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SYNTHESIS, STRUCTURE AND THERMAL DECOMPOSITION OF $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$

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The compound $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ was prepared and characterized by elemental analysis and vibrational spectra. The single crystal X-ray study revealed that the structure consists of $[Ni(NH_3)_6]^{2+}$ and $[VO(O_2)_2(NH_3)]^-$ ions. As a result of weak interionic interactions $V'\cdots O_p$ (O_p–peroxo oxygen), $([VO(O_2)_2(NH_3)]^-)_2$ dimers are formed in the solid-state. The thermal decomposition of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ is a multi-step process with overlapped individual steps; no defined intermediates were obtained. The final solid products of thermal decomposition up to 600°C were $Ni_2V_2O_7$ and V_2O_5.

Keywords: *ammine complexes, IR spectra, thermal decomposition, X-ray structure*

Introduction

The peroxo complexes of transition metals are of great interest as molecular precursors for preparation of oxide materials [1]. The use of peroxo complexes for this purpose may be effective especially in the case of multimetallic oxide-materials, for preparation of which well-defined and water soluble compounds are usually lacking. As the final products are often obtained by thermal treatment of the precursors, the investigation of thermal decomposition of pertinent coordination compounds is of great importance for material chemistry [2, 3].

The present paper describes the synthesis, characterization and thermal decomposition of a bimetallic compound containing volatile ammine ligand in both cationic and anionic parts of the compound.

Experimental

Materials

V_2O_5 was prepared by thermal decomposition (at 500°C) of previously purified NH_4VO_3. All other chemicals were of analytical grade and used as received. Vanadium(V) was determined by titration with 0.1 M $FeSO_4$ in presence of H_3PO_4 and diphenylamine as indicator [4]. The peroxide content was determined by potentiometric titration with potassium permanganate. Nitrogen was determined by CHN analyzer 1106 (Carlo Erba).

Synthesis of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$

$NiSO_4\cdot 7H_2O$ (1.40 g; 5 mmol) was dissolved in aqueous solution of NH_3 (25 mL; w=25%). Solid NH_4VO_3 (0.59 g; 5 mmol) was then added and after dissolution, the solution of H_2O_2 (10 mL; w=30%) was dropwise added. The resulting green solution was stored at –5°C for 72 h, and ethanol (20 mL; φ=96%) was then added. Green crystals were isolated after 24 h, washed with ethanol and dried at 5°C. Anal. cald. for $H_{24}N_8O_{10}NiV_2$: N, 24.5%; O_2^{2-}, 28.0%; V, 22.3%; found: N, 22.7%; O_2^{2-}, 27.5% and V, 21.9%.

Methods

The IR spectra in nujol mulls were recorded on a FTIR Nicolet Magna 750 spectrometer. The Raman spectrum of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ was registered on a FT RA model FRA 106/S connected to a FTIR spectrometer FS 55 Equinox (Bruker); a Nd:YAG laser (1.064 μm, 350–500 mW) was used.

The single crystal diffraction data were collected with a KM4 CCD diffractometer with a four-circle area-detector (KUMA Diffraction, Poland), and equipped with an Oxford Cryostream Cooler (Oxford Cryosystems, UK). The ω scan technique with different κ and φ offsets for covering a whole independent part of reflections in the 2–25° θ range was performed. The cell

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Table 1 Crystal data and structure refinement for $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$

