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Thermal and spectral studies of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with 3-(anilinomethylene)-2-methoxychroman-4-one

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Abstract The complexes Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 3-(anilinomethylene)-2-methoxychroman-4-one were synthesized and characterized by elemental analysis, conductivity, infrared and UV–Vis spectroscopy, ^{1}H NMR, X-ray diffraction patterns, magnetic susceptibility and thermal analysis (TG/DTG/DSC). The X-ray analysis shows that the studied compounds crystallize in the triclinic crystal system and they are no isostructural complexes. The unit cell parameters for these chelates were presented. The molecules of solvent are in the outside coordination sphere of the complexes. The chelates have different thermal stability and they decompose in air atmosphere in three steps. The coordination of metal ions is through nitrogen atom from ligand and oxygen atom present in 4-position of γ-pyrone. The studied chelates have electrolyte (1:1) and non-electrolyte nature. They are high-spin complexes with octahedral coordination and the weak ligand fields.

Keywords Complexes · Chromanone · TG-DSC · IR · X-ray powder diffraction

Introduction

The synthesis of complexes of metal ions with heterocycles ligands is currently subject of considerable interest, mainly as an approach to materials with novel physicochemical properties and biological activity. Compounds containing the chromone skeleton are an important class of compounds which occurs naturally in plants. They have anti-inflammatory, antibacterial, antitumor, antioxidant, antiHIV, anticancer, antiviral and antiallergenic properties [1–7]. In addition, 3-formylochromone and its derivatives inhibit a human protein phosphatase PTP1B [8]. 3-Formylochromones (4-oxo-4H-1-benzopyran-3-carboxaldehydes) are relevant for two reasons. They show a significant biological activity and they can be used as substrates for various reactions [9]. 4-Oxo-4H-1-benzopyran-3-carboxaldehyde contains three electron deficient sites (C-2, C-4 and –CHO) suitable for nucleophilic attack [10]. The products of the condensation of 3-formylochromone with primary amines depend on the conditions of the reactions [4, 10–15]. It was proved that the reaction of chromones with primary amines proceeded via nucleophilic 1,4-addition with the opening of the pyrone ring [14]. The condensation 3-formylchromone with aniline allows to obtain yellow crystals of 3-(anilinomethylene)-2-methoxychroman-4-one. The synthesis, structure and some of physicochemical properties of 3-(anilinomethylene)-2-methoxychroman-4-one were presented in previous article [16].

The aim of this study was to obtain the complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 3-(anilinomethylene)-2-methoxychroman-4-one and to determine their properties. The thermal behaviour of these compounds was investigated by using thermogravimetric (TG) and differential scanning calorimetry (DSC) methods. Thermal characterizations let us evaluate the assumed position of crystallization water molecules in the outer or inner spheres of coordination, determine the endo- or exo-effects connected with such processes as: dehydration,

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melting, crystallization, oxidation, reduction and estimate the strength of bonding between atoms or groups of atoms and ions. Their spectral (IR, UV–Vis), structural (^{1}H NMR, X-ray diffraction patterns, conductivity) and magnetic properties were also studied.

Experimental

Physical measurements

Elemental analysis for C, H was performed using a Perkin-Elmer CHN 2400 analyser. The contents of M(II) were established by using ED XRF spectrophotometer (Canberra-Packard). The melting point of analysed complexes was measured using BÜCHI Melting Point B-540. The FTIR and UV–Vis spectra of complexes were recorded over the range 4000–400 cm^{-1} and 200–800 nm, respectively, using M-80 spectrophotometer (Carl Zeiss, Jena). The X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss, Jena) diffractometer using Ni filtered CuK$_\alpha$ radiation. The measurements were made within the range $2\theta = 4$–80° with a step equal to 0.5°. The X-rayan programme was used for determining position and peak intensities. The TREOR programme was used for calculating the unit cell parameters from the collection of data, which had been obtained from the X-rayan programme [17]. Thermal stability and decomposition of the complex were determined by Setaram Setsys 16/18 derivatograph, recording TG, DTG and DSC curves. The measurement was made at heating rate of 10 K min^{-1} with full scale. The samples (6.54–7.66 mg) were heated in ceramic crucible in air to 1273 K. The magnetic moment was determined at room temperature using Gouy method. Magnetic susceptibility measurements were made on magnetic balance (Sherwood Scientific Ltd., Cambridge MSB-MK1) using Hg[Co(SCN)$_4$] as a calibrant. The correction for diamagnetism [18] of the constituent atoms was calculated from the equation:

$$\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{M}} \cdot \mathrm{T})^{1/2} \qquad (1)$$

The ^{1}H NMR spectra of the ligand and its complexes were recorded with a Brucker Avance 300 instrument using d$_6$-DMSO solution and TMS as internal standard. The measurements were made at 25 °C. Molar conductance was measured with a PHYWE 13701.93 conductometer (10^{-3} mol dm^{-3} CH_3OH solution was used).

