

## SOME FIRST ROW TRANSITION METAL COMPLEXES OF NICOTINAMIDE AND NICOTINIC ACID

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Some complexes of the chlorides and bromides of manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) with nicotinamide and nicotinic acid have been prepared. These complexes have stoichiometry  $ML_2X_2$  where  $M$  is a metal ion,  $L$  is an organic ligand and  $X$  is a halide ion. Spectral and magnetic properties indicate that these compounds have octahedral polymeric structures. The decomposition of the complexes was studied by thermogravimetry and differential thermal analysis. In only one instance was a decomposition product of the formula  $MLX_2$  obtained. Its structure was also octahedral.

Pyridine compounds, ranging in complexity from nicotine to monosubstituted pyridines like nicotinamide and nicotinic acid play an important role in the metabolism of all living cells. Nicotinamide and nicotinic acid are of biological origin: nicotinamide being an important component of the hydrogen-carrying co-enzymes nicotinamide-adenine dinucleotide and nicotinamide adenine dinucleotide phosphate; while nicotinic acid is an essential vitamin. Many stable complexes of metal salts with nicotinic acid and nicotinamide are known [1–6]. In this paper, we report a study of the chloro- and bromo-complexes of nicotinamide and nicotinic acid with the first row transition metals, manganese(II), iron(II), cobalt(II), nickel(II) and copper(II). No thermal decomposition data have been previously reported in the literature for these compounds. The electronic spectra, magnetic measurements and the far infrared spectra have only received little attention.

Information about the stereochemistry of the compounds has been obtained by studying the magnetic moment over the temperature range 300–100 K for each of the compounds isolated from solution while the electronic spectra and infrared spectra have been recorded for each complex. The thermal decomposition of the compounds has also been studied.

### Experimental

Three methods of preparation were used:

(A) The complexes were prepared by addition of either a warm ethanolic solution of nicotinamide (9 : 100 parts by weight) or a boiling ethanolic solution of nicotinic acid (6 : 100 parts by weight), to the appropriate warm ethanolic solu-

tion of the metal halide in a 2 : 1 molar ratio. The precipitated complexes were washed with ethanol and ether and dried over calcium chloride.

(B) This method was similar to (A) except that the preparation was carried out under dry nitrogen.

(C) A complex prepared by method (A) was heated on a thermobalance at a fixed temperature until constant weight was obtained.

The complexes prepared by these methods are listed in Table 1. Reference are given to previous preparations. Where no reference is given it is believed that this is a new compound.

Table 1  
Analysis of compounds

Compound	Method of preparation	Metal found	Halide found	Metal theory	Halide theory	References
Mn(ANA) <sub>2</sub> Cl <sub>2</sub> ·H <sub>2</sub> O	A	14.12	18.24	14.15	18.27	
Mn(ANA) <sub>2</sub> Cl <sub>2</sub>	B	14.80	19.11	14.84	19.15	[1, 3]
Mn(ANA) <sub>2</sub> Br <sub>2</sub>	A	11.94	34.80	11.97	34.81	[1]
Mn(NA) <sub>2</sub> Cl <sub>2</sub>	A	14.76	18.98	14.77	19.06	[1]
Mn(NA)Cl <sub>2</sub>	B	22.02	28.50	22.08	28.52	
Mn(NA) <sub>2</sub> Br <sub>2</sub>	A	11.87	34.64	11.92	34.67	[1]
Fe(ANA) <sub>2</sub> Cl <sub>2</sub>	C	15.08	19.12	15.10	19.14	
Fe(NA) <sub>2</sub> Cl <sub>2</sub>	C	15.01	19.02	15.02	19.03	
Co(ANA) <sub>2</sub> Cl <sub>2</sub>	A	15.74	18.92	15.75	18.95	[2, 4]
Co(ANA) <sub>2</sub> Br <sub>2</sub>	A	12.71	34.50	12.73	34.51	
Co(NA) <sub>2</sub> Cl <sub>2</sub>	A	15.65	18.83	15.67	18.85	
Co(NA) <sub>2</sub> Br <sub>2</sub>	A	12.66	34.34	12.67	34.37	
Ni(ANA) <sub>2</sub> Cl <sub>2</sub> ·2H <sub>2</sub> O	A	14.30	17.26	14.32	17.30	
Ni(ANA) <sub>2</sub> Cl <sub>2</sub>	B	15.66	18.96	15.70	18.96	[2, 3, 5]
Ni(ANA) <sub>2</sub> Br <sub>2</sub>	A	12.66	34.50	12.69	34.53	[5]
Ni(NA) <sub>2</sub> Cl <sub>2</sub>	A	15.60	18.84	15.62	18.86	[5]
Ni(NA) <sub>2</sub> Br <sub>2</sub>	A	12.60	34.36	12.63	34.38	[5]
Cu(ANA) <sub>2</sub> Cl <sub>2</sub>	A	16.76	18.74	16.78	18.76	[6]
Cu(ANA) <sub>2</sub> Br <sub>2</sub>	A	13.55	34.20	13.58	34.22	[6]
Cu(NA) <sub>2</sub> Cl <sub>2</sub>	A	16.66	18.64	16.69	18.66	
Cu(NA) <sub>2</sub> Br <sub>2</sub>	A	13.52	34.04	13.52	34.07	

