J. Inorg. Nucl. Chem., 1964, Vol. 26, pp. 2177 to 2184. Pergamon Press Ltd. Printed in Northern Ireland

THERMAL DECOMPOSITION OF NITROGEN LIGATED NICKEL (II) COMPLEXES AND ISOLATION OF NEW COMPOUNDS

A. K. MAJUMDAR, A. K. MUKHERJEE and ARUN K. MUKHERJEE
Department of Inorganic and Analytical Chemistry,
Jadavpur University, Calcutta-32, India

(*Received* 12 *December* 1963; *in revised form* 24 *April* 1964)

Abstract—Thermal decomposition of nitrogen ligated complexes of the type NiL_4X_2 and NiL_2X_2 has been studied and a few new compounds have been isolated.

DURING our study of the physical and chemical properties of the nitrogen ligated nickel (II) complexes of the types NiL_4X_2 (where L = pyridine, β- and γ-picolines, benzylamine and aniline; X = Cl^-, Br^-, I^-, NCS^- and ClO_3^-) and NiL_2X_2 (where L = pyridine, α-, β- and γ-picolines, piperidine, quinoline, isoquinoline, O-toluidine and aniline and X = Cl^-, Br^- and I^-), the pyrolysis curves obtained indicated the existence of new compounds which could not be prepared otherwise. This paper reports the isolation of some of the compounds of the types NiL_2X_2 and $NiLX_2$ (Table 1).

TABLE 1.—ANALYSIS OF PRODUCTS OBTAINED DURING THERMAL DECOMPOSITION

Compound	Colour	Ni(%)		X(%)	
		theo.	found	theo.	found
Ni(Pyridine)Cl_2	pale yellow	28·12	28·02	34·02	34·10
Ni(β-picoline)Cl_2	pale yellow	26·35	26·30	31·88	31·94
Ni(γ-picoline)Cl_2	pale yellow	26·35	26·33	31·88	31·96
Ni(Pyridine)$(NCS)_2$	yellow	23·14	23·13	—	—
Ni(Quinoline)Cl_2	pinkish brown	22·69	22·64	27·45	27·48
Ni$(Pyridine)_2Cl_2$	light blue	20·40	20·41	24·68	24·71
Ni$(\beta$-picoline$)_2Cl_2$	pale yellow	18·60	18·49	22·49	22·45
Ni$(aniline)_2Cl_2$	pale green	18·60	18·59	22·49	22·56

While this investigation was in progress a note[1] appeared on the thermal decomposition of tetrapyridine nickel (II) chloride.

EXPERIMENTAL

Materials

Of the nickel complexes studied, the tetraligated pyridine[2] and the bisligated quinoline[3] and α-picoline[4] complexes are known. They were prepared according to the methods suggested in their respective references.

(1) D. H. BROWN, R. H. NUTTAL and D. W. A. SHARP, *J. Inorg. Nucl. Chem.* **25**, 1067 (1963).
(2) F. REITZENSTEIN, *Z. Anorg. Chem.* **11**, 254 (1895); **18**, 269 (1898).
(3) D. M. L. GOODGAME and M. GOODGAME, *J. Chem. Soc.* **207**, (1963).
(4) Sister M. DENNIS GLONEK, Brother COLUMBA CURRAN and J. V. QUAGLIANO, *J. Amer. Chem. Soc.* **84**, 2014 (1962); A. V. LOGAN and D. W. CARLE, *J. Amer. Chem. Soc.* **74**, 5224 (1952).

The methods for the preparation of the other complexes and their properties will be described in a subsequent paper. The purity of the compounds was checked by analysis (Table 2).