Empirical formula	$H_{24}N_8NiO_{10}V_2$
M	456.81 g mol^{-1}
Temperature of measuring	–153(2)°C
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a=5.9196(8) Å α=105.149(11)° b=7.5216(10) Å β=93.821(11)° c=9.0155(12) Å γ=97.343(11)°
volume	382.18(9) Å^3
Z, Calculated density	1, 1.9849 g cm^{-3}
Absorption coefficient	2.477 mm^{-1}
F(0 0 0)	234
Crystal size	0.40·0.30·0.30 mm
θ range for data collection	4.15 to 25.00°
Limiting indices	$-6\le h\le 7$, $-8\le k\le 8$, $-9\le l\le 10$
Reflections collected / unique	2565/1323 [R(int)=0.0533]
Completeness to 2 θ=25.00:	99.2%
Max. and min. transmission	0.5236 and 0.4374
Data / restraints / parameters	1323/0/101
Goodness-of-fit on F^2	1.090
Final R indices [I > 2σ(I)]	R_1=0.0330, wR_2=0.0875
R indices (all data)	R_1=0.0339, wR_2=0.0884
Extinction coefficient	0.000(4)
Largest diff. peak and hole	0.630 and –0.502 e Å^{-3}

parameters were refined from all strong reflections. The data reductions were carried out using the CrysAlis RED (Oxford Diffraction, UK) program. The structures were determined by SHELXS-97 [5] and refined by SHELXL-97 [6], the data for publication were prepared by SHELXL and PARST [7], and the figure by Diamond [8]. The crystal data and refinement details are given in Table 1. The X-ray powder diffraction patterns were obtained on a Philips PW 1050 diffractometer using CuK$_\alpha$ radiation.

The thermal analysis under dynamic conditions was performed on a STD 2960 (TA Instruments) enabling a simultaneous collection of TG, DTG and DTA curves. The experimental parameters: air atmosphere, sample mass 25 mg, heating rate 10°C min^{-1}, Pt crucible. The temperature interval was 20–600°C. KNO_3, $KClO_4$ and K_2SO_4 (Chemcomex) were used as reference standards for the temperature calibration of DTA. The interrupted thermal treatment was accomplished on a Derivatograph Q 1500 D (MOM, Hungary). The experimental parameters: as formerly, with the exception of sample mass – 100 mg.

Results and discussion

Synthesis and characterization

The dark green complex $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ was prepared by crystallization from the $NiSO_4\cdot 7H_2O–NH_4VO_3–NH_3–H_2O_2–H_2O$–ethanol system. A necessary condition for the successful synthesis is the addition of ethanol after at least 72 h, otherwise $[Ni(NH_3)_6]SO_4$ crystallized out of the solution. The solid complex is stable at room temperature for a few days.

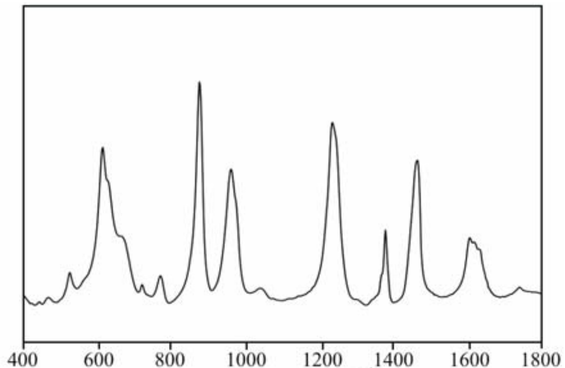

Fig. 1 IR spectrum of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$

Table 2 Characteristic bands in infrared spectrum of $[Ni(NH3)_6][VO(O_2)_2(NH_3)]_2$

$\tilde{\nu}$/cm^{-1}	Assignment
3466 s	$\nu_{as}+\nu_{s(NH_3)}$
3342 vs	$\nu_{as}+\nu_{s(NH_3)}$
3275 sh	$\nu_{as}+\nu_{s(NH_3)}$
3234 s	$\nu_{as}+\nu_{s(NH_3)}$
3140 vs	$\nu_{as}+\nu_{s(NH_3)}$
1631 sh	$\delta_{as(NH_3)}$
1617 sh	$\delta_{as(NH_3)}$
1605 vs	$\delta_{as(NH_3)}$
1235 vs	$\delta_{s(NH_3)}$
961 vs	$\nu_{(V=O)}$
877 vs	$\nu_{(O_p-O_p)}$
771 s	$\rho_{r(NH_3)}$
664 sh	$\nu_{(V-O_p)}$
631 sh	$\nu_{(V-O_p)}$
615 vs	$\nu_{(V-O_p)}$
527 s	$\nu_{(V-O_p)}$
444 vw	$\nu_{(Ni-N)}+\nu_{(V-N)}$