Materials

The 4-oxo-4H-1-benzopyran-3-carboxaldehyde and aniline used for the preparation of 3-(anilinomethylene)-2-methoxychroman-4-one were produced by Aldrich Chemical Company. The chlorides of respective metal ions were used as the hydrated and anhydrous salts (i.e. $MnCl_2{\cdot}4H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$ and $ZnCl_2$) and produced by Polish Chemical Reagents in Gliwice (Poland).

Synthesis

The preparation of 3-(anilinomethylene)-2-methoxychroman-4-one was presented in previous article [15].

The hot methanolic solution (80 mL) of 3-(phenyloaminomethylene)-2-methoxy-chroman-4-one (2 mmol, 0.563 g) was added dropwise to a hot stirred water–methanol (1:1, 20 mL) solution of corresponding metal(II) salts (1 mmol). The mixtures were constant stirring for 3 h (T = 333 K, pH = 5.3). The solution was cooled overnight at room temperature (slow evaporation). The precipitated complexes were filtered off, washed several times with cold methanol and dried at 303 K to constant mass.

Results and discussion

The properties of complexes Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 3-(anilinomethylene)-2-methoxychroman-

Table 1 The colours, molar mass, melting points and elemental analysis data of analysed complexes

Complex	Colour	Fw/g mol^{-1}	M.p./K	C/%		H/%		N/%		M/%	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Mn	Yellow	784.5	407	56.59	56.97	5.35	5.31	3.67	3.74	7.00	7.27
Co	Dark green	764.5	469	53.37	53.74	4.97	4.87	3.66	3.80	7.70	7.95
Ni	Light green	764.3	550	53.38	53.36	4.97	4.79	3.66	3.75	7.68	7.84
Cu	Grey	769.1	463	53.05	53.02	4.94	4.66	3.64	3.34	8.26	8.37
Zn	Yellow	717.0	530	56.90	57.10	4.46	4.49	3.90	3.74	9.12	9.36

Mn $[MnL_2(CH_3OH)Cl]Cl{\cdot}2CH_3OH$, *Co* $[CoL_2(H_2O)Cl]Cl{\cdot}3H_2O$, *Ni* $[NiL_2(H_2O)Cl]Cl{\cdot}3H_2O$, *Cu* $[CuL_2Cl_2]{\cdot}4H_2O$, *Zn* $[ZnL_2Cl_2]{\cdot}H_2O$ and *L* $C_{17}H_{15}NO_3$

4-one were studied. The compounds were characterized by elemental analysis (Table 1), FTIR, UV–Vis and ^{1}H NMR spectroscopy, X-ray powder diffraction, thermal methods, magnetic and conductivity measurements.

Infrared spectroscopy

The FTIR spectra of 3-(anilinomethylene)-2-methoxychroman-4-one and its complexes were registered (Table 2)

