J Therm Anal Calorim (2010) 101:1019–1026
DOI 10.1007/s10973-009-0605-3

Manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with 4-oxo-4H-1-benzopyran-3-carboxaldehyde

Thermal, spectroscopic and magnetic characterization

Agnieszka Dziewulska-Kułaczkowska

Received: 30 July 2009 / Accepted: 17 November 2009 / Published online: 2 December 2009

Abstract The complexes Mn(II), Co(II), Ni(II) and Zn(II) with 4-oxo-4H-1-benzopyran-3-carboxaldehyde were synthesized and characterized by elemental analysis, infrared and UV spectroscopy, X-ray diffraction patterns, magnetic susceptibility, thermal gravimetric analysis, conductivity and also solubility measurements in water, methanol and DMF solution at 298 K. They are polycrystalline compounds with various formula and different ratio of metal ion:ligand. Their formula are following: $[MnL_2(H_2O)](NO_3)_2{\cdot}2H_2O$, $[CoL_2](NO_3)_2{\cdot}3H_2O$, $[NiL_2](NO_3)_2{\cdot}3H_2O$, $[CuL_2](NO_3)_2{\cdot}H_2O$ and $[ZnL_3](NO_3)_2$, where $L = C_{10}H_6O_3$. The coordination of metal ions is through oxygen atoms present in 4-position of γ-pyrone ring and of aldehyde group of ligand. Chelates of Mn(II), Co(II), Ni(II) and Cu(II) obey Curie–Weiss law and they are high-spin complexes with the weak ligand fields. The thermal stability of analyzed complexes was studied in air at 293–1,173 K. On the basis of the thermoanalytical curves, it appears that thermal stability of anhydrous analysed chelates changed following: Cu (423 K) $<$ Zn (438 K) $\sim$ Co (440 K) $<$ Ni (468 K). The gaseous products of thermal decomposition of those compounds in air atmosphere are following: CO_2, CO, NO_2, N_2O, hydrocarbons and in case of hydrates also water. The molar conductance data confirm that the all studied complexes are 1:2 electrolytes in DMF solution.

Keywords Complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) · Chromone · Thermal stability · FTIR spectra · Magnetic susceptibility

Introduction

4-Oxo-4H-1-benzopyran-3-carboxaldehyde (chromone 3-carboxaldehyde, $C_{10}H_6O_3$) is the derivative of the parent chromone compounds especially occurring in the plants, which are heterocyclic compounds containing oxygen [1–3]. Chromones are compounds, which contain γ-pyrone nucleus fused to benzene ring at the 5- and 6-position. Molecules, contain in their structure chromone ring, have attracted attention because of their interesting biological properties. Many of them show antifungal, antiallergic, antiviral, antihypertensive and anticancer activities [4–7]. Additionally, chromone derivatives are essential, for the synthesis of many important oxygen heterocyclics, pyrazoles and xantones [6].

The aim of this work was to synthesize metal chelates of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) ions with chromone 3-carboxaldehyde and investigated using various techniques. The present work concerned with thermal, spectral and magnetic properties of analyzed complexes.

Experimental

Physical measurements

Elemental analysis for C, H was performed using a Perkin-Elmer CHN 2400 analyser. The contents of M(II) ions were established by ASA method with the use of ASA 880 spectrophotometer (Varian). The FTIR and UV–VIS spectra of complexes were recorded over the range 4,000–400 and 200–400 nm, respectively, using M-80 spectrophotometer (Carl-Zeiss, Jena). The gaseous products of thermal decompositions of studied compounds were identified by the

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A. Dziewulska-Kułaczkowska (✉)
Department of General and Coordination Chemistry, Maria Curie-Sklodowska University, 20-031 Lublin, Poland
e-mail: akulaczkowska@wp.pl

recording of TG-FTIR spectra in the range 4,500–500 cm^{-1} in the TG-FTIR system using Mettler-Toledo Star System. The measurements were carried out in argon atmosphere at a heating rate of 20°min^{-1}. The samples of masses ranging from 10.72 to 16.91 mg were heated to 1,273 K. The argon flowed at a rate of 50 mL min^{-1}. The X-ray diffraction patterns were taken on a HZG-4 (Carl-Zeiss, Jena) diffractometer using Ni filtered CuK_{α} radiation. The measurements were made within the range $2\theta = 4$–80° by means of the Bragg–Brentano method. Thermal stability and decomposition of the complex was determined by Setaram Setsys 16/18 derivatograph, recording TG, DTG and DSC curves. The measurement was made at heating rate of 10 K/min with full scale. The samples (7.16–7.78 mg) were heated in ceramic crucible in air to 1,173 K. Magnetic susceptibilities of polycrystalline samples of 4-oxo-4H-1-benzopyran-3-carboxaldehyde of Mn(II), Co(II), Ni(II) and Cu(II) were measured by the Gouy method using a sensitive Cahn RM-2 balance. Measurements were carried out at a magnetic field strength of 9.9 kOe. $\mathrm{Hg[Co(SCN)_4]}$ with the magnetic susceptibility of 1.644×10^{-5} $\mathrm{cm^3\ g^{-1}}$ was employed as calibrant. The correction of diamagnetism of the constituent atoms was calculated by using Pascal's constants [8]. The magnetism of the samples was found to be field independent. The magnetic moments were calculated according to following equation:

