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Complexation of metal ions with dioxime of dialdehyde starch

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Abstract

Dialdehyde starch (30%) from periodate-oxidized potato starch was converted into its dioxime (DASOX). The dioxime was coordinated to the Ca, Cd, Co (II), Cu (II), Fe (II), Mg, Mn (II), Ni (II), Pb (II), and Zn ions. Particular metal ions were chelated to a different extent. In the complexes, one mole of a metal ion was coordinated on from 9 to 80 moles of the DASOX units. Similarly as pure DASOX, the metal complexes decomposed thermally in four steps. The coordination to all metal ions except Fe (II) increased temperature of the thermal decomposition and, except Cu (II), they also increased the rate of the first decomposition stage. After coordination the ligand decomposed more profoundly than in the free stage. Computational simulations pointed to the nitrogen atoms of the dioxime C=N moiety and the oxygen atom of the former pyranose ring as the coordination sites.

Keywords: Macro ligands; Metal complexes; Oximes; Polysaccharides; Thermal analysis

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1. Introduction

Potential and versatile bioactivity of various oximes and their metal complexes (Hall, Lee, Ibrahim, Khan, & Bouet, 1997; Jurisson & Lydon, 1999; Mansuy, Battioni, & Battioni, 1989) induced steadily growing interest in oxime co-ordination compounds. Oximes reveal certain insecticidal, miticidal, and nematocidal activity, they inhibit arginase (Custot et al., 1996) and, some oximes are intermediates in the biosynthesis of nitrogen oxide (Mansuy et al., 1989), and radiopharmaceuticals in brain tumor diagnostics because of their traversing the blood–brain barrier (Blower, 1998; Dilworth & Parrott, 1998). Certain metallic complexes of furan oximes exhibited cytotoxicity in murine and human tissue cultured cell lines (Hall, Lee, Ibrahim, Khan, & Bouet, 1997). Oximes were also used as antidote against organophosphorus poisons (Rachaman et al., 1979). Oxime metal chelates exhibited higher antimicrobial activity than free ligand (Mehta & Nagarkoti, 2002). Biological functions of oximes and their in vivo metabolism are evidently dependent on their chelation with metal ions (Custot et al., 1996). Chelating ability of oximes is utilized in chemical trace metal analysis (Patel, Ray, & Patel, 1992). In metallurgy, oximes provide isolation, separation, and extraction of various metal ions (Filippov, Joussemet, & Houot, 2000; Jin, Michel, & Noble, 1989; Mahmoud, Nakamura, & Akiba, 1997).

In this paper ligation of dialdehyde starch dioxime (DASOX, Fig. 1) with the Ca, Cd, Co(II), Cu(II), Fe(II), Mg, Mn(II), Ni(II), Pb(II), and Zn ions is presented.

Relevant complexes are characterized and their structures elucidated.

2. Experimental part

Dialdehyde starch (DAS) oxidized in 30% was prepared from potato starch in the periodate-oxidation with electrochemical recovery of the oxidant (Para, Karolczyk-Kostuch, Hajdon, & Tomasik, 2000). Its solubility in water at 25 °C reached 1.8%. HPLC-determined molecular weight profile was as follows: 18% <1000, 77% between 1000 and 40 000, and 5% between 40,000 and 170,000 amu.

Dialdehyde starch dioxime (DASOX) was prepared from DAS and hydroxylamine hydrochloride, reagent grade (POCh Gliwice, Poland) according to Para et al. (2000).