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

Frequency/cm^{-1}						Assignment
L	Mn	Co	Ni	Cu	Zn	
–	3420br	3400br	3392br	3428br	3448br	ν(OH)
3128vw	3132w	3276w	3144w	3248w	3264w	ν(NH)
3068w	3060w	3052w	3056w	3041w	3048w	ν(CH)
2936m	2972vw	2968vw	2944vw	2920vw	2964vw	$\nu_{as}(CH_3)$
2900m	2912vw	2924vw	2904vw	2904vw	2924vw	
2824m	2876vw	2876vw	2824vw	2852vw	2864vw	$\nu_s(CH_3)$
1652vs	1644vs	1648vs	1648vs	1648vs	1640vs	ν(C=O)chromanone carbonyl
1608vs	1608vs	1608s	1608vs	1608vs	1608s	ν(C=C)
1596vs	1588s	1584s	1596vs	1596vs	1596s	ν(C=C)
1584m	1588m	1564m	1584	1584m	1588m	ν(C=C), γ_w(N–H)
1568m	1556m	1556m	1560m	1556m	1560m	
1480s	1472vs	1472vs	1480s	1480s	1480s	ν(C=C), $\delta_{as}(CH_3)$
1468vs	1460m	1460s	1468vs	1468vs	1468s	
1440s	1440s	1440m	1440s	1440m	1432m	ν(C–O)
1384s	1380m	1384s	1384m	1384m	1404m	ν(C–CHO), ν(C–N)
1356m	1360m	1356m	1356m	1356m	1356m	ν(C–CHO), $\delta_s(CH_3)$
1284vs	1280s	1277s	1279s	1280s	1271s	ν(C–C), ν(C–O–C), ν(C–N)
1236m	1232w	1232w	1236w	1236w	1236m	ν(C–C)
1204s	1212m	1212m	1204m	1208m	1208w	δ_{as}(CH), ν(C–N)
1192w	1192w	1192w	1192vw	1188vw	1172vw	ν(CH), δ(COC)
1148m	1148m	1148m	1148m	1148m	1148w	δ(COC)
1104m	1108m	1108m	1104m	1104m	1104m	δ(OCC)
1068vs	1068s	1068s	1068vs	1068vs	1064m	γ_{wach}(CH), ν_s(C–O–C),
1016s	1012s	1012s	1016s	1016s	1012m	ν(C–C)
972m	952s	952s	972m	972m	956m	δ (C–CHO),
932vs	908m	908w	932s	932s	908w	δ(CCC)
868m	856vw	844vw	860w	848vw	884vw	δ(CCC), γ(CH)
808w	808vw	808vw	808vw	808vw	812vw	δ(CCC), γ(CH)
752vs	752vs	752vs	752vs	756vs	764vs	γ(CH)
684m	684m	684m	684m	692m	696m	γ(CH)
–	532m	516m	540m	542m	544m	ν(M–O)
504m	500w	500w	504w	496w	496w	γ(COC)
–	440m	484m	516m	480m	456m	ν(M–N)
472w	416vw	416vw	408vw	416vw	416vw	γ(C=O)
–	376w	392w	380w	372w	372w	ν(M-Cl)
312vw	312vw	308vw	312vw	308vw	320vw	γ(CCC), δ(O-(CH$_3$))

L $C_{17}H_{15}NO_3$, *Mn* $[MnL_2(CH_3OH)Cl]Cl\cdot 2CH_3OH$, *Co* $[CoL_2(H_2O)Cl]Cl\cdot 3H_2O$, *Ni* $[NiL_2(H_2O)Cl]Cl\cdot 3H_2O$, *Cu* $[CuL_2Cl_2]\cdot 4H_2O$, *Zn* $[ZnL_2Cl_2]\cdot H_2O$, *vs* very strong, *s* strong, *m* medium, *w* weak, *vw* very weak, *br* broad, ν stretching, δ deformation in plane, γ deformation out of plane, *as* asymmetric, *s* symmetric

[9, 16, 19–22]. In the IR spectra of complexes the broad band with the value of maximum frequency at 3392–3448 cm^{-1}, characteristic of ν(OH) vibrations confirms the presence of the water (and methanol for complex of Mn(II)) molecules. The bands at 2904–2972 cm^{-1} and 2824–2876 cm^{-1} may be assigned to asymmetric and symmetric stretching vibrations of the $\nu(CH_3)$ group, respectively from *methoxy*-substituent. The very strong band at 1284 cm^{-1} in the spectrum of ligand was attributed to the ν(C–N). The shifting of this band in the spectra of complexes to lower frequency compared with free 3-(anilinomethylene)-2-methoxychroman-4-one suggests a coordination of metal ions through nitrogen atom. The very strong band of ν(C=O) from chromanone in the spectrum of free ligand was registered at 1652 cm^{-1}. In the spectra of analysed complexes this band is shifted to lower frequency, it results in the participation of carbonyl oxygen of chromanone in the coordination of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). New bands which are not present in the spectrum of free ligand appeared in the range of 516–544 cm^{-1}, 440–516 cm^{-1} and 372–392 cm^{-1} were attributed to ν(M–O), ν(M–N), ν(M–Cl) vibrations, respectively. The spectra of ligand and its complexes display splitted bands in the range of 3008–3276 cm^{-1}, which may be assigned to ν(N–H···O). The presence of intramolecular hydrogen bond between N–H···O was confirmed in the structure of 3-(anilinomethylene)-2-methoxychroman-4-one [16].

