

THERMAL INVESTIGATION OF 1,2-PROPANEDIAMINE COMPLEXES OF NICKEL(II) IN THE SOLID PHASE

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Thermal studies have been carried out on $[\text{NiL}_3]\text{X}_2 \cdot n \text{H}_2\text{O}$, where $L = 1,2$ -propanediamine; $X = \text{Cl}^-$, Br^- , SCN^- , $1/2 \text{SO}_4^{2-}$ and $1/2 \text{SeO}_4^{2-}$; and $n = 2, 1.5$ and 0 . $[\text{Ni}_2\text{L}_5(\text{NCS})_2](\text{SCN})_2$ and $[\text{NiL}_2\text{SO}_4]$ have been synthesized pyrolytically in the solid-state from their mother diamine complexes. The deaquation behaviour of $[\text{NiL}_3]\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ appears interesting, and its monohydrate undergoes a solid-state reaction (88 – 102°) without mass loss, showing an exothermic peak at 95°C ($\Delta H = -5.1 \text{ kJ mole}^{-1}$).

Wendlandt et al. earlier reported thermal investigations on diamine complexes of Ni(II) [1–4]. We recently made exhaustive studies on the thermal behaviour of nickel(II) diamine complexes [5–9]. The results encouraged us to perform further investigations. The present paper deals with the thermal behaviour of 1,2-propanediamine complexes of nickel(II) in the solid state.

Experimental

The metal salts used were all of analytical reagent grade purity. 1,2-Propanediamine (L) was purified by repeated distillation.

Preparation of the complexes

$[\text{NiL}_3]\text{Cl}_2 \cdot 2 \text{H}_2\text{O}$ (1), $[\text{NiL}_3]\text{Br}_2 \cdot 1.5 \text{H}_2\text{O}$ (2) and $[\text{NiL}_3](\text{SCN})_2$ (3): 1,2-propanediamine (4 mmole) was added dropwise to NiX_2 ($X = \text{Cl}^-$, Br^- or SCN^-) (1 mmole) dissolved in ethanol, with vigorous stirring. When the resulting mixture was stirred, fine pink crystals immediately separated out. The crystals were collected by filtration, washed thoroughly with ethanol, and dried over fused CaCl_2 in a desiccator.

$[\text{NiL}_3]\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ (4) and $[\text{NiL}_3]\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ (5): 1,2-propanediamine (4 mmole) was added dropwise with vigorous stirring to $[\text{Ni}(\text{NH}_3)_6]\text{AO}_4$ ($A = \text{S}$ or

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Se) (1 mmole) in ethanolic suspension. During stirring of the resulting mixture for 3–4 h, the desired complex separated out as a fine pink powder. It was collected by filtration, washed thoroughly with ethanol, and dried over fused CaCl_2 in a desiccator.

$[\text{NiL}_3]\text{SO}_4 \cdot \text{H}_2\text{O}$ (4B) and $[\text{NiL}_3]\text{SO}_4$ (4C): These were prepared by keeping complex (4) at 100 and 165°, respectively.

$[\text{NiL}_2\text{SO}_4]$ (4D) and $[\text{Ni}_2\text{L}_5(\text{NCS})_2](\text{SCN})_2$ (3A): These were synthesized by keeping complexes (4) and (3) at 245 and 220°, respectively, in a dinitrogen gas atmosphere. Thermal analysis was stopped when no more diamine was lost, as evidenced by weight constancy. Analytical, magnetic and electronic (mull) spectral data for the above complexes are presented in Table 1.

Thermal measurements

The thermal analysis was carried out with a Shimadzu DT-30 thermal analyser. A constant flow of dinitrogen gas (30 ml min^{-1}) was maintained. Platinum crucibles were used. The heating rate was 10 deg min^{-1} . The particle size of the samples was within 150–200 mesh. Aluminium oxide was used as reference. Indium metal was used as calibrant for the evaluation of enthalpy change. Table 2 lists the thermal data.

