Thermochimica Acta, 162 (1990) 375–387
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

INFRARED, THERMAL AND STRUCTURAL PROPERTIES OF FIRST TRANSITION SERIES METAL CHLORIDE AND PERCHLORATE COMPLEXES OF QUINOXALINE

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(Received 6 November 1989)

ABSTRACT

The chloride complexes of divalent Mn, Fe, Co, Ni, Cu and Zn containing one or two quinoxaline molecules and different numbers of H_2O molecules, when subjected to thermal analysis under dynamic N_2 atmosphere, decomposed to the metal chloride which then gave the metal oxide. The chlorides of Cu and Zn partly sublimed.

The perchlorate complexes contained two or three quinoxaline molecules and in the case of Mn, Fe and Zn did not decompose to pure metal perchlorate during the heating before an explosion occurred; this depended on the heating rate.

The IR spectra of the complexes show M–N bands under 500 cm^{-1}, confirming the quinoxaline coordination. Copper in particular shows a tendency to form polymeric structures. The correlation between the results and the complex structure is discussed.

INTRODUCTION

We have recently prepared and solved the crystal structure of two quinoxaline copper complexes: *catena*-μ-perchlorate-0,0′-tris-μ-quinoxaline-*N,N′*-dicopper(I) perchlorate [1] and triaquabis(quinoxaline)copper(II) perchlorate [2]. Other physical properties were discussed with respect to their structures. We have now extended this study to other quinoxaline complexes of first transition-series metal chlorides and perchlorates. The syntheses, TG curves and IR spectra of the complexes and comparison with earlier data are reported in this paper together with a discussion of their structures.

EXPERIMENTAL

Reagents, syntheses and analyses of the complexes

The chloride complexes were prepared by refluxing quinoxaline (0.005 mol) and $MCl_2 \cdot xH_2O$ (0.005 mol) in 100 ml of absolute ethanol on a water

TABLE 1

Analytical data for the metal chloride and perchlorate complexes of quinoxaline (Q)

Complex	Analysis			
	M.W.	Colour	Metal (%)	
			Calc.	Found
$MnQCl_2 \cdot H_2O$	274.01	Yellow	20.05	19.8
FeQ_3Cl_2	517.20	Green	10.80	10.9
$CoQCl_2 \cdot 1.5H_2O$	287.00	Blue	20.53	20.5
$NiQCl_2 \cdot 3H_2O$	313.80	Yellow	18.71	18.8
$CuQCl_2 \cdot H_2O$	282.61	Green	22.48	22.6
$ZnQCl_2 \cdot H_2O$	284.45	White	22.98	22.5
$ZnQ_2Cl_2 \cdot H_2O$	414.60	White	15.77	15.8
$MnQ_2(ClO_4)_2 \cdot 5H_2O$ [a]	604.21	Yellow	9.09	9.1
$FeQ_3(ClO_4)_2 \cdot 5H_2O$	735.27	Green	7.60	7.6
$CoQ_2(ClO_4)_2 \cdot 6H_2O$ [b]	626.23	Blue	9.41	9.4
$NiQ_2(ClO_4)_2 \cdot 6H_2O$	626.00	Yellow	9.38	9.3
$ZnQ_2(ClO_4)_2 \cdot 6H_2O$	632.67	White	10.33	10.4

[a] H_2O: 14.90 (calc.), 16.5 (found).
[b] H_2O: 17.26 (calc.), 17.3 (found); ClO_4: 31.76 (calc.), 30.5 (found).

bath for 15 min; the precipitates were left for several weeks, then filtered, washed with ether and dried. A quinoxaline : metal ratio of 2 : 1 was used for manganese and zinc. The copper complex was recrystallised from ethanol–water (9 : 1) solution. The metal salts used, $MnCl_2 \cdot 4H_2O$, $FeCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $ZnCl_2$ (Fluka or Merck), were of the best available quality.

The perchlorate complexes were synthesised by refluxing quinoxaline (0.005 mol) and $M(ClO_4)_2 \cdot 6H_2O$ (0.005 mol) in 30 ml of ethylacetate for 30 min; the precipitate was left for several days, then filtered, washed with ethylacetate and ether, and dried. The metal perchlorate hexahydrates (Fluka and Merck) were also of the best available quality.

The metal contents were determined by EDTA titrations. After cation exchange, the perchlorate content was determined as acid with a known NaOH solution, and H_2O was determined by the Karl–Fisher method [3]. The analytical results are presented in Table 1.