Electronic absorption spectroscopy

The electronic absorption data of studied chelates are given in Table 3. In the spectrum of the ligand, the band at maximum 332 nm (30118 cm^{-1}) is due to the chromanone ring $\pi-\pi^*$ transition. The absorption band at 398 nm (25078 cm^{-1}) may be attributed to the $n-\pi^*$ transition within the aminomethylene group, influenced by the intramolecular charge transfer within the ligand molecule. During the formation of the complexes, these bands are shifted to longer wavelength, suggesting that the nitrogen atom is coordinated to the metal ions. The comparison of UV spectra of 3-(anilinomethylene)-2-methoxychroman-4-one and its chelates clearly shows that the absorption bands characteristic of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) are bathochromically shifted in methanol solution of ligand [23–25].

X-ray diffraction patterns

The X-ray diffraction patterns were made for all analysed complexes (Fig. 1). For complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) every 2θ peak position was used in the calculation. The X-ray analysis shows that the studied compounds crystallize in the triclinic crystal system and they are no isostructural complexes. The unit cell parameters for these compounds are presented in Table 3. The values of cell volume for analysed complexes are in the range of 1077-1973 $Å^3$ [17, 26].

Thermal analysis

The thermal stability of 3-(anilinomethylene)-2-methoxychroman-4-one of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was studied in the range 303–1273 K in air atmosphere. The thermal behaviour of the synthesized complexes

Table 3 The data of conductivity, magnetic moment, frequency of electronic bands and the unit cell parameters for the analysed complexes

Properties	Complex				
	Mn	Co	Ni	Cu	Zn
$\Lambda/cm^2\ \Omega^{-1}\ mol^{-1}$	87.6	97.5	101.2	54.8	15.2
$\mu_{eff}/\mu B$	6.1	4.8	3.2	1.7	Diam.
Wavenumber/nm (cm^{-1})	383 (26109)	381 (26246)	385 (25974)	401 (24937)	400 (24998)
	439 (22779)	438 (22831)	441 (22675)	425 (23529)	439 (22779)
		533 (18761)	525 (19047)	534 (18726)	
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
a/Å	9.62	10.36	9.82	8.15	7.68
b/Å	12.49	14.67	14.27	9.67	9.67
c/Å	17.30	14.43	17.82	16.81	17.69
α/°	75.18	110.19	55.52	83.78	96.36
β/°	74.84	105.39	72.16	95.14	101.53
γ/°	80.04	60.36	72.89	107.05	56.77
V/$Å^3$	1928	1778	1937	1257	1077

Mn $[MnL_2(CH_3OH)Cl]Cl\cdot 2CH_3OH$, *Co* $[CoL_2(H_2O)Cl]Cl\cdot 3H_2O$, *Ni* $[NiL_2(H_2O)Cl]Cl\cdot 3H_2O$, *Cu* $[CuL_2Cl_2]\cdot 4H_2O$, *Zn* $[ZnL_2Cl_2]\cdot H_2O$, *L* $C_{17}H_{15}NO_3$