Spectral measurements

Infrared spectra in KBr ($4000\text{--}250 \text{ cm}^{-1}$) were recorded with a Perkin–Elmer IR 783 spectrophotometer. Electronic spectra of mulls ($800\text{--}350 \text{ nm}$) were recorded with a Pye Unicam SP8-150 spectrophotometer.

Magnetic measurements

The effective magnetic moments were evaluated from magnetic susceptibility measurements with an EG and G PAR vibrating sample magnetometer model 155 at room temperature.

Results and discussion

$[\text{NiL}_3]\text{Cl}_2 \cdot 2 \text{H}_2\text{O}$ (1) *

The i.r., electronic and magnetic data suggest that the ligands are chelated and the complex possesses the O_h configuration. It becomes anhydrous at 150° in two-steps (Table 2, Fig. 1), through formation of the monohydrate. The anhydrous species starts to decompose at 185° and transforms to NiCl_2 through the formation of $[\text{NiL}_2\text{Cl}_2]$, $[\text{NiLCl}_2]$, $[\text{NiL}_{0.66}\text{Cl}_2]$ and $[\text{NiL}_{0.33}\text{Cl}_2]$ as intermediates. Its decomposi-

* $[\text{NiL}_3]\text{X}_2$, where $\text{X} = \text{Cl}^-$ or Br^- , melts down swells up during decomposition. To avoid swelling, thermal investigation of these complexes was carried out following intimate mixing of the samples with inert alumina (50% by weight).

Table 1 Analytical, magnetic and electronic spectral data of 1,2-propanediamine (L) complexes of nickel(II)

Compound	Compound No.	Colour	Nickel	Elemental analyses, % ^a			$\mu_{\text{eff.}}$ (B. M.)	$\lambda_{\text{max.}}$ nm
				Nitrogen	Halogen/ Sulphur/ Selenium			
[NiL ₃]Cl ₂ · 2 H ₂ O	1	Pink	15.06 (15.14)	21.72 (21.66)	18.01 (18.31)	2.95	521, 334	
[NiL ₃]Br ₂ · 1.5 H ₂ O	2	Pink	12.48 (12.55)	17.92 (17.96)	33.5 (34.18)	3.01	522, 334	
[NiL ₃](SCN) ₂	3	Pink	14.80 (14.79)	28.30 (28.23)	15.89 (16.13)	3.11	520, 332	
[Ni ₂ L ₅ (NCS) ₂](SCN) ₂ ^b	3A	Bluish pink	16.27 (16.32)	27.17 (27.24)	17.41 (17.79)	3.09	542, ~ 350 (sh)	
[NiL ₃]SO ₄ · 2 H ₂ O	4	Pink	14.20 (14.22)	20.30 (20.35)	7.24 (7.75)	3.11	524, 338	
[NiL ₃]SO ₄ · H ₂ O ^b	4B	Pink	14.81 (14.87)	21.19 (21.28)	7.81 (8.10)	3.09	524, 338	
[NiL ₂ SO ₄] ^b	4D	Very pale pink	19.30 (19.39)	18.51 (18.49)	10.18 (10.57)	2.94	~ 550 (sh), ~ 352 (sh)	
[NiL ₃]SeO ₄ · 2 H ₂ O	5	Pink	12.71 (12.77)	18.20 (18.27)	16.87 (17.17)	3.10	524, 337	

^a Figures in parentheses are the required percentage; ^b Synthesized in the solid state.

