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Studies of the thermal dehydration reaction of $NiSO_4$ complexes with adenosine

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Abstract

Hydrated complexes of $NiSO_4$ with adenosine have been obtained and their thermal dehydration processes have been studied. Changes in the coordination sphere have been examined. The Ni(II) ions are in six-coordination in all the complexes. The adenosine molecules are bonded to the Ni(II) through the N-7 atom. Water molecules are bonded directly to the Ni(II) and via hydrogen bonds in the crystal lattice. Sulfate anions are linked as monodentate ligands in two of the dehydrated salts.

INTRODUCTION

Adenosine (Fig. 1), a constituent of nucleic acids, forms bonds with metal ions through nitrogen or oxygen [1, 2]; however in dehydrated complexes, the water molecules can be in competition as a ligand with both adenosine and anions. In this work, the main emphasis is placed on the synthesis of maximally hydrated nickel(II) salts with adenosine (ado). The complexes of adenosine and 9-methyladenine [3, 4] were reported to be anhydrous or dihydrated, whereas more water molecules were bonded in salts with ATP [5]. The aim of this paper is to analyse modifications in the coordination sphere brought about by thermal dehydration, because detachment of water molecules may change both the coordination number and the type of metal–ligand bonds. Adenosine may bind with metal ion through the N-7, N-3, and N-1 atoms [6–8]. The studies described here will help to clarify the preferred ligating sites of ado in the presence of water molecules. Sulfate anions [9] are able to form various types of bonds with metal ions, such as terminal or bridging, in complexes with low degrees of hydration; this will be discussed below.

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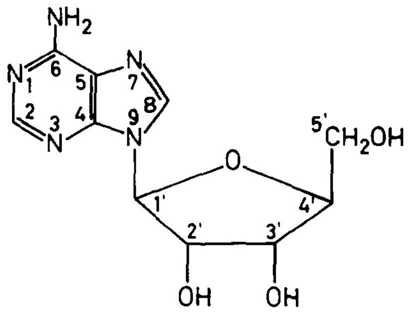

Fig. 1. Adenosine, ado.

EXPERIMENTAL

Adenosine p.a. was purchased from Reanal, Budapest and used without further purification. The $NiSO_4 \cdot 6H_2O$ p.a. was from POCH Gliwice and was used in 0.5 M water solution for syntheses. Complexes were prepared by direct reaction of aqueous solutions of $NiSO_4$ with adenosine in a 1:1, 1:2, and 1:3 ratio, as described previously [6]. Compound 2 (Table 1) was obtained by addition of 2 mmol of ado in 25 ml of hot water to 2 mmol of Ni(II) in 100 ml of ethanol. The reaction mixture was heated under reflux for 2 days. After evaporation of solvents the residue was mixed with acetone, left for 24 h, filtered and dried in a vacuum for 24 h. Synthesis in methanol solution gave compound 3. Intermediate hydrates were obtained by heating the maximally hydrated salt at constant temperatures established by analysis of the dehydration process from the DTG, DTA and TG curves. A heating temperature 5°C lower than the temperature of the onset of dehydration was chosen. Heating was discontinued when the weight of sample became constant. IR spectra were performed on an FT-IR Bruker JFS 113v spectrometer using KBr discs and 200 scans. Far-IR spectra were measured on polyethylene

TABLE 1

Results of elemental analyses

Compound	Ni (%)		C (%)		H (%)		N (%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1 $NiSO_4(ado) \cdot 7H_2O$	10.8	10.7	21.6	21.9	4.7	4.9	12.9	12.8
2 $NiSO_4(ado) \cdot 7H_2O \cdot EtOH$	9.4	9.9	24.6	24.2	5.6	5.6	12.1	11.8
3 $NiSO_4(ado) \cdot 8H_2O$	10.1	10.4	21.0	21.2	4.9	5.1	12.4	12.4
4 $NiSO_4(ado) \cdot 4H_2O$	11.6	11.9	24.5	24.3	4.4	4.3	14.5	14.2
5 $NiSO_4(ado)_2 \cdot 6H_2O$	7.1	7.4	30.4	30.1	4.6	4.8	17.3	17.6
6 $NiSO_4(ado)_2 \cdot 3H_2O$	7.8	7.9	32.0	32.3	4.4	4.3	18.7	18.8
7 $NiSO_4(ado)_3 \cdot 12H_2O$	4.8	5.0	30.3	30.7	5.2	5.4	18.0	17.9
8 $NiSO_4(ado)_3 \cdot 7H_2O$	5.4	5.4	33.0	33.3	4.8	4.9	19.0	19.4

windows and CsI discs. Electronic spectra were performed on a Specord M-40 (Carl-Zeiss Jena) with a reflection adapter, using MgO as a reference material. Thermal studies were made on an OD-102 Derivatograph (Paulik and Paulik, MOM Budapest). The atmosphere over the sample was air pumped by a water pump, the heating range was to 250°C, and the heating rate was $5°C\,min^{-1}$. Sample mass was 100 mg, the TG sensitivity was 50 mg, the reference material was Al_2O_3, and the grain size was <0.02 mm. Carbon, hydrogen and nitrogen analyses were determined by semi-microanalysis. Nickel was determined by complexometric titration with EDTA after previous mineralization of the salts. The results of the elemental analyses and the formulae of the complexes are presented in Table 1.