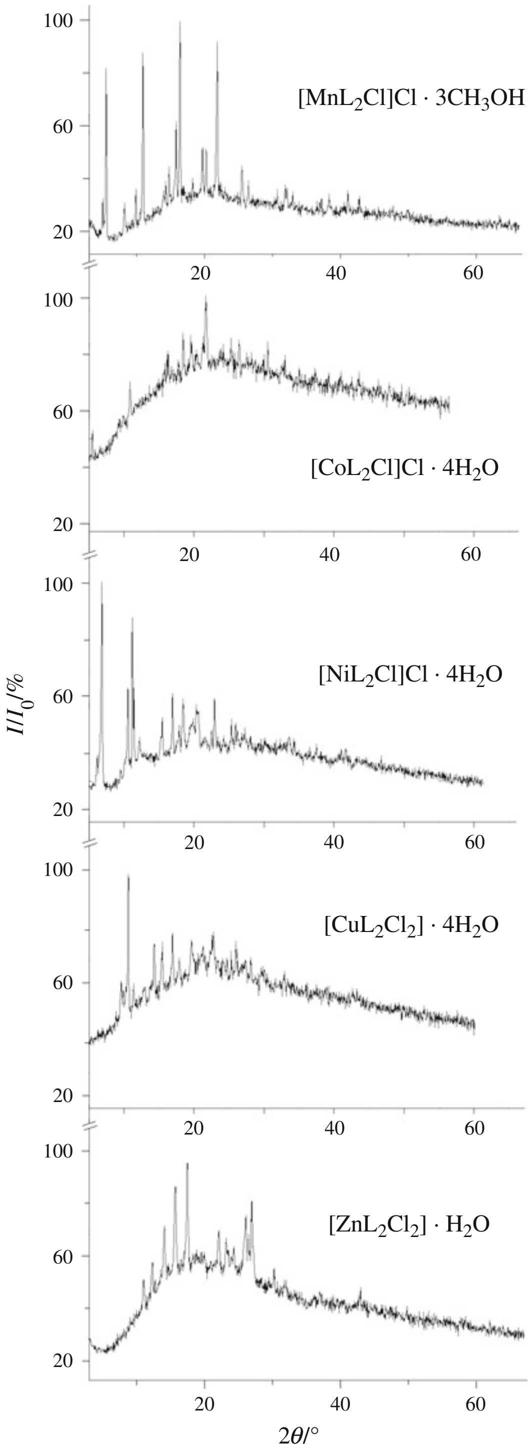


Fig. 1 Dependence of I/I_0 versus 2θ for analysed complexes

was characterized on the basis of TG/DTG and DSC methods. The baseline was obtained by running empty crucibles under the same measurements conditions (atmosphere, flow rate, initial temperature and heating rate). The data of thermal decomposition of studied compounds are listed in Table 4. Thermoanalytical curves of $[Ni(C_{17}H_{15}NO_3)_2(H_2O)Cl]Cl \cdot 3H_2O$ and $[Zn(C_{17}H_{15}NO_3)_2Cl_2] \cdot H_2O$ are presented as examples (Figs. 2, 3).

The TG curves of analysed chelates shows three decomposition steps. The first step corresponds to the loss of water and methanol molecules. Considering the temperatures at which the dehydration process of 3-(anilinomethylene)-2-methoxychroman-4-one Co(II), Ni(II), Cu(II) and Zn(II) takes place and the way by which it proceeds, it is possible to assume that the molecules of water (and methanol) are differently bound in the respective complexes. According to Nikolaev et al. [27] and Singh et al. [28], water eliminated below 424 K can be regarded as water of crystallization. Furthermore water eliminated above this temperature is coordinated to the central ion [29]. In studied compounds of Mn(II), Co(II) and Ni(II) only one chloride atom is coordinated to the metal ion. Moreover the magnetic moments of these chelates are in a good agreement with literature data what suggest octahedral arrangement of the ligands around the metal ion. For these reasons, it seems that one water molecule (methanol for Mn(II)) is coordinated to the metal ion. Furthermore the compounds lose molecules of water and methanol which are present in outside and inside of coordination sphere of respective chelates in one step [30–33]. The process of desolvation connected with endothermic effect is observed in DSC (sometimes splitted). The thermal analysis data show that the number of water and methanol molecules is in a good agreement with that defined by elemental analysis. The desolvation process for studied compounds starts in the range 313–351 K and finishes in the range 381–438 K (Table 4). The observed mass loss for this stage is in the range 2.6–12.5% (calcd. 2.51–12.23%). In the all complexes, a plateau is obtained after the first step which corresponds to the formation of stable dehydrated or desolvated metal complexes. The values of enthalpy of desolvation process for complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), which were calculated from DSC curves are equal to 40.8, 11.0, 11.1, 19.0 and 31.1 kJ mol^{-1}, respectively. The second stage of decomposition of analysed compounds occurs in the temperature range 438–485 K and corresponds to the decomposition of the organic part. According to registered TG/DTG and DSC curves of the studied chelates, the organic part of the complexes may decompose in one or more steps with the possibility of formation of one, two or three intermediate unstable products. The last stage of decomposition is accompanied by a broad exothermic effect in DSC curves. The final solid inorganic products are stable metal oxides Mn_2O_3, Co_3O_4, NiO, CuO and ZnO. Decomposition effects of the analysed complexes were used to obtain information about their thermal stability, properties, nature of the final products and desolvation process. The metal percentages calculated from the metal

Table 4 The data of thermal decomposition processes for analysed complexes in air atmosphere