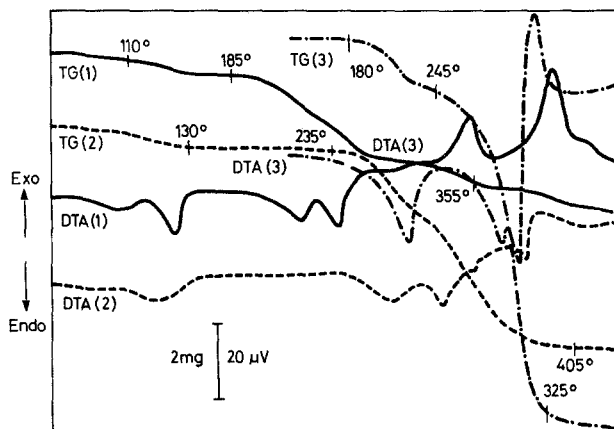


Fig. 1 Thermal curves of ———, $[\text{NiL}_3]\text{Cl}_2 \cdot 2 \text{H}_2\text{O}$ (1), sample mass 6.85 mg; - - - - -, $[\text{NiL}_3]\text{Br}_2 \cdot 1.5 \text{H}_2\text{O}$ (2), sample mass 11.01 mg; - · - · -, $[\text{NiL}_3](\text{SCN})_2$ (3), sample mass 16.25 mg

Table 2 Thermal parameters of 1,2-propanediamine (L) complexes of nickel(II)

Decomposition reactions	Temperature range, °C	DTA peak temperature, °C	
		Endo	Exo
$[\text{NiL}_3]\text{Cl}_2 \cdot 2 \text{H}_2\text{O}$ (1) \rightarrow $[\text{NiL}_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$	75–110	105	—
$[\text{NiL}_3]\text{Cl}_2 \cdot \text{H}_2\text{O} \rightarrow [\text{NiL}_3]\text{Cl}_2$	110–150	145	—
$[\text{NiL}_3]\text{Cl}_2 \rightarrow [\text{NiL}_2\text{Cl}_2]$	185–242	235	—
$[\text{NiL}_2\text{Cl}_2] \rightarrow [\text{NiLCl}_2]$	242–285	263	—
$[\text{NiLCl}_2] \rightarrow [\text{NiL}_{0.33}\text{Cl}_2]$	285–360	—	355
$[\text{NiL}_{0.33}\text{Cl}_2] \rightarrow \text{NiCl}_2$	360–550	—	412
$[\text{NiL}_3]\text{Br}_2 \cdot 1.5 \text{H}_2\text{O}$ (2) \rightarrow $[\text{NiL}_3]\text{Br}_2 \cdot \text{H}_2\text{O}$	50–80	75	—
$[\text{NiL}_3]\text{Br}_2 \cdot \text{H}_2\text{O} \rightarrow [\text{NiL}_3]\text{Br}_2$	80–130	110	—
$[\text{NiL}_3]\text{Br}_2 \rightarrow [\text{NiL}_2\text{Br}_2]$	235–295	280	—
$[\text{NiL}_2\text{Br}_2] \rightarrow \text{NiBr}_2$	295–395	315, 370	375
$[\text{NiL}_3](\text{SCN})_2$ (3) \rightarrow $[\text{NiL}_{2.5}(\text{NCS})](\text{SCN})$ (3A)	180–225	220	—
$[\text{NiL}_{2.5}(\text{NCS})](\text{SCN}) \rightarrow \text{NiS} + \text{S} + \text{C}$	235–335	292, 305	315
$[\text{NiL}_3]\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ (4) \rightarrow $[\text{NiL}_3]\text{SO}_4 \cdot \text{H}_2\text{O}$ (4A)	50–88	82	—
$[\text{NiL}_3]\text{SO}_4 \cdot \text{H}_2\text{O} \rightarrow [\text{NiL}_3]\text{SO}_4 \cdot \text{H}_2\text{O}$ (4B)	88–102	—	95
$[\text{NiL}_3]\text{SO}_4 \cdot \text{H}_2\text{O} \rightarrow [\text{NiL}_3]\text{SO}_4$ (4C)	130–165	160	—
$[\text{NiL}_3]\text{SO}_4 \rightarrow [\text{NiL}_2\text{SO}_4]$ (4D)	180–250	238	250
$[\text{NiL}_2\text{SO}_4] \rightarrow [\text{NiLSO}_4]$	265–330	—	315, 327
$[\text{NiLSO}_4] \rightarrow [\text{NiL}_{0.5}\text{SO}_4]$	330–405	—	385
$[\text{NiL}_{0.5}\text{SO}_4] \rightarrow \text{NiO}$	405–510	—	495
$[\text{NiL}_3]\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ (5) \rightarrow $[\text{NiL}_3]\text{SeO}_4 \cdot \text{H}_2\text{O}$	40–85	78	—
$[\text{NiL}_3]\text{SeO}_4 \cdot \text{H}_2\text{O} \rightarrow [\text{NiL}_3]\text{SeO}_4$	85–125	120	—
$[\text{NiL}_3]\text{SeO}_4 \rightarrow [\text{NiL}_2\text{SeO}_4]$	210–265	260	—
$[\text{NiL}_2\text{SeO}_4] \rightarrow \text{NiSeO}_4$	265–305	—	295

