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Studies of the thermal dehydration reaction of $Ni(ClO_4)_2$ complexes with adenosine

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Abstract

Hydrated complexes of $Ni(ClO_4)_2$ 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 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. Perchlorate anions are linked as a monodentate ligand in 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 the detachment of water molecules may change both the coordination number and 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. The studied perchlorate complexes of adenine [9], adenosine [10], theophylline [11] and guanine [12] showed different ways of anion and amine binding. Perchlorate anions are able to form various types of bonds with metal ions, such as terminal or bridging, in complexes with low degrees of hydration [13]; this will be discussed below.

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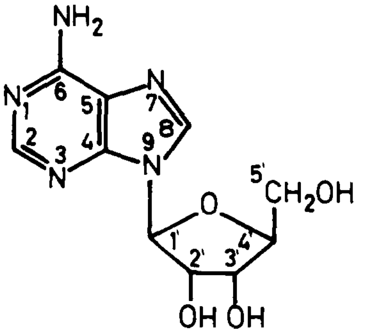

Fig. 1. Adenosine (ado).

EXPERIMENTAL

Adenosine p.a. grade was purchased from Reanal, Budapest and used without further purification. The $Ni(ClO_4)_2 \cdot 6H_2O$ was obtained from nickel carbonate and $HClO_4$ p.a. grade, both from POCh Gliwice, using 0.5 M solution in water for syntheses. Complexes were prepared by reaction of aqueous solutions of $Ni(ClO_4)_2$ with adenosine in 1:1, 1:2 or 1:3 ratio as described previously [6]. Salt 4 (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 solution was heated under reflux for 8 h. After evaporation of solvents, the residue was treated with acetone left for 24 h, filtered off and dried in vacuo for 24 h. Synthesis in aqueous methanol gave salt 1. Intermediate hydrates were obtained by heating the maximally hydrated salt at a constant temperature established by analysis of the DTG, DTA and TG curves of the dehydration process. The heating temperature was chosen 20°C higher than the temperature of onset of dehydration. Heating was discontinued when the weight of the sample

TABLE 1

Results of elemental analysis

Compound	Ni (%)		C (%)		H (%)		N (%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1 $Ni(ClO_4)_2(ado) \cdot 6H_2O$	9.3	9.3	19.1	19.0	3.8	4.0	11.3	11.1
2 $Ni(ClO_4)_2(ado) \cdot 2H_2O$	10.1	10.5	21.6	21.4	3.2	3.0	12.2	12.5
3 $Ni(ClO_4)_2(ado) \cdot 3H_2O$	9.8	10.1	21.0	20.7	3.4	3.3	11.8	12.1
4 $Ni(ClO_4)_2(ado) \cdot 6H_2O \cdot C_2H_5OH$	8.7	8.6	21.0	21.2	4.5	4.6	10.1	10.3
5 $Ni(ClO_4)_2(ado)_2 \cdot 5H_2O$	6.4	6.7	27.1	27.2	4.0	4.1	15.6	15.9
6 $Ni(ClO_4)_2(ado)_2 \cdot 2H_2O$	7.3	7.1	28.8	29.0	3.4	3.6	17.3	16.9
7 $Ni(ClO_4)_2(ado)_3 \cdot 5H_2O$	5.4	5.1	31.7	31.3	4.5	4.3	18.1	18.3
8 $Ni(ClO_4)_2(ado)_3 \cdot 2H_2O$	5.2	5.4	32.8	32.9	4.3	3.9	19.6	19.3

became constant. IR spectra were recorded on a Bruker JFS 113v FT-IR spectrometer using KBr discs and 200 scans. Far IR spectra were measured with a polyethylene window and CsI discs. Electronic spectra were obtained on a Specord M-40 (Carl-Zeiss Jena) with reflection adapter and with MgO as a reference material, or in the range 11 500–7000 cm^{-1} on a Specord NIR (Carl-Zeiss Jena) using samples in a nujol mull on Whatman 1 chromatographic paper. Thermal studies were made with 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 up to 250°C, and the heating rate was 2.5°C min^{-1}. Other parameters were sample mass 50 mg, TG sensitivity 50 mg, reference material Al_2O_3, grain size <0.06 mm. The C, H, N, analyses were performed by semi-microanalysis. Nickel was determined by complexometric titration with EDTA after mineralisation 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

Results of the thermal analyses are shown in Table 2. The dehydration starts at 48–55°C as an endotherm. At least three water molecules are lost in a one-step process. This process is much slower than in the other