Substance	ΔT/K	DTG_{max}/ K	DSC_{max}/K	Mass loss/%		n	Product of decomp. in solid state
				Calcd.	Found		
$[MnL_2(CH_3OH)Cl]Cl\cdot 2CH_3OH$	325–438	395	−351	12.23	12.5	3	$[MnL_2Cl]Cl$
$[MnL_2Cl]Cl$	456–760	705	+699	–	47.7	–	Intermediate products
Intermediate products	825–928	864	+881	89.94	90.3	–	Mn_2O_3
$[CoL_2(H_2O)Cl]Cl\cdot 3H_2O$	341–416	389	−386	9.42	9.7	4	$[CoL_2Cl]Cl$
$[CoL_2Cl]Cl$	481–521	506	+508	–	19.9	–	Intermediate products
Intermediate products	738–926	782	+629/+780	89.50	89.8	–	Co_3O_4
$[NiL_2(H_2O)Cl]Cl\cdot 3H_2O$	313–388	345	−343	9.42	9.2	4	$[NiL_2Cl]Cl$
$[NiL_2Cl]Cl$	485–613	569	+567	–	25.3	–	Intermediate products
Intermediate products	733–876	784	+700/+ 831	90.23	89.7	–	NiO
$[CuL_2Cl_2]\cdot 4H_2O$	341–415	391	−358	9.36	9.1	4	$[CuL_2Cl_2]$
$[CuL_2Cl_2]$	468–553	509	+509	–	13.5	–	Intermediate products
Intermediate products	733–961	866	+763/+ 868	89.66	89.2	–	CuO
$[ZnL_2Cl_2]\cdot H_2O$	351–381	362	−369	2.51	2.6	1	$[ZnL_2Cl_2]$
$[ZnL_2Cl_2]$	438–578	519	+551	–	15.1	–	Intermediate products
Intermediate products	783–941	901	+756/+903	88.65	88.8	–	ZnO

L $C_{17}H_{15}NO_3$, ΔT temperature ranges of decomposition processes, n number of water or methanol molecules lost in the thermal decomposition, − endothermic, + exothermic

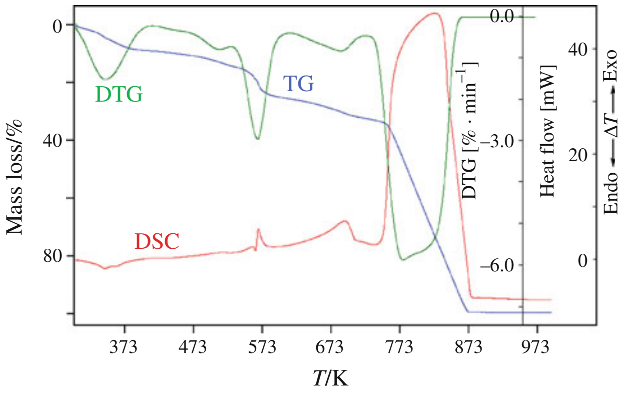


Fig. 2 TG, DTG and DSC curves for complex of Ni(II) in air atmosphere

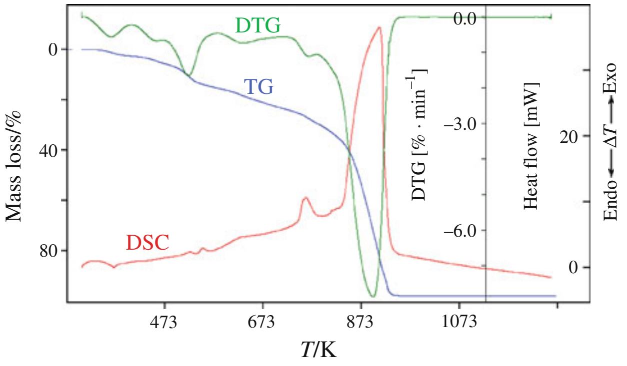


Fig. 3 TG, DTG and DSC curves for complex of Zn(II) in air atmosphere

oxide residues were found to be a good agreement with the results of elemental analysis. A comparison of temperatures of the first and second step of decomposition of the complexes was made (Fig. 4). These temperatures do not vary regularly with increasing atomic number of elements. In the first step, the most stable is Zn(II) complex and next the thermal stability of anhydrous complexes increases in order: Zn(II) < Mn(II) < Cu(II) < Co(II) < Ni(II).