tion pattern from the stage of $[\text{NiL}_2\text{Cl}_2]$ is very similar to that of $[\text{Ni}(\text{N,N-diethyl-1,2-ethanediamine}_2\text{Cl}_2)]$ reported earlier [6].

$[\text{NiL}_3]\text{Br}_2 \cdot 1.5 \text{H}_2\text{O}$ (2) *

This complex also possesses O_h geometry. Dehydration at 50° and the complex becomes anhydrous at 130° through formation of the monohydrate as intermediate.

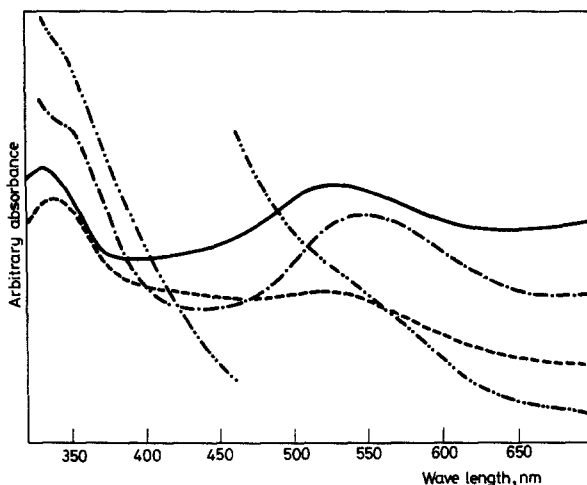


Fig. 2 Electronic spectra of ———, $[\text{NiL}_3](\text{SCN})_2$ (3); - · - · -, $[\text{Ni}_2\text{L}_5(\text{NCS})_2](\text{SCN})_2$ (3A); - - - -, $[\text{NiL}_3]\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ (4); - - - - -, $[\text{NiL}_2\text{SO}_4]$ (4D)

The decomposition pattern of $[\text{NiL}_3]\text{Br}_2$ is very complicated. It decomposes to a nonisolable intermediate, $[\text{NiL}_2\text{Br}_2]$ and then decomposes to NiBr_2 through several nonisolable intermediates.

$[\text{NiL}_3](\text{SCN})_2$ (3)

This undergoes decomposition to metal sulphide (Fig. 1) via an isolable intermediate $[\text{Ni}_{2.5}(\text{NCS})](\text{SCN})$ (3A) *, which is very interesting. The electronic spectra (mull) (Fig. 2) and magnetic moment of species (3A) suggest that the complex possesses octahedral geometry. The i.r. spectra of complexes (3) and (3A) show some differences. Complex (3) displays bands at 2062 and 745 cm^{-1} , due to ν_{CN} and ν_{CS} vibrations of anionic thiocyanate. Complex (3A) has ν_{CN} and ν_{CS} at 2062 and 745 cm^{-1} for anionic thiocyanate, and at 2097 and 775 cm^{-1} for coordinated N-bonded thiocyanate (Fig. 3) [10, 11]. Further, the metal:ligand ratio in complex

* Conductance data on complex (3A) could not be taken due to its insolubility in noncoordinating solvents.

