabilization energy of a tetrahedral as compared with an octahedral environment for most electronic configurations.

The actual structures adopted by the various phases are not known but it is likely that the complexes with smaller amounts of base have lattices in which there is considerable halide bridging as has previously been postulated for the corresponding cobalt complexes.<sup>(1.2)</sup> In spite of the lack of knowledge of precise details the broad outline of the thermal decompositions is clear and may be summarized:

$$\begin{split} \text{NiL}_4 X_2(\text{oct.}) &\rightarrow \text{NiL}_2 X_2(\text{oct.}) \rightarrow \text{NiL} X_2(\text{oct.}) \\ (\text{where } X = \text{Cl or Br}) \\ &\rightarrow \text{Ni}_3 L_2 X_6(\text{oct.}) \rightarrow \text{Ni} X_2(\text{oct.}); \\ \text{NiL}_6 I_2(\text{oct.}) \rightarrow \text{NiL}_4 I_2(\text{oct.}) \rightarrow \text{NiL}_2 I_2(\text{tet.}) \\ &\rightarrow \text{NiI}_2 + \text{NiO}; \\ \text{NiL}_2 X_2(\text{tet.}) \rightarrow \text{NiL} X_2(\text{oct.}) \rightarrow \text{Ni} X_2 \\ (\text{where } X = \text{Cl or Br}) \end{split}$$

The actual mode of thermal decomposition is not known and as it was not possible to determine melting points for all phases it cannot be said definitely that all transitions occurred in the liquid phase when major lattice rearrangements are required to go from one phase to another.

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