Magnetic measurements

The magnetic moment of Mn(II), Co(II), Ni(II) and Cu(II) complexes were measured at room temperature (Table 3). The value of magnetic moment for manganese(II) complex is 6.1 μB corresponding to five unpaired electrons and octahedral coordination. The magnetic moment for Co(II) complex is 4.8 μB, suggesting an approximate high-spin octahedral geometry of ligands around cobalt(II) (octahedral normal range for Co(II) complexes is 4.3–5.2 μB). Divalent Ni^{2+} cation ($3d^8$) should exhibit a magnetic moment for two unpaired electrons (octahedral normal range is 2.8–3.2 μB and tetrahedral is 3.4–4.0 μB). The value of magnetic moment at room temperature of the 3-(anilinomethylene)-2-methoxychroman-4-one of Ni(II) is 3.2 μB, what indicates its octahedral geometry. The

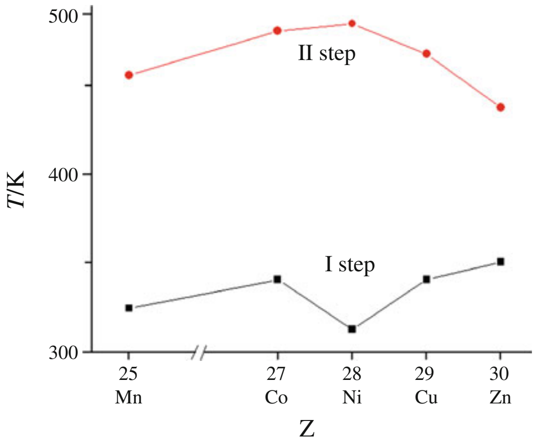


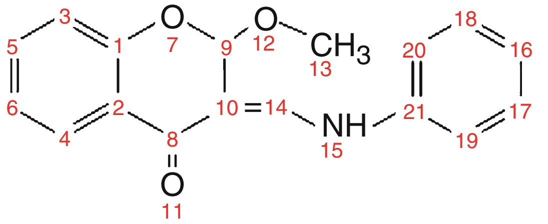
Fig. 4 Variation in initial temperatures of the first and second step of decomposition of the complexes versus atomic number

magnetic moment of the Cu(II) complex at room temperature is 1.7 μB which shows one unpaired electron and is typical for distorted octahedral copper(II) chelates. The Zn(II) complex is diamagnetic as expected for d^{10} configuration. The experimental data suggest that 3-(anilinomethylene)-2-methoxychroman-4-ones of Mn(II), Co(II), Ni(II) and Cu(II) are high-spin complexes with weak ligand fields. [34–36].

^{1}H NMR

^{1}H NMR spectra of 3-(anilinomethylene)-2-methoxychroman-4-one and its five complexes in DMSO solution were measured and the assignments of spectral data are listed in Table 5. All the signals detected in the ^{1}H NMR spectra of the free ligand molecule were also found in the appropriate spectra of analysed complexes. The calculated chemical shifts for ligand strongly correlate with experimental values. For most of the hydrogens, the predicted error is within the 0.0–3.1% range. The highest value of predicted error for proton signal of 15 NH is 7.6%, which is likely to be caused by hydrogen bond (N–H···O) between proton of nitrogen atom and oxygen from chromanone. This hydrogen bond is observed in the structure of 3-(anilinomethylene)-2-methoxychroman-4-one [16]. The spectra of the complexes with Mn(II), Co(II), Ni(II) and Cu(II) show very wide signals due to the paramagnetic nature of these metals. In the spectra of free ligand and its complexes in DMSO-d_6 solution, the aromatic proton signal is shown at

Table 5 The experimental and theoretical shifts for 3-(anilinomethylene)-2-methoxychroman-4-one and its complexes with metal ions



