

THE PREPARATION AND THERMAL ANALYSIS STUDIES
ON SOME FIRST ROW TRANSITION METAL COMPLEXES
OF 2-AMINOPYRIMIDINE

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Complexes of 2-aminopyrimidine with the chlorides, bromides and iodides of cobalt(II), zinc(II) and also with the chlorides and bromides of manganese(II), nickel(II) and copper(II) have been prepared. The chloride complex of iron(II) was also obtained. The stereochemical configurations of the complexes were deduced using spectral and magnetic properties. The decomposition of the complexes was studied by thermogravimetry and differential thermal analysis.

A great deal of interest has been shown in the pyrimidines due to their biological importance as components of the nucleic acids. Many compounds of therapeutic importance contain the pyrimidine ring system. Sulphadiazine, a sulphonamide of 2-aminopyrimidine, is an antibiotic, while phenobarbitol which contains the pyrimidine ring system is a barbiturate. The pyrimidines provide potential binding sites for metal ions and any information on their coordinating properties is important as a means of understanding the role of metal ions in biological systems. Several complexes have been previously prepared [1-4]. This present paper describes the preparation of the complexes formed between the halides of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II) and 2-aminopyrimidine together with the results of their thermal analysis, visible spectra, infrared spectra and magnetic measurements.

Experimental

Three methods of preparation were used:

A. The complexes were prepared by dissolving the hydrated transition metal halide in absolute ethanol and adding a saturated solution of the ligand dissolved in ethanol. The complexes were washed with ethanol and dried at 80°.

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.

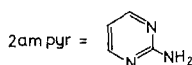
Magnetic susceptibility measurements were made by the Gouy method over the temperature range 300–100 K using a Newport variable temperature balance and as calibrant, Hg [Co(SCN)₄]. Each susceptibility value has been corrected for diamagnetism using Pascal's constants [5]. The values so corrected are represented by X_M^{Corr} in Table 2. The reciprocals of X_M^{Corr} plotted against the absolute temperature and the values of μ and θ in the Curie-Weiss equation, $\mu = 2.84 [X_M^{\text{Corr}} (T - \theta)]^{1/2}$ are obtained [6]. Electronic spectra were obtained on a Beckman ACTA M1V spectrophotometer. Infrared absorption spectra (KBr discs) were obtained with a Perkin-Elmer 257 Infrared Spectrophotometer. Far infrared spectra were obtained on a Perkin-Elmer 577 Spectrophotometer.

Results

The complexes of manganese are colourless and have stoichiometry Mn(2-ampyr)X₂ (Table 1). No stoichiometric compound of manganese(II) iodide could be prepared. Thermal decomposition studies of the compounds showed no intermediate decomposition steps. The chloro-complex undergoes two exothermic

Table 1
Analysis of compounds

Compound	Method of preparation	Metal (found)	Halide (found)	Metal (theory)	Halide (theory)
Mn(2-ampyr)Cl ₂	A	24.82	32.06	24.87	32.09
Mn(2-ampyr)Br ₂	A	17.70	51.52	17.73	51.58
Fe(2-ampyr)Cl ₂	B	25.14	31.90	25.17	31.96
Co(2-ampyr)Cl ₂	A	26.20	31.50	26.20	31.52
Co(2-ampyr)Br ₂ · 2H ₂ O	A	13.20	35.90	13.24	35.92
Co(2-ampyr) ₂ Br ₂	C	14.38	39.06	14.41	39.10
Co(2-ampyr)I ₂ · 2H ₂ O	A	13.24	57.16	13.28	57.18
Co(2-ampyr)I ₂	C	14.42	62.18	14.45	62.26
Ni(2-ampyr)Cl ₂	A	26.06	31.52	26.10	31.55
Ni(2-ampyr)Br ₂ · H ₂ O	A	17.64	48.16	17.70	48.19
Ni(2-ampyr)Br ₂	C	18.68	50.96	18.71	51.0
Ni(2-ampyr) ₂ Br ₂	A	14.32	39.12	14.35	39.13
Cu(2-ampyr)Cl ₂	A	27.64	30.84	27.68	30.89
Cu(2-ampyr)Br ₂	A	19.91	50.14	19.95	50.18
Zn(2-ampyr) ₂ Cl ₂ · 3H ₂ O	A	17.16	18.60	17.19	18.66
Zn(2-ampyr) ₂ Cl ₂	C	20.02	21.71	20.04	21.76
Zn(2-ampyr) ₂ Br ₂	A	15.72	38.48	15.75	38.22
Zn(2-ampyr) ₂ I ₂	A	12.81	49.82	12.84	49.86