TABLE 2

Results of thermal analysis

Compound	Heat effect	Temperature range (°C)			Weight loss (%)		Number of detached molecules
		T_i	T_m	T_f	Found	Calc.	
1 $Ni(ClO_4)_2(ado) \cdot 6H_2O$	Endo	55	92	173	11.1	11.4	$4H_2O$
	Exo	176	dec.	–			
2 $Ni(ClO_4)_2(ado) \cdot 2H_2O$	Endo	141	172	180	3.6	3.2	$1H_2O$
	Exo	192	dec.[a]	–			
3 $Ni(ClO_4)_2(ado) \cdot 3H_2O$	Endo	92	166	182	9.7	9.3	$3H_2O$
	Exo	188	dec.				
4 $Ni(ClO_4)_2(ado) \cdot 6H_2O \cdot C_2H_5OH$	Endo	32	60–91	110	7.0	6.8	C_2H_5OH
	Exo	120	192	dec.	7.9	8.0	$3H_2O$
5 $Ni(ClO_4)_2(ado)_2 \cdot 5H_2O$	Endo	49	117	168	6.5	6.1	$3H_2O$
	Exo	170	dec.	–			
6 $Ni(ClO_4)_2(ado)_2 \cdot 2H_2O$	Endo	155	173	192	4.2	4.3	$2H_2O$
7 $Ni(ClO_4)_2(ado)_3 \cdot 5H_2O$	Endo	48	108–115	163	5.0	4.7	$3H_2O$
	Exo	168	dec.	–			
8 $Ni(ClO_4)_2(ado)_3 \cdot 2H_2O$	Endo	157	178	186	3.6	3.3	$2H_2O$
	Exo	203	dec.				

[a] With explosion above 198°C.

adenosine complexes [6–8]. The TG curve has a line shape with low slope and without discrete sharp steps connected with the mass loss. The position of the maximum on the DTG for two salts extends over about 10°C, which points to a slow rate of dehydration. The dehydration process coincides with the decomposition of ado, which is connected with an exotherm on the DTA curve. Detached water molecules come both from positions adjacent to Ni(II) and from the crystal lattice, where they are bonded via a hydrogen bonding network. The anhydrous salts could not be isolated owing to the decomposition of ado. Intermediate hydrates were obtained with at least two water molecules. In these compounds, water molecules are bonded up to the onset of adenosine decomposition, which occurs around 190–203°C; from that temperature, the mass loss on the DTG and TG curves corresponds to an exotherm on the DTA curve. Free adenosine decomposes from 220°C. A decrease in the decomposition temperature has been observed previously for Ni(II) halide salts with ado [6–8], and may be caused by the influence of metal–ligand bonds and of the hydrogen-bonding network on the adenosine molecular bonds. The higher degree of hydration for the studied salts than for the adenine complexes [14, 15] may be stabilized by the stronger hydrogen bond network in the presence of ado and perchlorate anion. The DTA curve of salt 4 exhibits an additional endotherm which is connected with the loss of one ethanol molecule followed by dissociation of three water molecules. The proposed reaction mechanism was proved by means of the isolated salt 3.

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 $^3A_1 \rightarrow {}^3T_{2g}(F)\nu_1$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)\nu_2$, and $^3A_{1g} \rightarrow {}^3T_{1g}(P)\nu_3$. The ν_1 frequency ($10Dq$) has been calculated by the Underhill method [16] in which Dq and B parameters are determined from the ν_2 and ν_3 electronic spectral bands for Ni(II) in pseudo-octahedral or tetrahedral symmetry. The calculated values for the maximally hydrated compounds gave evidence that Ni(II) ions are in six-coordination [17]. Spectra of the dehydrated salts show bands which allow one to state that Ni(II) retains the coordination number. The changes of the ν_2 and ν_3 frequencies in comparison with the starting hydrates can be assumed to result from variation of the ligand field strength. Such shift to lower frequency is caused by the substitution of ligands such as water by ado and perchlorate.