$CaCl_2{\cdot}2H_2O$, $CdCl_2{\cdot}2{,}5H_2O$, $CoCl_2$, $CuCl_2{\cdot}2H_2O$, $FeCl_2{\cdot}4H_2O$, $MgCl_2{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, $NiCl_2$, $Pb(NO_3)_2$

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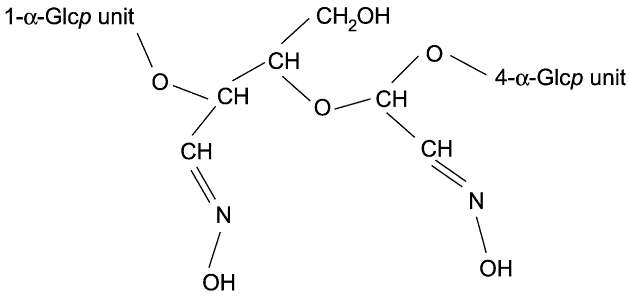


Fig. 1. Structure of dialdehyde starch dioxime.

and $ZnCl_2$, all analytical grade, were purchased from POCH Gliwice, Poland.

2.1. Average molecular weight of DAS

High pressure size exclusion chromatography system consisted of Shimadzu LC10A pump (Shimadzu Japan), Rheodyne model 7725i injector (Rheodyne, USA), TSKgel GMPWXL column (7.8 × 30 mm, TosoHaas, Japan), and differential refractive index detector Merck LaChrom L-7490 (Merck, Germany). Mobile phase consisted of 0.15 M $NaNO_3$, with 0.02% NaN_3 pumped with flow rate of 0.5 cm^3/min. Column was calibrated with set of 10 dextran standards (Polygen, Denmark) with M_w ranging from 1080 to 401300.

2.2. Preparation of complexes

DASOX (2 g) containing 0.004 mol oxime moieties was suspended in 0.5 M aqueous solution (10 cm^3) of a given metal salt and agitated gently for 3 h. The suspension was filtered under reduced pressure and washed on the filter with distilled water (3 × 20 cm^3). The solid was dried at 100 °C to the constant weight. The reaction yield was calculated in respect to the initial weight of the ligand.

2.3. Elemental analysis

Nitrogen content was estimated using the Dumas semimicro combustion analysis (Bobrański, 1956). The metal content was determined with inductively coupled plasma—atomic emission spectrometer ICP-AES, JY 238 ULTRACE JOBIN-YVON, (Longjumeau, France).

2.4. Solubility in water

Solubility was estimated gravimetrically according to Richter, Augustat, and Schierbaum (1968). Complexes (0.1 g) were dissolved in distilled water (8 cm^3) and agitated for 30 min in a water bath at 25 °C then centrifuged (5000 rpm for 10 min). Resulting transparent solution (5 cm^3) was transferred to the weighing dish of constant weight and evaporated to dryness at 120 °C.

2.5. UV absorption spectra

The spectra of 4.7×10^{-3} M aqueous solutions were recorded in 10 mm quartz cells using the UV–VIS Scanning Spectrophotometer, Shimadzu UV-2101 PC (Kyoto, Japan).

2.6. Raman spectra

FT Raman spectra were registered using a Bio-Rad FT Raman spectrometer (Cambridge, USA) with diode Spectra-Physics Nd: YAG laser providing the 1064 nm line.

2.7. EPR spectra

Experiments were carried out on X-band Bruker ESP-500 spectrometer (Karlsruhe, Germany) with the 100 kHz field modulation. The spectra were recorded at room temperature and at 77 K. EPR parameters were found by means of simulation with involvement of modified SIM 14 program (Lozos and Hoffman).

2.8. Thermal analysis (TG/DTG)

Samples (0.1 g) were heated from 21 to 500 °C in corundum crucibles in the open at the 10 K/min rate of temperature increase. Corundum particles $\phi = 8$ μm were taken as the standard. Analysis was performed with a computerized Paulik–Paulik–Erdey Q-1500-D (Budapest, Hungary) apparatus.

2.9. Magnetic susceptibility

The magnetic dc-susceptibility measurements were carried out using a commercial Quantum Design SQUID magnetometer (San Diego, USA) in the magnetic field of 2 T and in temperature range from 10 to 300 K. Effective magnetic moments of the metal ions were estimated from the slope of the inversed susceptibility, after taking diamagnetic background into account.