Apparatus and measurements

The TG curves were run on a Perkin–Elmer TGS-1 thermobalance. The sample weight was 2 mg, platinum crucibles were used, the heating rate was 5 or 2.5 °C min^{-1} and the atmosphere was dynamic nitrogen with a flow of about 35 ml min^{-1}.

IR spectra of KBr discs (1–20 mg compound: 200 mg KBr) were recorded on a Perkin–Elmer grating IR spectrophotometer, model 577 [4].

RESULTS AND DISCUSSION

IR spectra

The IR absorption bands of the chloride complexes with their assignments, and of quinoxaline for comparison, are presented in Table 2; those of the perchlorate complexes, and of quinoxaline perchlorate and cupric perchlorate hexahydrate are shown in Table 3. The spectra of the cuprous and cupric perchlorate complexes, and of quinoxaline for comparison, in the 1600–200 cm^{-1} range are shown in Fig. 1.

The IR spectrum of the hydrated cobalt chloride complex (4000–200 cm^{-1}) is quite different from those obtained earlier for cobalt(II) complexes with quinoxaline [5] and shows, in most cases, the quinoxaline bands, weakened and shifted to some extent, and also additional bands suggesting coordination to the metal atoms; this is the case for all the chloride complexes studied.

The quinoxaline complexes of monovalent and divalent metal ions show weak IR bands under 600 cm^{-1} due to metal–nitrogen bond vibrations. This

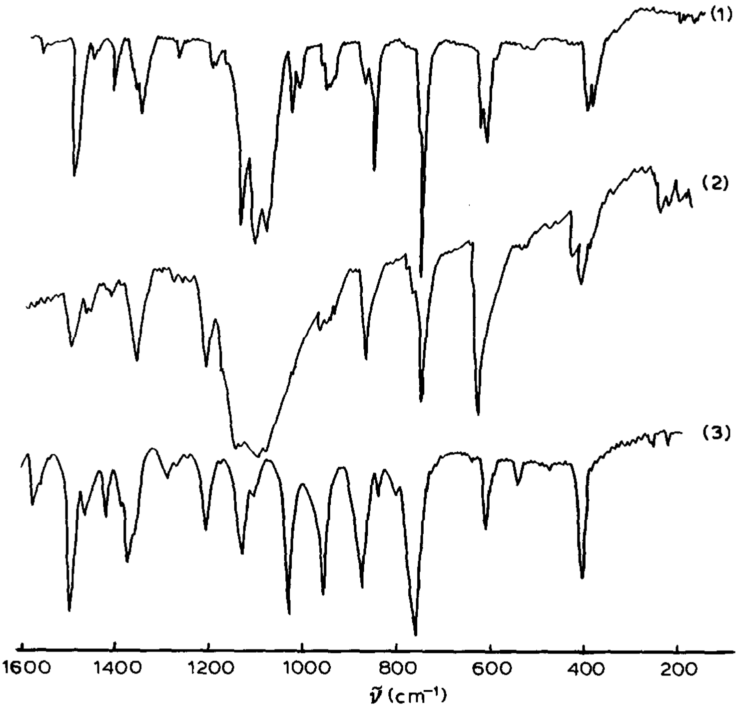

Fig. 1. Comparison of the IR spectra of two copper complexes and quinoxaline in the wavelength range 1600–200 cm^{-1}: 1, $[Cu_2Q_3(ClO_4)](ClO_4)$; 2, $[CuQ_2(H_2O)_3](ClO_4)_2$; 3, quinoxaline.

TABLE 2

IR frequencies (cm^{-1}) of the metal chloride complexes of quinoxaline [a]

