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Studies of the thermal dehydration reaction of NiI_2 complexes with adenosine

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Abstract

Hydrated complexes of NiI_2 with adenosine have been obtained and their thermal dehydration processes have been investigated. Changes in the coordination sphere have been studied. In all the salts, the Ni(II) ions are in six-coordination. The adenosine molecules are bonded to the Ni(II) through the N-7 atom, whereas the water molecules are bonded directly to the Ni(II) and via hydrogen bonds in the crystal lattice. Iodide anions are bonded to the metal ion in the terminal positions.

INTRODUCTION

Adenosine (Fig. 1), a constituent of nucleic acids, forms bonds with metal ions through nitrogen or oxygen [1,2]; however in hydrated 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, as detachment of water molecules may change both the coordination number and the type of metal–ligand bonds. Adenosine may bind with metal ions through the N-7, N-3 and N-1 atoms [6]. The studies described here will help to clarify the

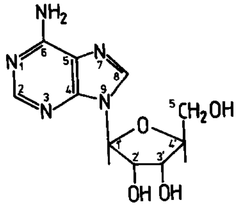

Fig. 1. Adenosine (ado).

preferred ligating sides of ado. Anions are able to form various types of bonds with metal ions, such as terminal or bridging bonds, in complexes with low hydration degrees; this will be discussed below.

EXPERIMENTAL

Adenosine p.a. was purchased from Reanal, Budapest and used without further purification. NiI_2 was prepared by reacting HI, freshly distilled from $NaHPO_2$, with $NiCO_3$ (p.a.) in 0.5M water solution for syntheses. Complexes were prepared by direct reaction in water of the NiI_2 solution with adenosine in a 1 : 1, 1 : 2, 1 : 3 ratio, as described previously [6]. Dehydrated salts were prepared by heating the hydrated salt at the temperature established by analysis of the DTG, DTA and TG curves of the dehydration process. IR spectra were performed on a Nicolet 5DXB FTIR spectrometer using KBr discs and 200 scans. Far-IR spectra were measured on a Perkin–Elmer 180 spectrophotometer using CsI discs. Electronic spectra were performed on a Specord M-40 (Carl–Zeiss Jena) with reflection adapter, with MgO as reference material. Thermal studies were made on an OD-102 Derivatograph (Paulik and Paulik, MOM Budapest). The atmosphere over the sample was air, pumped using a water pump, the heating range was up to 250 °C and the heating rate was 5 °C min^{-1}. The sample mass was 200 mg and the sensitivities were TG, 50 mg; DTA and DTG, 1/3 of the total effect. The reference material was Al_2O_3. The C, H, N analyses were determined by semi-microanalysis.

Nickel was determined by complexometric titration with EDTA after previous mineralisation of the salts. The dehydrated salts were obtained by heating the hydrated salts at a constant temperature established by analysis of the DTA, DTG and TG curves of the dehydration process; the temperature chosen for heating was 5 °C lower than the temperature of the onset of dehydration. The heating was discontinued when the weight of sample became constant. The results of the elemental analyses and the stoichiometric formulae of the salts are presented in Table 1.

TABLE 1

Results of elemental analysis

Compound	Ni (%)		C (%)		H (%)		N (%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc
$NiI_2(ado)\cdot 7H_2O$	8.4	8.3	16.8	17 0	3.7	4.0	9.8	9.9
$NiI_2(ado)\cdot 3H_2O$	9.4	9.3	18 8	18.9	3.0	3 2	11 1	11.0
$NiI_2(ado)_2\cdot 5H_2O$	6 1	6 3	25.4	25.6	4 1	3.8	14 7	14 9
$NiI_2(ado)_2\cdot 2H_2O$	6 4	6 6	27.4	27.2	3 8	3.6	15.8	15.7
$NiI_2(ado)_3\cdot 7H_2O$	4 6	4 7	28.8	29.0	4 3	4.5	16.4	16.9
$NiI_2(ado)_3\cdot H_2O$	5.0	5.2	32.0	31 8	3.5	3 9	18 1	18.5

RESULTS AND DISCUSSION

Thermal analysis

The results of the thermal analysis are presented in Table 2.

