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Semicarbazone of starch dialdehyde and its complexes with metal ions

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Abstract

Potato starch was oxidised with periodate to 14% dialdehyde product that was converted into its semicarbazone. Complexes of the semicarbazone with Ca, Cd, Co (II), Cu (II), Fe (II), Mg, Mn (II), Ni (II), Pb (II) and Zn are described. IR spectral analyses on the soluble fractions of the complexes showed that the carbonyl oxygen atoms and the C=N nitrogen atoms of the semicarbazone are involved in chelation of the metal atoms. The thermal analysis of complexes revealed two-step decomposition of the ligand and three-step decomposition of complexes. Particular metal ions are chelated to a different extent. One in six semicarbazone moiety is engaged in co-ordination of Cu (II), and in bonding of Mn (II) one in 40 semicarbazone moiety is involved. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Semicarbazone; Starch; Aldehyde

1. Introduction

There is ongoing semicarbazones of aldehydes because of their potential biological activity. Although such activity is known chiefly among derivatives of aromatic and heteroaromatic aldehydes, biological activity of derivatives of aliphatic aldehydes has also been reported (Tomasik & Schilling, 1999). Activity of aldehyde semicarbazones and thiosemicarbazones might be stimulated by co-ordination to some metal ions (Crim & Petering, 1967; Hall, Chen, Rajendran & West, 1996; Padhye & Kauffman, 1985; West, Padhye & Sonawane, 1991; West, Ingram, Kozub, Bain & Liberta, 1996). There are numerous structural studies on metal complexes with semicarbazones and thiosemicarbazones of aldehydes as the ligands (Battaglia, Ferrari & Boggia, 1994; Kumar & Chandra, 1993a; Patel & Agarwala, 1996; Soliman & Khattab, 1991; Souza, Sanz, Fernandez, Arquero, Gutierrez & Monge, 1991). Limited solubility of semicarbazones and thiosemicarbazones of some aldehydes make them potential traps of metal ions from industrial and municipal sewage. Biodegradability of such traps would be ecologically beneficial. Temporary soil detoxication from heavy metals with such ligands and protection of soil micro-organisms from the heavy metal ions might be taken into account. Finally, starch semicarbazone might be a useful carrier of some therapeutically beneficial micro-elements.

In this paper semicarbazone of low-oxidised (14%) starch dialdehyde was used as a ligand of complexes with Ca, Cd, Co (II), Cu (II), Fe (II), Mg, Mn (II), Ni (II), Pb (II), and Zn (Fig. 1).

2. Experimental part

2.1. Starch dialdehyde semicarbazone (DASSC)

The title compound was prepared from starch dialdehyde (DAS) that had been oxidised to 14% using sodium periodate with electrochemical recovery of the oxidant (Para, Karolczyk-Kostuch, Hajdon & Tomasik, 2000).

Dialdehyde starch (30 g) was introduced in a solution (250 cm^3) of semicarbazide hydrochloride taken in 30% excess with respect to the stoichiometric amount. Acid reaction mixture was neutralised with solid Na_2CO_3, then agitated at room temperature for 3 h. Resulting solid was collected on the vacuum filter and dried at 40 and then 90°C.

2.2. Determination of average molecular weight of DAS

The weight average molecular weight of starch dialdehyde was estimated using high performance size exclusion chromatography (HPSEC) with multiangle laser light scattering (MALLS) and refractive index detection. The system consisted of a pump (P2000, Spectra System, Palo Alto, USA), an injection valve (model 7021, Rheodyne, Palo Alto, USA), a guard column (TSK PWH, Tosoh Corporation, Tokyo, Japan). A MALLS detector Dawn-DSP-F (Wyatt Technology, Santa Barbara, CA) and differential

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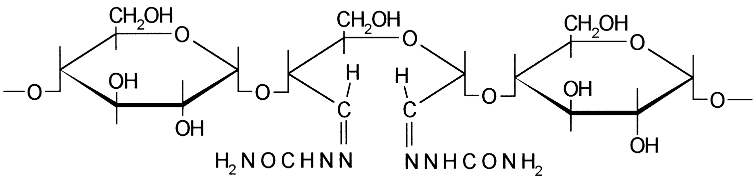


Fig. 1. Structure of DASSC.

refractive index detector (Model SE71, Shodex, Tokyo, Japan) were connected to the columns.

