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THE THERMAL, SPECTRAL AND MAGNETIC STUDIES OF CHLORO AND BROMO COMPOUNDS OF COBALT(II), NICKEL(II) AND COPPER(II) WITH MELAMINE

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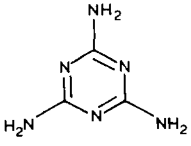
ABSTRACT

Compounds of melamine have been prepared with the chlorides and bromides of cobalt(II), nickel(II) and copper(II). The compounds, which have been characterised by analyses, magnetic moments, vibrational and electronic spectra, have polymeric octahedral structures. The thermal behaviour of these compounds has been studied by thermogravimetry (TG) and differential thermal analysis (DTA) techniques. The compounds, which are all hydrated, lose water of crystallisation followed by organic ligand to give the metal oxide.

INTRODUCTION

Melamine is an important industrial chemical with uses in resins and plastics. The reaction of melamine with formaldehyde gives thermosetting resins of industrial importance. The melamine-formaldehyde resins are used in making dinner ware and, under the brand name Formica, as decorative surface coatings for counter tops, tables and wall coverings. Melamine has a very stable heterocyclic structure with three ring-nitrogen atoms and three amine groups attached to the ring system. Thus, melamine provides six



Melamine ($C_3H_6N_6$)

potential bonding sites for metal ions so that any information on their corresponding properties and stability is important as a means of understanding the role of the metal ions in industrial processes. Furthermore, little information is available in the literature about this type of metallo-organic compound [1]. In this paper we have prepared new compounds and report the study of the complexes of melamine with the chloro and bromo compounds of cobalt(II), nickel(II) and copper(II), together with the results of the thermal analyses, electronic spectra and magnetic measurements. The thermal behaviour of melamine has been extensively investigated [2–8]. No thermal decomposition data on any of the complexes have been reported in the literature.

EXPERIMENTAL

Preparation of complexes

Two methods of preparation were used:

(A) Metal chloride or metal bromide (10 g) was dissolved in 100 cm^3 of warm water. Melamine (10 g) in 200 cm^3 of boiling water was then added and the resulting solution decreased in volume until ~ 100 cm^3 remained. The precipitated complexes were filtered, washed with boiling water and dried in a desiccator over calcium chloride.

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

Apparatus

Infrared spectra were obtained using KBr discs, 4000–1000 cm^{-1}, on a Perkin-Elmer Model 598 infrared spectrophotometer.

Raman spectra were obtained over the range 150–1000 cm^{-1} with an Anaspec Model 33 spectrometer and the 647.1 nm line of a krypton ion laser.

Electronic spectra were obtained on a Beckman ACTA M-IV spectrophotometer as solid diffuse reflectance spectra.

Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Each magnetic moment has been corrected for diamagnetism using Pascal's constants [9].

Thermal analysis studies were carried out on a Stanton Redcroft Model STA781 thermobalance. Thermogravimetry and differential thermal analysis curves were obtained at a heating rate of 6 °C min^{-1} in static air. In all cases the 20–900 °C temperature range was studied.

Metal ion analyses were obtained with a Perkin-Elmer Model 373 atomic absorption spectrophotometer. Carbon, hydrogen and nitrogen analyses were made using a Carlo Erba Model 1106 elemental analyser.

RESULTS AND DISCUSSION

The compounds isolated from solution are listed in Table 1. The stoichiometry of the compounds shows that the maximum number of melamine ligands present in any one compound is 2. All of the compounds are hydrated.

Table 2 lists the main bands in the vibrational spectra (4000–150 cm^{-1}). The spectra of the hydrated compounds show absorption bands in the region 3510–3200 cm^{-1}, $\nu(OH)$, and 1630–1580 cm^{-1}, $\delta(HOH)$, confirming the presence of water of crystallisation. The bands in the region 3350–3580 cm^{-1} have been assigned to the $\nu(NH_2)$ vibration, while those around 1660 cm^{-1} have been assigned to the $\delta(NH_2)$ vibration. The bands due to the $\nu(NH)$ vibrations undergo a change to higher frequency in the infrared spectra of the complexes, indicating that the nitrogen atom of the amine group is not involved in bonding to the metal atom [10]. The bonds due to the ring vibrations also show a change to higher frequency suggesting that coordination takes place between a ring nitrogen atom and the metal atom.