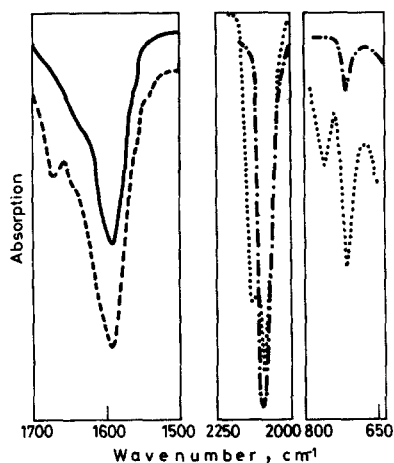
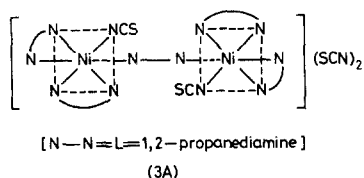


Fig. 3 IR spectra of ———, $[\text{NiL}_3]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (4); - - - - -, $[\text{NiL}_3]\text{SO}_4 \cdot \text{H}_2\text{O}$ (4B); - · - · - ·, $[\text{NiL}_3](\text{SCN})_2$ (3); ······, $[\text{Ni}_2\text{L}_5(\text{NCS})_2](\text{SCN})_2$ (3A)

(3A) helps us to predict that it should be dimeric and one of the ligands should be bridged to attain the O_h configuration. On the basis of the i.r. and electronic spectra and magnetic moment (Table 1) of complex (3A), the probable structure may be depicted as follows.

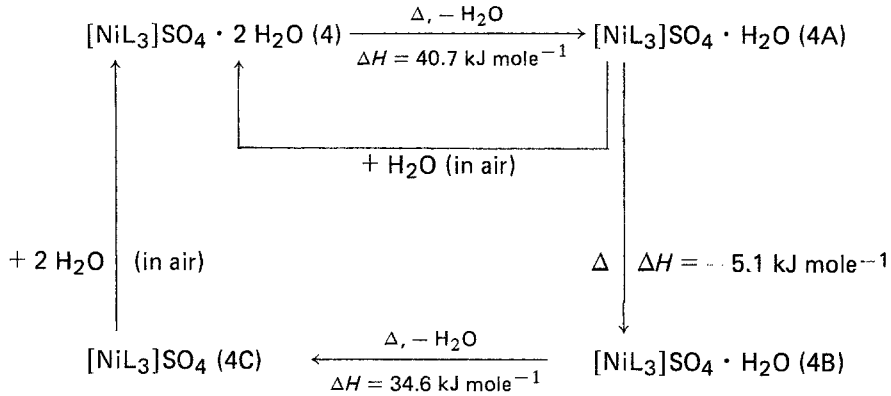


The thermal curves show that complex (3A) decomposes in a very complicated fashion. We earlier observed that the complex $[\text{Ni}(\text{en})_3](\text{SCN})_2$ where $\text{en} = 1,2$ -ethanediamine showed a phase transition, followed by melting and decomposition, with a steady weight loss in the TG curve [4]. Although complex (3) and $[\text{Ni}(\text{en})_3](\text{SCN})_2$ are of similar type, their modes of decomposition differ.

$[\text{NiL}_3]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (4)

The i.r. spectra, magnetic and electronic spectra (mull) show that complex (4) possesses an identical chromophore to complex (1). The deaquation behaviour of this complex appears very interesting. Deaquation starts at 50° , and yields the monohydrate (4A) at 88° , with an endothermic peak at 82° . The derived monohydrate (4A) transforms to (4B) with an exothermic peak at 95° [$\Delta H = -5.1 \text{ kJ mole}^{-1}$], with no mass loss in the TG curve (Fig. 4). Species (4B) starts to lose water at 130°

and becomes anhydrous (4C) at 165° (Scheme 1). The monohydrate (4B) is stable in air and is not hygroscopic at all, whereas the monohydrate (4A) is hygroscopic and instantaneously absorbs one molecule of water on exposure to air. Complex (4C)