In the infrared spectrum (Fig. 1, Table 2), all characteristic bands of coordinated ammonia molecule [9], as well as the bands of the $VO(O_2)_2$ group [10] can be observed. While the bands correspoding to the vibrations of $V-NH_3$ and $Ni(NH_3)_6$ groups cannot be distinguished, some interesting band shifts in comparison with the bands for $[Ni(NH_3)_6]Cl_3$ [9] and $NH_4[VO(O_2)_2(NH_3)]$ [10] were observed. Thus, there is only one band assignable to $\sigma_{s\,NH_3}$ at 1235 cm^{-1} (published data for $[Ni(NH_3)_6]Cl_3$ and $NH_4[VO(O_2)_2(NH_3)]$, respectively, are: 1176 and 1237 cm^{-1}). Moreover, the position of a band assigned to $\rho_{r(NH_3)}$ at 771 cm^{-1}, corresponds neither to $\rho_{r(NH_3)}$ for $[Ni(NH_3)_6]Cl_3$ (685 cm^{-1}) nor to $\rho_{r(NH_3)}$ for $NH_4[VO(O_2)_2(NH_3)]$ (711 cm^{-1}). Although, the structure of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ is composed of isolated ions (vide infra), such band shifts give evidence for some significant interactions between cations and anions in the solid state structure, which influence the infrared spectrum.

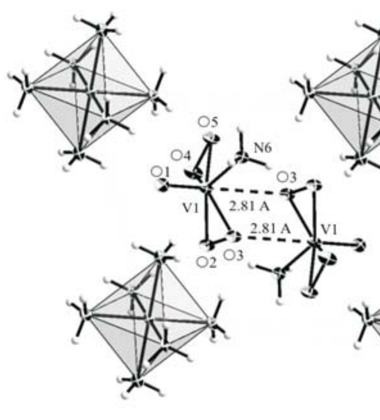

Fig. 2 The structure of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$. The deviation of the vanadium atom from the least squares pentagonal plane is 0.429Å

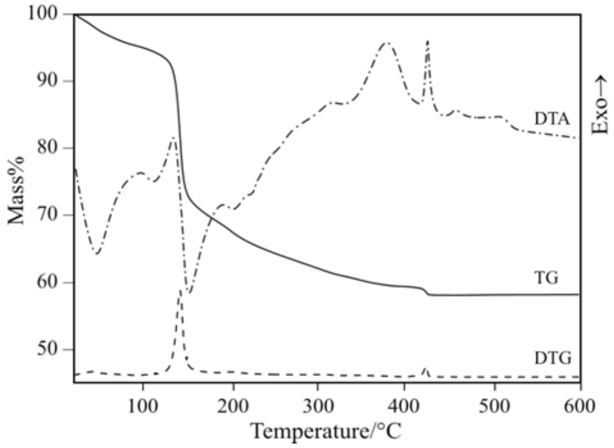

Fig. 3 Thermoanalytical curves of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$

The Raman spectrum was of low quality due to the luminescence of the sample. The most intensive Raman bands were at: 946 cm^{-1} [$\nu_{(V=O)}$]; 876 cm^{-1} [$\nu_{(O_p-O_p)}$] and 520 cm^{-1} [$\nu_{s(V-O_p)}$].

Crystal structure

The structure of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ consists of isolated $[Ni(NH_3)_6]^{2+}$ and $[VO(O_2)_2(NH_3)]^-$ ions held together by electrostatic forces and hydrogen bonds (Fig. 2).