Table 2.—Analysis of starting material

Compound	Found (%)			Required (%)		
	Ni	X	N	Ni	X	N
Ni(Pyridine)$_4$Cl$_2$	13·12	15·87	12·48	13·17	15·93	12·56
Ni(Pyridine)$_4$Br$_2$	10·89	30·08	10·43	10·97	29·92	10·47
Ni(Pyridine)$_4$I$_2$	9·30	40·66	8·89	9·33	40·39	8·90
Ni(Pyridine)$_4$(NCS)$_2$	11·92	—	17·10	11·96	—	17·12
Ni(Pyridine)$_4$(ClO$_3$)$_2$	10·80	—	10·21	10·83	—	10·34
Ni(β-picoline)$_4$Cl$_2$	11·68	14·14	11·10	11·70	14·16	11·16
Ni(β-picoline)$_4$Br$_2$	9·92	27·12	9·42	9·94	27·08	9·47
Ni(β-picoline)$_4$I$_2$	8·52	37·14	8·20	8·57	37·10	8·18
Ni(β-picoline)$_4$(NCS)$_2$	10·69	—	15·33	10·74	—	15·37
Ni(β-picoline)$_4$(ClO$_3$)$_2$	9·80	—	9·18	9·82	—	9·22
Ni(γ-picoline)$_4$Cl$_2$	11·69	14·13	11·21	11·70	14·16	11·16
Ni(γ-picoline)$_4$Br$_2$	9·91	27·06	9·40	9·94	27·08	9·47
Ni(γ-picoline)$_4$I$_2$	8·56	37·12	8·12	8·57	37·10	8·18
Ni(γ-picoline)$_4$(NCS)$_2$	10·71	—	15·32	10·74	—	15·37
Ni(γ-picoline)$_4$(ClO$_3$)$_2$	9·83	—	9·16	9·82	—	9·22
Ni(aniline)$_4$Cl$_2$	11·68	14·19	11·20	11·70	14·16	11·16
Ni(aniline)$_4$Br$_2$	9·95	27·10	9·30	9·94	27·08	9·47
Ni(aniline)$_4$I$_2$	8·60	37·14	8·30	8·57	37·10	8·17
Ni(benzylamine)$_4$Cl$_2$	10·50	12·70	9·98	10·52	12·74	10·04
Ni(benzylamine)$_4$Br$_2$	9·00	24·71	8·62	9·07	24·76	8·66
Ni(benzylamine)$_4$I$_2$	7·88	34·22	7·48	7·93	34·30	7·57
Ni(α-picoline)$_2$Cl$_2$	18·57	22·51	8·84	18·59	22·49	8·87
Ni(α-picoline)$_2$Br$_2$	14·47	39·40	6·81	14·50	39·53	6·92
Ni(quinoline)$_2$Cl$_2$	15·12	18·33	7·21	15·14	18·31	7·22
Ni(quinoline)$_2$Br$_2$	12·29	33·63	5·83	12·31	33·57	5·88
Ni(quinoline)$_2$I$_2$	10·27	44·53	4·89	10·28	44·50	4·91
Ni(pipiridine)$_2$Cl$_2$	19·56	23·73	9·34	19·58	23·69	9·30
Ni(pipiridine)$_2$Br$_2$	15·12	41·10	7·20	15·10	41·16	7·14
Ni(pipiridine)$_2$I$_2$	12·14	52·58	5·82	12·16	52·62	5·80
Ni(isoquinoline)$_2$Cl$_2$	15·16	18·36	7·21	15·14	18·31	7·22
Ni(isoquinoline)$_2$Br$_2$	12·30	33·60	5·87	12·31	33·57	5·88
Ni(isoquinoline)$_2$I$_2$	10·20	44·46	4·90	10·28	44·50	4·89
Ni(O-toluidine)$_2$Cl$_2$	16·92	20·60	8·13	17·08	20·65	8·15
Ni(O-toluidine)$_2$Br$_2$	13·52	37·02	6·45	13·56	36·98	6·47
Ni(O-toluidine)$_2$I$_2$	11·10	48·02	5·33	11·14	48·21	5·31
Ni(γ-picoline)$_2$Cl$_2$	18·52	22·54	8·72	18·60	22·49	8·87

Apparatus

A Chevenard Thermobalance of type 3 of A.D.A.M.E.L. of Paris, which registers photographically the loss in weight of the heated substance, as a function of temperature, was used. The occurrence of a horizontal in the curve is taken as evidence that the substance remains constant in weight throughout the temperature range corresponding to that horizontal. The rate of heating was 5°C per min, and the compounds were heated up to 700°C.