RESULTS AND DISCUSSION

Thermal analysis

The results of the thermal analyses are listed in Table 2. The dehydration starts at 51–65°C, the water molecules being lost in a two-step process. At least three water molecules become detached in the first step, which is connected with the dissociation of water molecules that can be bonded either directly to the metal ion or via hydrogen bonds in the crystal lattice. The second step of the dehydration reaction coincides with the decomposition of ado, which is why anhydrous salts could not be isolated. Intermediate hydrates (compounds 4, 6, 8) were obtained which

TABLE 2

Results of thermal analyses

Compound	Heat effect	Temperature (°C)			Weight loss (%)		Number of water molecules lost
		T_i	T_m	T_f	Found	Calc.	
1 $NiSO_4$(ado) · $7H_2O$	Endo	58	84	–			
	Endo	–	120	172	16.2	16.42	5
2 $NiSO_4$(ado) · $7H_2O$ · EtOH	Endo	37	112	125	7.8	7.74	EtOH
	Endo	–	155	182	9.4	9.09	3
	Exo	195	dec.	–	–	–	– [a]
3 $NiSO_4$(ado) · $8H_2O$	Endo	51	115	178	12.5	12.72	4
	Endo	185	dec.	–	–	–	– [a]
4 $NiSO_4$(ado) · $4H_2O$	Endo	190	dec.	–	–	–	– [a]
5 $NiSO_4(ado)_2$ · $6H_2O$	Endo	65	115	145	7.0	6.77	3
	Endo	165	dec.	–	–	–	– [a]
6 $NiSO_4(ado)_2$ · $3H_2O$	Endo	203	dec.	–	–	–	– [a]
7 $NiSO_4(ado)_3$ · $12H_2O$	Endo	55	128	182	7.8	7.68	5
	Endo	195	dec.	–	–	–	– [a]
8 $NiSO_4(ado)_3$ · $7H_2O$	Endo	182	dec.	–	–	–	– [a]

[a] Decomposition of ado prevents calculation of the H_2O loss.

contain 4, 3, and 7 water molecules. In these compounds, the water molecules remain bonded until the onset of adenosine decomposition, which occurs at about 210°C; from that temperature the mass loss on the DTG and TG curves is connected with an exothermic peak on the DTA curve. The decomposition of the free adenosine was found in 220–275°C range. A decrease in the decomposition temperature of ado has been observed previously for Ni(II) halide salts with ado [6–8] and can be caused by the influence of metal–ligand bonds and of the hydrogen-bonding network on the adenosine molecular bonds. The salts under discussion here are more hydrated than Ni(II) halide hydrates with adenine [10, 11]. Higher hydration degrees can be stabilized by the stronger hydrogen-bond network in the presence of ado and the sulfate anion. The DTA curve of compound 2 exhibits endothermic peaks which are related to the loss of one ethanol and three water molecules, whereas an exothermic peak above 195°C relates to the decomposition of ado. The proposed reaction mechanism had been proved by the isolated salt, compound 4.

Electronic spectra

The band positions and the calculated electronic parameters are given in Table 3. The electronic spectra of Ni(II) complexes in pseudo-octahedral symmetry exhibit three bands deriving from the transitions $^2A_1 \rightarrow {}^3T_{2g}(F)\nu_1$, $^2A_{2g} \rightarrow {}^3T_{1g}(F)\nu_2$, and $^3A_{1g} \rightarrow {}^3T_{1g}(P)\nu_3$. The calculated

TABLE 3

Electronic spectral parameters (cm^{-1})

Compound	ν_1 [a]	ν_2	ν_3	B [a]
1 $NiSO_4(ado) \cdot 7H_2O$	8180	13700	25250	9620
2 $NiSO_4(ado) \cdot 7H_2O \cdot EtOH$	8000	13450 14900	25200	9770
3 $NiSO_4(ado) \cdot 8H_2O$	8070	13550 14650	25150	9200
4 $NiSO_4(ado) \cdot 4H_2O$	7900	13250 14300	24450	9330
5 $NiSO_4(ado)_2 \cdot 6H_2O$	8360	14000 15400	25650	9710
6 $NiSO_4(ado)_2 \cdot 3H_2O$	7750	13000 14550	24100	9230
7 $NiSO_4(ado)_3 \cdot 12H_2O$	8100	13600 14750	25300	9730
8 $NiSO_4(ado)_3 \cdot 7H_2O$	7810	13100 14200	24200	9240

[a] Calculated from equations: $340Dq^2 - 18(\nu_2 + \nu_3)Dq + \nu_2\nu_3 = 0$; $B = \nu_2 + \nu_3 - 30Dq/15$.

and observed spectral parameters [12, 13] confirm that the Ni(II) ions are in six-coordination before and after the thermal dehydration reaction.