The vanadium atom is bonded to five oxygen and one nitrogen atoms in a distorted pentagonal pyramidal arrangement. The four oxygen atoms of the two peroxo groups and the nitrogen atom form the pentagonal plane and the double bonded oxygen atom is in apical position. There is a very weak interaction between the vanadium atom and the peroxo oxygen atom from the neighbouring anion [$d(V\cdots O_p)$=2.81 Å] (Fig. 2). The $[VO(O_2)_2(NH_3)]^-$ ions thus form weakly bonded dimers, in contrast to the structure of $NH_4[VO(O_2)_2(NH_3)]$ [11, 12] where the chains are formed as a result of the $V'\cdots O=V$ interactions.

The bond lengths (V1-O1 1.6143 (22), V1-O2 1.8985 (21), V1-O3 1.8992 (22), V1O4 1.8894 (21), V1-O5 1.8760 (19), V1-N6 2.1119 (25), O4-O5 1.4753 (29), O2-O3 1.4775 (30) and bond angles (O1-V1-O5 106.57, O1-V1-O4 105.55, O1-V1-O2 101.75, O1-V1-O3 106.08, O1-V1-N6 95.57, V1-O5-O4 67.42, V1-O4-O5 66.45, V1-O3-O2 67.08, V1-O2-O3 67.13) in the $[VO(O_2)_2NH_3]^-$ ion are comparable with those in structures of other six coordinated diperoxovanadate ions [11, 13, 14].

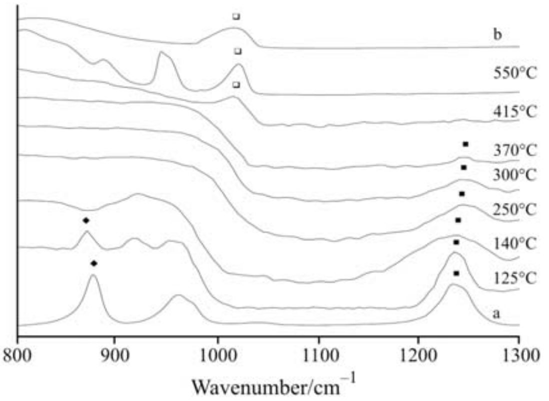

Fig. 4 IR spectra of intermediate products obtained by interruption of thermal decomposition of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ at 125, 140, 250, 300, 370, 415 and 550°C. a– $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ (20°C), b – V_2O_5; ■ – $\delta_{s(NH_3)}$, □ – $\nu_{(V=O)}$, ◆ – $\nu_{(O_p-O_p)}$

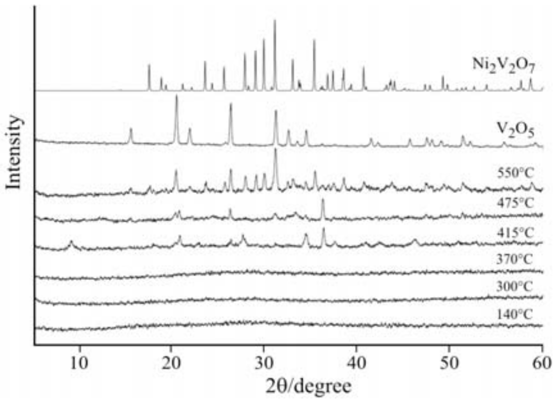

Fig. 5 X-ray powder diffraction patterns of $Ni_2V_2O_7$ [15], V_2O_5 and intermediate products obtained by interruption of thermal decomposition of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ at 140, 300, 370, 415, 475 and 550°C

The $[Ni(NH_3)_6]^{2+}$ cation possesses nearly regular octahedral structure with Ni–N bond lenghts 2.115–2.141 Å and bond angles for the *cis*-positioned N–Ni–N bonds in the interval 87.47–92.53°.

Thermal decomposition

The thermal decomposition of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ is a multi-step process in which the individual steps are overlapped (Fig. 3). The TG curve shows practically continuous mass loss. This is the reason why we were not able to isolate any intermediate as pure compound with defined composition and structure. Nevertheless, the stoichiometry of the thermal decomposition can be described by Eqs (1)–(3).

