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The thermal, spectral and magnetic studies of oxamic acid compounds of cobalt(II), nickel(II) and copper(II) ions

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Abstract

Cobalt, nickel and copper compounds with oxamic acid have been prepared in aqueous solution. The compounds have been characterised by analyses, magnetic moments, and vibrational and electronic spectra. They have the stoichiometry $ML_2(H_2O)_2$ and have octahedral structures. The thermal behaviour of these compounds has been studied by thermogravimetry and differential thermal analyses. The degradation processes for the cobalt and nickel complexes are similar, first losing two water molecules and then the organic ligand, to give the metal oxides. The copper complex loses first one water molecule, then the other water molecule and, finally, the organic ligand to give the metal oxide.

INTRODUCTION

The compound oxamic acid, $NH_2COCOOH$, has three donor sites for forming bonds with metal ions: the nitrogen atom of the NH_2 group, the oxygen atom of the CO group, and the oxygen atoms of the COOH group. This paper reports the thermal analysis studies of oxamic acid and of the complexes it forms with the transition metals cobalt, nickel and copper. Electronic spectroscopy and magnetic studies were used to obtain the stereochemistry of each metal complex and vibrational spectroscopy has been used to interpret the type of coordination which takes place to the metal ion.

EXPERIMENTAL

Preparation of compounds

Oxamic acid (0.05 mol) was dissolved in boiling water, and the resulting solution was neutralised by the addition of cobalt(II) carbonate. The

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solution was then filtered to remove any excess cobalt(II) carbonate and the filtrate was reduced in volume to yield the metal complex. This procedure was repeated using the carbonates of copper(II) and nickel(II).

Apparatus

The concentration of the metal ion was determined using a Perkin-Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen analyses were obtained using a Carlo Erba elemental analyser.

The IR spectra were obtained using KBr discs (4000–600 cm^{-1}) and polyethene discs (600–200 cm^{-1}) on a Perkin-Elmer spectrophotometer model 598.

The electronic spectra were obtained as solid diffuse reflectance spectra on a Beckmann Acta MIV spectrophotometer.

Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.

Thermal analysis studies were carried out on a Stanton Redcroft model STA 1500 thermobalance. The thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 10°C min^{-1} in static air over the temperature range of 20-800°C.

RESULTS AND DISCUSSION

The analytical results for the complexes are given in Table 1. The analytical data agree with the given formula proposed for the complexes.

Table 2, shows the wavenumbers of the IR absorption bands for oxamic acid and its complexes, together with the descriptions and assignments of the relevant wavenumbers. The absence of a broad intense band in the region 3500–2900 cm^{-1} would indicate that the water molecules are not present as water of crystallisation [1]. The bands due to the NH_2 vibrations are observed to move to higher wavenumbers on complexation, suggesting that no bonding has taken place between the nitrogen atoms of the NH_2

TABLE 1

Analyses of the compounds

Compound	Colour		Metal	C	N	H
$Co(C_2H_2NO_3)_2(H_2O)_2$	Pink	Theory	21.74	17.72	10.33	2.95
		Found	21.63	17.73	10.18	2.11
$Ni(C_2H_2NO_3)_2(H_2O)_2$	Green	Theory	21.67	17.74	10.34	2.95
		Found	21.24	17.10	9.88	2.38
$Cu(C_2H_2NO_3)_2(H_2O)_2$	Blue	Theory	23.04	17.42	10.16	2.92
		Found	22.32	17.62	9.38	2.04

TABLE 2

Infrared spectra 4000–200 cm^{-1}

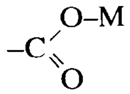
Compound	$\nu(NH_2)$	ν(COOH)	ν(C=O)	$\nu(COO^-)$	ν(C–O)	ν(M–O)
$C_2H_3NO_3$	3350 (s), 3240 (s)	1740 (s)	1678 (s)	–	1468 (m)	–
$Co(C_2H_2NO_3)_2(H_2O)_2$	3402 (s), 3230 (s)	–	1680 (s)	1660 (s)	1450 (m)	312 (s), 252 (m) $Co–OH_2$
$Ni(C_2H_2NO_3)_2(H_2O)_2$	3420 (s), 3240 (s)	–	1681 (s)	1664 (s)	1448 (m)	316 (s), 260 (m) $Ni–OH_2$
$Cu(C_2H_2NO_3)_2(H_2O)_2$	3422 (s), 3296 (s)	–	1679 (s)	1665 (s)	1456 (m)	330 (s), 246 (m) $Cu–OH_2$