The bands from the vibrational spectra (150–600 cm^{-1}) due to the $\nu(M-Cl)$, $\nu(M-Br)$ and $\nu(M-N)$ vibrations are listed in Table 2. The bands due to the $\nu(M-Cl)$ and $\nu(M-Br)$ vibrations, which are reported to be < 200 cm^{-1}, are consistent with similar modes in halogen-bridged polymeric octahedral structures in the solid state [11]. No peaks were observed in the spectra for $\nu(M-O)$ vibrations. The suggestion of a polymeric structure for these compounds is supported by the fact that they were found to be insoluble in most polar and non-polar solvents [11].

The position of the bands in the electronic spectra of the compounds (Table 3) together with the values for Dq would suggest that the metal ions are in an octahedral environment in these compounds [12]. The values obtained for the magnetic moments also agree with this prediction [13].

No single crystals of the compounds could be isolated from solution or by examination of the powder samples of each compound by different solvents. Thus without X-ray analysis, no definite structures can be described. However, the spectroscopic and magnetic data enable us to predict possible structures. It is thus postulated that the structure of the compound is a chain of metal atoms bonded to halogens with the melamine molecules above and below the plane of the metal hydrogen chain. The broadness of the $\nu(N-H)$ vibration in the melamine and the splitting of these vibrations is caused by strong hydrogen bonding [14]. This is still observed in the infrared spectra of the melamine complexes thus suggesting the presence of hydrogen bonding between individual melamine molecules in these compounds.

The TG and DTA diagrams for melamine and its chloro and bromo complexes of cobalt(II), nickel(II) and copper(II) are shown in Figs. 1–7.

The TG curve for melamine (Fig. 1) shows that the compound is thermally stable in the 20–260 °C region. Its pyrolitic decomposition starts at

TABLE 1

Analyses and magnetic moments

Compound	Method of preparation	Found				Calculated				μ (B.M.)
		M	C	H	N	M	C	H	N	
$CoCl_2(C_3H_6N_6)_2 \cdot H_2O$	A	14.32	16.96	3.32	41.22	14.72	17.99	3.49	41.98	5.28
$CoCl_2(C_3H_6N_6)_2$	B	15.10	18.26	3.02	42.78	15.42	18.84	3.14	43.95	–
$CoBr_2(C_3H_6N_6)_2 \cdot 2H_2O$	A	10.86	14.02	2.96	32.64	11.60	14.18	3.15	33.08	5.14
$CoBr_2(C_3H_6N_6)_2$	B	11.89	14.76	2.11	34.72	12.51	15.28	2.55	35.65	–
$NiCl_2(C_3H_6N_6)_2 \cdot 2H_2O$	A	13.62	13.87	3.43	60.06	14.08	17.26	3.84	40.28	3.02
$NiCl_2(C_3H_6N_6)_2$	B	14.96	18.20	2.87	43.17	15.37	18.85	3.14	43.98	–
$NiBr_2(C_3H_6N_6)_2 \cdot 2H_2O$	A	10.91	13.67	2.99	32.71	11.58	14.20	3.16	33.14	3.72
$NiBr_2(C_3H_6N_6)_2$	B	12.03	14.87	2.63	34.92	12.46	15.28	2.97	35.67	–
$CuCl_2(C_3H_6N_6)_2 \cdot 2H_2O$	A	14.83	16.52	2.87	39.04	15.03	17.00	3.78	39.74	2.02
$CuCl_2(C_3H_6N_6)_2$	B	16.03	18.01	2.76	42.97	16.43	18.62	3.10	43.63	–
$CuBr_2(C_3H_6N_6)_2 \cdot 2H_2O$	A	12.19	33.63	14.08	2.13	12.87	34.03	14.58	2.83	2.12
$CuBr_2(C_3H_6N_6)_2$	B	13.31	14.68	2.02	36.74	13.35	15.13	2.52	35.31	–

