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Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

PRIMARY ALIPHATIC AMINE COMPLEXES OF TRANSITION-METAL HALIDES

III. Thermal and spectroscopic characterization of solid methylamine complexes of nickel(II) halides

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Abstract

The hexakis(methylamine) complexes of nickel(II)-chloride, -bromide and -iodide have been prepared using-gas phase preparation procedure. The thermal decomposition starts with the release of four moles of the organic ligand. The bis(methylamine) intermediate decomposes in one step to the pure nickel(II) halide in the case of the chloride compound, however one and a half moles of methylamine containing intermediates were identified for the bromide and iodide analogues. The UV/VIS and the far IR spectra of the hexakis complexes show a typical octahedral environment around the central nickel(II) ion.

Keywords: complex, methylamine, mid- and far-IR, nickel(II) halides, thermal analysis, UV/VIS

Introduction

In the last few decades interest has grown in the thermal and structural properties of complexes with monodentate, nitrogen donor ligands (e.g. ammonia, pyridine and aniline) and transition metal halides. Because of the expected changes in the type of complex from ammonia to pyridine, the study of primary aliphatic amine compounds is of interest.

Extensive work has been undertaken on ammonia and pyridine complexes in the last few decades [1–2]. While preparation methods and the thermal properties of these compounds are well known, only a few papers report on the primary

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aliphatic amine amine complexes of transition metals [3–5]. Investigations within the first row of transition metal complexes are of interest in order to follow the changes in thermal properties from ammonia complexes to those containing aromatic systems.

Ephraim and Linn [3] report on the use of a complicated apparatus created for the preparation of primary aliphatic amine complexes formed with different transition metal halides (e.g. Zn, Cd, Co, Cu, Mn). In addition to these, they have published the temperature and heats of dissociation and other physicochemical constants of the light blue hexakis(methylamine)nickel(II) chloride ($NiCl_2\cdot 6CH_3NH_2$:T:413 K, Q:14.87 cal[1]).

Fifty three years later Uhlig and Steiger [4] reported on the thermal properties of hexakis(methylamine)nickel(II) chloride. The thermal degradation has been studied by heating these compounds in a vessel in an argon stream containing the amine. The decomposition scheme observed was as follows[2]:

$$Ni(CH_3NH_2)_6Cl_2 \rightarrow Ni(CH_3NH_2)_4Cl_2\ (140^\circ C) \quad (1)$$

$$Ni(CH_3NH_2)_6Cl_2 \rightarrow Ni(CH_3NH_2)_2Cl_2\ (\text{vacuum}) \quad (2)$$

The thermal intermediates have been isolated and the magnetic and spectroscopic properties studied.

Ludwig [5] reported for the very first time on the thermal behaviour of hexakis(methylamine)nickel(II) chloride using a conventional thermobalance with a separate DTA apparatus. The following decomposition scheme was given in the article [5][3].

$$[Ni(CH_3NH_2)_6]Cl_2 \rightarrow [Ni(CH_3NH_2)_4]Cl_2\ (60\text{–}110^\circ C) \quad (3)$$

$$[Ni(CH_3NH_2)_4]Cl_2 \rightarrow [Ni(CH_3NH_2)_3]Cl_2\ (125^\circ C) \quad (4)$$

$$[Ni(CH_3NH_2)_3]Cl_2 \rightarrow [Ni(CH_3NH_2)_2]Cl_2\ (155^\circ C) \quad (5)$$

$$[Ni(CH_3NH_2)_2]Cl_2 \rightarrow [Ni(CH_3NH_2)_{1.5}]Cl_2\ (190^\circ C) \quad (6)$$

The probable structure of the tris-complex and the thermal intermediate containing one and a half moles of ligand is discussed on the basis of the work published by Brown and Nuttall [6].

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[1] Units are given by the authors [3].

[2] The chemical reaction scheme was taken from [4].

[3] The chemical reaction scheme was taken from [5].

A careful comparison of the literature data has shown contradictions in the stoichiometry, decomposition scheme and the temperature of decomposition of these complexes. On the basis of our earlier observations [7–10] we decided to apply the solid-gas phase preparation to obtain solid primary aliphatic amine complexes. Stable nickel(II) chloride was selected in order to avoid oxidation processes.