$$\mu_{\mathrm{eff}} = 2.83(\chi_{\mathrm{M}} \cdot T)^{1/2}$$

Molar conductance was measured with a PHYWE 13701.93 conductometer (10^{-3}M DMF solution was used). The solubilities of analyzed complexes in methanol, DMF and water were measured at 293 K. Saturated solution of the obtained compounds were prepared under isothermal conditions. The contents of M(II) were determined by using ASA 880 spectrophotometer (Varian).

Materials

The 4-oxo-4H-1-benzopyran-3-carboxaldehyde used for the preparation of complexes was from Aldrich Chemical Company. The metal salts used were in the hydrated form, i.e. $\mathrm{Mn(NO_3)_2{\cdot}4H_2O}$, $\mathrm{Co(NO_3)_2{\cdot}6H_2O}$, $\mathrm{Ni(NO_3)_2{\cdot}6H_2O}$, $\mathrm{Cu(NO_3)_2{\cdot}3H_2O}$, $\mathrm{Zn(NO_3)_2{\cdot}6H_2O}$ and were purchased from Polish Chemical Reagents in Gliwice (Poland). All chemical used were reagent grade from and were used without further purification.

Preparation of complexes

An ethanolic solution (100 mL) of 4-oxo-4H-1-benzopyran-3-carboxaldehyde (5.7 mmol, 1 g) and ethanolic solution (30 mL) containing the nitrate(V) of the Mn(II), Co(II), Ni(II) and Cu(II) in mole ratio of 1:2 (and 1:3 for zinc(II) complex) were mixed with constant stirring for 6 h (T = 343 K, pH = 5.3). The solution was cooled overnight at room temperature. The precipitated complexes were filtered off, washed with cold ethanol and dried at 303 K to constant mass.

Results and discussion

The complexes of 4-oxo-4H-1-benzopyran-3-carboxaldehyde with Mn(II), Co(II), Ni(II) Cu(II) and Zn(II) were obtained as polycrystalline products with a metal ion to ligand ratio of 1:2 for Mn(II), Co(II), Ni(II) and Cu(II) and 1:3 for Zn(II). The colours of analyzed complexes are typical for M(II) ions of these elements (Table 1) and their formula are following: $\mathrm{[MnL_2(H_2O)](NO_3)_2{\cdot}2H_2O}$, $\mathrm{[CoL_2](NO_3)_2{\cdot}3H_2O}$, $\mathrm{[NiL_2](NO_3)_2{\cdot}3H_2O}$, $\mathrm{[CuL_2](NO_3)_2{\cdot}H_2O}$ and $\mathrm{[ZnL_3](NO_3)_2}$, where L = $\mathrm{C_{10}H_6O_3}$. All studied complexes were characterized by elemental analysis (Table 1).

Infrared spectroscopy

The FTIR spectra of 4-oxo-4H-1-benzopyran-3-carboxaldehyde and its complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were recorded (Table 2). In the spectra of Mn(II), Co(II), Ni(II) and Cu(II) complexes, the broad bands with maxima at 3,435–3,386 cm^{-1} are characteristic for υ(OH) vibration [9–18]. The strong bands υ(C=C) ring vibrations in the spectra of free ligand and all investigated

Table 1 The colours, formula weights, melting points and elemental analysis data of analyzed complexes