2.10. Computations

The heat of formation per one bond was calculated with HyperChem Pro 7.0 software. Semi-empirical ZINDO/1 optimisation method with the Fletcher-Reeves algorithm was applied (Fletcher, 1980). The calculations were performed for all possible complex structures derived from the involvement of the nitrogen and oxygen atoms leading to the formation of either single five- and six-, and, simultaneously, two five- and two six-membered rings.

Table 1
Characteristics of starch dialdehyde dioxime and its metal complexes

Central metal atom	Colour	Reaction yield[a] (%)	Aqueous solubility (%)	Elemental analysis			
				Nitrogen (%)		Metal ions	
				Calcd	Found	$g \times 10^{-3}$/(1g DASOX)	X[b]/(mol M)
None	White		6.1	4.93	4.73		
Ca	White	85	2.9	4.92	4.98	2.52	28
Cd	White	80	2.2	4.92	4.66	2.84	70
Co(II)	Buff	73	4.3	4.92	4.89	2.76	37
Cu(II)	Olive	58	5.0	4.87	4.32	11.75	9
Fe(II)	Yellow brown	81	5.4	4.90	4.54	5.25	19
Mg	White	84	2.6	4.93	5.01	0.73	58
Mn(II)	White	81	2.7	4.92	4.97	1.09	80
Ni(II)	Yellow	75	2.7	4.92	4.48	2.12	49
Pb(II)	White	63	3.8	4.88	4.21	9.65	37
Zn	White	72	3.4	4.92	4.45	1.46	80

[a] Calculated on DASOX.
[b] The number of moles of DASOX units.

3. Results and discussion

3.1. Physical properties of complexes

The yield of DASOX metal complexes was between 63 and 85% (Table 1).

All complexes were sparingly water-soluble solids. Complexation reduced solubility of the ligand (Table 1). Low aqueous solubility of DASOX metal complexes opens potential non-pharmacological applications. For instance, DASOX can be utilised for a temporary immobilisation of heavy metal ions in the soil. It might be beneficial for a crop production. In such manner beneficial soil micro-organisms sensitive to heavy metal and natural pesticides, for instance, entomopathogenic nematodes (Jaworska, Sepioł, & Tomasik, 1996, 1997) might be inhibited from toxic action of heavy metal ions in the period of their seasonal activity (Para & Ropek, 2000).

Nitrogen content in the complexes fairly well fitted theoretical values. Amount of the metal atoms involved in coordination to DASOX varied from 9 to 80 mol of ligand per one mole of metal ions. The Cu(II) and Fe(II) ions co-ordinated DASOX to the highest extent whereas the Mn(II) and Zn(II) ions co-ordinated to DASOX to the lowest extent (Table 1). Comparison of coordination properties of semicarbazone, thiosemicarbazone, hydrazone, and oxime of dialdehyde starch showed the lowest coordination ability for oxime, especially in respect to Cd(II), Ni(II) and Zn ions. The number of complexed metal ions was, in this case, four times lower (Para & Karolczyk-Kostuch, 2002a,b).

3.2. UV and Raman spectra

Table 2 presents the UV and Raman spectral characteristics of the ligand and its metal complexes.

In the UV spectrum of DASOX two absorption bands at 211.8 nm ($\varepsilon_{\max} = 3.871$) and 287.2 nm ($\varepsilon_{\max} = 1.726$) could be observed. Coordination to a metal had practically no influence on the position and intensity of the first spectral band. Also position of the second spectral band was insensitive to coordination but its intensity decreased to the extent dependent on the central metal ion. The decrease in the intensity was particularly significant in the spectra of the Co(II), Cu(II), Ni(II) and Zn(II) complexes (Table 2). As a rule, coordination to the metal ions resulted in a decrease of intensity of that band. Because the long wavelength band corresponded to local excitations it was not surprising that variation in its intensity was non-linear against the number of the metal ions co-ordinated to DASOX.

In the FTIR spectrum of the dialdehyde starch and its derivatives an intensive band at 1637 cm^{-1} assigned to water was present. It was a band typically residing in the spectra of starch and numerous its derivatives. It could be assigned to deformation vibrations in water molecules sorbed onto starch (Kazitsyna & Kypletskaya, 1971). It masked the ν(C=N) stretching vibrations in DASOX. Therefore, in order to elucidate the structure of complexes, the Raman spectra in the region of 4000–200 cm^{-1} were recorded instead.