Key: s, strong; m, medium.

group and the metal ions [2], the upward trend in wavenumbers indicating the presence of hydrogen bonding. A band at 1740 cm^{-1} in the IR spectrum of oxamic acid is due to the –COOH group. The spectra of the complexes confirms the absence of free carboxylic acid groups. A reduction in the $\nu(COO^-)$ compared to free $–CO_2H$ is observed which is characteristic of the type of chelation [3] shown in Scheme 1. The fact that little change is observed in the wavenumber of the ν(C=O) vibration for the C=O group suggests that bonding is not taking place between the C=O group and the metal atom. A band due to the C–O vibration is observed for oxamic acid and its metal complexes. The presence of coordinated water in the cobalt, nickel and copper complexes is shown by the bands at 312, 316 and 330 cm^{-1}, respectively. These bands have been assigned to the $M–OH_2$ vibration [4]. Metal–oxygen vibrations as a result of bonding between the carboxylate groups and the metal atoms are also reported in Table 2.

The electronic spectra and magnetic measurements are listed in Table 3. The position of the bands in the spectra of the cobalt and nickel complexes together with their magnetic moments, would suggest that the metal atoms are in an octahedral environment [7]. The copper compound has a broad band in its electronic spectrum between 10 000 and 15 000 cm^{-1}, suggesting that the copper atoms are in an octahedral environment in this compound [5]. A magnetic moment of 1.69 BM was obtained for this compound, indicating some weak copper–copper magnetic interaction.

The fact that the compounds were obtained as powders and not as single crystals means that no complete structure determination could be carried out. However, spectroscopic and magnetic data enable us to suggest the environment of the metal ion in each of the complexes. The compounds are



Scheme 1.

TABLE 3

Electronic spectra and magnetic moments

Compound	Band positions/cm^{-1}	d–d Transition	μ/BM
$Co(C_2H_2NO_3)_2(H_2O)_2$	8306 18860 21276 sh	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.85
$Ni(C_2H_2NO_3)_2(H_2O)_2$	9090 15625 25640	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	3.03
$Cu(C_2H_2NO_3)_2(H_2O)_2$	13320	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.69

Key: sh, shoulder.

considered to have a planar arrangement formed by bonding between two carboxylate groups and two water molecules to a metal ion. A six-coordinate environment for each metal ion is obtained by the metal ion bonding to oxygen atoms in adjacent layers.

The TG and DTA traces for oxamic acid and its metal complexes are shown in Figs. 1–4. The TG trace for oxamic acid, Fig. 1, shows that it is thermally stable in the range 20–150°C. Decomposition begins at 150°C and ends at 340°C with total elimination of the sample. The DTA trace, Fig. 1, shows an endothermic peak at 210°C due to fusion, followed by an exothermic peak corresponding to the decomposition of the oxamic acid. The TG and DTA traces for the cobalt, nickel and copper complexes of oxamic acid are shown in Figs. 2–4. The TG traces for the cobalt and nickel complexes show that they decompose at 136 and 148°C, respectively, with the loss of two molecules of water. These dehydration processes produce an endothermic peak on the DTA trace for each complex. The TG trace for each of the anhydrous complexes shows that they then decompose to

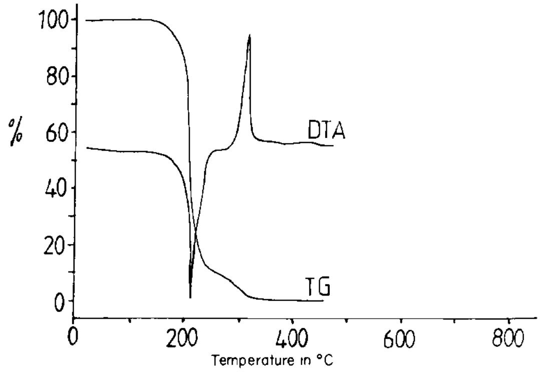


Fig. 1. TG and DTA trace of $C_2H_3NO_3$; sample weight = 9.52 mg.