(ANA) = nicotinamide (C<sub>6</sub>H<sub>6</sub>ON<sub>2</sub>)

(NA) = nicotinic acid (C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>N)

Thermal decomposition studies were carried out in air on a Stanton Redcroft Model TR-01 Thermobalance working at chart speed of 6 in/hr with DTA attachment (Table 2). Electronic spectra were obtained on a Beckman ACTA M-IV spectrophotometer.

Table 2  
TG data

Compound	Expected loss	Calculated, %	Actual, %
Mn(ANA) <sub>2</sub> Cl <sub>2</sub> ·H <sub>2</sub> O	H <sub>2</sub> O	4.64	4.04
	(ANA) <sub>2</sub>	62.93	64.19
Mn(NA) <sub>2</sub> Cl <sub>2</sub>	(NA)	33.09	35.42
	(NA)	33.09	34.89
Co(NA) <sub>2</sub> Cl <sub>2</sub>	NA	32.74	34.81
Ni(ANA) <sub>2</sub> Cl <sub>2</sub> ·2H <sub>2</sub> O	H <sub>2</sub> O	4.40	7.66
	H <sub>2</sub> O	4.40	4.27
	(ANA) <sub>2</sub>	59.59	59.63

Infrared absorption spectra (KBr discs) were obtained with a Perkin-Elmer Infrared Spectrophotometer. Far infrared spectra were obtained on a Beckman IR 720 M interferometer using a polythene matrix to support the complexes. Magnetic susceptibility measurements were made by the Gouy method using a Newport variable temperature balance and the calibrant Hg[Co(SCN)<sub>4</sub>]. The complexes were studied over the temperature range 300–100 K and the results fitted to the Curie-Weiss equation

$$\mu = 2.84 [\chi_M^{Corr} (T - \vartheta)]^{1/2}$$

Diamagnetic corrections were applied using the atomic diamagnetic susceptibilities tabulated by Figgis and Lewis [7]. The results were processed on the Napier College CTL Modular One computer using programme MAG [8].

## Results

The nicotinamide and nicotinic acid complexes of manganese(II) were obtained as pale pink and white powders, respectively. The compounds had stoichiometry Mn L<sub>2</sub>X<sub>2</sub> with the exception of bisnicotinamide manganese(II)chloride which has one molecule of water of crystallization. Thermal decomposition studies of Mn(ANA)<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O, (Fig. 1) showed that this compound underwent an endothermic reaction at 373 K with loss of the water molecule. A further endothermic reaction takes place with a further mass loss corresponding to a loss of two nicotinamide ligands at 590 K. Bisnicotinic acid manganese(II)chloride (Fig. 2) decomposes in two stages. Above 503 K a rapid endothermic decomposition takes place resulting in the formation of Mn(NA)Cl<sub>2</sub>. At 664 K a further endothermic mass loss occurs followed by an exothermic reaction at 840 K to give manganese(II)chloride.