reactions at 635 K and 785 K with mass loss corresponding to the organic material and halogen. The bromide compound undergoes an endothermic reaction at 605 K followed by an exothermic reaction at 780 K with mass loss corresponding to organic material and halogen. The visible absorption spectra (Table 3) show bands of low intensity. The bands in the spectrum are weak since any excitation of the ground state, which is 6S in the free ion, causes spin pairing and the formation of quartet or doublet states. Since the excited states have different spin multiplicities from the ground state, the transitions are spin-forbidden and are thus observed as weak transitions. The bands have been assigned to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$; ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$; ${}^6A_{1g} \rightarrow {}^4E_g(G)$, ${}^4A_{2g}(G)$. The magnetic moment of the bromide complex is similar to the spin only value for manganese(II) ions (~ 5.9 BM). This results from the fact that there are no higher T terms having the same multiplicity as the ${}^6A_{1g}$ ground state term so that no mixing occurs between the ${}^6A_{1g}$ term and the higher T terms. The chloride complex has a magnetic moment of 6.51 BM. This is probably due to some ferromagnetic impurity in the sample. The compounds obey the Curie-Weiss law (Table 2) with positive θ values. The far infrared spectra (Table 4) support an essentially octahedral environment for the manganese [7].

The iron complex has stoichiometry $Fe(2\text{-ampyr})Cl_2$ (Table 1). No stoichiometric complexes of iron(II) bromide and iron(II) iodide could be prepared. The preparations were carried out in a dry nitrogen atmosphere. Thermogravimetric studies showed that the chloro compound exhibited no intermediate decomposition steps. At 543 K the compound undergoes an exothermic reaction with loss of organic material and halogen. The visible spectrum (Table 3) showed an absorption band at 10.640 cm^{-1} which corresponds to the transition ${}^5T_{2g} \rightarrow {}^5E_g$. This would suggest an octahedral environment for the iron. The compound has a

Table 2
Magnetic data

Compound	Temp., K	Diamagnetic correction, 10^{-6}	$\chi_M^{\text{Corr}}, 10^{-6}$	$\mu/\text{B. M.}$	θ
$Mn(2\text{-ampyr})Cl_2$	293	84.05	17 946	6.51	26.4
$Mn(2\text{-ampyr})Br_2$	293	106.45	15 514	6.06	3.35
$Fe(2\text{-ampyr})Cl_2$	293	84.05	11 376	5.19	-38.8
$Co(2\text{-ampyr})Cl_2$	293	84.05	11 773	5.28	12.7
$Co(2\text{-ampyr})_2Br_2 \cdot 2H_2O$	292	156.9	10 647	5.01	-0.26
$Co(2\text{-ampyr})_2Br_2$	294	136.76	8 801	4.57	-20.8
$Co(2\text{-ampyr})I_2 \cdot 2H_2O$	288	142.38	7 861	4.27	2.78
$Ni(2\text{-ampyr})Cl_2$	294	84.05	4 962	3.43	-5.22
$Ni(2\text{-ampyr})Br_2 \cdot H_2O$	290	122.38	4 826	3.36	2.66
$Ni(2\text{-ampyr})_2Br_2$	298	150.9	2 997	2.68	-14.3
$Cu(2\text{-ampyr})Cl_2$	296	84.05	1 301	1.76	14.6
$Cu(2\text{-ampyr})Br_2$	296	106.45	1 140	1.65	51.7

Table 3

Electronic spectra, cm^{-1}

Manganese compounds

Octahedral environment (ground state ${}^6A_{1g}$)