TABLE 2

Vibrational spectra

Compound	Infrared				Raman				
		ν(NH)		$\delta(NH_2)$	Ring vibrations		ν(C–N–C)	ν(M–N)	ν(M–X)
$(C_3H_6N_6)$	3326(s)	3420(s)	3468(s)	1653(s)	982(s)	674(vs)	379(s)	–	–
$CoCl_2(C_3H_6N_6)_2$	3350(s)	3420(s)	3540(s)	1660(s)	987(s)	696(vs)	392(s)	565(s)	< 200(vw)
$CoBr_2(C_3H_6N_6)_2$	3330(s)	3410(s)	3524(s)	1670(s)	984(s)	684(vs)	385(s)	569(s)	< 200(vw)
$NiCl_2(C_3H_6N_6)_2$	3342(s)	3422(s)	3520(s)	1660(s)	992(s)	694(vs)	387(s)	575(s)	< 200(vw)
$NiBr_2(C_3H_6N_6)_2$	3332(s)	3430(s)	3508(s)	1670(s)	986(s)	680(vs)	383(s)	585(s)	< 200(vw)
$CuCl_2(C_3H_6N_6)_2$	3320(s)	3430(s)	3508(s)	1670(s)	983(s)	687(vs)	383(s)	559(s)	< 200(vw)
$CuBr_2(C_3H_6N_6)_2$	3325(s)	3418(s)	3516(s)	1662(s)	979(s)	681(vs)	379(s)	571(s)	< 200(vw)

vs, Very strong; s, strong; vw, very weak.

TABLE 3

Electronic spectra (cm^{-1})

Compound	Peak position (cm^{-1})	Dq	B	β
$CoCl_2(C_3H_6N_6)_2$	ν_1 8264 ν_2 14925 ν_3 18348	934	744	0.76
$CoBr_2(C_3H_6N_6)_2$	ν_1 8130 ν_2 14925 ν_3 18348	920	753	0.78
$NiCl_2(C_3H_6N_6)_2$	ν_1 7940 ν_2 14290 ν_3 24690	794	1010	0.97
$NiBr_2(C_3H_6N_6)_2$	ν_1 8510 ν_2 13700 ν_3 24720	851	859	0.83
$CuCl_2(C_3H_6N_6)_2$	ν_1 13300			
$CuBr_2(C_3H_6N_6)_2$	ν_1 13900			

259 ° C and finishes around 400 ° C with total elimination of the sample. The DTA curve shows a peak at 364 ° C corresponding to fusion. The value of the fusion enthalpy calculated from the area of this peak is 856 J g^{-1}. Liquid

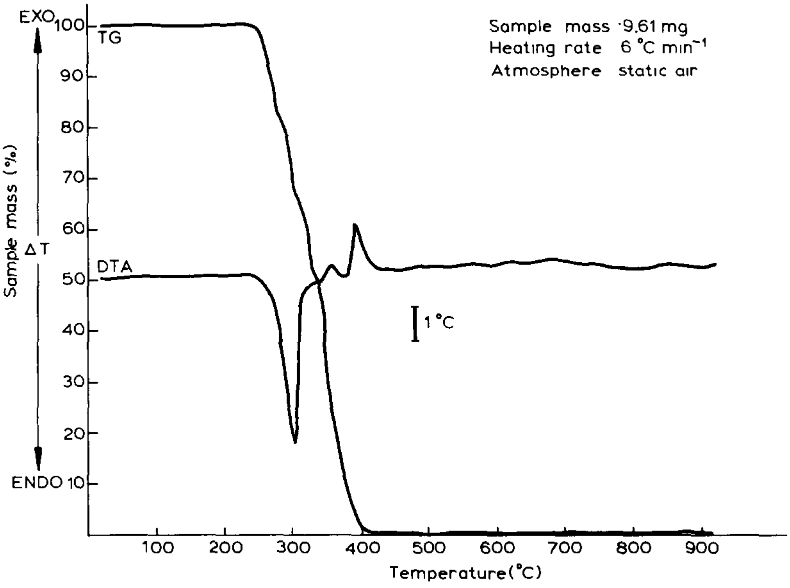


Fig. 1. Simultaneous TG and DTA curves of $C_3H_6N_6$.