Complex (L = $\mathrm{C_{10}H_6O_3}$)	Colour	Fw/g mol^{-1}	Mp/K	C/%		H/%		N/%		M/%	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\mathrm{[MnL_2(H_2O)](NO_3)_2{\cdot}2H_2O}$	Light pink	563.2	445	41.31	41.92	3.09	2.94	4.82	4.82	9.45	9.72
$\mathrm{[CoL_2](NO_3)_2{\cdot}3H_2O}$	Pink	585.2	473	41.03	40.69	3.07	2.48	4.78	5.41	10.07	10.31
$\mathrm{[NiL_2](NO_3)_2{\cdot}3H_2O}$	Green	584.9	470	41.04	41.43	3.08	2.79	4.78	5.17	10.04	10.42
$\mathrm{[CuL_2](NO_3)_2{\cdot}H_2O}$	Light green	553.8	423	43.36	43.29	2.53	2.41	5.06	5.14	11.47	11.71
$\mathrm{[ZnL_3](NO_3)_2}$	Creme	718.8	449	50.60	49.97	2.53	2.50	3.93	4.03	9.19	9.27

chelates appear at 1,579–1,554 cm^{-1} [9, 12, 14, 16, 19]. In the spectra of 4-oxo-4H-1-benzopyran-3-carboxaldehyde and its all analysed complexes were registered very strong band υ(C=O) of aldehyde group, which appear in the range of 1,700–1,664 cm^{-1} (Table 2). The strong band at 1,700 cm^{-1} in the spectra of the free ligand assigned to υ(C=O) of aldehyde group is changed by 16–36 cm^{-1} in the spectra of complexes, indicating coordination 4-oxo-4H-1-benzopyran-3-carboxaldehyde through carbonyl oxygen atom [9, 12, 14, 20]. The spectrum of free ligand show a very strong absorption band at 1,649 cm^{-1}, which is characteristic for the υ(C=O) of γ-pyrone. In the spectra of analyzed complexes, this absorption band has been shifted to the 1,619–1,617 cm^{-1} region indicating the coordination

Table 2 Frequencies of the maxima of the absorption bands for ligand and its complexes

Frequency/cm^{-1}						Assignment
L	Mn*	Co*	Ni*	Cu*	Zn*	
–	3423 b	3386 b,s	3386 b,s	3435 b	–	υ(OH)
3089 vw		3108 vw	3111 vw	3100 vw	3092 vw	υ(C–H)
3059 m	3046 w	3068 w	3068 w	3065 w	3053 w	υ(C–H)
2869 m	–	–	–	–	–	υ(C–H(O))
1963 m	–	1954 vw	1957 vw	1957 vw	1954 vw	Overtone γ(C–H)
1842 m	–	1834 vw	1833 vw	1833 vw	–	Overtone γ(C–H)
1700 vs	1684 vs	1674 vs	1672 vs	1664 vs	1674 vs	υ(C=O)
1649 vs	1617 vs	1619 vs	1619 vs	1618 vs	1617 vs	υ(C=O)
–	1579 m	1575s	1579 s	1566s	–	υ(C=C)
1560 s	1558 m	1556 s	1557 s	1554 s	1557 s	υ(C=C)
1464 s	1457 vs	1461 vs	1461 vs	1458s	1459 vs	υ(C–O)
1416 s	1415 s	1418 s	1419 s	1413 vs	1419 s	υ(O–C), δ(C–H)$_{sym}$
–	1390 w	1391 vs	1385 s	–	–	υ(N–O)
1360 s	1352 s	1353 vs	1353 vs	–	1351 m	υ(C–C(HO))
1336 m	–	–	–	–	–	υ(C–C), δ(C–H)
1309 m	1313 vs	1300 cs	1300 vs	1315 vs	1308 vs	υ(C–C), δ(C–H)
1269 m	–	1278 m	1279 m	1279 s	–	υ(C–O–C)$_{asym}$
1234 m	1231 m	1236 s	1237 s	1239 s	1235 s	υ(C–O–C)$_{asym}$, υ(N–O)
1192 s	–	1185 w	1180 w	–	–	δ(C–H)$_{sym}$
1144 s	1144 m	1143 m	1144 m	1144 m	1145 m	δ(C–O–C)
1101 m	1105 m	1105 m	1106 m	1106 m	1104 m	δ(OCC)
1027 m	1039 s	1030 s	1035 s	1023 m	1035 s	υ(C–O-C)$_{sym}$
956 s	970 m	978 m	981 m	986 m	975 m	δ(C–C(HO))
937 m	946 m	947 m	948 m	947 m	948 m	δ(C–H)
879 vw	865 s	868s	869s	870s	867s	δ(CCC), γ(C–H)
849 s	–	828 m	834 vw	–	–	δ(CCC), γ(C–H)
–	817 m	814 m	813 m	818 m	815 w	δ(N–O)
–	–	778 m	778s	778s	–	δ(N–O)
764 vs	762 s	758 s	759 m	759 s	763 s	γ(C–H)
688 s	691 m	692 s	692 m	692 s	690 m	γ(C–H)
644 s	645 vw	646 vw	647 vw	619 vw	646 w	γ(C–H)
–	558 m	564 m	570 s	578 s	541 s	υ(M–O)
544 m	532 s	548 m	554 m	–	–	υ((H)C=O)
–	508 m	511 m	512 m	514 m	511 m	υ(M–O)
459 m	–	–	–	–	–	γ(C=O)
416 m	419 w	422 w	425 w	425 w	417 w	γ(C=O)