RESULTS

The thermogravimetric results are given in the Figures. In many cases the complexes decompose in a stepwise fashion with the formation of definite intermediate compounds. Flat portions in the curves bear evidence to their existence. The decomposition temperatures of the complexes and of the intermediate compounds as well as their stability range are recorded in Table 3. The final product in the decomposition of all

TABLE 3

Complex	Decomposition temp. (°C)	Product	Stability range (°C)
$Ni(pyridine)_4Cl_2$	110; 190; 270	NiL_2Cl_2; $NiLCl_2$; $NiCl_2$	178–190; 220–270; 365–490
$Ni(\beta\text{-picoline})_4Cl_2$	115; 175; 260	NiL_2Cl_2; $NiLCl_2$; $NiCl_2$	160–175; 230–260; 365–490
$Ni(\gamma\text{-picoline})_4Cl_2$	145; 280	$NiLCl_2$; $NiCl_2$	240–280; 380–490
$Ni(benzylamine)_4Cl_2$	90; 260	NiL_2Cl_2; $NiCl_2$	220–260; 360–490
$Ni(aniline)_4Cl_2$	75; 232	NiL_2Cl_2; $NiCl_2$	140–232; 335–490
$Ni(quinoline)_2Cl_2$	175; 250	$NiLCl_2$; $NiCl_2$	210–250; 420–490
$Ni(O\text{-toluidine})_2Cl_2$	130	$NiCl_2$	250–490
$Ni(piperidine)_2Cl_2$	190; 300	$NiLCl_2$; $NiCl_2$	272–300; 370–500
$Ni(isoquinoline)_2Cl_2$	120; 200	$NiLCl_2$; $NiCl_2$	180–200; 260–490
$Ni(\alpha\text{-picoline})_2Cl_2$	60	$NiCl_2$	360–480
$Ni(\beta\text{-picoline})_2Cl_2$	110; 260	$NiLCl_2$; $NiCl_2$	230–260; 365–500
$Ni(\gamma\text{-picoline})_2Cl_2$	150; 280	$NiLCl_2$; $NiCl_2$	240–280; 365–490
$Ni(Pyridine)_2Cl_2$	170; 290	$NiLCl_2$; $NiCl_2$	220–270; 365–490
$Ni(aniline)_2Cl_2$	232	$NiCl_2$	335–490
$Ni(Pyridine)_4Br_2$	60; 195	$NiLBr_2$; NiOBr	175–190; 320–345
$Ni(\beta\text{-picoline})_4Br_2$	70;	NiOBr	320–345
$Ni(\gamma\text{-picoline})_4Br_2$	50	NiOBr	320–345
$Ni(benzylamine)_4Br_2$	95; 180	NiL_2Br_2; NiOBr	140–180; 310–490
$Ni(aniline)_4Br_2$	75; 225	NiL_2Br_2; $NiBr_2$	160–225; 290–490
$Ni(quinoline)_2Br_2$	150; 250	$NiLBr_2$; $NiBr_2$	240–250; 330–490
$Ni(isoquinoline)_2Br_2$	100; 200	a; NiOBr	190–200; 400–480
$Ni(O\text{-toluidine})_2Br_2$	120; 170	$NiLBr_2$; $NiBr_2$	165–170; 270–490
$Ni(Pyridine)_4I_2$	60; 132	NiL_2I_2; $NiLI_2$	125–132; 230–260
$Ni(\beta\text{-picoline})_4I_2$	100	NiL_2I_2	210–235
$Ni(\gamma\text{-picoline})_4I_2$	35	NiL_2I_2	90–150
$Ni(aniline)_4I_2$	150	NiI_2	240–255
$Ni(O\text{-toluidine})_2I_2$	80	NiI_2	220–260
$Ni(Pyridine)_4(NCS)_2$	155; 215; 320	$NiL_2(NCS)_2$; $NiL(NCS)_2$; $Ni(NCS)_2$	205–215; 285–320; 410
$Ni(\beta\text{-picoline})_4(NCS)_2$	150; 360	$NiL(NCS)_2$; $Ni(NCS)_2$	250–360; 410
$Ni(\gamma\text{-picoline})_4(NCS)_2$	130; 370	$NiL(NCS)_2$; $Ni(NCS)_2$	290–370; 440

a = no definite compound.

the complexes is nickel oxide, NiO, except in the cases of the isothiocyanate complexes where the end product is $Ni(NCS)_2$. Details of the weight loss, at each stage, are recorded in Tables 4, 5 and 6. From the Tables, it would appear though that in some cases the calculated and the experimental weight loss values do not agree satisfactorily with each other, the experimental values are good enough to predict the formation of such compounds.