The dehydration starts at 50–58 ° C; water molecules are lost in a one-step process. At least three water molecules become detached in this step, which is connected with the dissociation of the water molecules that can be bonded directly to metal ions or via hydrogen bonds in the crystal lattice. The second step of the dehydration reaction is associated with the decomposition of ado, which is why anhydrous salts could not be isolated. Intermediate hydrates were obtained which contain between 3 and 1 water molecules. In these compounds, the water molecules remain bound until the onset of adenosine decomposition, which occurs above 170 ° 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 free adenosine occurs in the 220–275 ° C range. Such a significant decrease in decomposition temperature has been observed previously in $NiCl_2$ (ado) salts [6] and can be ascribed to the influence of the metal–ligand bonds and of the hydrogen-bonding network on the adenosine molecular bonds. In comparison to $NiCl_2$ and $NiBr_2$ hydrates with adenosine [7], the salts under discussion are more hydrated. For the compounds studied, the dehydration reactions can be presented as

$$NiI_2(ado) \cdot 7H_2O \rightarrow NiI_2(ado) \cdot 3H_2O + 4H_2O \tag{1}$$

$$NiI_2(ado)_2 \cdot 5H_2O \rightarrow NiI_2(ado)_2 \cdot 2H_2O + 3H_2O \tag{2}$$

$$NiI_2(ado)_3 \cdot 7H_2O \rightarrow NiI_2(ado)_3 \cdot H_2O + 6H_2O \tag{3}$$

TABLE 2

Results of thermal analysis

Compound	Temperature range (° C)			Weight loss (%)		Number of detached water molecules
	T_i	T_m	T_f	Found	Calc	
$NiI_2(ado) \cdot 7H_2O$	55	90	145	11.0	10.5	4
$NiI_2(ado) \cdot 3H_2O$	122	185	dec.	–	–	–
$NiI_2(ado)_2 \cdot 5H_2O$	58	85	150	6 1	5.8	3
$NiI_2(ado)_2 \cdot 2H_2O$	114	190	dec.	–	–	–
$NiI_2(ado)_3 \cdot 7H_2O$	50	95	145	9.0	8.5	6
$NiI_2(ado)_3 \cdot H_2O$	106	195	dec.	–	–	–

TABLE 3

Electronic spectral parameters (cm^{-1})

Compound	ν_3	ν_2	ν_1 [a]	B [a]
$NiI_2(ado)\cdot 7H_2O$	27300	13700	8063	1121
$NiI_2(ado)_2\cdot 5H_2O$	26500	12700	7429	1127
$NiI_2(ado)_3\cdot 7H_2O$	26500	13500	7963	1075

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

Electronic spectra

The band positions and the calculated electronic parameters are given in Table 3. The electronic spectra of nickel(II) complexes in pseudo-octahedral symmetry exhibit three bands deriving from the transitions ${}^3A_{1g} \rightarrow {}^3T_{2g}(F)\nu_1$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)\nu_2$ and ${}^3A_{1g} \rightarrow {}^3T_{1g}(P)\nu_3$. The ν_1 frequency ($10Dq$) has been calculated by the Underhill [8] method in which the Dq and B parameters are determined from the ν_2 and ν_3 electronic spectral bands for nickel(II) in pseudo-octahedral or tetrahedral symmetry. The values thus obtained for the spectra of maximally hydrated salts show that the nickel(II) ions are in pseudo-octahedral symmetry [9]. The spectra of the dehydrated salts in the range above 20000 cm^{-1} exhibit complicated shapes, most probably arising from CT transitions in the presence of iodide anions [10]. This makes it impossible to isolate the ν_3 band, only ν_2 can be found at around 14100 cm^{-1}. The coordination number is most probably six, as in the maximally hydrated salts.

IR spectral analysis

The IR spectra of adenine, adenosine and their complexes have been investigated by many authors [3–5, 11–19]. Although adenosine is potentially a polydentate ligand, it binds with metal ions mostly as a monodentate ligand via the N-7. Evidence of this fact is provided by the spectrum of ado in the 500–1800 cm^{-1} range. Band frequencies and assignments to proper vibrations are shown in Table 4. An absorption band at 1712 cm^{-1} in free ado is shifted to 1682–1690 cm^{-1} in the studied salts; Tajmir-Riahi et al. [5] have associated this with the absence of a direct M–N-1 bond. A band associated with $-NH_2$ deformation vibrations appears at 1650–1659 cm^{-1} and a similar frequency of $-NH_2$ vibrations has been found in the spectra of complexes with 9-methyladenine [16] and adenosine [19], where $M-NH_2$ bonds were excluded.