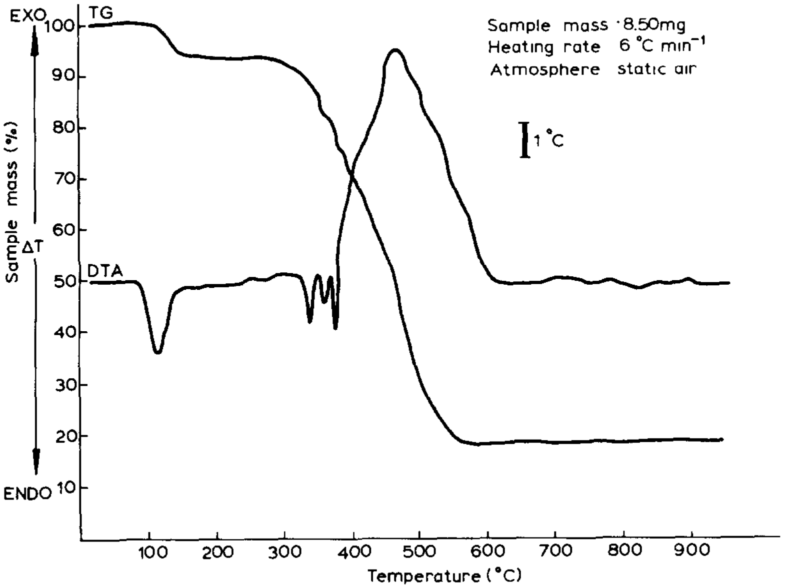


Fig. 2. Simultaneous TG and DTA curves of $CoCl_2(C_3H_6N_6)\cdot H_2O$.

melamine decomposed immediately with exothermic bands at 372 and 395 ° C.

The TG and DTA curves for the melamine complexes are shown in Figs.

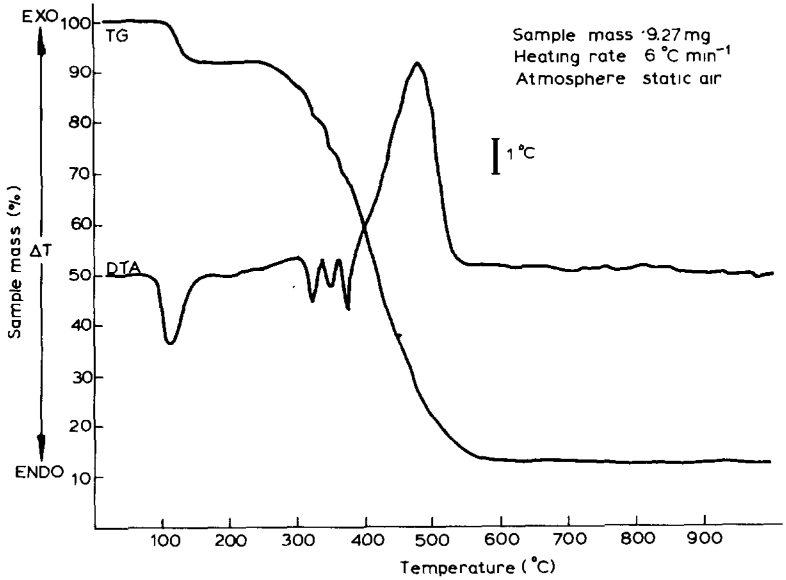


Fig. 3. Simultaneous TG and DTA curves of $CoBr_2(C_3H_6N_6)_2\cdot 2H_2O$.

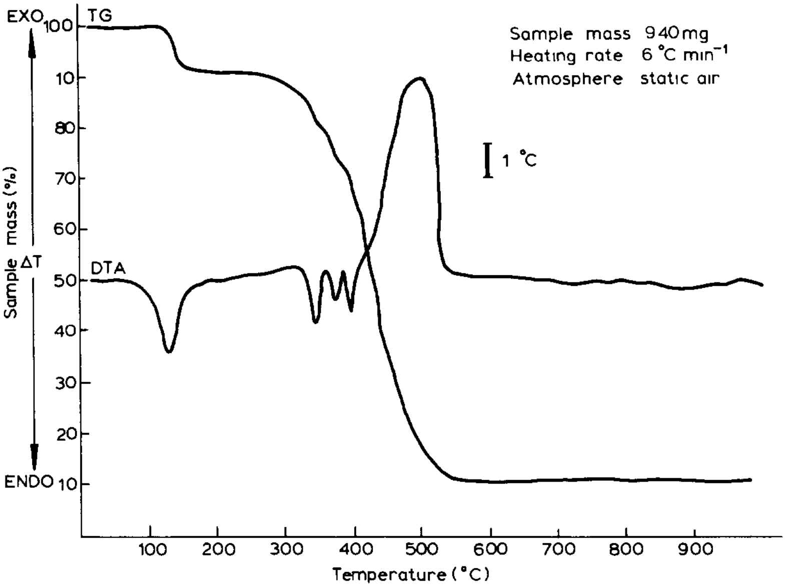


Fig. 4. Simultaneous TG and DTA curves of $NiCl_2(C_3H_6N_6)_2 \cdot 2H_2O$.