Experimental

Complexes of nickel(II) halides formed with primary aliphatic amines were prepared using a solid-gas phase preparation procedure. In the preparation nickel(II) halide hexahydrates (Reanal p.a.) were dehydrated at 350°C in a drying oven. After grinding to reduce the particle size, the pure nickel(II) halides were placed in a desiccator containing methylamine vapour (Jansen Chimica 40% water solution). The chemisorption occurred within a few days with frequent pulverising of the solid material. The progress of the reaction was followed by a change in colour from yellow to violet.

Table 1 Analyses of hexakis complexes

Complex		Nickel	Carbon	Nitrogen	Hydrogen
$[Ni(MeNH_2)_6]Cl_2$	theory [%]	18.58	22.81	26.60	9.57
	found [%]	18.7	23.0	26.3	9.6
$[Ni(MeNH_2)_6]Br_2$	theory [%]	14.50	17.80	20.75	7.47
	found [%]	14.3	17.9	20.8	7.5
$[Ni(MeNH_2)_6]I_2$	theory [%]	11.77	14.45	16.85	6.06
	found [%]	11.8	14.4	16.9	5.9

The nickel(II) content of the complexes was determined by complexometric titration. The carbon, hydrogen and nitrogen analyses were made using a Carlo-Erba elemental analyser (Table 1).

The thermoanalytical curves were recorded (Figs 1–3) on a MOM-OD2 Derivatograph with a heating rate of 5°C min^{-1} and a sample weight of 100 mg. Air and nitrogen atmosphere, platinum crucibles and 100 mg of α-aluminium oxide as reference material were applied.

The UV/VIS solid reflectance spectra were collected in the 200–2500 nm region using a Beckman Acta MIV spectrophotometer with $BaSO_4$ as reference material.

Infrared spectra of the samples were recorded by a DIGILAB FTS spectrophotometer using KBr discs (4000–400 cm^{-1} region) and nujol mulls in polyethylene matrix (600–40 cm^{-1} region).

Results

The thermal decomposition of the parent, hexakis(methylamine) complexes starts with the release of four molecules of methylamine ligand (Fig. 1).

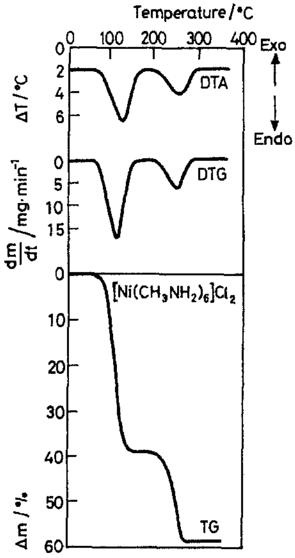

Fig. 1 Simultaneous thermoanalytical curves of $[Ni(CH_3NH_2)_6]Cl_2$

$$[Ni(CH_3NH_2)_6]Cl_2 \rightarrow [Ni(CH_3NH_2)_2Cl_2]\ (105^\circ C) \tag{7}$$

The bis-intermediates thus formed decompose in one step to the pure nickel halide in the case of the chloride complex, however, an additional intermediate was identified for the bromide and iodide analogues, containing one and a half moles of the ligand (Figs 1–3).

$$[Ni(CH_3NH_2)_2Cl_2] \rightarrow NiCl_2\ (245^\circ C) \tag{8}$$

$$[Ni(CH_3NH_2)_6]Br_2 \rightarrow [Ni(CH_3NH_2)_2Br_2]\ (150^\circ C) \tag{9}$$

$$[Ni(CH_3NH_2)_2Br_2] \rightarrow [Ni(CH_3NH_2)_{1.5}Br_2]\ (195^\circ C) \tag{10}$$

$$[Ni(CH_3NH_2)_{1.5}Br_2] \rightarrow NiBr_2\ (250^\circ C) \tag{11}$$

$$[Ni(CH_3NH_2)_6]I_2 \rightarrow [Ni(CH_3NH_2)_2I_2]\ (160^\circ C) \tag{12}$$

$$[Ni(CH_3NH_2)_2I_2] \rightarrow [Ni(CH_3NH_2)_{1.5}I_2]\ (230^\circ C) \tag{13}$$