Moisturised dialdehyde starch (1 g) with 10 cm^3 of water was suspended in dimethylsulfoxide (DMSO 90 cm^3). Then, the abs. ethanol was added for precipitation of the dialdehyde starch. The precipitate was centrifuged (2500 rpm, 20 min), washed with ethanol and dried under vacuum at room temperature. Then, the dialdehyde starch was dissolved in 2 M NaOH by stirring at 70°C for 1 h, neutralised with 2 M hydrochloric acid and filtered prior to the HPSEC injection.

2.3. Preparation of metal complexes

DASSC containing 0.005 mol of semicarbazone moieties (3 g) was suspended in 0.25 M aqueous solution of a given metal salt (20 cm^3) and agitated gently for 3 h. The following salts were used: $Ca(NO_3)_2\cdot 4H_2O$, $CdCl_2\cdot 2.5H_2O$, $CoCl_2$, $CuSO_4$, $FeCl_2\cdot 4H_2O$, $MgCl_2\cdot 6H_2O$, $MnSO_4\cdot 5H_2O$, $Ni(NO_3)_2\cdot 8H_2O$, $Pb(NO_3)_2$ and $ZnCl_2$. All salts were of analytical grade. They were purchased from POCH, Gliwice, Poland. Then the suspension was filtered under reduced pressure and washed on the filter with distilled water (3×20 cm^3). The solid was dried at 40°C then at 120°C until constant weight. The reaction yield was calculated with respect to the initial weight of the ligand.

2.4. Estimation of solubility

Solubility was estimated according to Richter (Richter, Augustat & Schierbaum, 1968). In the centrifuge cells complexes (0.1 g) was dissolved in distilled water (8 cm^3). The content of the measurement cell was 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. The weight of the residue was estimated.

2.5. 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, France.

2.6. IR spectra

The spectra were recorded in thin films developed on the krs-5 crystal by evaporation of solutions. The measurement range was 650–4000 cm^{-1}. The BIO-RAD, STS — 60V spectrophotometer (USA) was employed.

2.7. UV spectra

The spectra of 10^{-3} M aqueous solutions of particular

Table 1
Characteristics of starch dialdehyde semicarbazone and its metal complexes

Central metal atom	Reaction yield (%)	Water solubility (%)	Elemental analysis			IR bonds (cm^{-1})	
			Nitrogen (%)	Metal ions		υ(C=O)	υ(C=N)
				$g\ 10^{-5}$/Ig DASSC	X^a/mol Me		
None		5.4	6.78			1680	1585
Ca	80	3.4	6.61	244	15	1664	1572
Cd	72	1.4	6.20	433	23	1663	1561
Co (II)	79	3.5	6.80	293	18	1665	1567
Cu (II)	66	4.8	6.30	890	6	1660	1547
Fe (II)	76	2.4	6.38	194	25	1668	1576
Mg	77	2.6	6.44	75	28	1682	1586
Mn (II)	63	1.8	6.45	124	40	1673	1586
Ni (II)	76	3.7	6.23	550	9	1667	1571
Pb (II)	66	4.8	6.83	1835	10	1660	1561
Zn	72	2.2	6.29	289	20	1667	1557

[a] Number of moles of semicarbazone units.

Table 2
UV absorption spectra of dialdehyde starch semicarbazone and its metal complexes

Central metal atom	λ_{max} (nm)	A	λ_{max} (nm)	A
None	231	1.4588	286	0.7484
Ca	231	1.2925	286	0.6786
Cd	231	1.4769	286	0.7724
Co (II)	231	1.4233	286	0.7234
Cu (II)	231	1.3292	286	0.6465
Fe (II)	231	1.4687	286	0.7924
Mg	231	1.4735	286	0.7644
Mn (II)	231	1.4786	286	0.7606
Ni (II)	231	1.3340	286	0.6899
Pb (II)	231	1.3215	286	0.6966
Zn	231	1.4267	286	0.7335

salts and 10^{-4} M solutions of DASSC in above solutions of salts were recorded in 10 mm quartz cells. The Shimadzu UV — 2101 PC (Japan) apparatus was used.