L = L = $C_{10}H_6O_3$, Mn* = $[MnL_2(H_2O](NO_3)_2\cdot 2H_2O$, Co* = $[CoL_2](NO_3)_2\cdot 3H_2O$, Ni* = $[NiL_2](NO_3)_2\cdot 3H_2O$, Cu* = $[CuL_2](NO_3)_2\cdot H_2O$ and Zn* = $[ZnL_3](NO_3)_2$, *vs* very strong, *s* strong, *m* medium, *w* weak, *vw* very weak, *b* broad, υ stretching, δ deformation in plane, γ deformation out of plane, *as* asymmetric, *sym* symmetric of the 4-oxo-4H-1-benzopyran-3-carboxaldehyde through the oxygen atom present in 4-position of pyrone ring [6, 9, 12]. In the spectra of free ligand and its chelates, the frequencies bands $\upsilon(C–O–C)_{asym}$, $\upsilon(C–O–C)_{sym}$ and $\delta(C–O–C)$ are similar (Table 2), it suggests that γ-pyrone ring oxygen does not participate in coordination metal ions [9, 14, 17, 21]. The bands at 1,391–1,385 and 817–778 cm^{-1} registered in the spectra of complexes are absence in the spectrum of free ligand. These bands are assigned as $\upsilon(N–O)$ ionic nitrate [9, 12, 14]. In the spectra of complexes, the bands of metal ion–oxygen, $\upsilon(M–O)$ observed in the region 578–541 and 514–508 cm^{-1} and they are increase following: Zn(II) < Mn(II) < Co(II) < Ni(II) < Cu(II) [9, 12, 14, 22].

From comparison, the spectra of studied chelates result that spectra of Mn(II), Co(II), Ni(II) and Cu(II) are similar, but spectrum of Zn(II) is different. It is probably connected with ratio metal ion:ligand (1:3) in comparison to another analysed chelates (1:2). Suggested coordination of central ion for Co(II), Ni(II) Cu(II) and Zn(II) complexes was shown in Fig. 1.

FTIR spectra of gaseous products

The decomposition process with the gas product analysis was recorded for complexes Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 4-oxo-4H-1-benzopyran-3-carboxaldehyde. In Fig. 2, as example of the FTIR spectrum of gaseous products of thermal decomposition, Co(II) complex spectrum is presented. FTIR spectra of the gas phase products indicate that the decomposition of complexes is connected with the release of molecules of CO_2, CO, H_2O (H_2O in the case of hydrates), NO_2, N_2O and hydrocarbons. The characteristic valence and deformation vibration bands of water molecules in FTIR spectra appear in the wavenumber ranges of 3,950–3,500 and 1,570–1,320 cm^{-1}, respectively. The bands characteristic for CO_2 molecule vibrations occur in the following ranges: 2,450–2,250 and 700–600 cm^{-1}. The bands for hydrocarbons vibrations are observed at: 3,100–2,750 and 1,900–1,100 cm^{-1}. The double peak of band characteristic for CO molecule vibrations appears in the range of 2,250–2,000 cm^{-1}. The bands for NO_2 and N_2O