TABLE 3

Electronic spectral parameters (cm^{-1})

Compound	ν_3	ν_2	ν_1	Dq [a]	B [a]
1 $Ni(ClO_4)_2(ado) \cdot 6H_2O$	25900	13900 15200	8500	876	944
2 $Ni(ClO_4)_2(ado) \cdot 2H_2O$	25600	13300 15500	–	867	932
3 $Ni(ClO_4)_2(ado) \cdot 3H_2O$	25000	13500 15500	–	881	871
4 $Ni(ClO_4)_2(ado) \cdot 6H_2O \cdot C_2H_5OH$	25300	13500 15400	8400	874	910
5 $Ni(ClO_4)_2(ado)_2 \cdot 5H_2O$	25600	13200 15100	8200	848	947
6 $Ni(ClO_4)_2(ado)_2 \cdot 2H_2O$	25600	13300 15500	–	867	932
7 $Ni(ClO_4)_2(ado)_3 \cdot 5H_2O$	25500	13000 14000	8300	834	932
8 $Ni(ClO_4)_2(ado)_3 \cdot 2H_2O$	25500	13200 15100	–	851	941

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

Infrared spectral analysis

The IR spectra of adenine, adenosine and their complexes have been discussed by many authors [3–5, 18–26]. Although adenosine is potentially a polydentate ligand, it binds with metal ions mostly as a monodentate ligand via N-7. Evidence of this is provided by the spectrum of ado in the range 1800–500 cm^{-1}. Band frequencies and assignments to the appropriate vibrations are shown in Table 4. An absorption band at 1712 cm^{-1} in free ado is shifted to 1685–1675 cm^{-1} in the studied salts. Theophanides [5] connected the same finding with the absence of a direct M–N-1 bond. A band associated with $-NH_2$ deformation vibrations appears at 1660–1654 cm^{-1}, and similar frequencies have been found in the spectra of complexes with 9-methyladenine [23] and adenine [26], for which $M-NH_2$ bonds were excluded. Absorption bands at 1606, 1573 and 1506 cm^{-1} in the free ado spectrum, assigned to pyrimidine and imidazole skeletal vibrations, show no drastic changes (Table 4). Beauchamp and co-workers [27–31] analysed the positions of these bands and resolved the crystal structure of the complexes with one, two and three $MeHg^+$ moieties with adenine. The observed frequencies are similar to those found in $MeHg^+$ compounds where adenine had been metallated at N-7 and N-9. Coordination via N-7 can be proposed for the studied salts. Also, the positions of the bands at 1475 and 1425 cm^{-1} are close to those

TABLE 4

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

Adenosine	$Ni(ClO_4)_2$-(ado) · $6H_2O$	$Ni(ClO_4)_2$-(ado) · $2H_2O$	$Ni(ClO_4)_2$-(ado) · $3H_2O$	$Ni(ClO_4)_2$(ado) · $6H_2O$ · C_2H_5OH	$Ni(ClO_4)_2$-(ado)$_2$ · $5H_2O$	$Ni(ClO_4)_2$-(ado)$_2$ · $2H_2O$	$Ni(ClO_4)_2$-(ado)$_3$ · $5H_2O$	$Ni(ClO_4)_2$-(ado)$_3$ · $2H_2O$	Assignments
1712s	1690s	1692s	1688s	1692m	1688s	1692s	1687s	1689s	
1662s	1655s	1658s	1656s	1654s	1658s	1656s	1654s	1656s	δNH_2
1606s	1605s	1604s	1603s	1603s	1604s	1602s	1602s	1603s	Pyr. ring
1573s	1584m	1586s	1580s	1572s	1580s	1576m	1575m	1577m	Pyr. ring
1506s	1512w	1518w	1508m	1510w	1502s	1504m	1504m	1505w	Im. ring
1475m	1490m	1489m	1487m	1488m	1491m	1488m	1485m	1479m	N-7–C–
1425m	1432m	1438m	1435m	1434m	1430m	1432m	1433m	1436m	C-8–H–
1333s	1340w		1334m	1338w	1336m	1335m	1335m	1332m	Pyr. + im.
1303s	1310w	1318m	1308w	1309w	1312m	1308m	1306m	1306w	Pyr. + im.
	1640s	1646s	1644s	1642s	1644s	1638m	1638m	–	δH_2O
	724w	722m	719m	723m	715w	718w	716w	720w	ρH_2O
	558w	554m	560m	554m	570m	558m	552m	560m	ωH_2O
	1105s	1090s	1085s	1090–1110s	1108s	1078s	1080–1130s	1075s	$\nu_3 ClO_4$
		1125s	1122s			1125s		1125s	
	636m	628s	622s	628s	632s	624s	625s	626	$\nu_4 ClO_4$
		640s	639s			642s		640s	
		940m	938s			942s		938s	$\nu_1 ClO_4$
		462m	460m			465m		467m	$\nu_2 ClO_4$
	386m	396m	390m	380m	382m	390m	384m	395m	Ni–OH_2
		298m	292m			296m		299m	Ni–$OClO_3$
	236m	244m	240w	235w	232w	238w	244w	243w	Ni–N
		234w							

Key: s, strong; m, medium; w, weak; δ, deformation; ρ, rocking; ω, wagging; ν_3, asym. stretching Cl–O; ν_1, sym. stretching Cl–O; ν_4, sym. def. ClO_2; ν_2, asym. def. ClO_2; pyr., pyrimidine; im., imidazole.

observed in the spectra of nickel(II) complexes with nucleosides and nucleotides [5, 32, 33] where M–N-7 bonds are present.

