

*Short Communication*

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**THERMAL AND STRUCTURAL STUDIES OF THE CHLORO COMPLEXES OF COBALT AND COPPER WITH 2-AMINO-3-METHYLPYRIDINE**

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**Abstract**

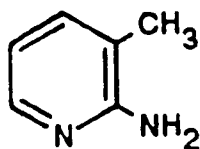
The chloro complexes of 2-amino-3-methylpyridine with cobalt(II) and copper(II) have been prepared in ethanolic solution and solid compounds have been isolated. The compounds have stoichiometry  $ML_2Cl_2$  where  $M$  is  $Co^{2+}$  or  $Cu^{2+}$  and  $L$  is 2-amino-3-methylpyridine. Spectral and magnetic studies have been used to obtain information about the environment of the metal ion in these compounds. The compounds have tetrahedral structures. The thermal decomposition of each compound has been studied using thermogravimetry and differential thermal analysis. Thermogravimetry studies show that the cobalt complex forms an intermediate compound before the metal oxide is produced while the copper compound undergoes decomposition with loss of organic ligand and the formation of copper chloride which then decomposes to give an oxide of copper.

The enthalpy of reaction for each of the processes has been calculated from the thermal analysis curves.

**Keywords:** chloro complexes of cobalt and copper, complexes, kinetics, structural studies

**Introduction**

The compound 2-amino-3-methylpyridine has two donor sites for forming bonds with metal ions: the nitrogen atom of the amino group and the nitrogen atom of the aromatic ring system

2-amino-3-methylpyridine (C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)

Information concerning the stereochemistry of each complex has been obtained from magnetic studies, electronic and far-infrared spectra. The type of coordination which takes place to the metal ions has been investigated using infrared spectroscopy. The thermal behaviour of each complex has been studied.

## Experimental

### *Preparation of the Metal Complexes*

The metal complexes were prepared by the addition dropwise with stirring of a solution of 2-amino-3-methylpyridine in ethanol (50:50) to a boiling solution of the metal halide (0.05 mol) in ethanol. When the precipitation was complete the product was isolated by filtration, washed with a minimum of ethanol, then di-ethyl ether and dried over calcium chloride in a dessicator.

### *Apparatus and Measurements*

The metal ion concentrations were determined using a Perkin Elmer Model 373 atomic absorption spectrophotometer and the carbon, nitrogen and hydrogen analyses using a Carlo Erba elemental analyser. The infrared spectra were obtained using KBr discs for the range 4000–600 cm<sup>-1</sup> and polyethylene discs for the range 600–200 cm<sup>-1</sup> on a Perkin Elmer IR spectrophotometer Model 598. The electronic spectra were obtained on a Beckmann Acta MIV spectrophotometer as diffuse reflectance spectra. Magnetic measurements were carried out by the Gouy method using Hg[Co(SCN)<sub>4</sub>]. The thermal analysis were carried out on a Stanton-Redcroft thermobalance Model STA 1500. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 10 deg·min<sup>-1</sup> in static air and over a temperature range of 20 to 800°C.

## Results and discussion

The metal complexes prepared are listed in Table 1. The analytical results agree with the stoichiometry of the compounds. The position of the bands in the electronic spectrum of the cobalt compound along with its magnetic moment, Table 2, clearly indicate that the cobalt ions are in a tetrahedral environment [1]. The copper compound has bands at 4950 cm<sup>-1</sup> and 13514 cm<sup>-1</sup> suggesting

that the copper ion is in a distorted tetrahedral environment [2]. The magnetic moment for this compound was 2.06 B.M.

**Table 1** Analysis of compounds

Compounds		Metal	Carbon	Nitrogen	Hydrogen
Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	Theory/%	17.03	41.64	16.18	4.65
	Found/%	16.81	41.23	15.86	4.31
Cu(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	Theory/%	18.65	42.30	16.44	4.73
	Found/%	18.41	42.01	16.19	4.31

**Table 2** Electronic spectra and magnetic moments

Compound	Colour	Band positions/cm <sup>-1</sup>	μ (B.M.)
Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	Blue	4424	4.71
		7142	
		15625	
Cu(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	Green-brown	4950	2.06
		13514	

**Table 3** Infrared spectra (4000–200 cm<sup>-1</sup>)

Compound	ν(NH <sub>2</sub> )		Ring Vibrations		ν(M–Cl)	ν(M–N)
C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	3333(s)	3196(s)	1602(s)	1585(s)	–	–
Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	3346(s)	3227(s)	1609(s)	1591(s)	325(s)	272(m)
					298(s)	
Cu(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	3341(s)	3221(s)	1610(s)	2589(s)	302(s)	240(m)

s strong; m medium

The main bands in the infrared spectra are listed together with their descriptions and assignments in Table 3. The infrared spectra of the metal complexes are similar to that of the 2-amino-3-methylpyridine in the 4000–600 cm<sup>-1</sup> range except that the bands due to the aromatic ring vibrations and the N–H vibrations are shifted to higher wavenumber on the formation of the complexes. This suggests that the nitrogen atom of the aromatic ring is coordinated to a metal atom [3] while there is no coordination through the nitrogen atom of the amino group [4].