$MnQCl_2 \cdot H_2O$	FeQ_3Cl_2	$CoQCl_2 \cdot 1.5H_2O$	$NiQCl_2 \cdot 3H_2O$	$CuQCl_2$	$ZnQCl_2 \cdot H_2O$	$ZnQ_2Cl_2 \cdot H_2O$	Q	Assignment
3700–2800s,br	3700–3100s,br	3380s,br	3160–2600s,br	3600–3140w,br	3500sh,br	3400w,br	3450m,vbr	$\nu_1(A_1, OH)$, $\nu(CH)$
		3210w			3320s,br			$\nu(CH)$
		3070w		3070w				$\nu(CH)$
	3040w	3050w		3040m		3050w	3060m,br	$\nu(CH)$
		3025w		3020m		3030w		$\nu(CH)$
		2980w			2750vs,br			c. and o.
						1910w,br	1930m,br	ν(ring)
						1860w	1830w,br	ν(ring)
	1620s	1633, 1620m			1650sh,br	1635w	1615m	ν(ring)
1600s,br	1605w	1605m	1610w,br		1600s	1608w		$\nu_2(A_1, OH)$
	1573w	1530w, 1520s	1545s,br		1562s	1575w	1570m	ν(ring)
1495s	1515s, 1478m	1480w	1500s	1503s	1498vs	1498vs	1498vs	δ(ring)
1460sh,br	1455m	1455w	1455w	1462m	1460s	1463s	1465m	δ(ring)
			1423w	1418w	1421m	1420w	1418m	δ(ring)
	1400s, 1380vs	1380s		1372w	1370sh	1380m	1385w	δ(ring)
1350s,br	1340s	1350m	1350s	1354s	1358vs	1357s, 1355w	1375s	δ(ring)
1310, 1295w	1275w	1270w	1295w	1313, 1280w	1290, 1270w	1282, 1265m	1290w	δ(ring)
1240sh	1258m, 1235w	1255w, 1240vw				1255, 1250w		$\delta(CH)$
1210s,br	1210s, 1190w	1213w, 1210s	1210s	1210, 1205s	1210vs	1213s, 1206w,	1210s	$\delta(CH)$

1141s	1142w, 1140vs	1140s	1145m	1142s	1145w,1140s	1147,1140s		δ(CH)
1130s	1130w		1135sh	1135s	1138w	1130vs	1130s	δ(CH)
1115, 1100m	1082w	1080w	1067w, 1058w	1095w	1088w	1095w	1100w	δ(CH)
1042s, 1060sh	1038w, 1030s	1038vs, 1010w	1048s, 1025m	1055s	1040s, 1015w	1045vs, 1030w	1028vs	δ(CH)
985sh, 960s	967w, 940m	968, 963w	962s	970s	995w, 968vs	962vs, 955w	953vs	δ(ring), δ(CH)
860s	874m, 862w	878, 867w	875w	875s	882vs	880w, 875s	870vs	δ(CH)
828m	836vs, 830w	848, 825s	850s, 845w		850, 830w	850, 825w	838w	δ(CH)
785m	780m, 775w	782m, 770w	786vw	780w	800, 787w	792m	800vw	δ(CH)
765m	760w	765w, 758s			776m, 765vs	770s, 762vs	760vs	δ(CH)
752vs	755s, 750w	755, 750w	755w, 743s	752vs				δ(ring)
					705m			ν(MCl)
	622m		660w, 615w,br	642w	636m	627m		δ(ring)
	604sh, 597vs	600vs					604m	ν(CN), ν(MN)
535vw	528w, 522s	532w, 524m	530w	545, 537w	538, 510m	537w	537w	ν(CN), ν(MN)
490w	482m	480m	470vw		482w,br	505w		ν(CN), ν(MN)
450w	460sh, 455vw	460w		465w	458vw			ν(CN), ν(MN)
	422vw		435w, 426m, 410w	428, 418m	408vs	418s, 409vs	405vs	δ(ring), ν(MN)
	388w, 380vs,br	390m, 385w						ν(MCl)
		310m		322m	333vs	345, 318w		ν(MCl)
	293m				292s			ν(MCl)
			235, 208w					ν(MCl)

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[a] Abbreviations: b, broad; m, medium; s, strong; sh, shoulder; v, very; w, weak; ν, stretching; δ, bending; c., combination; o., overtones.

TABLE 3

IR frequencies (cm^{-1}) of the metal perchlorate complexes of quinoxaline [a]