Compound	${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$	${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$	${}^6A_{1g} \rightarrow {}^4E_g(G), {}^4A_{1g}(G)$
Mn(2-ampyr)Cl ₂	18 520	21 645	23 810
Mn(2-ampyr)Br ₂	18 620	21 835	23 530

Iron compound

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

Compound	${}^5T_{2g} \rightarrow {}^6E_g$
Fe(2-ampyr)Cl ₂	10 640

Cobalt compounds

(i) Octahedral environment (ground state ${}^4T_{1g}(F)$)

Compound	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
Co(2-ampyr)Cl ₂	6666	17 545
Co(2-ampyr) ₂ Br ₂ · 2H ₂ O	6330, 7140, 8620	15 265, 15 950, 16 835

(ii) Tetrahedral environment (ground state ${}^4A_2(F)$)

Compound	${}^4A_2(F) \rightarrow {}^4T_1(F)$	${}^4A_2(F) \rightarrow {}^4T_1(P)$
Co(2-ampyr)I ₂	6850, 8335	14 285
Co(2-ampyr) ₂ Br ₂	6329, 7140, 8620	15 265, 15 950, 16 835

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(2-ampyr)Cl ₂	7810	13 160	22 990
Ni(2-ampyr) ₂ Br ₂	6800	12 660	21 740
Ni(2-ampyr)Br ₂	6710	12 740	23 150

Copper compounds

Octahedral environment (ground state 2E_g)

Compound	${}^2E_g \rightarrow {}^3T_{1g}$
Cu(2-ampyr)Cl ₂	14 285
Cu(2-ampyr)Br ₂	14 495

magnetic moment which agrees with an octahedral configuration for the iron and obeys the Curie–Weiss law with a negative value for θ . The variation of the magnetic moment with temperature is due to the presence of electron delocalization [7]. The far infrared spectrum (Table 4) supports an essentially octahedral environment for the iron [7].

The cobalt complexes have stoichiometry Co(2-ampyr)Cl₂, Co(2-ampyr)Br₂ · 2H₂O and Co(2-ampyr)I₂ · 2H₂O. Thermal decomposition studies show that the chloro compound has no intermediate decomposition steps but undergoes an exothermic reaction at 644 K with loss of organic ligand and halogen. The bromo and iodo complex (Figs 1 and 2) have two stage decompositions. The bromo complex undergoes an endothermic reaction at 465 K with mass loss corresponding to two molecules of water, followed by an exothermic reaction at 565 K with mass loss corresponding to organic ligand and halogen. The iodo complex undergoes an endothermic reaction at 480 K with mass loss corresponding to organic ligand and halogen. The compounds Co(2-ampyr)Cl₂, and Co(2-ampyr)₂Br₂ · 2H₂O have electronic spectra which are typical of octahedrally coordinated cobalt atoms [7]. The observed transitions are ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$. The magnetic data for the compounds (Table 2) agree with the suggestion of an octahedral arrangement of ligands around the cobalt atom with temperature dependent magnetic moments in the range 4.9–5.2 BM. The compounds obey the Curie–Weiss law with a positive θ value for the chloro compound and a negative θ value for the bromo compound. The far infrared spectra support an essentially octahedral environment for the cobalt [7]. The compounds Co(2-ampyr)₂Br₂ and Co(2-ampyr)I₂ have electronic spectra which would suggest tetrahedral structures. The observed transitions are ${}^4A_2(F) \rightarrow {}^4T_1(F)$ and ${}^4A_2(F) \rightarrow {}^4T_1(P)$. The magnetic data (Table 2) for the compounds would support a tetrahedral configuration with magnetic moments between 4.2–4.8 BM. The compounds obey the Curie–Weiss law with negative and positive values for θ . The far infrared spectra also supports a tetrahedral environment for the cobalt [12].