Table 4.—Weight loss data for the chloro complexes

Compound	Weight loss (%) NiL$_2$X$_2$ theo.	NiL$_2$X$_2$ found	NiLX$_2$ theo.	NiLX$_2$ found	NiX$_2$ theo.	NiX$_2$ found
Ni(Pyridine)$_4$Cl$_2$	28·2	29·2	53·2	55·5	70·8	74·3
Ni(β-picoline)$_4$Cl$_2$	37·1	37·6	55·7	53·9	74·1	74·6
Ni(γ-picoline)$_4$Cl$_2$	—	—	55·7	54·2	74·1	71·1
Ni(aniline)$_4$Cl$_2$	37·5	37·7	—	—	74·1	72·9
Ni(benzylamine)$_4$Cl$_2$	38·5	36·2	—	—	76·7	78·0
Ni(piperidine)$_2$Cl$_2$	—	—	28·0	29·0	56·9	57·3
Ni(O-toluidine)$_2$Cl$_2$	—	—	—	—	62·3	60·3
Ni(quinoline)$_2$Cl$_2$	—	—	33·3	32·6	66·6	65·3
Ni(isoquinoline)$_2$Cl$_2$	—	—	33·3	28·5	66·6	65·1

Table 5.—Weight loss data for the bromo complexes

Compound	Weight loss (%) NiL$_2$X$_2$ theo.	NiL$_2$X$_2$ found	NiLX$_2$ theo.	NiLX$_2$ found	NiX$_2$ theo.	NiX$_2$ found	NiOX (?) theo.	NiOX (?) found
Ni(Pyridine)$_4$Br$_2$	29·6	28·6	44·2	54·5	—	—	71·2	72·9
Ni(β-picoline)$_4$Br$_2$	—	—	—	—	—	—	73·8	69·6
Ni(γ-picoline)$_4$Br$_2$	—	—	—	—	—	—	73·8	72·1
Ni(aniline)$_4$Br$_2$	31·5	33·9	—	—	63·0	61·0	—	—
Ni(benzylamine)$_4$Br$_2$	33·1	31·1	—	—	66·3	62·2	—	—
Ni(quinoline)$_2$Br$_2$	—	—	27·1	29·8	54·0	56·0	—	—

Table 6.—Weight loss data for some iodo and isothiocyanato complexes

Compound	Weight loss (%) NiL$_2$X$_2$ theo.	NiL$_2$X$_2$ found	NiLX$_2$ theo.	NiLX$_2$ found	NiX$_2$ theo.	NiX$_2$ found
Ni(Pyridine)$_4$I$_2$	25·1	20·7	37·7	33·3	—	—
Ni(β-picoline)$_4$I$_2$	27·2	29·7	—	—	—	—
Ni(γ-picoline)$_4$I$_2$	27·2	23·4	—	—	54·3	46·8
Ni(aniline)$_4$I$_2$	—	—	—	—	54·3	53·7
Ni(benzylamine)$_4$I$_2$	—	—	—	—	57·8	57·9
Ni(Pyridine)$_4$(NCS)$_2$	32·2	24·3	48·3	46·5	64·4	62·5
Ni(β-picoline)$_4$(NCS)$_2$	—	—	51·1	49·7	68·1	67·2
Ni(γ-picoline)$_4$(NCS)$_2$	—	—	51·1	52·6	68·1	66·9