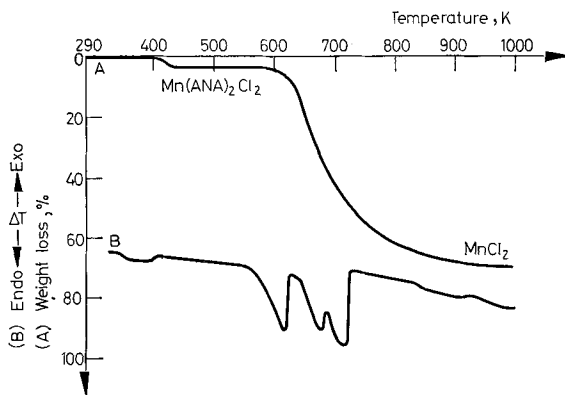


Fig. 1. TG (curve A) and DTA (curve B) of  $\text{Mn(ANA)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ . Sample weight: 76.8 mg; Atmosphere: Static air; Heating rate:  $4^\circ \text{ min}^{-1}$

Bisnicotinamide manganese(II)bromide and bisnicotinic acid manganese(II)-bromide showed no intermediate stages in their thermal decomposition. The visible absorption spectra, show as expected for  $d^5$  ions, weak bands which have been assigned to the transitions  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ ;  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ ;  ${}^6A_{1g} \rightarrow {}^4E_g(G)$ ;  ${}^4A_{1g}(G)$ . The magnetic moments (Table 3) are similar to those expected for manganese(II) ions ( $\sim 5.9$  B.M.) with the exception of  $\text{Mn(ANA)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  which has a value of 6.34 B. M. This is probably due to some distortion of the octahedral environment of the manganese(II) ion resulting in a small orbital contribution. The far infrared spectra support an essentially octahedral environment round the metal [9].

The iron(II)chloride compounds of nicotinamide and nicotinic acid are yellow in colour and have stoichiometry  $\text{FeL}_2\text{Cl}_2$ . No stoichiometric complexes of iron(II)-

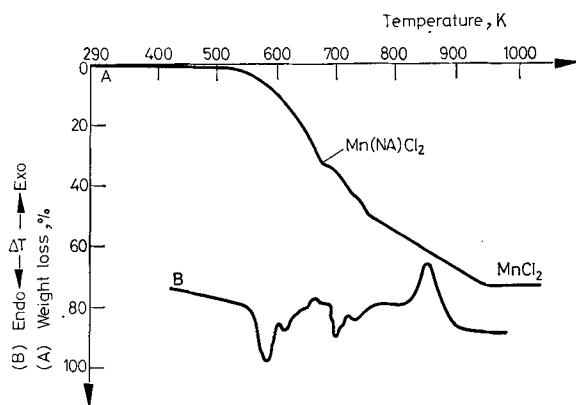


Fig. 2. TG (curve A) and DTA (curve B) of  $\text{Mn(NA)}_2\text{Cl}_2$ . Sample weight: 75.1 mg; Atmosphere: Static air; Heating rate:  $4^\circ \text{ min}^{-1}$

Table 3  
Magnetic data

Compound	Temperature, /K	Diamagnetic correction, /10 <sup>-6</sup>	$\chi_M^{\text{Corr}}/10^{-6}$	$\mu$ , B.M.	$\phi$
Mn(ANA) <sub>2</sub> Cl <sub>2</sub> ·H <sub>2</sub> O	298	120.80	16720	6.34	7.4
Mn(ANA) <sub>2</sub> Br <sub>2</sub>	298	128.80	15130	6.03	8.1
Mn(NA) <sub>2</sub> Cl <sub>2</sub>	298	115.80	14577	5.92	1.7
Mn(NA) <sub>2</sub> Br <sub>2</sub>	295	136.80	14948	5.96	7.5
Fe(ANA) <sub>2</sub> Cl <sub>2</sub>	297	106.60	14296	5.85	-20.4
Fe(NA) <sub>2</sub> Cl <sub>2</sub>	297	114.60	13805	5.75	-5.13
Co(ANA) <sub>2</sub> Cl <sub>2</sub>	295	106.60	13014	5.57	10.6
Co(ANA) <sub>2</sub> Br <sub>2</sub>	298	127.60	12337	5.45	8.1
Co(NA) <sub>2</sub> Cl <sub>2</sub>	295	114.60	12881	5.54	19.7
Co(NA) <sub>2</sub> Br <sub>2</sub>	295	135.60	12545	5.46	17.9
Ni(ANA) <sub>2</sub> Cl <sub>2</sub> ·2H <sub>2</sub> O	296	132.60	6151	3.83	-19.1
Ni(ANA) <sub>2</sub> Br <sub>2</sub>	293	127.60	5435	3.58	-8.6
Ni(NA) <sub>2</sub> Cl <sub>2</sub>	293	114.60	5078	3.46	-20.3
Ni(NA) <sub>2</sub> Br <sub>2</sub>	293	135.60	4874	3.39	-10.8
Cu(ANA) <sub>2</sub> Cl <sub>2</sub>	293	106.60	1253	1.72	-27.7
Cu(ANA) <sub>2</sub> Br <sub>2</sub>	290	127.60	1364	1.79	4.41
Cu(NA) <sub>2</sub> Cl <sub>2</sub>	297	114.6	1525	1.91	-3.62
Cu(NA) <sub>2</sub> Br <sub>2</sub>	292	135.6	1876	2.10	39.3