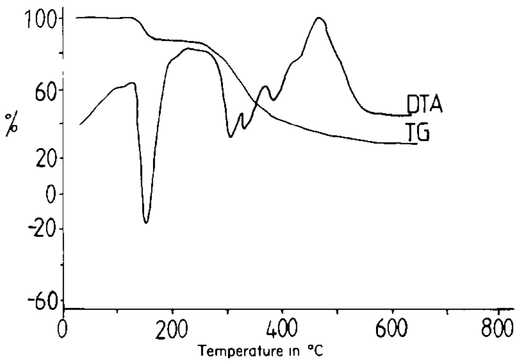


Fig. 2. TG and DTA trace of $Co(C_2H_2NO_3)_2(H_2O)_2$; sample weight = 10.12 mg.

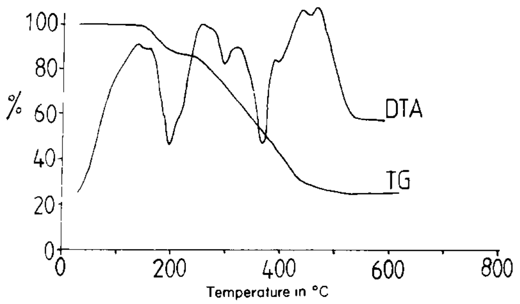


Fig. 3. TG and DTA trace of $Ni(C_2H_2NO_3)_2(H_2O)_2$; sample weight = 11.50 mg.

give the metal oxide. These decomposition processes are accompanied by endothermic and exothermic effects on the DTA traces. The TG trace for the copper complex shows that it first loses one water molecule at 135°C followed by a second water molecule at 162°C. The DTA trace indicates that these dehydration processes are accompanied by endothermic peaks. The TG trace shows that the anhydrous copper complex then decomposes to give copper(II) oxide. This decomposition process produces endothermic and exothermic effects in the DTA trace. The actual weight losses reported

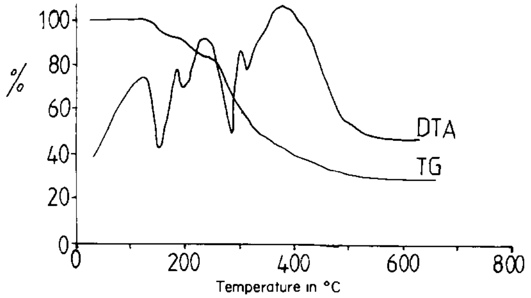


Fig. 4. TG and DTA trace of $Cu(C_2H_2NO_3)_2(H_2O)_2$; sample weight = 9.86 mg.

TABLE 4

Dehydration processes of metal complexes

Process	Temperature of decomposition/°C	Thermal nature of transformation
$Co(C_2H_2NO_3)_2(H_2O)_2 \rightarrow Co(C_2H_2NO_3)_2$	136	Endo
$Ni(C_2H_2NO_3)_2(H_2O)_2 \rightarrow Ni(C_2H_2NO_3)_2$	148	Endo
$Cu(C_2H_2NO_3)_2(H_2O)_2 \rightarrow Cu(C_2H_2NO_3)_2 \cdot H_2O$	135	Endo
$Cu(C_2H_2NO_3)_2 \cdot H_2O \rightarrow Cu(C_2H_2NO_3)_2$	162	Endo

Key: Endo, endothermic (from DTA) trace).

TABLE 5

Decomposition processes of oxamic acid and its metal complexes

Process	Temperature range/°C	Thermal nature of transformation	Residue in %		Weight loss in %	
			Calc.	Found	Calc.	Found
$C_2H_3NO_3$	150–340	Endo/exo	–	–	13.3	13.2
$Co(C_2H_2NO_3)_2 \rightarrow Co_3O_4$	209–582	Endo/exo	29.6	29.5	13.3	13.4
$Ni(C_2H_2NO_3)_2 \rightarrow NiO$	226–539	Endo/exo	27.6	27.5	6.5	6.4
$Cu(C_2H_2NO_3)_2 \rightarrow CuO$	246–548	Endo/exo	27.9	27.8	6.5	6.5

Key: Endo, endothermic; exo, exothermic (from DTA trace).

in Tables 4 and 5 for the decomposition processes of the metal complexes compare favourably with the calculated losses.

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