The chloro and iodo complexes of nickel(II) have stoichiometry Ni(2-ampyr)Cl₂ (Table 1). The reaction of nickel(II) bromide and 2-aminopyrimidine in ethanolic solution resulted in the isolation of a yellow complex of stoichiometry Ni(2-ampyr)Br₂ · H₂O and green complex of stoichiometry Ni(2-ampyr)₂Br₂. No stoichiometric compound of nickel(II) iodide could be prepared. Thermogravimetric studies on the chloro and the green bromo complex showed no intermediate decomposition steps. The chloro complex undergoes two exothermic reactions at

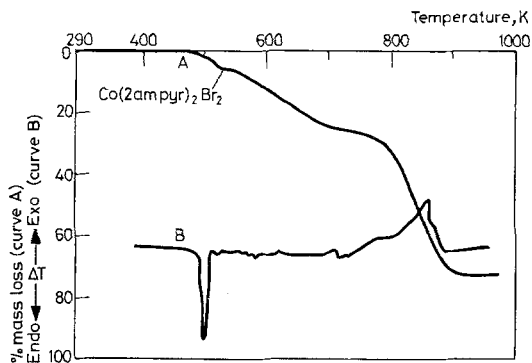


Fig. 1. TG (Curve A) and DTA (Curve B) of $\text{Co}(\text{2-ampyr})_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$. Sample weight: 93.0 mg. Atmosphere: Static air. Heating rate: 4 deg min^{-1}

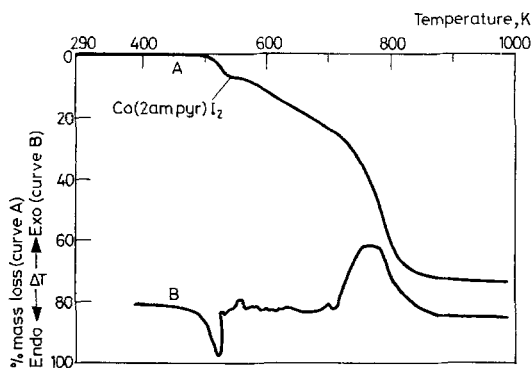


Fig. 2. TG (Curve A) and DTA (Curve B) of $\text{Co}(\text{2-ampyr})\text{I}_2 \cdot 2\text{H}_2\text{O}$. Sample weight: 108.8 mg. Atmosphere: Static air. Heating rate: 4 deg min^{-1}

673 K and 880 K with mass loss corresponding to organic ligand and halogen. The bromo complex undergoes two exothermic reactions at 665 K and 822 K with mass loss corresponding to organic ligand and halogen. The yellow bromo complex (Fig. 3) undergoes an endothermic reaction at 390 K with loss of a water molecule. A further endothermic reaction takes place at 620 K immediately followed by an exothermic reaction at 695 K with mass loss corresponding to organic ligand and halogen. The electronic absorption spectra (Table 3) is characteristic of nickel(II) in an octahedral environment. The observed transitions are ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, ${}^3\text{A}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$. The magnetic moments (Table 2) of the compounds are again typical of nickel(II) in an octahedral environment. The compounds obey the Curie-Weiss law with a positive θ value for the yellow bromo compound and negative θ values for the green bromo and chloro compounds. The far infrared spectra (Table 4) also support an essentially octahedral configuration for nickel [7].

The chloro and bromo complexes of copper are green and have stoichiometry $\text{Cu}(2\text{-ampyr})\text{X}_2$ (Table 1). Thermal decomposition studies show that no intermediate compounds are produced. By 530 K the mass loss corresponds to complete loss of organic ligand. The electronic spectra of the compounds are typical of copper in an octahedral environment [7]. The magnetic moments (Table 2) of the complexes are less than the spin only value. This indicates some copper-copper magnetic interaction in the compounds [8]. The compounds obey the Curie-Weiss law with positive values for θ . The far infrared spectra (Table 4) also support an octahedral configuration for these compounds [7].