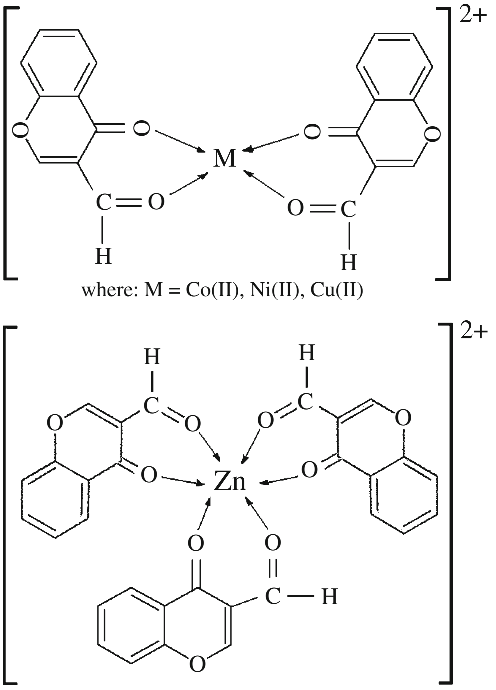

Fig. 1 Suggested coordination of central ions

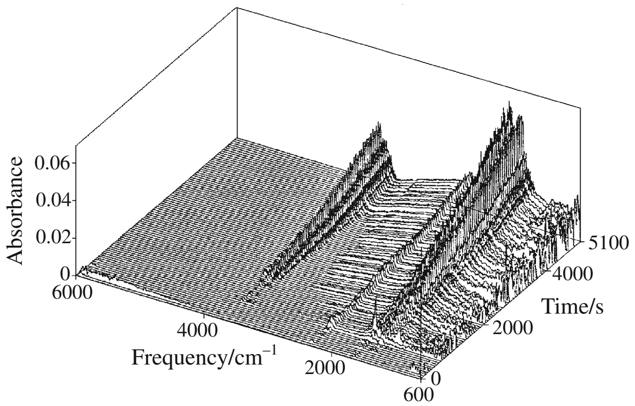

Fig. 2 The FTIR spectra of the gaseous products evolved during the decomposition of Co(II) complex

Table 3 The data of solubilities in methanol, DMF and water (at 293 K), conductivity and frequency of electronic bands of analysed complexes

Complex (L = $C_{10}H_6O_3$)	Solubility/mol dm^{-3}			$\Lambda/cm^2\ \Omega^{-1}\ mol^{-1}$	Wavenumber/nm
	CH_3OH	DMF	H_2O		
$[MnL_2(H_2O)](NO_3)_2\cdot 2H_2O$	3.4×10^{-2}	1.4×10^{-2}	1.7×10^{-3}	158.8	245, 296, 348
$[CoL_2](NO_3)_2\cdot 3H_2O$	3.7×10^{-2}	2.5×10^{-2}	3.6×10^{-3}	171.0	235, 266, 320
$[NiL_2](NO_3)_2\cdot 3H_2O$	3.8×10^{-2}	2.8×10^{-2}	4.4×10^{-3}	157.2	242, 265, 357
$[CuL_2](NO_3)_2\cdot H_2O$	2.1×10^{-2}	2.7×10^{-2}	3.8×10^{-3}	146.6	229, 262, 368
$[ZnL_3](NO_3)_2$	2.1×10^{-2}	1.8×10^{-2}	1.4×10^{-3}	146.1	238, 262, 359

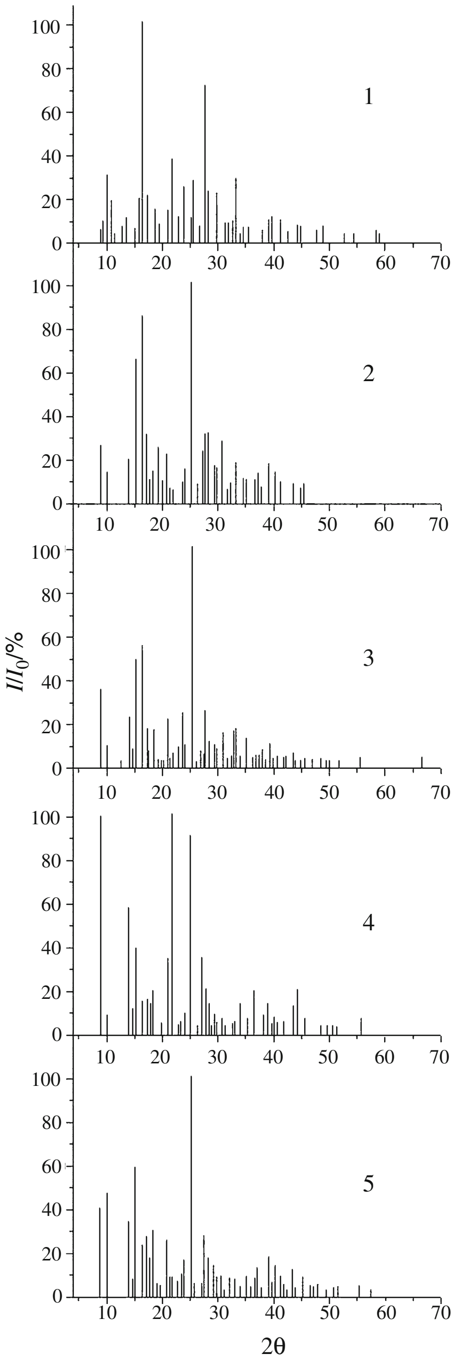

Fig. 3 Dependence of I/I_0 versus 2θ for Mn(II)(1), Co(II)(2), Ni(II)(3), Cu(II)(4) and Zn(II)(5) complexes

molecules are shown in the range of 1,900–1,100 cm^{-1} [12, 23, 24].