bromide could be prepared possibly because of the presence of iron(III) in the iron(II)bromide. The preparations were all carried out in a dry nitrogen atmosphere. Thermogravimetric studies on the chloro-compounds showed no intermediate decomposition steps. By 720 K the weight loss corresponded to the complete loss of organic material in each compound. The visible spectra exhibit a broad absorption band which is clearly split into two components in the region 14,500–18,500 cm<sup>-1</sup>. This would suggest an octahedral environment for the iron (Table 4). The two components represent transitions to the <sup>5</sup>E<sub>g</sub> state from

Table 4  
Electronic spectra, cm<sup>-1</sup>  
Manganese compounds  
Octahedral environment (Ground state <sup>6</sup>A<sub>1g</sub>)

Compound	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (G)	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> (G)	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> E <sub>g</sub> (G), <sup>4</sup> A <sub>1g</sub> (G)
Mn(ANA) <sub>2</sub> Cl <sub>2</sub>	18,870	21,270	23,200
Mn(ANA) <sub>2</sub> Br <sub>2</sub>	19,420	21,500	22,220
Mn(NA) <sub>2</sub> Cl <sub>2</sub>	19,040	21,460	22,960
Mn(NA)Cl <sub>2</sub>	—	21,600	23,010
Mn(NA) <sub>2</sub> Br <sub>2</sub>	19,040	21,740	22,960

## Iron compounds

Octahedral environment (Ground state  ${}^5T_{2g}$ )

Compound	${}^6T_{2g} \rightarrow {}^6E_g$	
Fe(ANA) <sub>2</sub> Cl <sub>2</sub>	14,800	18,500
Fe(NA) <sub>2</sub> Cl <sub>2</sub>	14,600	18,040

## Cobalt compounds

Octahedral environment (Ground state  ${}^4T_{2g}(F)$ )

Compound	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
Co(ANA) <sub>2</sub> Cl <sub>2</sub>	8,403	20,000
Co(ANA) <sub>2</sub> Br <sub>2</sub>	8,278	19,881
Co(NA) <sub>2</sub> Cl <sub>2</sub>	8,170	19,724
Co(NA) <sub>2</sub> Cl <sub>2</sub>	8,106	19,694
Co(NA) <sub>2</sub> Br <sub>2</sub>	8,078	19,802

## Nickel compounds

(Octahedral environment (Ground state  ${}^3A_{2g}(F)$ ))

Compound	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
Ni(ANA) <sub>2</sub> Cl <sub>2</sub>	8,865	14,599	25,641
Ni(ANA) <sub>2</sub> Br <sub>2</sub>	7,813	14,535	25,773
Ni(NA) <sub>2</sub> Cl <sub>2</sub>	8,150	14,556	25,575
Ni(NA) <sub>2</sub> Br <sub>2</sub>	8,503	14,641	25,707

## Copper compounds

Octahedral environment (Ground state  ${}^2E_g$ )

Compound	${}^2E_g \rightarrow {}^2T_{2g}$
Cu(ANA) <sub>2</sub> Cl <sub>2</sub>	13,440
Cu(ANA) <sub>2</sub> Br <sub>2</sub>	13,514
Cu(NA) <sub>2</sub> Cl <sub>2</sub>	12,905
Cu(NA) <sub>2</sub> Br <sub>2</sub>	12,610

the  ${}^5T_{2g}$  ground state. The compounds have magnetic moments which would agree with an octahedral configuration for the iron(II). They obey the Curie-Weiss law. The variation of the magnetic moment with temperature is due to electron

delocalization. A "T term" is split by spin-orbit coupling to produce levels whose energy differences are of the order of the Boltzmann factor,  $kT$ . Temperature will thus have a direct effect on the population of the levels. The far infrared spectra (Table 6) would agree with an octahedral environment [10] for the iron(II).