The spectrum of $Ni(ClO_4)_2(ado) \cdot 2H_2O$ (salt 2) in the 1400–1000 cm^{-1} range differs significantly from the others. A pair of bands at 1335 and 1305 cm^{-1} assigned to purine ring vibrations [15, 27] appears as a single band at 1318 cm^{-1}. The 1252 and 1127 cm^{-1} bands are shifted to 1290 and 1162 cm^{-1} respectively. The same shift has been observed in the spectra of $[(MeHg)_3(ad)]NO_3$ [25], and the crystal structure of this complex [28] has proved the presence of N-9, N-7, N-3 bonded adenine. The same ligating sites are the most probable in salt 2.

Analysis of the water deformation vibrations is difficult because of their overlap with $-NH_2$ deformation bands, which usually appear in the 1680–1630 cm^{-1} range. Coordinated water molecules show vibrational bands due to libration: rocking, wagging and twisting [13]. In the presented spectra, rocking and wagging vibration bands appeared in the ranges 728–710 and 560–550 cm^{-1} respectively. The above discussion leads to the assertion that ado molecules are bonded with Ni(II) through N-7 whereas water molecules are bonded directly to the metal ion, or by means of hydrogen bonds in the crystal lattice.

Perchlorate as a free anion possesses T_d symmetry and its IR spectra exhibits only two bands from the T_2 type vibrations at 1110 cm^{-1} (ν_3) and 630 cm^{-1} (ν_4) [13]. Spectra of the maximally hydrated compounds show single ν_4 and ν_3 bands in the range 640–620 cm^{-1} and 1130–1105 cm^{-1} respectively, from which we can state that perchlorate ions are not bonded directly to the metal ion. Spectra of the dehydrated salts exhibit doubly split ν_3 and ν_4 bands, and single bands arise from ν_1 and ν_2 vibrations at 930 and 460 cm^{-1} (Table 4). These bands point to lowering of the perchlorate symmetry from T_d to C_{3v} [13]. The lower symmetry of the anion is caused by the $Ni-OClO_3$ bond, which has been formed in place of the previously existing $Ni-OH_2$ bonds.

A list of the observed bands in the region 500–100 cm^{-1} is shown in Table 4. The Ni–N(ado) stretching vibration bands arise in the range 250–225 cm^{-1}, as had been found in the reported spectra of Ni–N(adenine) and Ni–N(ado) complexes [3, 4, 6–8, 26]. Because the positions of metal–ligand vibrational bands depend on coordination number [13], and spectra of the dehydrated salts exhibit bands in positions similar to those before dehydration reaction, this fact supports the assumption that there is no change of the coordination number. The medium intensity bands observed in all spectra at 390 cm^{-1} can be assigned to $Ni-O(H_2O)$ stretching vibrations according to previously found bands in the spectra of Ni(II) hydrates [34], adenine and ado complexes [6–8, 14, 15]. $Ni-OClO_3$ stretching vibration bands in the studied spectra for pseudo-octahedral symmetry can be assigned tentatively at about 290 cm^{-1} [35].

From analysis of the vibrational spectra, the most probable structure is six-coordination with adenosine bonded via N-7 and with water molecules bonded in the coordination sphere and by means of hydrogen bonding in the crystal lattice. Thermal dehydration does not change the coordination number, and adenosine is bonded in the same way as in the maximally hydrated salts. The metal environment for salts 1, 5 and 7 should be written as $[Ni(ado)_{1-3}(H_2O)_{5-3}](ClO_4)_2 \cdot nH_2O$, where $n = 1$, 1 and 2, whereas that for salt 4 is $[Ni(ado)(H_2O)_5](ClO_4)_2 \cdot H_2O \cdot C_2H_5OH$. The general formulae of dehydrated salts 2, 3, 6 and 8 can be written as $[Ni(OClO_3)_2 \cdot \mu\text{-}(ado)(H_2O)]$, $[Ni(OClO_3)_2(ado)(H_2O)_3]$, $[Ni(OClO_3)_2(ado)_2(H_2O)_2]$ and $[Ni(OClO_3)_2(ado)_3(H_2O)] \cdot H_2O$.

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