$MnQ_2(ClO_4)_2 \cdot 15H_2O$	$FeQ_3(ClO_4)_2 \cdot 5H_2O$	$CoQ_2(ClO_4)_2 \cdot 6H_2O$	$NiQ_2(ClO_4)_2 \cdot 6H_2O$	$[CuQ_2(H_2O)_3]_2(ClO_4)_2$	$[Cu_2Q_3(ClO_4)](ClO_4)$	$ZnQ_2(ClO_4)_2 \cdot 6H_2O$	$QH^+ClO_4^-$	$Cu(ClO_4)_2 \cdot 6H_2O$	Assignment
3240s, vbr	3240s, vbr	3240s, br	3240vs, br	3400m, br			3240w	3390vs, br	$\nu_1(A_1, OH)$, $\nu(CH)$
							3200w		$\nu(CH)$
				3050w	3050w	3060w	3090w		$\nu(CH)$
					3000vw	3020w	3070w		$\nu(CH)$
	1990vw						1990w		ν(ring)
	1935vw		1940w			1945w	1920w		ν(ring)
	1840w		1840w			1835w	1865w		ν(ring)
1625vs, br	1650m	1650m, br	1650s	1620w, br		1730, 1720w	1620m		ν(ring), $\nu(ClO_4^-)$
1605sh	1600m		1620m			1605w	1605w	1610s	$\nu(ClO_4^-)$, $\nu_2(A_1, OH)$
1575vw	1575w	1577vw	1580w		1570vw	1575w	1575m		ν(ring)
1555vw	1555w		1560w				1540w		ν(ring)
1495s	1495s	1495s	1500vs	1495m	1495s	1500vs	1517s		δ(ring)
1460m	1460s	1465m	1465s	1465w	1460w	1465s	1455m		δ(ring)
1417w	1420w	1415w	1420m	1415w	1415m	1420w	1400w		δ(ring)
1385vw	1385sh		1400vw				1385s		δ(ring)
1370m	1370sh	1375w	1380sh		1367w	1380m			δ(ring)
1355m	1355m	1355s	1360s	1355m	1355m	1355vs	1355m		δ(ring)
1290w	1290vw	1290w	1295w	1280vw	1280w	1285s	1280w		δ(ring)
1265vw	1267vw	1265w	1270w	1265vw		1265m	1250w		δ(ring)
1210m	1210m	1210s	1215s	1208m	1210w	1210s	1215s		$\nu(ClO_4^-)$
1200vw		1200sh			1200w	1200w	1195w	1180vw	$\nu(ClO_4^-)$

				1135sh	1140vs	1140vs		1150vs	$\nu_3(ClO_4^-)$, δ(CH)
1100vs, br	1100vs, br	1100vs	1100vs, br	1085vs	1110, 1090vs	1100vs	1100vs	1115, 1090vs	$\nu_3(ClO_4^-)$, δ(CH)
1030s	1035m	1040w	1035m	1025sh	1035m	1040vs	1030w		δ(CH)
1010w	1010w	1030w	1000w		1020m		1010w		δ(CH)
958s	960m	960s	965s	955w	960m	950vs	965w		δ(CH)
938m	940w	940w	940w	940vw	950m	940m	945w	940m	$\nu_1(ClO_4^-)$, δ(ring)
930vw	930vw		930w				920m		δ(ring)
880m	880sh		885vw		885w		890w		δ(CH)
870, 865m	870s	870s	875s	870m	860s	870vs			δ(CH)
855m	855sh		845w				850s		δ(CH)
830vw	830vw		835w			825w	825w		δ(CH)
795vw	795vw	790w	800w			795m	790w		δ(CH)
770sh	770s	770s	775s			770vs	770s		δ(CH)
755, 750m	755sh	760s	760w, 745m	750s	755vs	765vs	757s		δ(ring)
635sh	635sh	635sh	635sh		635m	635vs	630s	640s	$\nu_4(ClO_4^-)$
625m	625m	625s	625m	625s	625m	625vs	620s	630s	$\nu_4(ClO_4^-)$
	600w						600s		δ(ring)
530w	530w	535, 530w	535, 530w	535w		535w	525m		ν(CN), ν(MN)
490w	487w	505w	490w			510w	490m		ν(CN), ν(MN)
				455vw		450vw	455w		ν(CN), ν(MN)
		415m		425w	410m	417s			ν(MN)
	400m	405s	400sh	412m	400m	407vs	400w		ν(CN), ν(MN)
398s	395m		395m	405w			390m		ν(CN), ν(MN)
								300, 290vw	ν(MCl)
		275vs						265w	ν(MCl)
								240m	ν(MCl)

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[a] For abbreviations see Table 2 footnote.

is shown in Fig. 1 for the two copper perchlorate complexes studied and the bands of the spectra and their assignments [1,2] are given in Table 3.

The very strong, broad bands at 3400 cm^{-1} ($\nu_{as}(OH) = \nu_3(B_1)$) shown by the metal salt hydrates are masked by the ligand bands of the chloro and perchlorate complexes, as shown in Tables 2 and 3.