$$[Ni(CH_3NH_2)_{1.5}I_2] \rightarrow NiI_2\ (290^\circ C) \tag{14}$$

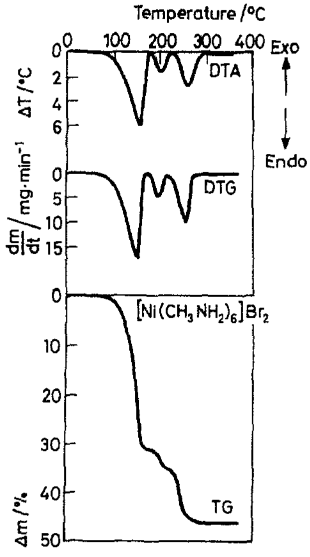

Fig. 2 Simultaneous thermoanalytical curves of $[Ni(CH_3NH_2)_6]Br_2$

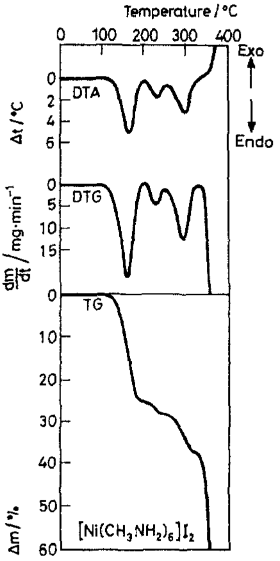

Fig. 3 Simultaneous thermoanalytical curves of $[Ni(CH_3NH_2)_6]I_2$

This thermal decomposition scheme is slightly different from those published earlier in the literature [3–5]. We did not observe the tetrakis- and the tris-intermediates, and the decomposition products containing one and a half moles of methylamine were identified only for the bromide and the iodide analogues. The thermal stability of the parent, hexakis(methylamine) complexes increases from the chloride to the iodide analogue. Although the ionic radii of the halogens, and thus the steric hindrance increases in the same order, the polarizability of the ions increasing from chloride to iodide seems to be more marked.

Table 2 Electronic spectra of the complexes

$[Ni(MeNH_2)_6]Cl_2$	$[Ni(MeNH_2)_6]Br_2$	$[Ni(MeNH_2)_6]I_2$	Assignment
	cm^{-1}		
8389	8368	9843	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$
16806	15082	16892	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$
27027	25641	26738	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$
43103	42553	42553	charge transfer band
839	837	984	$-10Dq$
1068	969	881	B (Racah parameter)
0.99	0.89	0.81	β (nephelauxetic parameter)

Table 3 Infrared spectra (4000–40 cm^{-1}) of the hexakis complexes

No.	$[Ni(MeNH_2)_6]Cl_2$	$[Ni(MeNH_2)_6]Br_2$	$[Ni(MeNH_2)_6]I_2$	Assignment
		cm^{-1}		
1	3283	3276	3261	$\nu_{as}(NH_2)$
2	3180	3174	3177	$\nu_s(NH_2)$
3	2996, 2972	2993, 2965	2992, 2967	$\nu_{as}(CH_3)$
4	2930, 2901	2903, 2898	2927, 2899	$\nu_s(CH_3)$
5	1615	1605	1612	$\beta_s(NH_2)$
6	1492	1490	1488	$\delta_{as}(CH_3)$
7	1468	1463	1466	$\beta_s(CH_3)$
8	1239	1235	1236	$\beta_s(NH_2)$
9	1061	1054	1056	$\delta_e(CH_3)$
10	1001	1000	1006	$\nu(C–N)$
11	643, 607	606	621, 589	$\delta_{as}(NH_2)$
12	330	332	359	$\nu(Ni–N)$
13	248	241	226	$\delta(N–Ni–N)$
14	141, 112, 94	106, 71	81, 72, 63	Lattice

The observed weight changes during the thermal decomposition corroborated the expected stoichiometry.

In the UV/VIS region three main absorption bands were observed (Table 2) indicating an octahedral symmetry around the central nickel(II) ion, realized via nickel-nitrogen bonds in the inner coordination sphere and counter halide ions in the unit cell. The ligand field (−10*Dq*) parameter increases from the chloride to the iodide compounds, however, the reverse order was obtained for the β nephelauxetic parameter. This indicates the dominance of the covalent character of the nickel(II)-nitrogen bond for the $[Ni(MeNH_2)_6]X_2$ type compounds, in which the halides are in the outer coordination sphere.

In the 4000–400 cm^{-1} region of the IR spectra (Table 3) significant changes were not observed compared to the spectra of the free methylamine, although one ν(Ni–N) stretching and one δ(N–Ni–N) deformation vibrations were assigned in the far IR spectra in agreement with the expected O_h symmetry of the complexes. These bands, however, are slightly deformed and this effect becomes more marked with the increasing ionic radii of the anion, because of steric interactions. The wavenumbers of the ν(Ni–N) bands increase from the chloride to the iodide analogue in agreement with the observed increasing thermal stability. In addition to the metal ligand vibration, some lattice bands occur at low wavenumbers.

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