Decomposition of tetraligated complexes

Chloro complexes. Tetrapyridine, tetra(β-picoline), tetra(γ-picoline), tetra(aniline) and tetra(benzylamine) complexes decompose stepwise when heated in the presence of air (Fig. 1)

$$NiL_4X_2 = NiL_2X_2 + 2L$$
$$NiL_2X_2 = NiLX_2 + L$$
$$NiLX_2 = NiX_2 + L$$
$$NiX_2 + \tfrac{1}{2}O_2 = NiO + X_2$$

However, the pyrolysis curves do not indicate the existence of bis(γ-picoline) and mono(aniline) nickel chloride. The intermediate compounds NiL_2Cl_2 and $NiLCl_2$ were isolated after heating the tetraligated complexes at the required temperature and their compositions confirmed by elemental analysis (Table 1). Though the existence of mono(benzylamine) derivative could be inferred from the small horizontal in the curve near 300°, attempts to isolate it met with no success.

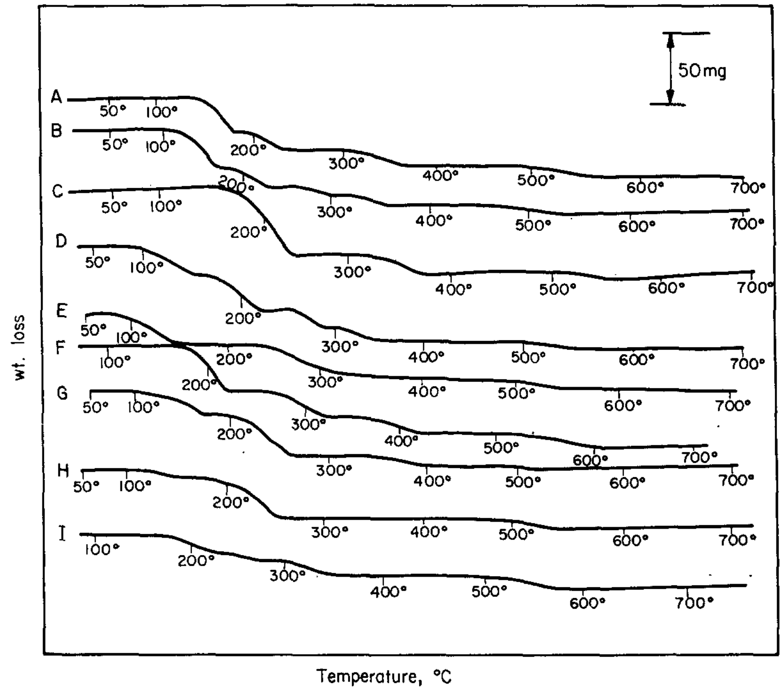

FIG. 1.—Thermolysis curves of chloro complexes.

A. $Ni(Py)_4Cl_2$; B. $Ni(\beta\text{-Pic})_4Cl_2$; C. $Ni(\gamma\text{-Pic})_4Cl_2$; D. $Ni(benzylamine)_4Cl_2$; E. $Ni(aniline)_4Cl_2$; F. $Ni(quinoline)_2Cl_2$; G. $Ni(Isoquinoline)_2Cl_2$; H. $Ni(O\text{-}toluidine)_2Cl_2$; I. $Ni(Pipi)_2Cl_2$

Bromo complexes. All the bromo complexes decompose to nickel oxide with the intermediate formation of the bis(derivative) and nickel bromide (Fig. 2, Table 5). The curves do not suggest the presence of $NiLBr_2$. The almost horizontal line between 320° and 345°, for complexes with L = pyridine, β-picoline, γ-picoline and isoquinoline, agrees with the formation of a pale yellow unstable compound whose composition could not be determined with certainty though the height corresponds to NiOBr (Table 5), and it appears to be oxidizing in character. This product changes rapidly to green on exposure.

Iodo complexes. The pyrolysis curves of the iodo complexes (Fig. 3) descend continuously until the NiO state is reached. In some cases the existence of the complexes NiL_2I_2 and $NiLI_2$ as well as of NiI_2 can be deduced from the weight loss data (Tables 3 and 6), but as these temperatures fall on the slope of the curves, attempts to isolate them failed. The long horizontal, between 400° and 550°, in the decomposition curve of tetra(γ-picoline) nickel iodide (Fig. 3C), does not agree to any definite compound.