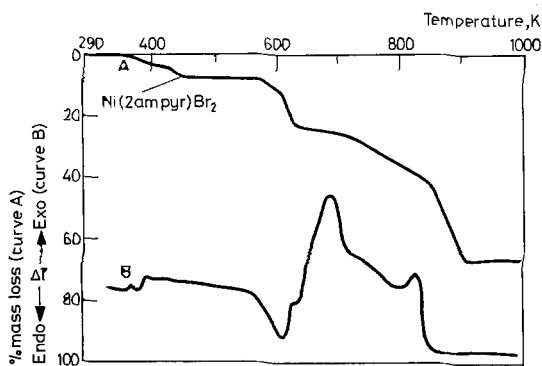


Fig. 3. TG (Curve A) and DTA (Curve B) of $\text{Ni}(2\text{-ampyr})\text{Br}_2 \cdot \text{H}_2\text{O}$. Sample weight: 82.1 mg. Atmosphere: Static air. Heating rate: 4 deg min^{-1}

Table 4
Infrared spectra ($4000\text{--}200 \text{ cm}^{-1}$)

Compound	$\nu_a(\text{NH}_2)$	$\nu_s(\text{NH}_2)$	$\delta(\text{NH}_2)$	Ring vibrations	$\nu(\text{M} - \text{X})$
2-ampyr	3310	3165	1628	1550, 1450	—
$\text{Mn}(2\text{-ampyr})\text{Cl}_2$	3440	3360	1640	1575, 1495	226
$\text{Mn}(2\text{-ampyr})\text{Br}_2$	3440	3360	1630	1570, 1490	206
$\text{Fe}(2\text{-ampyr})\text{Cl}_2$	3430	3360	1625	1570, 1490	215
$\text{Co}(2\text{-ampyr})\text{Cl}_2$	3430	3360	1630	1570, 1495	210
$\text{Co}(2\text{-ampyr})\text{Br}_2 \cdot 2\text{H}_2\text{O}$	3360	—	1645	1590, 1565, 1485	242
$\text{Co}(2\text{-ampyr})_2\text{Br}_2$	3320	—	1635	1590, 1560, 1475	336
$\text{Co}(2\text{-ampyr})\text{I}_2$	3440	3310	1630	1590, 1560, 1485	226
$\text{Ni}(2\text{-ampyr})\text{Cl}_2$	3455	3365	1635	1575, 1495	240
$\text{Ni}(2\text{-ampyr})\text{Br}_2$	3440	—	1615	1570, 1480	232
$\text{Ni}(2\text{-ampyr})_2\text{Br}_2$	3405	3305	1615	1575, 1485	224
$\text{Cu}(2\text{-ampyr})\text{Cl}_2$	3375	3320	1645	1575, 1500	246
$\text{Cu}(2\text{-ampyr})\text{Br}_2$	3400	3285	1630	1568, 1490	235
$\text{Zn}(2\text{-ampyr})_2\text{Cl}_2$	3300	3180	1635	1595, 1560, 1485	328, 310, 290
$\text{Zn}(2\text{-ampyr})_2\text{Br}_2$	3360	3184	1645	1595, 1555, 1480	232
$\text{Zn}(2\text{-ampyr})_2\text{I}_2$	3360	3124	1632	1590, 1565, 1490	210

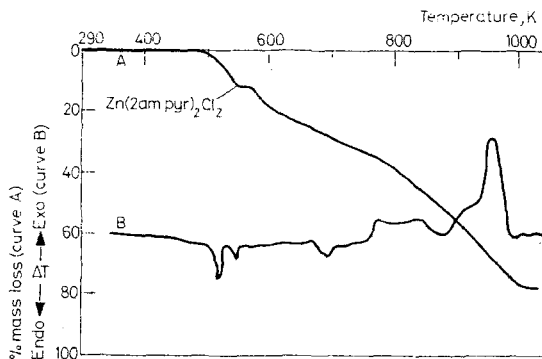


Fig. 4. TG (Curve A) and DTA (Curve B) of $\text{Zn}(2\text{-ampyr})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$. Sample weight: 64.2 mg. Atmosphere: Static air. Heating rate: 4 deg min^{-1}