In general, in the spectra of all the complexes, the band at 3250–3000 cm^{-1} is due to C–H stretching vibrations of the quinoxaline molecules. The strong, medium or weak bands in the 3000–700 cm^{-1} range are assigned to combination and overtone bands or stretching and deformation bands of the quinoxaline rings with individual overlaps as noted in Tables 2 and 3.

The strong band at 1610 cm^{-1} observed in the spectra of metal salt hydrates and due to OH bending ($\nu_2(A_1(OH))$) vibrations is missing, masked or shifted in the complex spectra. This must be due to hydrogen-bond formation in the crystals [1,2].

The bands (cm^{-1}) 1150vs, 1115vs, 1090vs, 940m, 640s and 630s due to ClO_4 vibrations in the spectrum of $Cu(ClO_4)_2 \cdot 6H_2O$ are shifted, split or even missing from the same regions in the spectra of the perchlorate complexes suggesting ionic or bridging bidentate perchlorate.

The IR spectra of the chloride complexes clearly show the strong band found at 953 cm^{-1} in the quinoxaline spectrum [5] in the 1000–900 cm^{-1} region; it is generally split into a doublet which suggests quinoxaline coordination [1]. It has earlier been assumed [6] that this band indicates the coordination of pyrazine to the central atom.

The very sharp single peaks at 780–750 cm^{-1} may characterise bidentate quinoxaline [5] and the doublet or triplet may indicate the monodentate quinoxaline. The two quinoxaline peaks at 604 cm^{-1} (in-plane deformation) and 405 cm^{-1} (out-of-plane deformation) are generally shifted to higher frequencies, the former to 640–597 and the latter, split, to around 430–400 cm^{-1}.

In general, the weak, medium or strong bands below 600 cm^{-1} at 500–490, 455–415 and 405–390 cm^{-1} are assigned to ν(M–N) stretching vibrations due to quinoxaline coordination to the metal ions in the complexes, and those below 390 cm^{-1} are due to ν(MCl) vibrations.

According to the non-splitting or splitting of the 760–750 cm^{-1} band in the spectra of the complexes, the quinoxaline molecules were bidentate in the cuprous and cupric perchlorate complexes studied, which is in agreement with their structural data [1,2], and monodentate in other perchlorate complexes studied.

Among the chloride complexes, the manganese and copper chloride complexes contained bidentate quinoxalines and the other chloride complexes studied contained monodentate quinoxalines. For the copper(II) chloride complex, this was confirmed by X-ray analyses [7]. The copper(II) chloride and perchlorate complexes studied have polymeric structures with bridging quinoxalines, chloride and perchlorate ions [1,7]. The disappearance of the band at 1620–1610 cm^{-1} due to $\nu(ClO_4^-)$ vibrations is also typical for the copper(I) perchlorate complex studied [1].

TG data

The results of the thermal analyses of the complexes are presented in Tables 4 and 5 and in Figs. 2 and 3. In Table 4, the TG data, obtained in a

TABLE 4

TG data for the metal chloride complexes of quinoxaline (Q) [a]

Process	TG		
	Temp. range (°C)	Residue (%)	
		Found	Calc.
$MnQCl_2 \cdot H_2O \downarrow$	– 30		
$MnQCl_2$	55–140	93.3	93.4
$MnCl_2$	350–410	46.4	45.9
MnO	590 →	24.8	25.9
$FeQ_3Cl_2 \downarrow$	– 95		
$FeCl_2$	280–430	22.4	24.5
FeO	760 →	14.2	13.9
$CoQCl_2 \downarrow$	– 30		
$CoQ_{0.5}Cl_2$	70–105	75.6	75.0
$CoQ_{0.25}Cl_2$	175–205	62.1	62.5
$CoCl_2$	270–365	50.7	49.9
CoO	575 →	29.5	28.8
$NiQCl_2 \cdot 3H_2O \downarrow$	– 35		
$NiQCl_2$	70– 93	77.6	82.8
$NiCl_2$	320–350	42.4	41.3
NiO	555 →	23.1	23.8
$CuQCl_2 \cdot 1.5H_2O \downarrow$	– 70		
$CuQCl_2 \cdot H_2O$	80–110	96.7	96.9
$CuCl_2$	340	45.0	46.1
CuO	525 →	5.4	27.3
$CuQCl_2 \downarrow$	–245		
$CuCl_{1.5}$	305–365	44.6	44.1
CuO	545 →	8.6	30.1
$ZnQCl_2 \cdot H_2O \downarrow$	–117		
$ZnQCl_2$	190–210	93.8	93.7
$ZnCl_2$	388–395	48.5	47.9
ZnO	490 →	19.8	28.6
$ZnQ_2Cl_2 \cdot H_2O \downarrow$	– 85		
$ZnQCl_2$	150–190	66.6	64.3
$ZnCl_2$	345–365	33.9	32.9
ZnO	465 →	8.1	19.6

[a] Heating rate, 5°C min^{-1}; dynamic N_2 atm, 35 ml min^{-1}.