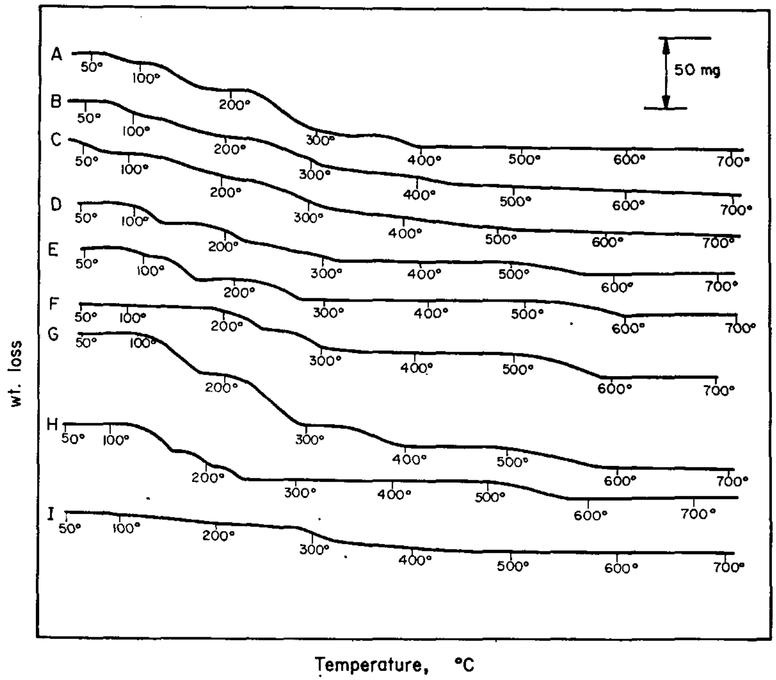

FIG. 2.—Thermolysis curves of bromo complexes.

A. $Ni(Py)_4Br_2$; B. $Ni(\beta\text{-}Pic)_4Br_2$; C. $Ni(\gamma\text{-}Pic)_4Br_2$; D. Ni(benzylamine)$_4Br_2$; E. Ni(aniline)$_4Br_2$; F. Ni(quinoline)$_2Br_2$; G. Ni(Isoquinoline)$_2Br_2$; H. Ni(O-toluidine)$_2Br_2$; I.Ni(Pipi)$_2Br_2$

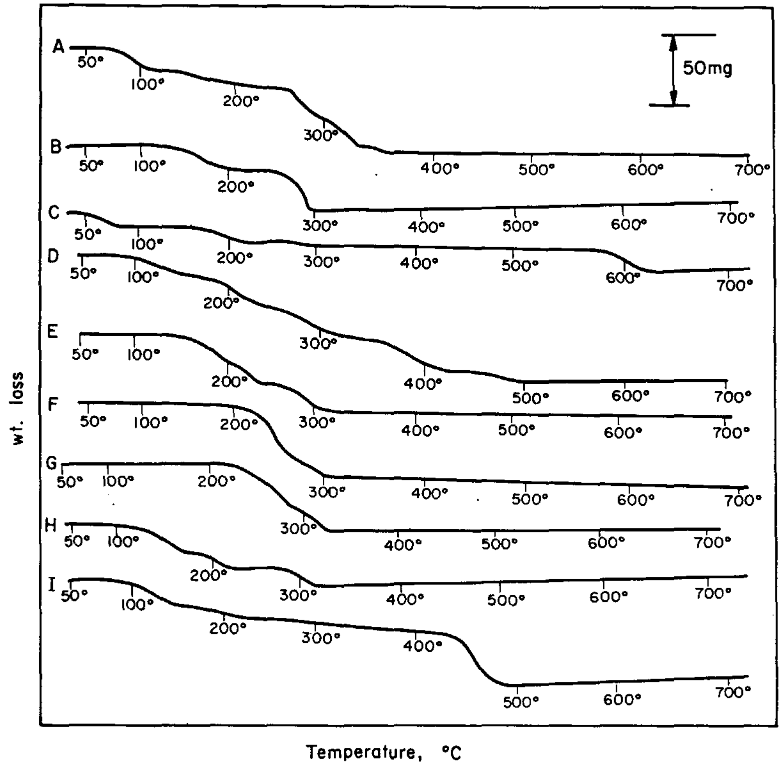

FIG. 3.—Thermolysis curves of iodo-complexes.