Number of atom[a]	Ligand δ/ppm		Error/%	$\Delta\delta = \delta_{(\text{complex})} - \delta^{b}_{(\text{ligand})}$/ppm				
	Theor.	Exp.		Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
3 CH	7.15	7.26	1.5	0.00	0.01	0.02	0.03	0.03
4 CH	7.77	7.77	0.0	0.01	0.01	0.01	0.01	0.01
5 CH	7.47	7.50	0.4	0.09	0.00	0.09	0.01	0.00
6 CH	7.17	7.38	2.9	0.00	0.00	0.00	0.01	0.00
9 CH	6.18	6.19	0.1	0.02	0.04	0.02	0.03	0.04
13 CH_3	3.36	3.50	4.1	0.22	0.03	−0.19	−0.16	−0.17
14 CH	6.97	6.94	0.4	0.04	0.05	0.05	0.04	0.03
16 CH	6.72	6.91	2.8	0.21	0.23	0.22	0.22	0.22
17 CH	7.11	7.00	1.5	0.02	0.03	0.03	0.02	0.02
18 CH	7.11	7.06	0.7	−0.04	−0.04	0.04	0.06	−0.04
19 CH	6.68	6.88	2.9	0.52	0.53	0.52	0.51	0.53
20 CH	6.68	6.89	3.1	0.52	0.53	0.52	0.51	0.53
15 NH	13.16	12.15	7.6	0.28	0.27	0.28	0.28	0.29

Error indicates the predicted relative percentage error theoretical versus experimental, Δ indicates the difference in chemical shift between non-complexed and complexed 3-(phenyloaminomethylene)-2-methoxychroman-4-one

[a] the final assignment is based on the analysis of the data from theoretical calculation

[b] the experimental chemical shift difference between NMR signals for ligand and its complexes

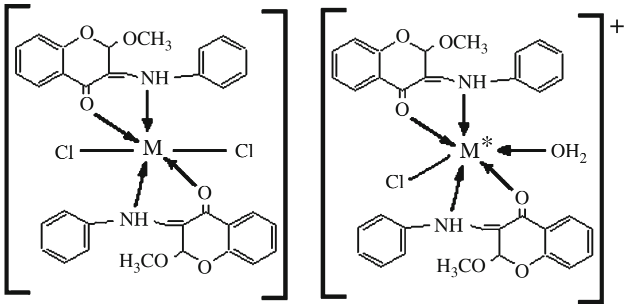


Fig. 5 Suggested coordination of central ions, where M = Cu(II), Zn(II) and M* = Co(II), Ni(II)

6.35–7.78 ppm regions. The signals at 3.50 ppm for ligand and 3.31–3.72 ppm for chelates are caused by the presence of *methoxy*-group. These signals in the spectra of complexes are obtained downfield and upfield in comparison with respective signals in the spectrum of free ligand. These shifts may be due to the possibility of the formation of intramolecular hydrogen bonding with the oxygen atom from $–OCH_3$. In the structure of 3-(anilinomethylene)-2-methoxychroman-4-one, the hydrogen bonds occur between nitrogen and oxygen atoms from chromone as well as between oxygen atom from *methoxy*-group and –CH in the six-membered ring [16]. The proton at nitrogen atom in the free ligand (12.15 ppm) is shifted downfield to 11.86–11.87 ppm on complexation. This observation suggests that the ligand coordinates to the metal ions through the nitrogen atom [15, 37–40].

Molar conductivity of complexes

The molar conductance of complexes Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 3-(anilinomethylene)-2-methoxychroman-4-one was measured in $0.001\ \mathrm{mol{\cdot}dm^{-3}}$ CH_3OH solution (Table 3). Their values are in the range of $15.2–101.2\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$. These values indicate a 1:1 electrolyte nature for Mn(II), Co(II) and Ni(II) compounds, thus these complexes may be formulated as $[ML_2Cl]Cl$. The complexes of Cu(II) and Zn(II) are non-electrolyte indicating that both the two chloride anions are involved in coordination to the respective M(II) ions. It also suggests six coordinate formulation for these complexes. Thus, these compounds may be formulated as $[ML_2Cl_2]$ where M = Cu(II) and Zn(II) [41–43].

Conclusions

On the basis of the studies described above (elemental analysis data, ^{1}H NMR and FTIR spectroscopy, molar conductance and thermogravimentric analysis) the coordination of metal ions in analysed complexes is suggested (Fig. 5). The investigated complexes were obtained as crystalline solvates with different number of solvent molecules. The molecules of solvent occur in the outside coordination sphere of complexes. The studied compounds are stable in air at room temperature and they have electrolyte (1:1) and non-electrolyte nature. Their desolvation runs in one step above 313 K. In all cases, the anhydrous metal complexes undergo exothermic decomposition reactions to give the metal oxide. The X-ray analysis shows that investigated chelates crystallize in the triclinic crystal system and they are no isostructural complexes. The suggested coordination of metal ions to ligand is through oxygen and nitrogen atoms from 3-(anilinomethylene)-2-methoxychroman-4-one.

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