2-7. The dehydration processes which take place in one stage can be observed in the 30-126 °C range. The observed weight losses for these processes are in good agreement with the theoretical values. The expected

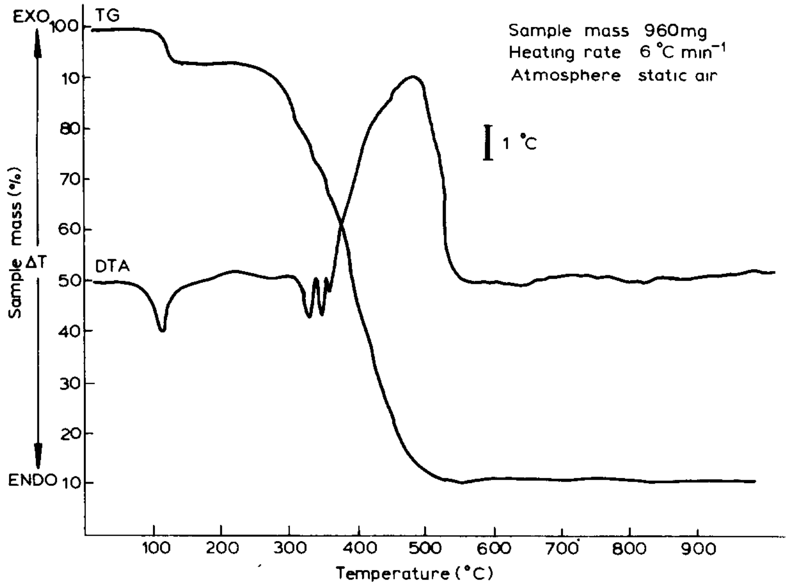


Fig. 5. Simultaneous TG and DTA curves of $NiBr_2(C_3H_6N_6)_2 \cdot 2H_2O$.

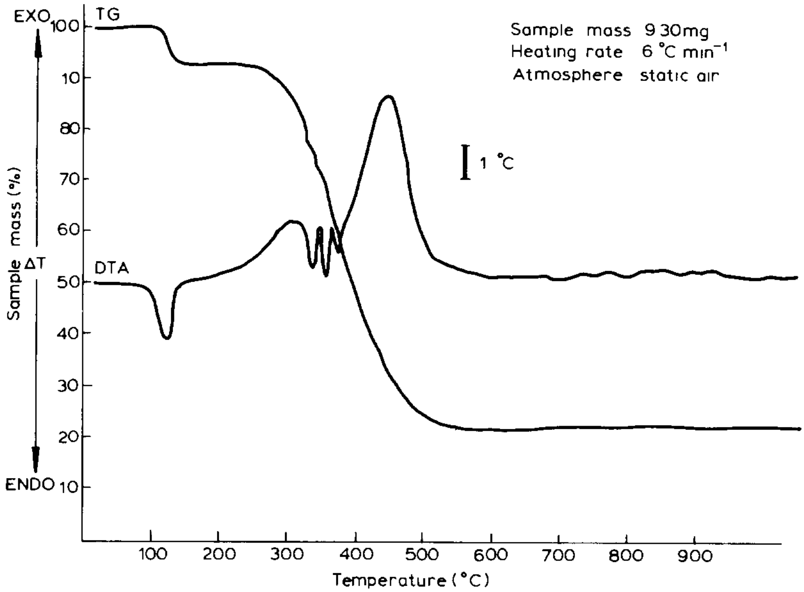


Fig. 6. Simultaneous TG and DTA curves of $CuCl_2(C_3H_6N_6)_2 \cdot 2H_2O$.

endothermic peaks for the dehydration processes associated with the complexes are present in the DTA curves. The dehydration enthalpies have been calculated and are given in Table 4A. The anhydrous compounds are stable

