Thermochimica Acta, 216 (1993) 249–254
Elsevier Science Publishers B.V., Amsterdam

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

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(Received 10 June 1992)

Abstract

Hydrated complexes of $Ni(NCS)_2$ with adenosine have been obtained and their thermal dehydration processes have been studied. Changes in the coordination sphere have been studied. 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. Thiocyanate anions are bonded as monodentate ligands in terminal positions.

INTRODUCTION

Adenosine (Fig. 1), a constituent of nucleic acids, forms bonds with metal ions through nitrogen or oxygen atoms [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. The complexes of adenosine and 9-methyladenine [3, 4] were reported to be anhydrous or dihydrated. More water molecules were found in salts with nucleotides [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 type of the metal–ligand bond. Adenosine may bind with the 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 adenosine in the presence of water molecules. Thiocyanate anions [9] are able to form various types of bond with metal ions, such as terminally by means of N or S atoms, or bridging in complexes with low degrees of hydration; this is discussed below.

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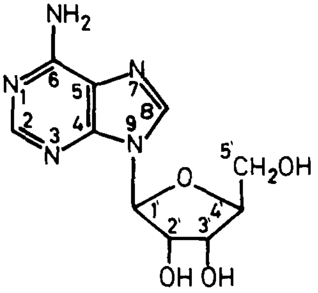

Fig. 1. Adenosine (ado).

EXPERIMENTAL

Adenosine (p.a., Reanal, Budapest) was used without further purification. $Ni(NCS)_2$ was prepared by reacting HNCS with $NiCO_3$. HNCS was obtained by a cationic exchange process on 0.1 M KNCS solution over Dowex X-8 50W and used instantly to react with $NiCO_3$. Complexes were prepared by direct reaction of aqueous solutions of $Ni(NCS)_2$ with adenosine in 1:1, 1:2 and 3:2 ratios, as described previously [6]. The 3:2 synthesis gave salt **1** (Table 1). The intermediate hydrates **3** and **5** were obtained by heating the maximally hydrated salts **1** and **4** at constant temperature established by analysis of the DTG, DTA and TG curves of the dehydration process. The heating temperature was chosen 5 K lower than the temperature of the onset of dehydration. Heating was discontinued when the weight of the sample became constant. IR spectra were performed on an FT-IR Bruker JFS 113v spectrometer using KBr discs and 200 scans. Electronic spectra were performed on a Specord M-40 (Carl-Zeiss, Jena) with reflection adapter, with 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 to 523 K, and the heating rate 5 K min^{-1}. The sample mass was 100 mg, the TG sensitivity was 50 mg, the reference material was Al_2O_3, and the size of grain was <0.06 mm. C, H

TABLE 1

Results of elemental analysis (ado = adenosine)

Compound	Ni (wt.%)		C (wt.%)		H (wt.%)		N (wt.%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1 $Ni(NCS)_2(ado) \cdot 6H_2O$	10.4	10.7	26.3	26.2	4.4	4.5	17.6	17.8
2 $Ni(NCS)_2(ado) \cdot 4H_2O$	11.4	11.1	27.8	28.0	4.1	3.9	19.1	19.2
3 $Ni(NCS)_2(ado) \cdot 3H_2O$	12.1	11.8	29.2	29.0	3.8	3.8	20.0	19.8
4 $Ni(NCS)_2(ado)_2 \cdot 6H_2O$	7.3	7.2	32.3	32.0	4.7	4.5	20.5	20.6
5 $Ni(NCS)_2(ado)_2 \cdot 3H_2O$	7.9	7.7	34.8	34.6	4.3	4.2	21.9	22.0

and N analyses were determined by semi-micro analysis. Nickel was determined by complexometric titration with EDTA after previous mineralisation of the salts. The results of the elemental analyses and stoichiometric formulae of the complexes are presented in Table 1.

RESULTS AND DISCUSSION

Thermal analysis

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

The dehydration starts at 308–318 K, water molecules are lost in a two-step process, and in one salt in a three-step process (Table 2). At least two water molecules become detached in the first step, which is connected with the dissociation of water molecules which can be bonded directly to a metal ion or via hydrogen bonds in the crystal lattice. The second step of the dehydration reaction coincides with the decomposition of adenosine, which is why anhydrous salts could not be isolated. Intermediate hydrates **3** and **5** were obtained with two and three water molecules respectively. Water molecules are bonded until the onset of adenosine decomposition, which occurs about 483 K; from that temperature the mass loss on the TG curve is connected with an exothermic peak on the DTA curve. The decomposition of the free adenosine was found in the range 493–548 K. Decrease in decomposition temperature has been observed previously for Ni(II) halide salts with adenosine [6–8] and can be caused by the influence of metal–ligand bonds and of the hydrogen-bonding network on the adenosine molecular bonds. In comparison to Ni(II) halide hydrates with adenine [10, 11], the salts under discussion are more hydrated. Higher hydration degrees can be stabilised by a stronger hydrogen-bond network in the presence of adenosine. The DTA curve of salt **4** exhibits two endothermic peaks on DTA, which are related to the loss of three and two

TABLE 2

Results of thermal analysis (ado = adenosine)