The Raman spectrum of DAS exhibited an intensive band at 1732 cm^{-1} assigned to the ν(C=O) stretching vibrations in the aldehyde carbonyl group. This band vanished in the spectrum of DASOX confirming formation of dioxime. In a consequence, the band at 1656 cm^{-1} attributed to the ν(C=N) stretching vibrations (Yildiz, Misir, Tüfekci, & Gök, 1998) could be observed (Table 2). This band was fairly sensitive to coordination. As a result of reduced electron density at the nitrogen atom caused by coordination to the metal cation, it moved in the spectra of all complexes to a lower frequency (1643–1647 cm^{-1}). In all spectra this band was asymmetric. There was a milder

Table 2
UV and Raman spectra of dialdehyde starch dioxime and its metal complexes

Central metal atom	UV				Raman shift	
	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}	ν(C=N I) (cm^{-1})	ν(C=N II) (cm^{-1})
None	211.8	3.871	287.2	1.726	1656	
Ca	210.8	3.724	287.2	1.532	1645	1586
Cd	210.2	3.648	287.0	1.444	1647	1584
Co(II)	209.4	3.581	286.6	0.953	1646	1602
Cu(II)	209.2	3.587	286.0	0.720	1643	1599
Fe(II)	208.6	3.665	286.0	1.023	1644	1598
Mg	210.2	3.778	286.6	1.576	1647	
Mn(II)	209.2	3.740	286.7	1.347	1647	
Ni(II)	209.3	3.563	287.0	0.922	1645	
Pb(II)	209.8	3.624	286.0	1.089	1647	1600
Zn	208.8	3.577	286.8	0.870	1646	

slope on its red side. In the spectra of the Ca(II), Cd(II), Co(II), Cu(II), Fe(II), and Pb(II) complexes of several oximes a weak band in range of 1584–1602 cm^{-1} used to be seen (Serbest, Değirmencioğlu, Karaböcek, & Güner, 2001; Yilmaz, Kandaz, Özkaya, & Koca, 2002). In the spectra of DASOX complexes, both C=N groups appeared at closely the same frequency and, therefore, they were indistinguishable. Possibly, they manifested in form of asymmetry of the 1656 cm^{-1} band. One could conclude that nitrogen atoms of both coordinated oxime groups were not equivalent to one another. In the spectra of Mg(II), Mn(II), Ni(II) and Zn(II) complexes the band at that frequency was not observed, similarly as in the spectrum of free DASOX.

3.3. EPR spectra

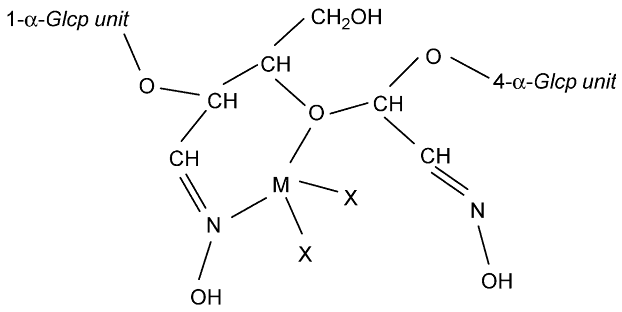
The EPR spectrum of polycrystalline Cu(II) complex recorded at room (RT) and liquid nitrogen temperature (LNT) contained two peaks. From the spectra, the $g\|$ (parallel) and $g\perp$ (perpendicular) values were found (2.47 (RT) and 2.48 (LNT) and 2.05 (RT and LNT) respectively). The observed trend: $g\| > g\perp > g_e$ (2.0023) observed for the Cu(II) complexes showed that the unpaired electron was present in the $d_{x_2-y_2}$ orbital of the Cu(II) atom (Casanova, Alzuet, Borras, David, & Gatteschi, 1993). Kivelson and Neiman (1961) have shown that $g\|$ was moderately sensitive providing indication of the covalent character of the bonding. For the ionic environment, $g\|$ was above 2.3 and for a covalent environment it was below 2.3. Because for complexes under study $g\|$ was above 2.3 the ionic nature of the complexes could be postulated. G-parameter from expression $G = (g\| - 2)/(g\perp - 2)$ exceeded 4. Thus, exchange interactions between Cu(II) centers in the solid complex were negligible (Hathway & Billing, 1970).