2.8. Thermal analysis

Samples (approximately 100 mg) were heated in open in corrundum crucibles. Range of heating was from room temperature to 500°C with the rate of temperature increase of 10 K/min. Corrundum $\varphi = 8$ μm was used as the standard. Computerised Paulik-Pulik-Edey Q-1500D instrument (Hungary) was used.

2.9. Magnetic susceptibility

It was measured using Faraday's method on a Cahn RG automatic electrobalance of own construction in a magnetic field of $H = 3.66$ kOe and temperature range from liquid nitrogen to 325 K. Weight of sample of the cobalt complex was 0.02345 g.

3. Results and discussion

Characteristics of complexes are given in Table 1.

In the IR spectra the bands near 1680 and 1580 cm^{-1} are specific for $\upsilon_{C=O}$ and $\upsilon_{C=N}$ in the semicarbazone moiety, respectively. After complexation to metal ions they shifted towards lower frequency by 12–20 cm^{-1} and 9–38 cm^{-1} for carbonyl and azine stretching modes, respectively. For small ligands corresponding shifts might reach even 30 and 50 cm^{-1}, respectively (Ibrahim, Chebli, Khan & Bouet, 1999; Kumar and Chandra, 1993b). Observed band shifts are evident in such cases common for all metal ions tested, except for Mn (II) and Mg, that chelation takes place with involvement at two of these coordination centers. Lower band shifts in the case of macro ligand studied in this project may suggest that the metal central atoms are additionally inter- and intra-molecularly coordinated to other potential O- and N-coordination centers. Coordination of the ligand to Mn (II) perturbed solely the position of $\upsilon_{C=O}$ but band of $\upsilon_{C=N}$ remained at original place. Therefore, one might assume that the Mn (II) ion was not chelated and the O-center was preferred by this ion as the coordination site. The Mg ion did not influence the position of either characteristic bands of the ligand. Therefore, that ion is considered as non-coordinating to the ligand. Ions of that metal may be sorbed on the surface of DASSC. Elemental analysis showed that from the quantitative point of view Cu (II) was most efficiently coordinated to the ligand because in the complex one Cu (II) ion was ascribed to six structural units of the macro ligand. On the contrary, one Mn (II) ion was bound in the element composed of 40 structural units of the ligand.

In the UV–Vis region of the spectra DASSC absorbs at 231 nm ($A = 1.4588$) and 286 nm ($A = 0.7484$). After complexation the absorption bands did not shift but their intensities declined to various extent. Table 2 presents the effect of coordination of DASSC to various metal ions upon the intensity of both spectral bands.

One may see that only coordination to Ca, Cu (II), Ni (II) and Pb (II) ions caused a noticeable effect on the absorption intensity. In shorter wavelengths, more intensive band was always more sensitive to the coordination. Other metal ions caused almost negligible decrease in the intensity of both spectral bands. These observations qualitatively correspond with the frequency of the coordination of these metals to DASSC. Four exceptionally spectrophotometrically active metal ions were bound to every from sixth to 15th coordination site. The other metal ions coordinated from every 18th to 40th site.

The thermal properties of metal complexes have been investigated as one of the most interesting topic in the field of coordination chemistry (Aravindakshan & Muraleedharan, 1990). DASSC retained certain hygroscopicity, which is typical for polysaccharides. It held 5.4% of humidity. All metal complexes of DASSC also contained similar amount of water (Table 3). Only magnesium sorption complex of DASSC held less water and it confirms the different character ascribed to that complex. In the temperature range 20–500°C DASSC lost 68% of its weight. The thermal decomposition of DASSC proceeded in two steps.