A. $Ni(Py)_4I_2$; B. $Ni(\beta\text{-}Pic)_4I_2$; C. $Ni(\gamma\text{-}Pic)_4I_2$; D. Ni(benzylamine)$_4I_2$; E. Ni(aniline)$_4I_2$; F. Ni(quinoline)$_2I_2$; G. Ni(Isoquinoline)$_2I_2$; H. Ni(O-toluidine)$_2I_2$; I. Ni(Pipi)$_2I_2$

Chlorate complexes. The chlorate complexes decompose slowly from the very beginning. At about 300°, the decomposition is abrupt with the loss of both chlorine and oxygen, resulting in the formation of NiO (Fig. 4).

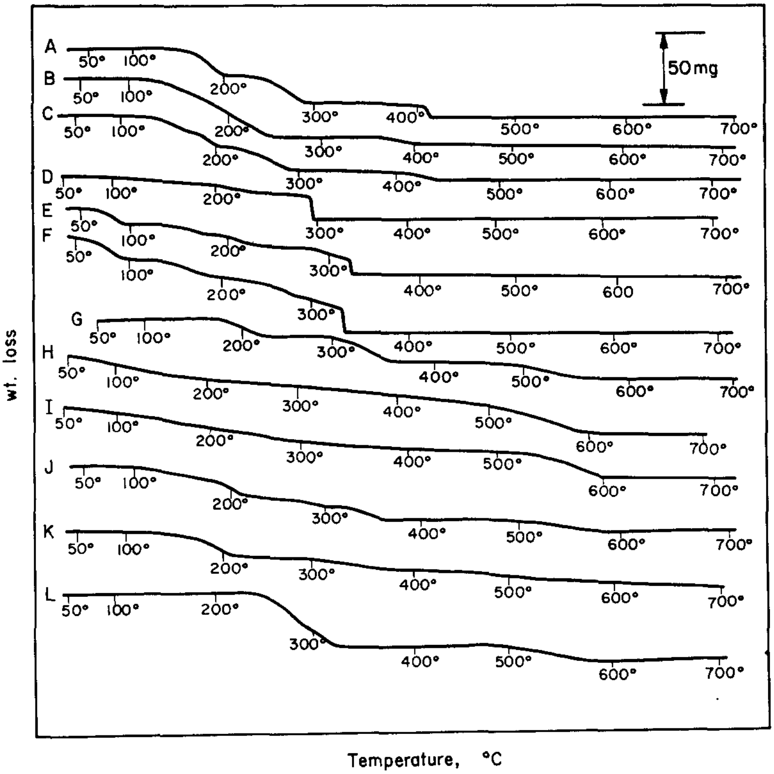

FIG.—4. Thermolysis curves of chlorate, isothiocyanate and some bis-ligated complexes. A. $Ni(Py)_4(NCS)_2$; B. $Ni(\beta\text{-Pic})_4(NCS)_2$; C. $Ni(\gamma\text{-Pic})_4(NCS)_2$; D. $Ni(Py)_4(ClO_3)_2$ E. $Ni(\beta\text{-Pic})_4(ClO_3)_2$; F. $Ni(\gamma\text{-Pic})_4(ClO_3)_2$; G. $Ni(Py)_2Cl_2$; H. $Ni(\alpha\text{-Pic})_2Cl_2$; I. $Ni(\alpha\text{-Pic})_2Br_2$; J. $Ni(\beta\text{-Pic})_2Cl_2$; K. $Ni(\gamma\text{-Pic})_2Cl_2$; L. $Ni(aniline)_2Cl_2$

Isothiocyanate complexes. The pyrolysis curve for $Ni(Py_4(NCS)_2$ Fig. 4A, Table 6), as obtained, does not agree with that of DUVAL.[5] The compound has been found to be stable upto 155° and not upto 63°, as reported. Further, the course of the curve is difficult to interpret. Nowhere any evidence for the existence of the compound, $Ni(Py)_3(NCS)_2$, as suggested by him, could be had. The horizontal between 285° and 320° corresponds to $Ni(Py)(NCS)_2$ which has been actually isolated (Table I).