Electronic absorption spectroscopy

The electronic spectra in the range of 200–400 nm of studied complexes and the free ligand were recorded. The spectrum of the 4-oxo-4H-1-benzopyran-3-carboxaldehyde exhibits three main peaks at 233, 257 and 321 nm. The absorption values of studied chelates were presented in Table 3, and they are shifted in comparison with bands in spectra of ligand. These changes indicate that complexes are formed. UV spectra clearly indicated that the absorption bands characteristic for Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} are bathochromically shifted in methanol solutions of 4-oxo-4H-1-benzopyran-3-carboxaldehyde.

X-ray diffraction patterns

The X-ray diffraction patterns of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with 4-oxo-4H-1-benzopyran-3-carboxaldehyde were recorded (Fig. 3). The analysis of the diffractograms suggests that the chelates are polycrystalline compounds with different structures [25]. The structures of the complexes have not been determined because single crystals have not been obtained.

Thermal analysis

The thermal stability of complexes of 4-oxo-4H-1-benzopyran-3-carboxaldehyde with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was studied in air at 293–1,173 K. The thermal decomposition data are collected in Table 4. Thermoanalytical curves of TG, DTG and DSC for $[Mn(C_{10}H_6O_3)_2(H_2O)](NO_3)_2\cdot 2H_2O$, $[Co(C_{10}H_6O_3)_2](NO_3)_2\cdot 3H_2O$ and $[Zn(C_{10}H_6O_3)_3](NO_3)_2$ are presented (Fig. 4) as examples.

The manganese(II) complex is stable up to 365 K and during further heating dehydrated in two steps. In the first stage, this compound loses two water molecules and next above 423 K it loses one water molecules. Considering the temperature at which the dehydration process of the complex takes place and the way by which it proceeds, it is possible to assume that there are two water molecules that may be outer and one water inner coordination sphere of complex [26, 27]. Anhydrous Mn(II) complex heated decomposes to unstable intermediate compounds and to Mn_2O_3, which is final product of thermal decomposition this compound in air. The complex 4-oxo-4H-1-benzopyran-3-carboxaldehyde with Co(II) is stable up to 323 K. Above this temperature, cobalt compound is dehydrated in two steps losing 1.5 and 1.5 water molecules, respectively. Anhydrous $[Co(C_{10}H_6O_3)_2](NO_3)_2$ at 440 K decomposes to CoO with formation intermediate, unstable products. The trihydrate of Ni(II) and monohydrate of Cu(II) complexes dehydrated in one step at 328 K and 393 K, respectively, and next gradually decomposed to, respectively, oxides (NiO, CuO) with formation intermediate, unstable compounds. The anhydrous Zn(II) complex is stable up to 438 K. Above this temperature, it decomposes to unstable compounds and next to ZnO, which is final product of its decomposition, in air atmosphere.

Table 4 Data of thermal decomposition processes for analyzed complexes in air atmosphere

Substance L = $C_{10}H_6O_3$	ΔT/K	Mass loss/%		n	Product of decomposition in solid state
		Calcd.	Found		
$[MnL_2(H_2O)](NO_3)_2{\cdot}2H_2O$	365–388	6.19	6.1	2	$[MnL_2(H_2O)](NO_3)_2$
$[MnL_2(H_2O)](NO_3)_2$	423–446		38	1	Intermediate products
Intermediate products	453–693	86.4	86.5	–	Mn_2O_3
$[CoL_2](NO_3)_2{\cdot}3H_2O$	323–390	4.61	4.6	1.5	$[CoL_2](NO_3)_2{\cdot}1.5H_2O$
$[CoL_2](NO_3)_2{\cdot}1.5H_2O$	431–438	9.23	8.9	1.5	$[CoL_2](NO_3)_2$
$[CoL_2](NO_3)_2$	440–508		38	–	Intermediate products
Intermediate products	603–633	87.19	m	–	CoO
$[NiL_2](NO_3)_2{\cdot}3H_2O$	328–453	9.23	9.4	3	$[NiL_2](NO_3)_2$
$[NiL_2](NO_3)_2$	468–548		37.6	–	Intermediate products
Intermediate products	563–638	87.23	m	–	NiO
$[CuL_2](NO_3)_2{\cdot}H_2O$	393–413	3.25	3.3	1	$[CuL_2](NO_3)_2$
$[CuL_2](NO_3)_2$	423–433		22.2	–	Intermediate products
Intermediate products	443–713	85.16	85.3	–	CuO
$[ZnL_3](NO_3)_2$	438–518		39	–	Intermediate products
Intermediate products	553–778	88.56	88.7	–	ZnO

ΔT = temperature ranges of decomposition processes, n = number of water molecules lost in the thermal decomposition

The final products of decomposition of complexes Mn(II), Co(II), Ni(II) Cu(II) and Zn(II) were identified by X-ray diffraction on the powder.