All of the cobalt complexes prepared from solution have stoichiometry  $\text{CoL}_2\text{X}_2$ . Bisnicotinic acid cobalt(II)chloride (Fig. 3) showed a point of inflection on its thermogravimetric curve at a temperature of 643 K corresponding to the compound  $\text{Co(NA)Cl}_2$ . However, no complex of this stoichiometry could be isolated. The other compounds underwent endothermic reactions, with loss of organic ligand and halogen. The visible spectra is characteristic of cobalt in an octahedral environment [11]. The observed transitions are  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ;  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ . The tran-

Table 5  
Infrared spectra 4000–650  $\text{cm}^{-1}$

(a) Nicotinamide complexes

Compound	$\nu_{\text{as}}(\text{NH}_2)$	$\nu_{\text{s}}(\text{NH}_2)$	$\delta(\text{NH}_2)$	Ring vibrations		$\nu(\text{C}=\text{O})$
ANA	3375	3175	1620	1598	1580	1680
$\text{Mn(ANA)}_2\text{Cl}_2$	3410	3200	1625	1601	1579	1665
$\text{Mn(ANA)}_2\text{Br}_2$	3440	3210	1630	1610	1585	1670
$\text{Fe(ANA)}_2\text{Cl}_2$	3420	3210	1634	1610	1590	1675
$\text{Co(ANA)}_2\text{Cl}_2$	3420	3210	1630	1608	1585	1670
$\text{Co(ANA)}_2\text{Br}_2$	3420	3200	1620	1600	1578	1660
$\text{Ni(ANA)}_2\text{Cl}_2$	3420	3210	1630	1609	1585	1670
$\text{Ni(ANA)}_2\text{Br}_2$	3420	3200	1620	1605	1580	1665
$\text{Cu(ANA)}_2\text{Cl}_2$	3420	3180	1630	1612	1588	1710
$\text{Cu(ANA)}_2\text{Br}_2$	3440	3220	1630	1612	1590	1670

(b) Nicotinic acid complexes

Compound	$\nu(\text{O}-\text{H})$	$\nu(\text{C}=\text{O})$	$\delta(\text{O}-\text{H})$	Ring vibrations		$\nu(\text{C}=\text{O})$
NA	2480	1420	1310	1600	1590	1710
$\text{Mn(NA)}_2\text{Cl}_2$	ca 2700	1425	1320	1610	1590	1700
$\text{Mn(NA)}_2\text{Br}_2$	ca 2700	1425	1315	1610	1590	1710
$\text{Fe(NA)}_2\text{Cl}_2$	ca 2700	1425	1315	1610	1590	1700
$\text{Co(NA)}_2\text{Cl}_2$	ca 2700	1425	1315	1610	1590	1698
$\text{Co(NA)}_2\text{Br}_2$	ca 2700	1425	1310	1610	1590	1698
$\text{Ni(NA)}_2\text{Cl}_2$	ca 2700	1425	1310	1610	1590	1700
$\text{Ni(NA)}_2\text{Br}_2$	ca 2700	1425	1310	1608	1590	1698
$\text{Cu(NA)}_2\text{Cl}_2$	ca 2700	1425	1305	1612	1590	1710
$\text{Cu(NA)}_2\text{Br}_2$	ca 2700	1425	1311	1614	1590	1710

Table 6  
Infrared spectra 650–50 cm<sup>-1</sup>

Compound	$\nu (M-X)$	$\nu (M-N)$
Mn(ANA) <sub>2</sub> Cl <sub>2</sub>	200	284
Mn(NA) <sub>2</sub> Cl <sub>2</sub>	224	282, 346
Mn(ANA) <sub>2</sub> Br <sub>2</sub>	236	286
Mn(NA) <sub>2</sub> Br <sub>2</sub>	248	276, 338
Fe(ANA) <sub>2</sub> Cl <sub>2</sub>	244, 160	282, 346
Fe(NA) <sub>2</sub> Cl <sub>2</sub>	230, 110	284, 348
Co(ANA) <sub>2</sub> Cl <sub>2</sub>	260, 136	326
Co(NA) <sub>2</sub> Cl <sub>2</sub>	242, 125	288, 346
Co(ANA) <sub>2</sub> Br <sub>2</sub>	248	286
Co(NA) <sub>2</sub> Br <sub>2</sub>	252	280, 340
Ni(ANA) <sub>2</sub> Cl <sub>2</sub>	248sh, 210	276
Ni(NA) <sub>2</sub> Cl <sub>2</sub>	254, 204	284, 342
Ni(ANA) <sub>2</sub> Br <sub>2</sub>	258, 226	292, 336sh.
Ni(NA) <sub>2</sub> Br <sub>2</sub>	256, 166	280, 344
Cu(ANA) <sub>2</sub> Cl <sub>2</sub>	222, 166	346
Cu(NA) <sub>2</sub> Cl <sub>2</sub>	226, 206	272, 348
Cu(ANA) <sub>2</sub> Br <sub>2</sub>	246, 206	276
Cu(NA) <sub>2</sub> Br <sub>2</sub>	240, 218	278, 330