3.4. The magnetic moment

The magnetic susceptibility for the Co(II) and Cu(II) complexes at different temperatures successfully fitted the Curie–Weiss law. The effective magnetic moments were 3.38 and 1.82 B.M, respectively. The value of 3.38 B.M. for Co(II) complex indicated three unpaired electrons. This would be consistent with the tetrahedral coordination (Cupertino, McPartlin, & Zissimos, 2001). In this case an inverse relationship between the magnitude of the orbital contribution and the strength of the ligand field was found (Cotton & Wilkinson, 1962). The magnetic moment, $\mu_{eff} = 1.82$ B.M. for the Cu(II) complex was very close to the value for one unpaired spin and was in the range normally observed for the Cu(II) complexes with non-degenerated B_{1g} ground state (Jayaramudu & Reddy, 1999). The expected range for magnetically diluted Cu(II) complexes spread over the range of 1.7–2.2 B.M. Several complexes with the magnetic moments below this range indicated antiferromagnetic coupling. Copper used to form a number of compounds with the Cu–Cu distances short enough to provide significant Cu–Cu interactions but in no case these distances corresponded to the Cu–Cu bonds (Cotton & Wilkinson, 1972).

3.5. Structure of complexes

Frequently, ligands containing the oxime moiety and oxygen atoms utilized simultaneously the nitrogen and oxygen atoms as coordination centers for metal ions (El-Mottaleb, Ramadan, El-Mehasseb, & Issa, 1997; Mokhir et al., 2002). The structure presented in Fig. 2



X=Cl, NO_3,

Fig. 2. Potential structure of metal complexes of dialdehyde starch dioxime.

proposed for the complexes of the metal ions and DASOX followed the same assumption.

The structure in Fig. 2 had the lowest heat of formation (from −677.8 to −711.3 kJ/bond for particular metal ions). It was the most stable and dominant species. Little differences in calculated values of heat of formation, of the order of a dozen kilojoules for different structures for the same metal ion, did not preclude other ways of coordination with nitrogen and oxygen atoms.

3.6. Thermal decomposition

Thermal properties of metal complexes have been investigated as one of the most interesting topic in the field of coordination chemistry (Hudák, & Košturiak, 1999; Moustafa, 1997). DASOX retained residual water entrapped in the polysaccharide structure.

This was typical for polysaccharides, particularly for starch. All DASOX metal complexes also contained similar amount of water (3.0–4.2%) (Fig. 3, Table 3). In the temperature range of 21–400 °C DASOX lost 57.7% of its weight. Weight loss for complexes is slightly higher and ranged from 59.2 to 64.6%, except the Fe(II) complex which lost 87.3% of its weight. This might suggest either catalytic activity of metal compounds in decomposition of carbonizate resulting from thermolysis of DAS above approximately 350 °C or involvement of corresponding metal oxides in the carbonizate decomposition.

After evolution of water the ligand and complexes decomposed in four further stages. First, between 170 and 210 °C the complexes lost 13.6–15.9% of their weight.