From the comparison of the TG curves of analyzed complexes results that studied compounds have various stability in air and different ways of decomposition. The scheme shows decomposition of investigated chelates:

$$[MnL_2(H_2O)](NO_3)_2{\cdot}2H_2O \Rightarrow [MnL_2(H_2O)](NO_3)_2 \Rightarrow \text{unstable products} \Rightarrow Mn_2O_3$$

$$[CoL_2](NO_3)_2{\cdot}3H_2O \Rightarrow [CoL_2](NO_3)_2 1.5H_2O \Rightarrow [CoL_2]\ (NO_3)_2 \Rightarrow \text{unstable products} \Rightarrow CoO$$

$$[NiL_2](NO_3)_2{\cdot}3H_2O \Rightarrow [NiL_2](NO_3)_2 \Rightarrow \text{unstable products} \Rightarrow NiO$$

$$[CuL_2](NO_3)_2{\cdot}H_2O \Rightarrow [CuL_2](NO_3)_2 \Rightarrow \text{unstable products} \Rightarrow CuO$$

$$[ZnL_3](NO_3)_2 \Rightarrow \text{unstable products} \Rightarrow ZnO$$

On the basis of the thermoanalytical curves, it appears that thermal stability of anhydrous analysed chelates changed following: Cu (423 K) < Zn (438 K) ~ Co (440 K) < Ni (468 K). The various ways of thermal decomposition for analyzed complexes may be result from the influence central ions on properties of complexes.

Magnetic measurements

The magnetic susceptibility of the Mn(II), Co(II), Ni(II) and Cu(II) with 4-oxo-4H-1-benzopyran-3-carboxaldehyde was measured in the temperature range of 76–303 K. The complex of zinc(II) is, as expected, diamagnetic. The paramagnetic dependences of magnetic susceptibility value as a function of temperatures are given in Fig. 5.

The values of magnetic susceptibilities of Mn(II), Co(II), Ni(II) and Cu(II) complexes obey the Curie–Weiss law, as they decrease gradually with rising temperature. They give information about the magnetic interaction between paramagnetic centres. As a rule, if the χ_M values increase with rising temperatures this indicates the anti-ferromagnetic interaction but when the χ_M values decrease with an increase in temperature the magnetic interaction is ferromagnetic. The χ_M values for analysed complexes show a gradual decrease with rising temperature. It indicates the tendency to a ferromagnetic interaction between metal ions [8, 28]. The magnetic moment values experimentally determined for Mn(II), Ni(II) and Cu(II) complexes were found to be in the ranges: 5.96–6.24, 3.12–3.21, 1.66–1.78 BM, respectively. The experimental data reveal that the magnetic moments for these compounds are connected with a spin-only moments. Their theoretical values at room temperatures are equal to 6.24 BM for Mn(II), 3.18 BM for Ni(II) and 1.67 BM for Cu(II). In the case of Co(II) complex the μ_{eff} are equal to 5.16–5.54 BM. The magnetic moment measured for Co(II) complex at room temperature is 5.54 BM. This value differs from μ_{os} value 3.88 BM. This relatively a large difference results from a spin–orbital coupling [8, 24, 28–30].

The experimental data suggest that Mn(II), Co(II), Ni(II) and Cu(II) complexes are the high-spin complexes