The curves due to $Ni(\beta\text{-picoline})_4(NCS)_2$ (Fig. 4B) and $Ni(\gamma\text{-picoline})_4(NCS)_2$ (Fig. 4C) are similar to that of the pyridine derivative. The curves fail to indicate the presence of $NiL_3(NCS)_2$ or $NiL_2(NCS)_2$, but the horizontal levels near 300° correspond more closely to $NiL(NCS)_2$.

Pyrolysis of bis-ligated complexes. The bis-ligated chlorocomplexes, NiL_2Cl_2 (where L = pyridine, α-, β- and γ-picolines, piperidine, quinoline, isoquinoline, aniline and O-toluidine), decompose in a stepwise fashion (Figs. 1 and 4).

$$NiL_2Cl_2 \rightarrow NiLCl_2 \rightarrow NiCl_2 \rightarrow NiO.$$

[5] C. DUVAL, *Inorganic Thermogravimetric Analysis*, p. 227. Elsevier (1953).

The compounds $NiLCl_2$ (where L = pyridine, quinoline, β- and γ-picolines) could be isolated after heating either the tetraligated or the bisligated complexes at the required temperature, and their composition confirmed by the elemental analysis (Table 1), while in other cases, where L = α-picoline, piperidine, isoquinoline, aniline and O-toluidine, though indications for such complex formation are there, their actual isolation was not possible as the horizontal portion of the curves at that stage was either very short or slanting.

The bromocomplexes, NiL_2Br_2 (where L = quinoline and isoquinoline), decompose ultimately to NiO possibly through the intermediate formation of $NiLBr_2$ and $NiBr_2$ (Fig. 2). In the case of Ni(O-toluidine)$_2$Br$_2$ the slight horizontal at 165°C tallies approximately to Ni(O-toluidine) Br_2 (Fig. 2H). However, this could not be isolated in the pure state. The end product of other bromocomplexes is NiO, but the actual course of the curve is difficult to interpret. Only the horizontal level, near 400°, agrees with the composition $NiBr_2$.

The iodocomplexes (Fig. 3) decompose until NiO is formed. In most cases there are no intermediate horizontal levels. Only with bis(O-toluidine) nickel iodide (Fig. 3H) the level between 220° and 260° corresponds to NiI_2.

DISCUSSION

The thermal stability order of the complexes NiL_4X_2 follows the same sequence as that of the pure compounds NiX_2 e.g. $NCS^- > Cl^- > ClO_3^- > Br^- > I^-$, except in the case of the aniline, bis(quinoline) and bis(isoquinoline) derivatives, where the stability order is $I^- > Br^- > Cl^-$. Thus while in the former the ligands follow the order of the spectrochemical series, in the latter they observe the order of the nephelauxetic series.

If we compare the first decomposition points of the chlorocomplexes, for example, we find that for the tetraligated derivatives the stability follows the sequence γ-picoline > pyridine > β-picoline > benzylamine > aniline. For the bisligated complexes the order, however, is aniline > piperidine > quinoline > pyridine > γ-picoline > O-toluidine > isoquinoline > β-picoline > α-picoline. Again the thermal stability sequence, for the bromocomplexes, NiL_4Br_2, in order of decreasing stability is benzylamine > aniline > β-picoline > pyridine > γ-picoline and for the iodocomplexes, NiL_4I_2, the sequence is aniline > β-picoline > benzylamine > pyridine > γ-picoline. The basicity of the ligand is not the sole factor to govern the stability of the complexes. Moreover, from these data alone it is not possible to find any recognizable relation between the thermal stability of the complexes and their composition with respect to L and X^-. The steric factor along with varying contributions of σ and π bonding may be suggested to play a significant part. Of course, it may be realized that the stability of the above complexes is influenced more by their reaction with air rather than by their relative resistance to pyrolysis.