The chloro compound of zinc has stoichiometry $\text{Zn}(2\text{-ampyr})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ while the bromo and iodo compounds have stoichiometry $\text{Zn}(2\text{-ampyr})_2\text{X}_2$ (Table 1). Thermal decomposition studies show that the chloro compound undergoes an endothermic reaction at 380 K with loss of three molecules of water followed by a further endothermic reaction at 523 K and an exothermic reaction at 654 K with mass loss corresponding to organic material and halogen. The bromo and iodo complexes have no intermediate stages in their decomposition. They undergo endothermic reactions at 499 K and 477 K with loss of organic material followed by exothermic reactions at 702 K and 721 K with loss of halogen. The complexes show bands in their far infrared spectra at $303\text{--}328 \text{ cm}^{-1}$ and $277\text{--}291 \text{ cm}^{-1}$ for $\nu(\text{Zn}-\text{Cl})$, $232\text{--}242 \text{ cm}^{-1}$ for $\nu(\text{Zn}-\text{Br})$ and $207\text{--}211 \text{ cm}^{-1}$ for $\nu(\text{Zn}-\text{I})$. The values (Table 4) agree with literature values [9] for ZnX frequencies of tetrahedral compounds.

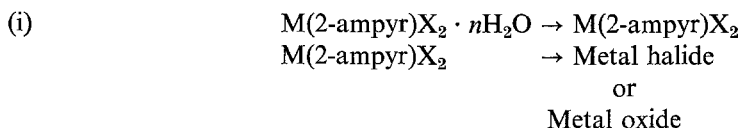
Discussion

The stoichiometry of the compounds show that the maximum number of 2-aminopyrimidine molecules present in any one compound is two. All of the compounds are anhydrous with the exception of $\text{Co}(2\text{-ampyr})\text{Br}_2 \cdot 2\text{H}_2\text{O}$, $\text{Co}(2\text{-ampyr})\text{I}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(2\text{-ampyr})\text{Br}_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}(2\text{-ampyr})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$. The infrared spectra of these compounds show medium absorption bands present in the region $3470\text{--}3450 \text{ cm}^{-1}$, $\nu(\text{OH})$ and $1640\text{--}1630 \text{ cm}^{-1}$, $\delta(\text{HOH})$ which clearly confirm the presence of water of crystallisation. Evidence that the presence of water is purely lattice water in the compounds $\text{Co}(2\text{-ampyr})\text{I}_2 \cdot 2 \text{H}_2\text{O}$, $\text{Ni}(2\text{-ampyr})\text{Br}_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(2\text{-ampyr})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ is given by the absence of typical bands of coordinated water [10]. However the presence of a weak band at 310 cm^{-1} in $\text{Co}(2\text{-ampyr})\text{Br}_2 \cdot 2 \text{H}_2\text{O}$ would suggest that the water molecules are coordinated to the cobalt atom [11]. Furthermore the water is lost in the compounds $\text{Co}(2\text{-ampyr})\text{I}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(2\text{-ampyr})\text{Br}_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(2\text{-ampyr})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ at around

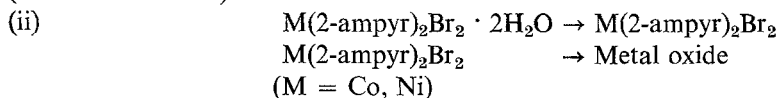
373 K whereas the water in the compound $\text{Co}(2\text{-ampyr})_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$ is lost at 465 K. In general terms the sequence of decomposition of the complexes from TG studies (Table 5) is:

Table 5
TG data of complexes showing expected and actual percentage mass loss for water and 2-aminopyrimidine

Compound	Ligand removed	Expected loss	
		calc., %	actual, %
$\text{Co}(2\text{-ampyr})_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$	H_2O	8.09	5.59
	$2\text{-ampyr} + \text{Br}_2$	78.66	74.73
$\text{Co}(2\text{-ampyr})\text{I}_2 \cdot 2\text{H}_2\text{O}$	H_2O	8.12	7.9
	$2\text{-ampyr} + \text{I}_2$	78.61	74.26
$\text{Ni}(2\text{-ampyr})\text{Br}_2 \cdot \text{H}_2\text{O}$	H_2O	5.43	5.48
	$2\text{-ampyr} + \text{Br}_2$	76.87	69.55
$\text{Zn}(2\text{-ampyr})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	H_2O	14.19	13.71
	$2\text{-ampyr} + \text{Cl}_2$	68.63	69.47