The 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 [20–24] have analysed the positions of these bands and determined the crystal structure of the

TABLE 4

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

Adenosine	$NiI_2(ado) \cdot 7H_2O$	$NiI_2(ado) \cdot 3H_2O$	$NiI_2(ado)_2 \cdot 5H_2O$	$NiI_2(ado)_2 \cdot 2H_2O$	$NiI_2(ado)_3 \cdot 7H_2O$	$NiI_2(ado)_3 \cdot H_2O$	Assignments
1712s	1684m	1688m	1685m	1688m	1682m	1690sh	N-1 proton ado
1662s	1655s	1659s	1656s	1660s	1655s	1660s	NH_2 def.
1606s	1610s	1608s	1609s	1609s	1606s	1612s	Pyrim. ring skel.
1573s	1574m	1578m	1574m	1575m	1578m	1574m	Imid. ring skel.
1506m	1508m	1511m	1506m	1510m	1508m	1512m	Pyrim. ring skel.
1475s	1489s	1495s	1490s	1492s	1488s	1495s	N-7–C–
1425m	1436s	1439s	1435s	1438s	1434s	1440s	C-8–H
1333s	1335s	1340m	1336s	1342m	1337m	1341m	Pyrim. ring
1303s	1309s	1306m	1305m	1308m	1306m	1310m	Pyrim. ring
	1648s	1645sh	1642sh	1640sh	1648s	1638sh	H_2O def.
	715m	720m	714w	718w	710w	720w	H_2O rock
	555m	560m	578m	565m	565m	568m	H_2O wag
	245w	258m	248m	256w	246w	259	Ni–N
	228w	232w	230w	233w	230w	235	Ni–N
	378s	380m	382m	383m	385m	389m	Ni–O(H_2O)
		170s		176s	178m		Ni–I
		149w		149w	140m		Ni–I

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

complexes with one, two and three $MeHg^+$ moieties with adenine. The observed frequencies are similar to those found in $MeHg^+$ complexes with two molecules of adenine. This may be caused by bonding through N-7 and N-9 in adenine and N-7 in adenosine. Moreover, the bands at 1475 and 1425 cm^{-1} are close to those observed in the spectra of nickel(II) complexes with nucleotides [5,25,26] where M–N-7 bonds are present. Analysis of the water deformation vibrations is difficult due to their overlapping 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 [27]. In the spectra of the salts, rocking and wagging vibration bands appeared at 700–720 cm^{-1} and 550–580 cm^{-1} respectively.

The environment of the Ni(II) ion can be derived on the basis of the preceding discussion. Adenosine molecules are bonded with Ni(II) through the N-7 and water molecules are bonded directly to the metal ion. Uncoordinated water molecules are bonded by means of hydrogen bonds in the crystal lattice. The observed bands in the 500–100 cm^{-1} region are listed in Table 4. The Ni–N stretching vibrations bands arise in the 228–268 cm^{-1} range. Ni–N(adenine) and Ni–N(ado) stretching vibrations bands were found in the same region [3,4,19]. Metal–ligand vibrational bands depend on coordination number [27]. The spectra of the dehydrated NiI_2–ado salts exhibit bands in similar positions. This supports the assumption that there is no change in coordination number in the studied salts. The medium intensity bands observed in all spectra at around 380 cm^{-1} can be assigned to $Ni–O(H_2O)$ stretching vibrations, in good agreement with bands previously found for $Ni–O(H_2O)$ in the spectra of Ni(II) hydrates [28], adenine and ado complexes [6,7]. Terminal M-I stretching bands in pseudo-octahedral symmetry appear below 200 cm^{-1}. Frequencies in the range characteristic for terminal Ni–I bonds [29,30] are reported in Table 4. The calculated ratio $\nu NiI/\nu NiCl = 0.58$ is in good agreement with that reported by Nakamoto [27]. The spectra discussed above show that iodide ions are bonded with the Ni(II) ions in terminal positions in the dehydrated salts only.

Analysis of the vibrational spectra indicates that the most probable coordination is six, with adenosine bonded via the N-7, iodides in the terminal position and water molecules bonded in the coordination sphere and by means of hydrogen bondings in the crystal lattice. Thermal dehydration does not change the coordination number and the ligands are bonded in the same way as in the maximally hydrated salts. The nearest surrounding should be written as follows: $[Ni(ado)_{1-3}(H_2O)_{5-3}]I_2 \cdot (1-3)H_2O$ for the maximally hydrated salts and $[NiI_2(ado)_{(1-3)}H_2O_{(3-1)}]$ for the dehydrated salts.

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