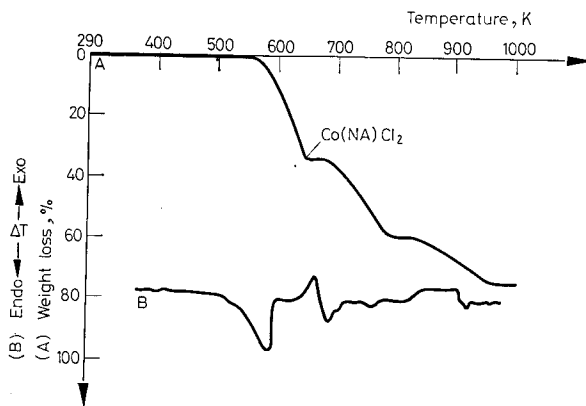


Fig. 3. TG (curve A) and DTA (curve B) of Co(NA)<sub>2</sub>Cl<sub>2</sub>. Sample weight: 45.1 mg; Atmosphere: Static air; Heating rate: 4° min<sup>-1</sup>

sition  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  was not observed. The magnetic data for the compound are in accord with an octahedral environment for the cobalt(II). The spin only value for a d<sup>7</sup> ion is  $2[S(S + 1)]^{1/2} = 3.87$  B. M. and the higher magnetic moments observed for the octahedral complexes are due to a significant orbital contribution



due to the interaction of the  ${}^4T_{1g}(P)$  and  ${}^4A_{2g}(F)$  states. All of the compounds exhibit a satisfactory dependence on the Curie-Weiss law. The far infrared spectra support an essentially octahedral environment round the cobalt(II).

The complexes of nickel(II) have in general stoichiometry  $NiL_2X_2$ , an exception being the complex formed between nicotinamide and nickel(II)chloride which has stoichiometry  $NiL_2Cl_2 \cdot 2H_2O$ . Thermogravimetric studies show that this complex (Fig. 4) has a two-stage decomposition. The compound undergoes an endothermic

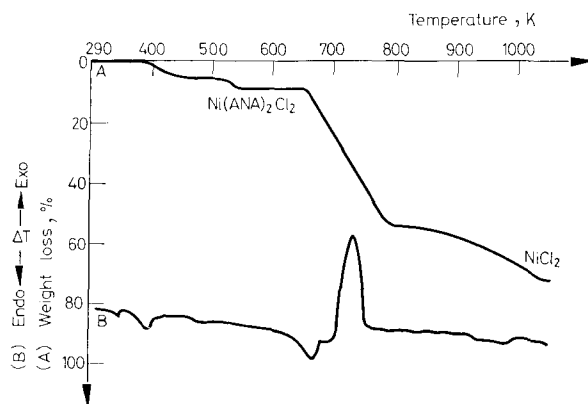


Fig. 4. TG (curve A) and DTA (curve B) of  $Ni(ANA)_2Cl_2 \cdot 2H_2O$ . Sample weight: 91.4 mg; Atmosphere: Static air; Heating rate:  $4^\circ \text{ min}^{-1}$

reaction at 373 K with mass loss of two molecules of water. A second endothermic reaction takes place at 640 K followed by an exothermic reaction at 725 K. The mass loss corresponds to that of the organic ligand. The other nickel compounds undergo endothermic reactions with loss of organic ligand and finally loss of halogen. The complex formed between nicotinic acid and nickel(II) chloride was obtained as a light green powder similar to the hydrated nicotinamide complex. Both of the corresponding bromide compounds were obtained as pale yellowish green powders. The visible absorption spectra are typical of octahedrally coordinated nickel atoms. The observed transitions are  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ;  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ;  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ . The prediction of an octahedral structure for these compounds is further supported by the fact that the compounds have temperature independent magnetic moments in the range 3.4–3.8 B.M. The compounds obey the Curie-Weiss law. The far infrared spectra also support an octahedral configuration for these compounds (II).