Compound	Heat effect	Temperature range (K)			Weight loss (wt.%)		Number of detached water molecules
		T_i	T_m	T_f	Found	Calc.	
1 $Ni(NCS)_2(ado)\cdot 6H_2O$	Endo	312	–[a]	469	14.4	14.0	4
2 $Ni(NCS)_2(ado)\cdot 4H_2O$	Endo	318	440	475	7.1	7.0	2
	Exo	483	Dec.	–			
3 $Ni(NCS)_2(ado)\cdot 3H_2O$	Endo	437	466	Dec.	7.4	7.3	2
4 $Ni(NCS)_2(ado)_2\cdot 6H_2O$	Endo	308	361	382	6.6	6.5	3
	Endo	385	403	434	4.4	4.6	2
	Exo	437	Dec.	–			
5 $Ni(NCS)_2(ado)_2\ 3H_2O$	Endo	420	445	Dec.	4.8	4.7	2

[a] Very broad minimum 350–460 K.

H_2O molecules, whereas the exothermic peak above 437 K is related to decomposition of adenosine. The second dehydration step in salt **5** proceeds at higher temperature than in the maximally hydrated **4**. This can be connected with the changes in the composition of the coordination sphere. A different thermal dehydration process had been observed for salt **1**. The shapes of the DTA and DTG curves for salt **1** do not allow determination of T_m. The DTA baseline is sloping towards the exothermic until it reaches 312 K, when it becomes endothermic. From that point, the DTG exhibits the mass loss process but the effect is stretched in the range 350–460 K.

Spectral analysis

The IR spectra of adenine, adenosine and their complexes have been discussed by many authors [3–5, 12–19]. Band frequencies and assignments to proper vibrations are shown in Table 3. The presence of absorption bands in the range 1684–1695 cm^{-1} and 1650–1654 cm^{-1} allows the statement to be made that adenosine is not bonded with Ni(II) by means of N-1 or $-NH_2$ [5, 12–15]. Absorption bands at 1606, 1573 and 1506 cm^{-1} in the free adenosine spectrum show no drastic changes in the studied spectra (Table 3). Beauchamp and co-workers [20–24] observed similar positions of these bands in the spectra of CH_3Hg complexes containing N-7 and N-9-bonded adenine, confirmed by X-ray analysis. The same method of adenosine coordination can be proposed for the salts studied. 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, 25, 26] in which M–N–7 bonds are found. The presence of the water deformation vibrations in the range 1648–1640 cm^{-1} and libration bands [9] from rocking and wagging at 744–717 cm^{-1} and 558–541 cm^{-1} respectively, confirms the coordination of water molecules.

The position of the $\nu(C{=}N)$ and $\nu(C{=}S)$ vibration bands in salts spectra are in the range which is characterisitc for the N-bonded thiocyanates (Table 3) [9].

Electronic spectra of the salts studied exhibit a ν_2 band in the range 14 900–15 400 cm^{-1}. The position of ν_2 is characteristic of six-coordinated Ni(II) [27]. Band ν_3 appears at 25 900 cm^{-1} only in the spectra of salt **3**. The spectra of the other salts exhibit in this range broad and intensive CT bands [27]. There is no change of coordination number during the thermal dehydration reaction of the salts.

From electronic and vibrational spectra analysis the most probable structure is six-coordination, with adenosine bonded via N-7 and 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 molecules are bonded in the same way

TABLE 3

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

Adenosine	$Ni(NCS)_2(ado) \cdot 6H_2O$	$Ni(NCS)_2(ado) \cdot 4H_2O$	$Ni(NCS)_2(ado) \cdot 3H_2O$	$Ni(NCS)_2(ado)_2 \cdot 6H_2O$	$Ni(NCS)_2(ado)_2 \cdot 3H_2O$	Assignment
1712s	1684m	1695m	1688m	1685m	1691m	
1662s	1653s	1652s	1650s	1653s	1645s	NH_2 def.
1606s	1600s	1596s	1598s	1600s	1599s	Pyrimidine ring
1573s	1577m	1580m	1578m	1576s	1578s	Pyrimidine ring
1506m	1507w	1508w	1508m	1505w	1513w	Imidazole ring
1475m	1496m	1493m	1488m	1490m	1485m	Imidazole ring
1425m	1435m	1434m	1426s	1422s	1426s	Imidazole ring in plane
1333s	1335s	1335s	1336s	1338s	1336s	Purine
	2092s	2101s	2079s	2090s	2088s	ν(C=N) (NCS)
	862w	860m	742m	868m	867m	ν(C=S) (NCS)
	1648s	1647a	1644s	1645s	1640s	H_2O def.
	736w	744w	718w	719w	717w	H_2O rocking
	541w	550m	558m	549w	556w	H_2O wagging

Key: s, strong; m, medium; w, weak.

as in the maximally hydrated salts. Thiocyanate anions are bonded in the terminal position. The nearest surrounding should be written $[Ni(NCS)_2(ado)_{1,2}(H_2O)_{3,2}] \cdot nH_2O$, where $n = 3$, 1, 0, 4, 1 respectively for salts **1**, **2**, **3**, **4**, **5**).

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