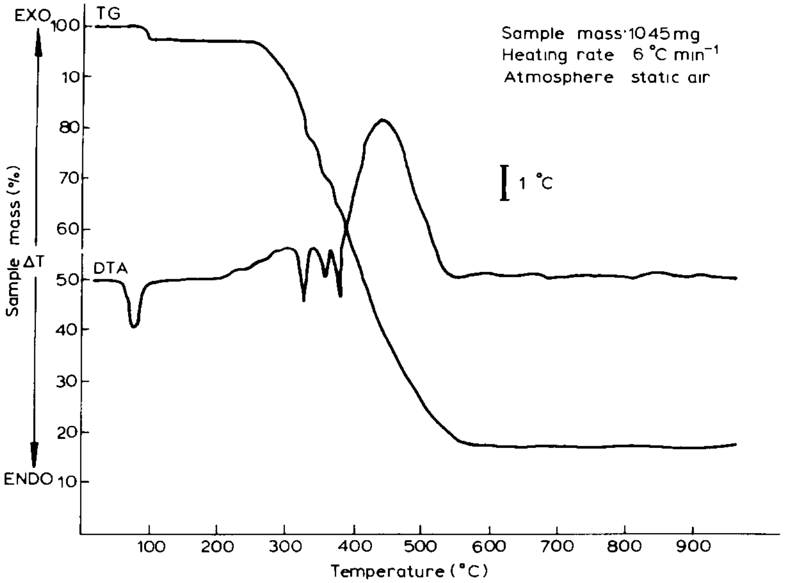


Fig. 7. Simultaneous TG and DTA curves of $CuBr_2(C_3H_6N_6)_2 \cdot 2H_2O$.

TABLE 4A

Dehydration processes

Reaction	Initial temp. (°C)	Thermal nature of reaction	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$C_3H_6N_6(s) \rightarrow C_3H_6N_6(l)$	364	endo	0	0	107.85
$CoCl_2(C_3H_6N_6)_2 \cdot H_2O \rightarrow CoCl_2(C_3H_6N_6)_2$	126	endo	4.5	6.0	40.8
$CoBr_2(C_3H_6N_6)_2 \cdot 2H_2O \rightarrow CoBr_2(C_3H_6N_6)_2$	106	endo	7.1	8.0	30.7
$NiCl_2(C_3H_6N_6)_2 \cdot 2H_2O \rightarrow NiCl_2(C_3H_6N_6)_2$	126	endo	8.6	9.0	55.2
$NiBr_2(C_3H_6N_6)_2 \cdot 2H_2O \rightarrow NiBr_2(C_3H_6N_6)_2$	104	endo	7.1	6.0	10.6
$CuCl_2(C_3H_6N_6)_2 \cdot 2H_2O \rightarrow CuCl_2(C_3H_6N_6)_2$	107	endo	8.5	7.0	49.4
$CuBr_2(C_3H_6N_6)_2 \cdot 2H_2O \rightarrow CuBr_2(C_3H_6N_6)_2$	99	endo	7.0	3.0	6.7

TABLE 4B

Decomposition reactions for anhydrous compounds

Reaction	Temp. range (°C)	Thermal nature of reaction	Weight loss (%)	
			Calc.	Found
$(C_3H_6N_6) \rightarrow$ pyrolytic reaction	259–400	exo	0	0
$CoCl_2(C_3H_6N_6)_2 \rightarrow Co_3O_4$	279–550	exo	79.9	81.0
$CoBr_2(C_3H_6N_6)_2 \rightarrow Co_3O_4$	258–557	exo	84.1	86.5
$NiCl_2(C_3H_6N_6)_2 \rightarrow NiO$	269–521	exo	82.1	89.0
$NiBr_2(C_3H_6N_6)_2 \rightarrow NiO$	254–548	exo	85.2	90.0
$CuCl_2(C_3H_6N_6)_2 \rightarrow CuO$	258–530	exo	81.2	77.0
$CuBr_2(C_3H_6N_6)_2 \rightarrow CuO$	255–575	exo	84.5	82.0

over a narrow temperature range and then show decomposition to the metal oxide with the metal complex losing organic ligand and halogen. The residual weights are in good agreement with the theoretical values from the metal oxides. In the DTA curves the main decomposition processes corresponds to an endothermic reaction followed by an exothermic reaction (Table 4B). Two smaller peaks corresponding to endothermic reactions are observed in each of the complexes at around 370 and 390 °C. These correspond to points of inflection on the TG curves for the complexes. However, attempts to isolate intermediate compounds of suitable stoichiometry were unsuccessful.

The stoichiometry of the residue of the pyrolytic decomposition of the metal melamine complexes was established by metal analysis on the residues.

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