IR spectra analysis

The IR spectra of adenine, adenosine and their complexes have been discussed by many authors [3–5, 14–22]. Band frequencies and assignments are shown in Table 4. The absorption bands in the ranges 1675–1685 and 1654–1660 cm^{-1} indicate that adenosine is not bonded with Ni(II) by means of the N-1 or $-NH_2$ [5, 19, 22]. The absorption bands at 1606, 1573 and 1506 cm^{-1} in the free ado spectrum, show no major changes in the studied spectra (Table 4). Beauchamp and coworkers [23–27] observed similar positions of these bands in the spectra of CH_3Hg complexes, where N-7- and N-9-bonded adenine was found and structures confirmed by X-ray analysis. The same type of ado coordination can be proposed for the studied salts. Moreover the position of the bands at 1475 and 1425 cm^{-1} are close to those observed in the spectra of Ni(II) complexes with nucleosides and nucleotides [5, 28, 29] where M–N-7 bonds were present. Analysis of the water deformation vibrations (1680–1630 cm^{-1}) is difficult due to their overlapping with $-NH_2$ deformation bands. In the analyzed spectra, the coordinated water molecules show libration bands [9] from rocking and wagging at 724–714 cm^{-1} and 575–556 cm^{-1}.

Spectra of the maximally hydrated and of some of the dehydrated salts show single ν_4 and ν_3 bands from sulfate vibrations (Table 4), which suggests that there are no direct bonds between metal ion and sulfate. The spectra of compounds 4 and 6 exhibit doubly split ν_3 and ν_4 bands and, in addition, single bands arising from ν_1 at 960 and 965 cm^{-1} and ν_2 at 428, and 430 cm^{-1} occur, which can be connected with $Ni–OSO_3$ bonds.

The Ni–N(ado) stretching vibration bands occur in the 242–228 cm^{-1} range, as in the reported spectra of Ni complexes with ado and adenine [3, 4, 6–8, 22]. The medium intensity bands observed in all spectra at around 380 cm^{-1} can be assigned to $Ni–O(H_2O)$ stretching vibrations. The observed frequencies are identical with previously assigned bands in the spectra of Ni(II) hydrates [30] and of complexes of ado and adenine [6–8, 10, 11]. The $Ni–OSO_3$ stretching vibrations bands in the studied spectra for the pseudo-octahedral symmetry can be assigned tentatively to about 250 cm^{-1}.

From vibrational spectra analysis, the most probable structure is six-coordination with adenosine bonded via N-7, with water molecules being bonded in the coordination sphere and by means of hydrogen bondings in the crystal lattice. Thermal dehydration does not change the coordination number; the adenosine is bonded in the same way as in the maximally hydrated salts. The formulae for compounds 1, 2, 3, 5, 7 and 8

TABLE 4

Characteristic IR spectral frequencies (cm^{-1}) [a]

Adenosine	$NiSO_4(ado) \cdot 7H_2O$	$NiSO_4(ado) \cdot 7H_2O \cdot EtOH$	$NiSO_4(ado) \cdot 8H_2O$	$NiSO_4(ado) \cdot 4H_2O$	$NiSO_4(ado)_2 \cdot 6H_2O$	$NiSO_4(ado)_2 \cdot 3H_2O$	$NiSO_4(ado)_3 \cdot 12H_2O$	$NiSO_4(ado)_3 \cdot 7H_2O$	Assignments
1662s	1654s	1656s	1658s	1660s	1655s	1660s	1656s	1658s	$-NH_2$ def
1606s	1612s	1614s	1610s	1604s	1611s	1605s	1615s	1612s	Pyr. ring skel
1573s	1570s	1569s	1566s	1572m	1568s	1574m	1572m	1570m	Im. ring skel
1506m	1509m	1508m	1510m	1505w	1508m	1504w	1509m	1507m	Im. ring skel
1475s	1488s	1486s	1495s	1497s	1492s	1485s	1493s	1496s	N-7–C-8
1425m	1432s	1434s	1429m	1436s	1431m	1438s	1430s	1432s	C-8–H
	724m	718m	720w	714w	715m	719w	722w	723w	H_2O rock
	565m	568m	575m	556m	560m	564m	569w	558m	H_2O wag
	234w	228w	232w	240w	233w	242w	233w	235w	Ni–N
	385m	382m	379m	388m	385m	386m	383m	384m	Ni–O(H_2O)
	252m	256m	255m	248m	250m	253m	256m	250m	Ni–OSO_3
	1124s	1110s	1105s	1080s	1118s	1075s	1105s	1110s	$\nu_3(SO_4)$
				1130s		1125s			
	618m	623m	620m	634m	625m	634m	630m	628m	$\nu_4(SO_4)$
				652s		658m			

[a] Key: s, strong; m, medium; w, weak; sh, shoulder.

can be written as $[Ni(ado)_{1-3}(H_2O)_{5-3}]SO_4 \cdot nH_2O$, where $n = 2, 2, 3, 2, 9$ and 4, respectively. The dehydrated salts, compounds 4 and 6, are $[Ni\text{-}(OSO_3)ado(H_2O)_4]$ and $[Ni(OSO_3)(ado)_2(H_2O)_3]$, respectively.

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