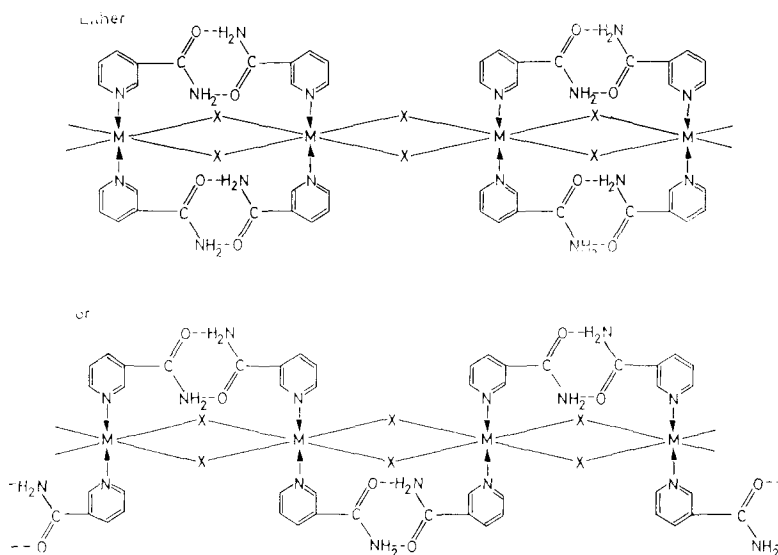
The copper complexes have stoichiometry  $CuL_2X_2$ . Thermogravimetric studies show that no intermediate compounds are formed and that the isolated compounds undergo endothermic reactions with loss of two molecules of organic ligand. The magnetic data listed in Table 2, are unable to differentiate between

octahedral and tetrahedral arrangements. Thus the evidence for structural assignment is from spectral data. The compounds show a broad absorption band in the region  $13,000-14,500\text{ cm}^{-1}$  and this suggests a distorted octahedral configuration [12, 13]. The far infrared spectra would also agree with an octahedral structure [14, 15].

### Discussion

The stoichiometry of the compounds prepared shows that the maximum number of nicotinamide and nicotinic acid ligands present in any one compound is two. The nicotinamide and nicotinic acid are thus acting as monodentate ligands in these compounds. All of the compounds were anhydrous with the exception of bisnicotinamide manganese(II)chloride and bisnicotinamide nickel(II)chloride which had respectively one and two molecules of water of crystallization attached. The infrared spectra of the hydrated complexes have a broad band from  $3680\text{ cm}^{-1}$  to lower frequency and this is considered to be due to a O-H stretching vibration of the water molecule. This band is absent in the anhydrous complexes. The absence of a band at  $315\text{ cm}^{-1}$  would suggest that the water is not coordinated to metal ion [16] but is present as water of crystallization. This is further borne out from the thermal decomposition data (Figs 1 and 4). Without X-ray analysis, no definite structures can be described. However, spectroscopic and magnetic data available enable us to predict structures, and we can also use other chemical properties to help us. The magnetic moments, visible spectra and far infrared spectra suggests that these compounds have octahedral structures. The infrared spectra of the solid, free ligands are almost identical to those of their complexes in the region  $2000-625\text{ cm}^{-1}$ . This suggests no shift in the  $\nu(\text{C}=\text{O})$  or  $\delta(\text{N}-\text{H})$  bands. However, a difference in spectra is observed in the  $3100-3600\text{ cm}^{-1}$  region for the  $\nu(\text{N}-\text{H})$  bands of the nicotinamide complexes. The number of bands increases to five in the complexes in contrast to two intense bands with a separation of about  $150\text{ cm}^{-1}$  in the spectrum of the free ligand. In the spectrum of the complexes there is an intense band at about  $3410\text{ cm}^{-1}$  which is separated from the lowest frequency band (ca  $3200\text{ cm}^{-1}$ ) of similar intensity by more than  $200\text{ cm}^{-1}$ . This indicates that the nitrogen atoms of the amino group are not bonded to a metal [17]. Similarly the  $\nu(\text{O}-\text{H})$  bands of the nicotinic acid are split into bands, including two moderately intense bands at about  $2700$  and  $2600\text{ cm}^{-1}$  suggesting that the oxygen atoms of the hydroxyl groups are not bonded to a metal. The infrared spectra of a dilute solution of nicotinamide in tetrachloromethane gives bands at  $3540$  and  $3420\text{ cm}^{-1}$  which are assigned to free  $\text{NH}_2$ ,  $\nu(\text{N}-\text{H})$ . Comparison of the spectrum of nicotinamide, as a potassium bromide disc, shows that the frequencies of these bands are lowered to  $3375$  and  $3170\text{ cm}^{-1}$ . This is considered to be due to the transition from the monomer to the dimer form of the molecule by intermolecular dimerization  $\text{NH} \dots \text{O}$  (2, 4, 6). Similar results are observed for nicotinic acid with strong to medium absorption bands between  $2750$  and  $2300\text{ cm}^{-1}$  [18, 19].