Scheme 1

is also hygroscopic and absorbs two molecules of water from the atmosphere to yield the original species (4). This absorption of water probably takes place proportionately. It may be corroborated by the fact that the nature of the deaquation profile remains the same even on the partial absorption of water, i.e. $< 2 \text{H}_2\text{O}$. The differences in the thermal profiles of $[\text{NiL}_3]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ and $[\text{NiL}_3]\text{SO}_4 \cdot x\text{H}_2\text{O}$ ($x < 2 \text{H}_2\text{O}$) are only

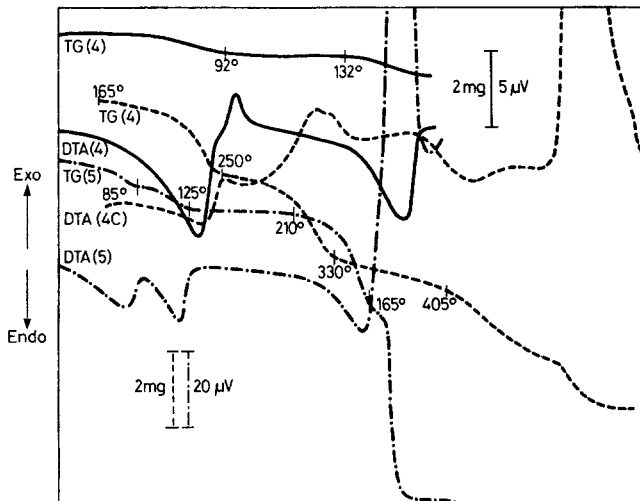


Fig. 4 Thermal curves of —, $[\text{NiL}_3]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (4), sample mass 10.78 mg; - - - -, $[\text{NiL}_3]\text{SO}_4$ (4C), sample mass 10.60 mg; - · - · - ·, $[\text{NiL}_3]\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ (5), sample mass 16.06 mg

in the TG weight loss and the areas of the three DTA curves relating to the deaquation phenomenon.

The exothermic peak at 95° may be due to the following reasons: (i) configurational changes around the central metal ion as in Lifschitz salts [12], (ii) conformational changes of the individual chelate rings [8], and (iii) formation of hydrogen-bonds between the lattice water molecule and the SO_4^{2-} oxygen or the NH_2 hydrogen of the ligand. However, the almost identical electronic mull spectral and magnetic data on complexes (4) and (4B) preclude any difference in the orientation of the donor atoms about the central metal ion. I.r. spectra of complexes (4), (4B) and rehydrated (4C) were taken and their spectral band positions with respect to the ligand vibrations were almost identical. This shows that the chelate conformations in complexes (4) and (4B) remain unaltered. We observed a peculiar difference in the bending vibration region of the H_2O molecule between complexes (4) and (4B) (Fig. 3). Normally, the lattice water absorbs at 1630–1600 cm^{-1} for HOH bending [13]. But this can shift upward by 10–50 cm^{-1} upon H-bond formation [14]*. Complex (4) shows a prominent shoulder at $\sim 1635 \text{ cm}^{-1}$ in the i.r. spectrum, whereas (4B) HOH bending bands at 1672 cm^{-1} and 1645 cm^{-1} (sh). It may therefore be suggested that the symmetry of the water molecule is appreciably lowered in complex (4B) and the water molecules are situated in different ways in the crystal lattices of (4) and (4B). Hence, it is clear that the water molecule is strongly hydrogen-bonded, probably through either the SO_4^{2-} oxygen or the NH_2 hydrogen or both, and this hydrogen-bond formation takes place here just after the elimination of one molecule of H_2O from complex (4), with an exothermic peak at 95° in the DTA profile (Fig. 4). The elimination of the water molecule from complex (4B) at a high temperature also corroborates the hydrogen-bonding phenomenon.