TABLE 5

TG data for the metal perchlorate complexes of quinoxaline (Q) [a]

Process	TG		
	Temp. range (°C)	Residue (%)	
		Found	Calc.
$MnQ_2(ClO_4)_2\cdot 5H_2O$ ↓	- 53		
$MnQ_2(ClO_4)_2\cdot H_2O$	87–110	89.5	88.1
$MnQ(ClO_4)_2$	200–235	62.7	63.6
(Explosion)	235–285	–	–
$MnQ_2(ClO_4)_2\cdot 5H_2O$ [b] ↓	- 70		
$MnQ_2(ClO_4)_2\cdot H_2O$	105–125	89.5	88.1
$MnQ(ClO_4)_2$	215	63.7	63.6
$Mn(ClO_4)_2$	260	42.9	42.0
Mn_3O_4	603 →	12.5	12.6
$FeQ_3(ClO_4)_2\cdot 5H_2O$ ↓	- 48		
$FeQ_3(ClO_4)_2\cdot H_2O$	88– 95	89.5	90.2
$FeQ_3(ClO_4)_2$	116–130	85.2	87.8
(Explosion)	130–207	–	–
$CoQ_2(ClO_4)_2\cdot 6H_2O$ ↓	- 67		
$CoQ_2(ClO_4)_2\cdot 2H_2O$	95–125	89.2	88.5
$CoQ_2(ClO_4)_2$	170	82.7	82.7
$Co(ClO_4)_2$	365–400	40.7	41.2
CoO	715 →	12.0	12.0
$NiQ_2(ClO_4)_2\cdot 6H_2O$ ↓	- 65		
$NiQ_2(ClO_4)_2\cdot 2H_2O$	90–130	89.1	88.5
$NiQ_2(ClO_4)_2$	193	78.2	82.7
$Ni(ClO_4)_2$	330	41.3	41.2
NiO	720 →	9.3	11.9
$[CuQ_2(H_2O)_3](ClO_4)_2$ ↓	- 70		
$[CuQ_2(H_2O)_2](ClO_4)_2$	110–135	96.8	96.9
$Cu(ClO_4)_2$	270–295	44.1	45.5
CuO	670 →	8.4	13.8
$[Cu_2Q_3(ClO_4)](ClO_4)$ [b] ↓	- 80		
$[Cu_2Q(ClO_4)](ClO_4)$	122–148	68.5	63.7
$[Cu_2Q_{0.5}(ClO_4)](ClO_4)$	195–205	55.7	54.6
CuCl	255–260	23.1	27.6
CuO	473 →	3.4	22.2
$ZnQ_2(ClO_4)_2\cdot 6H_2O$ ↓	- 50		
$ZnQ_2(ClO_4)_2\cdot 4H_2O$	90	95.4	94.3
$ZnQ_2(ClO_4)_2$	170	84.2	82.9
$ZnQ(ClO_4)_2$	280	63.0	62.3
(Explosion)	300		
$ZnQ_2(ClO_4)_2\cdot 6H_2O$ [b] ↓	- 42		
$ZnQ_2(ClO_4)_2\cdot 4H_2O$	64	95.0	94.3
$ZnQ_2(ClO_4)_2$	173	77.6	82.9
$ZnQ(ClO_4)_2$	248	64.3	62.3
$ZnCl_2$	348	25.6	21.6
(Sublimation)	348–630	–	–