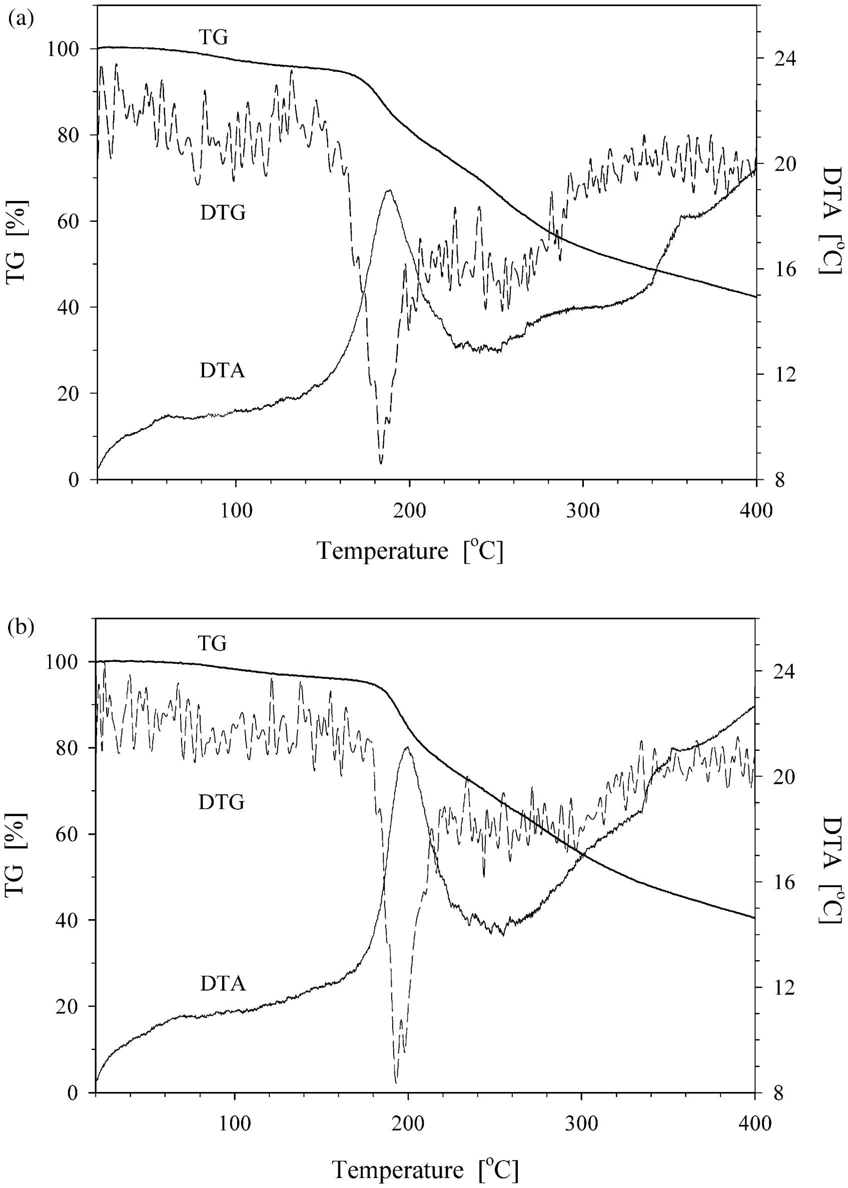


Fig. 3. Thermogram of dialdehyde starch dioxime (a) and its Pb(II)-complex (b).

Table 3
Thermal analysis (TG, DTG) of dialdehyde starch dioxime and its metal complexes