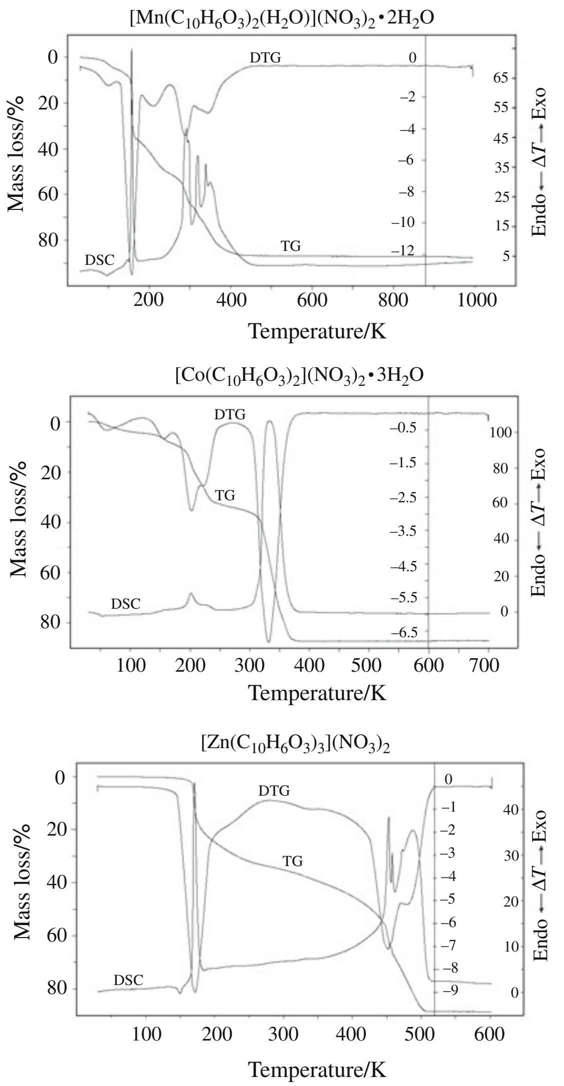

Fig. 4 TG, DTG and DSC curves for Mn(II), Co(II) and Zn(II) complexes in air

with the weak ligand fields. They probably crystallized as monomers.

Molar conductivity and solubility of complexes

The molar conductance of complexes 4-oxo-4H-1-benzopyran-3-carboxaldehyde with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) measured in 0.001 mol dm^{-3} DMF solution (Table 3). Their values are in the range of 146.1–171.0 cm^2 Ω^{-1} mol^{-1} and they fall in the expected range for 1:2 electrolytes [31–33]. It indicates that in the all analysed chelates the two nitrate(V) anions lie outside of coordination sphere.

The solubility of investigated complexes was measured in H_2O, CH_3OH and DMF solutions (Table 3) at 298 K. These values are in the order of 10^{-2} mol dm^{-3} (for CH_3OH and DMF) and 10^{-3} mol dm^{-3} (for H_2O). From the solubility data, it appears that 4-oxo-4H-1-benzopyran-3-carboxaldehyde may not be used for the separation of Mn(II)–Co(II)–Ni(II)–Cu(II)–Zn(II) by ion-exchange chromatography or by extraction methods because of the low difference in their solubility values.

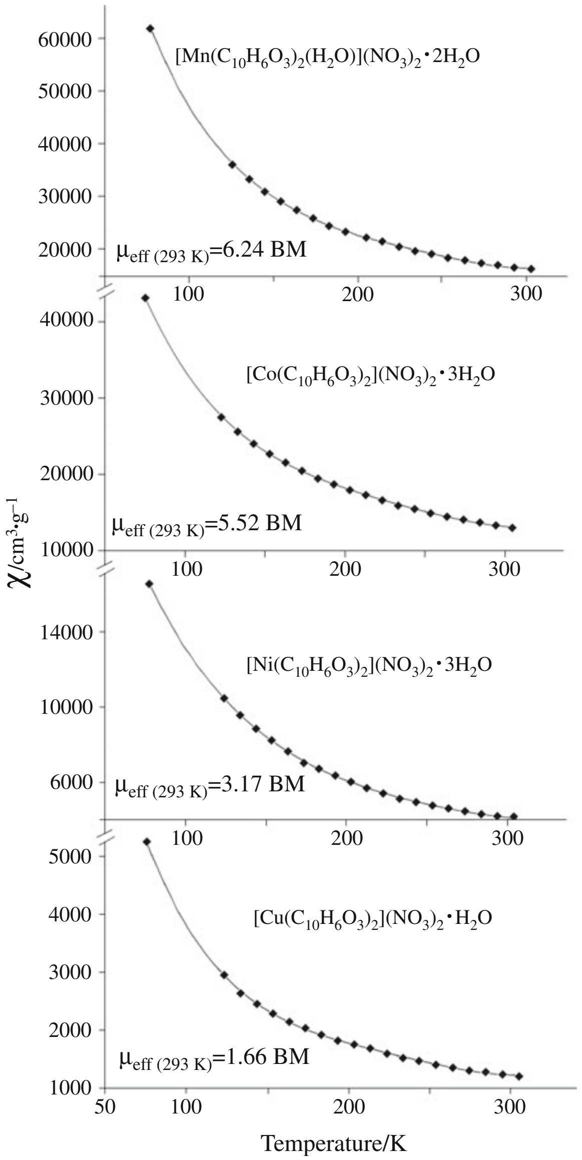

Fig. 5 Relationship between the values of magnetic susceptibilities of Mn(II), Co(II), Ni(II) and Cu(II) complexes versus temperature

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