In the first step of thermal decomposition (20–120°C, Eq. (1)), two molecules of ammonia are released (calcd. mass loss 7.5, found 6.4%):

$$[Ni(NH_3)_6][VO(O_2)_2NH_3]_2 \xrightarrow{\Delta t} \{Ni(NH_3)_4[VO(O_2)_2(NH_3)]_2\} + 2NH_3 \qquad (1)$$

This process is manifested on the DTA curve by two endothermic peaks at 49 and 114°C. The IR spectrum of the product obtained by interruption of the thermal decomposition at 125°C clearly shows the presence of the peroxo ligand in the sample (Fig. 4). We suppose that ammonia molecules are released from the $[Ni(NH_3)_6]^{2+}$ ions under formation of $\{Ni(NH_3)q[VO(O_2)_2(NH_3)]_2\}$ while in the other case a coordinatively unsaturated product $\{Ni(NH_3)_6V_2O_2(O_2)_4\}$ would be formed.

In the second step of decomposition (120–160°C, Eq. (2)), two oxygen and two ammonia molecules are released (calcd. mass loss 21.5, found 21.7%):

$$\{Ni(NH_3)_4[VO(O_2)_2(NH_3)]_2\} \xrightarrow{\Delta t} \{Ni(NH_3)_4(VO_3)_2\} + 2O_2 + 2NH_3 \qquad (2)$$

On the DTA curve this step is expressed by a strong exothermic effect at 137°C and the ensuing strong endothermic effect at 154°C. The IR spectrum of the product obtained at 140°C (Fig. 4) exhibits no $\nu_{(O_p-O_p)}$ band, but the strong band corresponding to $\delta_{s(NH_3)}$ can be still seen in the spectrum. The broad IR bands in the region of V–O stretches give evidence of the oligomeric or polymeric character of the supposed $\{Ni(NH_3)_4(VO_3)_2\}$ product.

The third step of decomposition (160–550°C, Eq. (3)) is accompanied by release of the remaining four ammonia molecules (calcd. mass loss 14.9, found 13.8%):

$$2\{Ni(NH_3)_4(VO_3)_2\} \xrightarrow{\Delta t} Ni_2V_2O_7 + V_2O_5 + 8NH_3 \qquad (3)$$

The DTA curve exhibits, besides small effects, intense exothermic peaks at 380 and 426°C. As the mass loss in the temperature range 350–550°C is relatively small, we suppose that these peaks correspond to the formation of a polymeric structure and/or a crystallization process. As can be seen from X-ray powder diffraction (XPD) patterns (Fig. 5), the intermediate products obtained up to 370°C are X-ray amorphous. Starting with the temperature 415°C, the diffractions of V_2O_5 are observed in the XPD patterns, besides diffractions of some unidentified intermediate product(s). The latter diffractions gradually disappear with increasing temperature, and are absent in the XPD pattern of the product obtained at 550°C. The XPD pattern of the final product exhibits diffractions corresponding to V_2O_5 and $Ni_2V_2O_7$ (Fig. 5).

The IR spectra of the decomposition intermediates (Fig. 4) enable to follow the release of coordinated ammonia molecules from the sample, e.g. using the strong band of $\delta_{s(NH_3)}$ at 1235 cm^{-1}. It is clearly shown that NH_3 ligand is present in the sample until 370°C. The IR spectrum of the sample obtained at 415°C exhibits the characteristic band of V_2O_5 at 1020 cm^{-1}, assigned to $\nu_{(V=O)}$.

The overall thermal decomposition process of $[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2$ is described by Eq. (4):

$$2[Ni(NH_3)_6][VO(O_2)_2(NH_3)]_2 \xrightarrow{\Delta t} Ni_2V_2O_7+V_2O_5+16NH_3+4O_2 \quad (4)$$

(calcd. mass loss 43.8, found 41.9%).

Supplementary material

Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666;
e-mail: crysdata@fiz-karlsruhe.de,

http://www.fiz-karlsruhe.de/ecid/Internet/en/DB/icsd/depot_anforderung.html), on quoting the deposition number CSD–416935.

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