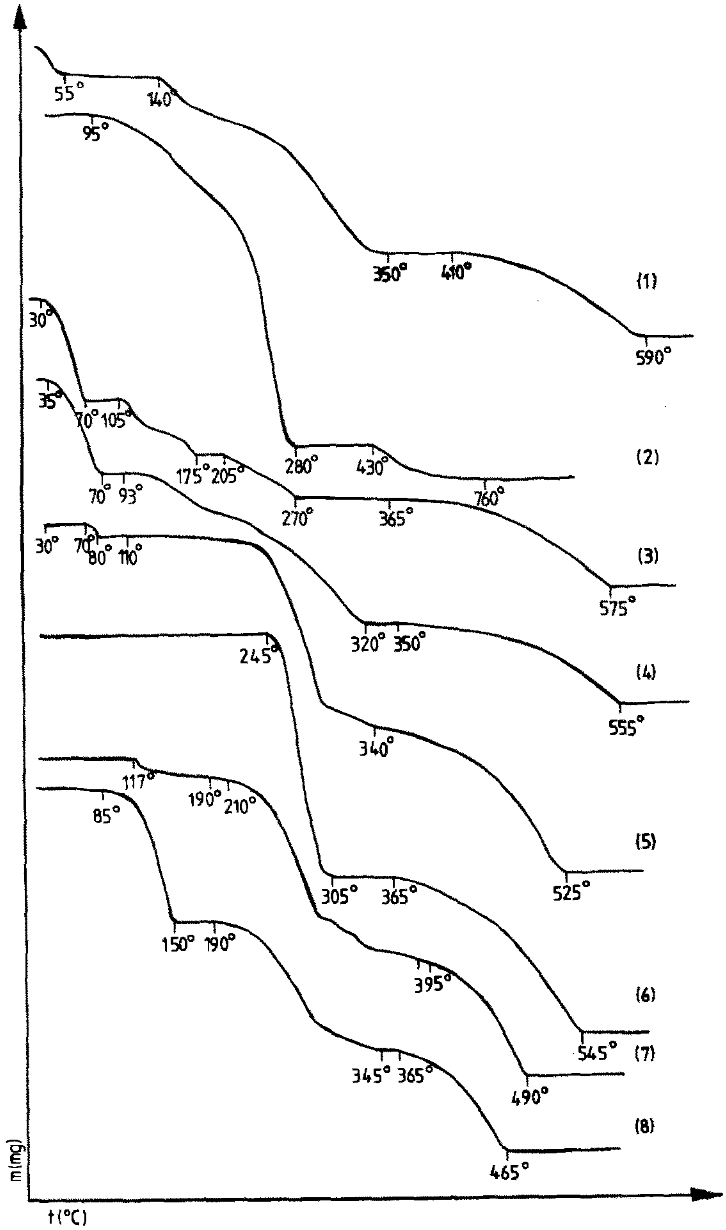

Fig. 2. TG curves of the metal chloride complexes of quinoxaline in dynamic nitrogen atmosphere: 1, $MnQCl_2 \cdot H_2O$; 2, FeQ_3Cl_2; 3, $CoQCl_2$; 4, $NiQCl_2 \cdot 3H_2O$; 5, $CuQCl_2 \cdot 1.5H_2O$; 6, $CuQCl_2$; 7, $ZnQCl_2 \cdot H_2O$; 8, $ZnQ_2Cl_2 \cdot H_2O$. Heating rate, 5 °C min^{-1}.

dynamic nitrogen atmosphere, are compared for the chloro complexes. Water and quinoxaline molecules escape successively from the complexes, the losses occurring in the temperature ranges 30–190 °C (H_2O) and 93–388 °C (H_2O + Q or Q).