Complex (4C) starts to decompose at 180°, and becomes $[\text{NiL}_2\text{SO}_4]$ (4D) at 250°. On further heating, $[\text{NiL}_2\text{SO}_4]$ starts to decompose at 265°, and transforms to NiO through the formation of nonisolable $[\text{NiLSO}_4]$ and $[\text{NiL}_{0.5}\text{SO}_4]$ as intermediates. The bis species (4D) is almost white in colour. Its electronic spectrum (mull) (Fig. 2) and magnetic data (Table 1) suggest that it possesses O_h geometry. The i.r. spectral data suggest that the ligands are chelated and possess *cis* configurations (4D) [5, 7]. It is not possible to assign the coordination pattern of SO_4^{2-} to the central metal ion as the ligand also absorbs in the region 1200–1000 cm^{-1} , where the ν_3 vibration of SO_4^{2-} appears, but the attainment of hexacoordination of the Ni atom in the complex $[\text{NiL}_2\text{SO}_4]$ suggests the bidentate character of the SO_4 group.

$[\text{NiL}_3]\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ (5)

Physicochemical studies suggest that this complex possesses O_h geometry, like complex (1). Dehydration starts at 40° and the anhydrous complex is obtained at

* Although the stretching mode of the water molecule is more informative here, it is very difficult to assign this in the presence of the NH_2 stretching mode, because the stretching mode of the water molecule shifts towards the lower frequency region due to H-bonding [14].

125° through the formation of nonisolable monohydrate species as 85° as intermediate (Fig. 4). The anhydrous species starts to decompose at 210° and transforms to NiSeO₄ at 305° through the formation of a nonisolable intermediate [NiL₂SeO₄] at 265°. It is interesting that complexes (4) and (5) are similar in composition, but differ as concerns the deaquation phenomenon. Another interesting observation is that NiSO₄ and NiSeO₄ do not yield hydrated complexes with 1,2-ethanediamine [7]. This suggests that both the diamine and the SO₄²⁻ anion are probably responsible for the solid-state reaction of [NiL₃]SO₄ · H₂O (4A).

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Zusammenfassung — Thermische Untersuchungen wurden an [NiL₃]X₂ · n H₂O ausgeführt, wobei L = 1,2-Propandiamin; X = Cl⁻, Br⁻, SCN⁻, 1/2 SO₄²⁻ und 1/2 SeO₄²⁻; n = 2, 1.5 und 0. [Ni₂L₅(NCS)₂](SCN)₂ und [NiL₂SO₄] wurden ausgehend von den entsprechenden Diaminkomplexen pyrolytisch im festen Zustand synthetisiert. Das Dehydratisierungsverhalten von [NiL₃]SO₄ · 2 H₂O scheint interessant zu sein, und beim entsprechenden Monohydrat wird eine ohne Massenverlust verlaufende Festkörperreaktion (88–102°) beobachtet, die sich durch einen exothermen Peak bei 95 °C (ΔH = - 5.1 kJ mol⁻¹) zu erkennen gibt.

Резюме — Проведено термическое исследование комплексов типа [NiL₃]X₂ · nH₂O, где L = 1,2-пропандиамин, X = Cl⁻, Br⁻, SCN⁻, 1/2 SO₄²⁻, 1/2 SeO₄²⁻, а n = 2, 1.5 и 0. Комплексы типа [Ni₂L₅(NCS)₂](SCN)₂ и [NiL₂SO₄] были получены в твердом состоянии путем пиролиза соответствующих диаминовых комплексов. Дегидратация комплекса [NiL₃]SO₄ · 2 H₂O протекает с потерей одной молекулы воды, а образующийся моногидрат затем в области температур 88–102° подвергается твердотельной реакции без потери веса, показывая при этом экзотермический пик при 95 °C ΔH = - 5.1 кдж · моль⁻¹.