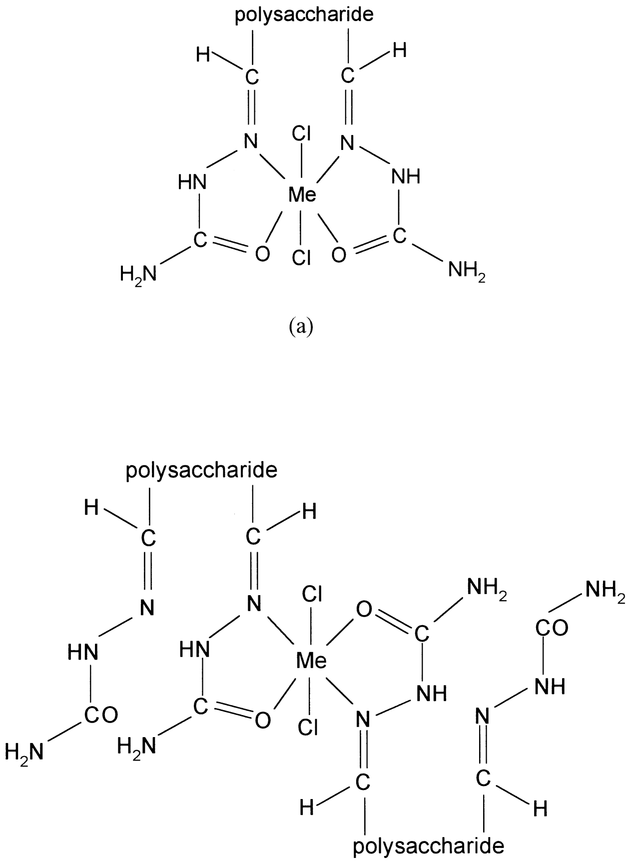
The first step at 226°C with the 23.2% weight loss can correspond to the glassy transition and decomposition of the structure as a whole. This assumption is drawn from the studies by Kapuśniak, Ciesielski, Kozioł and Tomasik (1999) as well as Tomasik, Wiejak and Bączkowicz (1986) on thermolysis of starch. The second decomposition step of DASSC, associated with the 17.4% weight loss may be related to the similar behaviour of starch on thermolysis (Kapuśniak et al., 1999; Tomasik et al., 1986). Coordination of DASSC to metal ions affects mainly its decomposition pattern with almost the same weight loss. Decomposition of complexes proceed, as a rule, in three steps. The first step for all complexes except Cu (II), Ni (II) and Pb (II) has its temperature maximum slightly higher than corresponding maximum for DASSC. Thus, one may say that complexation of DASSC with all metal ions except Cu (II), Ni (II),

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

Central metal atom	Temperature range (°C)	Corresponding weight loss (%)	Minimum of the DTG peak (°C)
None	20–165	5.4	100
	200–260	23.2	226
	260–302	17.4	277
	20–500	68.1	
Ca	20–165	4.4	100
	203–247	13.9	235
	247–275	11.6	252
	275–325	20.1	287
	20–500	71.6	
Cd	20–165	7.8	100
	200–244	12.0	233
	244–272	10.3	248
	272–318	18.3	287
	20–500	68.5	
Co (II)	20–165	7.7	100
	200–242	11.4	234
	242–268	9.4	260
	268–310	18.8	284
	20–500	69.4	
Cu (II)	20–165	4.2	100
	180–230	10.6	221
	230–270	12.0	245
	270–314	16.8	285
	20–500	64.7	
Fe (II)	20–165	7.9	100
	198–241	12.0	229
	241–270	11.5	244
	270–315	18.2	289
	20–500	74.4	
Mg (II)	20–165	2.0	100
	197–256	19.3	243
	256–266	3.8	261
	266–318	21.8	287
	20–500	68.4	
Mn (II)	20–165	6.8	100
	200–257	17.6	239
	257–276	7.3	266
	276–318	17.3	290
	20–500	70.4	
Ni (II)	20–165	7.6	100
	200–230	8.7	222
	230–268	12.9	258
	268–318	18.5	291
	20–500	69.2	
Pb (II)	20–165	6.5	100
	190–225	9.0	218
	225–269	13.6	236
	269–329	20.4	298
	20–500	68.5	
Zn (II)	20–165	5.0	100
	200–260	17.5	234
	260–281	8.1	274
	281–322	17.2	295
	20–500	68.0	