(Where $n = 1$ or 2)



Without X-ray analysis, no definite structures can be described. However spectroscopic and magnetic data available enable us to predict structures. When the infrared spectrum of the solid free ligand is compared to that of the complexes in the region $2000-625 \text{ cm}^{-1}$ it is found that the bands due to $\nu_s(\text{NH}_2)$, $\nu_a(\text{NH}_2)$, $\delta(\text{NH}_2)$ and ring vibrations (Table 4) move to higher frequency suggesting that coordination takes place through one of the nitrogen atoms in the pyrimidine ring and the nitrogen atom of the amine group. The exceptions are $\text{Co}(2\text{-ampyr})_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$, $\text{Co}(2\text{-ampyr})_2\text{Br}_2$ and $\text{Ni}(2\text{-ampyr})_2\text{Br}_2$ where little change in frequency is observed for the N-H vibration of the amine group, thus suggesting that in these compounds coordination takes place through a nitrogen atom of the pyrimidine ring. The compound $\text{Co}(2\text{-ampyr})_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$ has an octahedral structure. For the compounds of stoichiometry $\text{M}(2\text{-ampyr})\text{X}_2$ an octahedral structure of a metal halogen chain with each metal having four bonds to halogen atoms giving the formula MX_2 and the pyrimidine ligands attached above and below the planes of the MX_2 chain through the lone pairs of electrons on the nitrogen atoms to two adjacent metal atoms giving a formula of $\text{MX}_2(\text{LIGAND})$.

For the compound $\text{Ni}(2\text{-ampyr})_2\text{Br}_2$ the structure suggested is again a chain structure of metal-halogen atoms, MX_2 with two ligands bonded above and below the plane of the chain to each metal atom through a lone pair of electrons on the pyrimidine ring nitrogen giving a formula of $\text{MX}_2(\text{LIGAND})_2$. The bands corresponding to $\nu(\text{MX})$ in the low frequency infrared spectra of these two types of structure are consistent with similar modes in the halogen bridged polymeric octahedral compounds (12). The compounds $\text{Co}(2\text{-ampyr})_2\text{Br}_2$, $\text{Co}(2\text{-ampyr})\text{I}_2$ and $\text{Zn}(2\text{-am-pyr})_2\text{Cl}_2$, $\text{Zn}(2\text{-ampyr})\text{Br}_2$ and $\text{Zn}(2\text{-ampyr})\text{I}_2$ have tetrahedral structures.

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RÉSUMÉ — Les complexes de l'amino-2 pyrimidine avec les chlorures, bromures et iodures de cobalt(II), zinc(II) ainsi qu'avec les chlorures et bromures de manganèse(II), nickel(II) et cuivre(II) ont été préparés. Le complexe formé avec le chlorure de fer(II) a aussi été obtenu. Les configurations stéréochimiques des complexes ont été déduites des propriétés spectrales et magnétiques. La décomposition thermique des complexes a été étudiée par thermogravimétrie et analyse thermique différentielle.

ZUSAMMENFASSUNG — Komplexe von 2-Aminopyrimidinen mit den Chloriden, Bromiden und Jodiden von Kobalt(II), Zink(II) und den Chloriden und Bromiden von Mangan(II), Nickel(II) und Kupfer(II) wurden hergestellt. Der Chloridkomplex von Eisen(II) wurde ebenfalls erhalten. Die stereochemischen Konfigurationen der Komplexe wurden aus spektralen und magnetischen Eigenschaften abgeleitet. Die Zersetzung der Komplexe wurde durch Thermogravimetrie und Differentialthermoanalyse untersucht.

Резюме — Получены комплексы 2-аминопириимидина с хлоридами, бромидами и иодидами кобальта(II) и цинка(II), а также с хлоридами и бромидами марганца(II), никеля(II) и меди(II). Получен также комплекс с хлоридом железа(II). Исследование спектральных и магнитных свойств этих комплексов позволило установить их стереохимические конфигурации. Разложение комплексов изучено с помощью термогравиметрии и термического анализа по производной.