The metal-chloride and metal-nitrogen bands have been assigned for each of the complexes. The values listed for the metal-chloride bands in Table 3, support the suggestion made earlier for a tetrahedral environment for the metal ions [5].

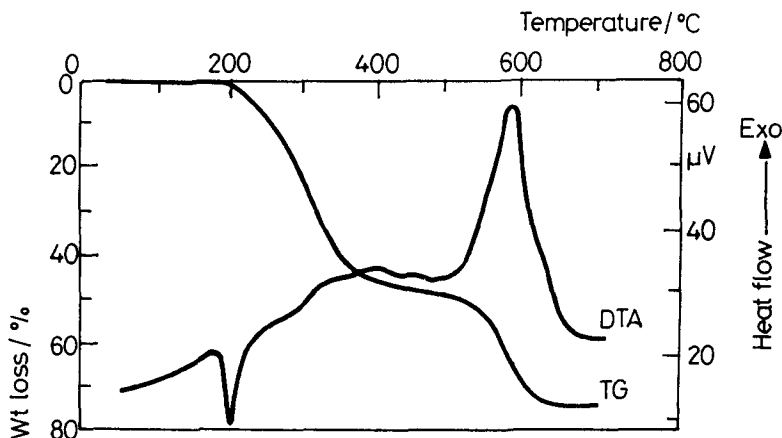


Fig. 1 TG and DTA curves for  $\text{Co}(\text{C}_6\text{H}_8\text{N}_2)\text{Cl}_2$

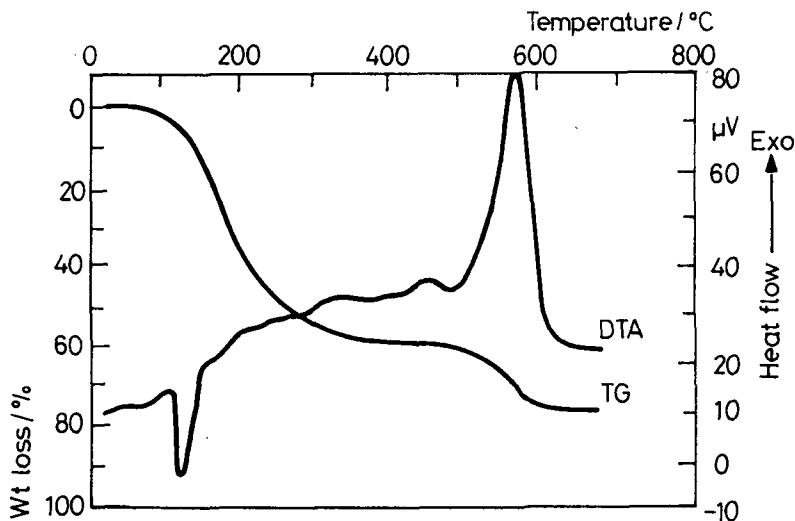


Fig. 2 TG and DTA curves for  $\text{Cu}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2$

The fact that the compounds were isolated from ethanolic solution as powders and not as single crystals means that no complete structure determination can be made. However spectroscopic and magnetic data enable us to predict that the metal ions are in a tetrahedral environment with the nitrogen atom of the aromatic ring in two different 2-amino-3-methylpyridine molecules being bonded to a metal ion along with two chloride ions to give the four coordinate environment for each metal ion.

The TG and DTA traces for the metal complexes are shown in Figs 1 and 2. The cobalt complex, Fig. 1, is stable up to 176°C when it then undergoes an en-

**Table 4** Thermal decomposition processes

Starting Material	Decomp. temp./ °C	Product	Weight		Enthalpy/ kJ·mol <sup>-1</sup>
			Calc.	Expt.	
Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	176 (ENDO)	Co <sub>2</sub> (C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>4</sub>	48.86	46.00	17
	378 (EXO)	Co <sub>3</sub> O <sub>4</sub>	29.96	29.20	296
Cu(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	92 (ENDO)	CuCl <sub>2</sub>	61.66	61.28	20
	398 (EXO)	CuO	15.67	15.80	160

ENDO Endothermic; EXO Exothermic (from DTA trace)

dothemic reaction with loss of one and a half molecules of 2-amino-3-methylpyridine to give Co<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)Cl<sub>4</sub>. This is followed by an exothermic reaction and loss of the remaining 2-amino-3-methylpyridine and chlorine to give Co<sub>3</sub>O<sub>4</sub>. The copper complex, Fig. 2, is stable up to 92°C when it undergoes an endothermic reaction with loss of two molecules of 2-amino-3-methylpyridine to give cobalt(II) chloride. A subsequent exothermic reaction takes place and CuO is obtained. The observed weight losses, obtained from the TG traces, for the different processes associated with these compounds compare favourably with the theoretical values in Table 4. In the DTA traces these processes correspond to endothermic or exothermic effects, Table 4. The reaction enthalpy for each of the decomposition processes is also listed in Table 4.

## References

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