and Pb (II) stabilised the DASSC macro structure. Regardless of the metal ion in the complexes lost in this first step significantly reduces its weight. It can be rationalised in terms of the oxidative character of the decomposition of DASSC in the first step. Carboxylic groups formed at this stage could be inhibited from decarboxylation by the formation of metal carboxylates. The next decomposition step localised for all complexes between 240 and 260°C could be ascribed to thermal decomposition of these carboxylates and other concerted and consecutive processes. The third thermal effect in the case of complexes can be related to the second decomposition step of DASSC. As a rule its maximum is by 9–18°C higher than that for DASSC itself. Since it is doubtful that metal either, oxides or carbonates, could interact with matrix remaining after former decomposition of DASSC the assumption that metal ions had their influence on the course of decomposition of DASSC in the earlier steps is sound.

Generally, metal ions co-ordinated two semicarbazone ligands (Battaglia et al., 1994; Kumar & Chandra, 1993a; Patel & Agarwala, 1996; Soliman & Khattab, 1991; Souza et al., 1991). Such moieties in the case of DASSC might be available either from the same oxidised glucose unit (a) or from two different glucose units residing closely enough



(a)

(b)

Fig. 2. Potential structures of metal complexes of DASSC.

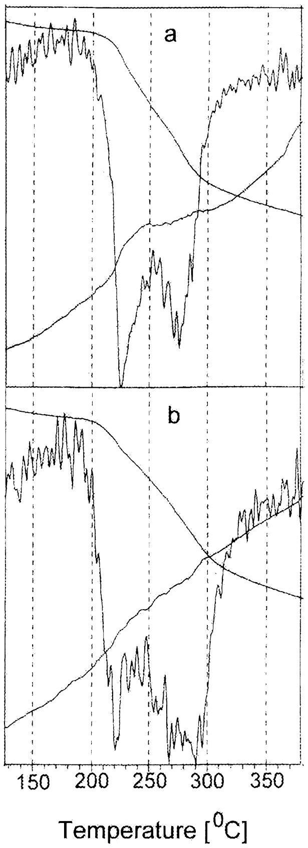


Fig. 3. Thermogram of DASSC (a) and its Ni (II) complex (b).

in the space offered for one ligand each (b) as shown in Fig. 2.

Heats of formation calculated from the energy of bonds in complexes of the (a)- and (b)-type were between −26,500 and −29,000 and −52,850 and −57,450 kJ mol^{-1}, respectively. Energies of the formation of these complexes per one bond were between −1020 and −1115 and −1150 and 1250 kJ, respectively. Calculated magnitudes were independent of the degree of substitution of the ligand with metal. DASSC average molecular weight was estimated for 1.6 kDA. The Curie constant, $C = 9.20 \times 10^{-4}$ K cm^3 g^{-1} determined for the Co (II) complex was used for the calculation of magnetic susceptibility for its potential structures (a) and (b). $M_{\rm ef}$ available were 3.4 and 4.9 BM for the (a)- and (b)-type structures, respectively. High-spin complexes with Co (II) have 4.7–5.2 BM whereas low-spin Co (II) complexes are characterised by the values of 2.2–2.7 BM (Cotton & Wilkinson, 1972). All these estimations indicated preferences for the ligation according to the (b)-pattern. However, inspection of the pattern of the thermograms of DASSC and its Ni (II) complex reveals that the main DTG peak is relatively uniform whereas the thermogram of the Ni (II) complex is rich in several transitions. It might suggest that, in fact, the complex is a combination of complexes of different structure. This variety of compounds of that mixture could be rationalised in terms of a complex polymeric structure in which all co-ordination sites may be unavailable to satisfy available co-ordination sites of the central atoms (Fig. 3).

4. Conclusions

Semicarbazone of starch dialdehyde of the 14% oxidation ligated such metal ions as Ca, Cd, Co (II), Cu (II), Fe (II), Mn (II), Ni (II), Pb (II) and Zn. The Mg anion solely sorbed and did not co-ordinate to the ligand. Degree of saturation of the ligand with metal ions was different for particular central metal atoms. Complexes with involvement of co-ordination sites belonging to two different structural units were formed rather than chelates. High-spin complexes were formed.

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