Thus the infrared spectra would suggest that adjacent nicotinamide and nicotinic acid molecules are linked by hydrogen bonds in the compounds. The far infrared spectra reported in Table 6 would suggest that the compounds have polymeric octahedral structures. Absorption bands in the  $300-350\text{ cm}^{-1}$  region and in the  $270-290\text{ cm}^{-1}$  region are considered to be due to metal-nitrogen vibrations whilst those occurring from  $260-150\text{ cm}^{-1}$  are thought to arise from metal-halogen vibrations [14]. The suggestion of polymeric octahedral structures is supported by the poor solubility of the compounds in polar and non-polar solvents [20]. The compounds are thus considered to have polymeric octahedral structures with the adjacent nicotinamide and nicotinic acid molecules linked by hydrogen bonds. Possible structures for the nicotinamide complexes are shown below.



The nicotinic acid complexes would have similar structures.

It is suggested that the thermal decomposition product, nicotinic acid manganese(II)chloride,  $\text{MnLCl}_2$ , has a double layer chain structure in which each chlorine is acting as a bridge between three manganese atoms with the nicotinic acid molecules in transpositions [9].

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RÉSUMÉ — Plusieurs complexes donnés par les chlorures et bromures de manganèse(II), fer(II), cobalt(II), nickel(II) et cuivre(II) avec le nicotinamide et l'acide nicotinique ont été préparés. Ces complexes répondent à la formule stœchiométrique  $ML_2X_2$ , où  $M$  représente l'ion métallique,  $L$  un ligand organique et  $X$  un ion halogène. Les propriétés spectrales et magnétiques indiquent que ces composés ont une structure polymère octaédrique. La décomposition de ces complexes a été étudiée par thermogravimétrie et par analyse thermique différentielle. Dans un seul cas un produit de décomposition de formule  $MLX_2$  a été obtenu. Sa structure est également octaédrique.

ZUSAMMENFASSUNG — Einige Komplexe der Chloride und Bromide von Mangan(II), Eisen(II), Cobalt(II), Nickel(II) und Kupfer(II) mit Nikotinamid und Nikotinsäure wurden hergestellt. Diese Komplexe sind von der Stöchiometrie  $ML_2X_2$ , wobei  $M$  ein Metallion,  $L$  ein organischer Ligand und  $X$  ein Halogenidion ist. Die spektralen und magnetischen Eigenschaften deuten auf oktaedrische Polymerstrukturen dieser Komplexe hin. Die Zersetzung der Komplexe wurde durch Thermogravimetrie und Differentialthermoanalyse untersucht. In einem einzigen Falle wurde ein Zersetzungsprodukt der Formel  $MLX_2$  erhalten, dessen Struktur ebenfalls oktaedrisch war.

Резюме — Получены некоторые комплексы хлоридов и бромидов марганца(II), железа(II), кобальта(II), никеля(II) и меди(II) с никотинамидом и никотиновой кислотой. Комплексы имеют стехиометрический состав  $ML_2X_2$ , где  $M$  — ион металла,  $L$  — органический лиганд,  $X$  — галогидный ион. Спектральные и магнитные свойства указывают, что эти соединения имеют октаэдрическую полимерную структуру. Разложение комплексов изучено с помощью термогравиметрии и дифференциального термического анализа. Только в одном случае был получен продукт разложения общей формулы  $MLX_2$ , структура которого также октаэдрическая.