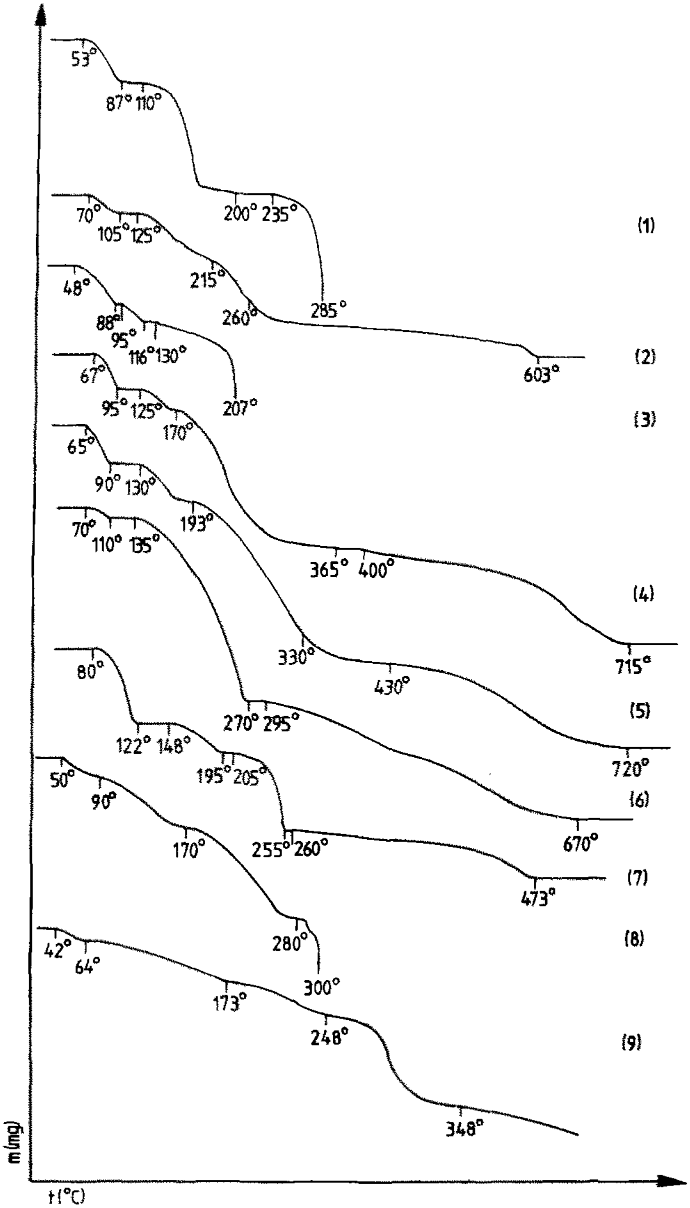

Fig. 3. TG curves of the metal perchlorate complexes of quinoxaline in dynamic nitrogen atmosphere: 1, $MnQ_2(ClO_4)_2 \cdot 5H_2O$; 2, $MnQ_2(ClO_4)_2 \cdot 5H_2O$; 3, $FeQ_3(ClO_4)_2 \cdot 5H_2O$; 4, $CoQ_2(ClO_4)_2 \cdot 6H_2O$; 5, $NiQ_2(ClO_4)_2 \cdot 6H_2O$; 6, $[CuQ_2(H_2O)_3](ClO_4)_2$; 7, $[Cu_2Q_3(ClO_4)](ClO_4)$; 8, $ZnQ_2(ClO_4)_2 \cdot 6H_2O$; 9, $ZnQ_2(ClO_4)_2 \cdot 6H_2O$. Heating rate 2.5 °C min^{-1} for curves 2, 7 and 9, and 5 °C min^{-1} for the others.

The metal chlorides remaining are oxidised at 270–760 °C to the corresponding metal monoxides. A large amount of the cupric and zinc chlorides sublime at this stage. The iron complex contains three quinoxaline molecules, the zinc complex two or one, and the other complexes one. The water content varies from zero to three water molecules.

The effect of the heating rate on the thermal stability and the reducibility in the case of the perchlorate complexes in a dynamic nitrogen atmosphere are also presented in Table 5 and Fig. 3 for the manganese, iron, copper and zinc complexes. When the decomposition proceeds without explosion, the quinoxaline molecules escape in 1–3 steps: in the temperature ranges 170–365 ° C (1), 125–348 ° C (2) and 80–255 ° C (3), respectively. The metal perchlorate remaining explodes at 130–300 ° C, depending on the case. Increasing the heating rate from 2.5 to 5 ° C min^{-1} accelerates the decomposition process; the quinoxaline molecules escape in 1–2 steps, and the temperature ranges are generally somewhat lowered. For the iron perchlorate complex, however, the TG curves are similar at the 2.5 and 5 ° C min^{-1} heating rates.

Allan et al. [8] recently prepared a set of quinoxaline complexes of manganese, cobalt, nickel and copper chlorides and bromides. They reported that compounds of MX_2Q stoichiometry decompose with loss of one molecule of quinoxaline to give the metal halide. This is in agreement with the conclusion derivable from the decomposition of the chloride complexes studied here.

The decomposition reactions of all the complexes follow a pattern in which the ligand molecules escape in steps according to the strength of their bonding to the central metal atom in agreement with the values of the anisotropic temperature factors [1,2,7,9].

CONCLUSION

In general, the mixed quinoxaline complexes of divalent transition metal ions show variable compositions and crystal structures. Some have a hydrogen-bond network stabilising the crystal structure, but in some only van der Waals forces are effective. The main structure types are monomeric and polymeric structures. The thermal, magnetic, reflectance and IR spectral properties are in accordance with the structure and nature of the complexes.

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