Temperature range (°C)	20–130		170–210			210–240		240–300		300–400		20–400
Central metal atom	WL[a] (%)	$tg\alpha$[b]	WL (%)	DTG[c] (°C)	$tg\alpha$	WL (%)	$tg\alpha$	WL (%)	$tg\alpha$	WL (%)	$tg\alpha$	WL (%)
None	4.1	−0.057	14.4	183	−0.50	9.8	−0.27	15.8	−0.32	11.5	−0.11	57.7
Ca	4.0	−0.046	15.3	197	−0.76	8.5	−0.28	16.3	−0.27	15.5	−0.12	60.9
Cd	4.1	−0.045	18.1	198	−2.81	7.0	−0.24	17.7	−0.30	16.5	−0.14	64.6
Co(II)	3.7	−0.036	14.0	198	−0.54	9.9	−0.35	16.5	−0.28	14.8	−0.12	59.9
Cu(II)	4.0	−0.057	14.3	186	−0.42	8.1	−0.31	16.2	−0.27	14.8	−0.12	59.6
Fe(II)	4.2	−0.054	40.0	180	−13.6	5.2	−0.10	12.9	−0.23	22.3	−0.24	87.3
Mg	3.3	−0.041	15.9	194	−0.85	8.0	−0.27	16.1	−0.28	14.7	−0.12	59.2
Mn(II)	3.7	−0.039	15.4	197	−0.73	7.3	−0.28	17.2	−0.27	14.9	−0.12	59.8
Ni(II)	4.0	−0.044	15.7	192	−0.57	8.4	−0.30	16.2	−0.28	14.2	−0.12	61.3
Pb(II)	3.0	−0.030	15.8	194	−0.68	8.7	−0.26	15.7	−0.27	15.1	−0.12	59.6
Zn	3.3	−0.032	15.3	194	−0.79	8.9	−0.29	16.4	−0.27	14.9	−0.12	60.1

[a] Corresponding weight loss.
[b] The slope of appropriate parts of the TG curve.
[c] Main peak.

Only the weight loss from the Cd(II) and Fe(II) complexes was higher, 18.1 and 40.0%, respectively. In the subsequent stage from 210 to 240 °C all complexes lost 7.0–9.9% of their weight and only Fe(II) complex lost 5.2%. Between 240 and 300 °C the weight loss was also between 15.7 and 17.7% (only for Fe(II) it reached 12.9%). In the fourth step of decomposition the free ligand lost 11.5% of its weight. For metal complexes the weight loss was slightly higher, this is, 14.2–16.5% except Fe(II) complex where 22.3% of the weight was lost.

The complex decomposition began at higher temperature (186–198 °C—minimum of the DTG peak) compared with ligand decomposition temperature (183 °C), which showed a little increase in the stability as a result of complexation. The Fe(II) complex was exceptional. The minimum of the DTG peak was slightly lower. It appeared at 180 °C.

The rate of decomposition for particular stages was characterized by the slope ($tg\alpha$) of appropriate parts of the TG curve. $tg\alpha$ for the first stage of decomposition for most complexes was in the range of −0.54 to −0.85 while for the ligand, $tg\alpha = -0.50$. For the Cd(II) and Fe(II) complexes these values were essentially higher: −2.8 and −13.6, respectively. $tg\alpha$ for the Cu(II) complex, was slightly lower than for the ligand (−0.42). Therefore, despite the fact that the decomposition began at slightly higher temperature, the rate of the decomposition was higher, especially for the Cd(II) and Fe(II) complexes. All metal ions except Cu(II) catalyzed the first step of decomposition.

The rate of the second stage of decomposition was similar for the ligand ($tg\alpha = -0.27$) and complexes ($tg\alpha$ from −0.24 to −0.35) and was slightly lower for the Fe(II) complex ($tg\alpha = -0.10$).

The rate of the third step of decomposition was the highest for the ligand ($tg\alpha = -0.32$). For Cd(II) and Fe(II) complexes the estimated values were −0.30 and −0.23, respectively, and for the other compounds from −0.27 to −0.28. This stage was stabilized by all metal ions.

The rate of the fourth stage of decomposition, $tg\alpha = -0.11$ to -0.14, was comparable for the ligand and all complexes except the Fe(II) complex.

One could see that all metal ions except Cu(II) increased the rate of the first step of decomposition and, simultaneously, slightly decreased the rate of the third step. Except the Fe(II) complex, the decomposition rate of the second and fourth step was not influenced by the complexation. Different situation was met in the case of the Fe(II) complex. The Fe(II) atom was the sole metal atom decreasing temperature of the complex decomposition.

4. Conclusions

Dialdehyde starch dioxime coordinated metal ions. Degree of saturation of the ligand with metal ions was different for particular central metal atoms. The C=N and C–O–C groups were potential sites of coordination. Coordination of the metal ions, except Fe(II), increased temperature of decomposition of the ligand.

Acknowledgements

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