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SYNTHESIS AND THERMAL DECOMPOSITION OF $[Ni_2(C_4H_4O_6)_2]\cdot 7H_2O$

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Abstract

The paper describes the synthesis, characterization and thermal decomposition of nickel(II) bis(tartrato) nickelate(II) heptahydrate $[Ni_2(C_4H_4O_6)_2]\cdot 7H_2O$. The complex was characterized by elemental analysis, magnetic moment measurement, infrared, ESR and electronic spectroscopy. The experimental evidences indicate that complex is likely to have metal bonding. The thermal decomposition of the complex produced NiO in air at about 360°C and in nitrogen at about 380°C as the final product. Some of the intermediates produced during the thermolysis were isolated by temperature arrest technique and identified by analytical and spectroscopic methods. A tentative reaction mechanism is proposed for the thermal decomposition of the complex in air and nitrogen.

Keywords: decomposition, dehydration, metal–metal bond, tartrate complex

Introduction

The synthesis, characterization and thermal decomposition of a large number of tartrato complexes of transition and non-transition metals have been reported by different workers [1–4]. The preparation and thermal decomposition of a series of oxalato complexes have already been reported [5–10] from these laboratories. The photodecomposition of potassium ferrioxalate by near ultraviolet and visible light in 0.1N H_2SO_4 is exploited for following the photochemical reactions by chemical actinometer [11]. It should be interesting to replace potassium ferrioxalate by a complex like nickel(II) bis(tartrato) nickelate(II) since only NiO is expected to remain in the residue of the complex after irradiation. The complex may be tried for photoinitiation of photopolymerization reaction as done with iron(III) tris(oxalato) ferrate(III) tetrahydrate $Fe[Fe(C_2O_4)_3]\cdot 4H_2O$ at room temperature [21] since the complex is stable at room temperature. This paper reports the synthesis, characterization and thermal decomposition of the hitherto unknown $Ni[Ni(tart)_2]\cdot 7H_2O$ in both air and nitrogen atmosphere.

Experimental

Preparation of the compounds

Nickel(II) hydroxide, prepared from nickel chloride was made free from chloride. It was dissolved in glacial acetic acid and heated on a steam bath. The solution

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was filtered and a greenish compound was precipitated by dropwise addition of stoichiometric amount of hot saturated solution of *L*(+) tartaric acid in glacial acetic acid. The compound was filtered off and repeatedly washed with hot distilled water, ether and acetone to remove foreign substances. Finally, the compound was dried over $CaCl_2$ in vacuum [5]. The water content was determined gravimetrically and the nickel content was also estimated gravimetrically as bis(dimethyl glyoximato) nickel(II). Carbon and hydrogen were estimated by Thomas CH analyser. Analysis: calculated for $[Ni_2(C_4H_4O_6)_2]\cdot 7H_2O$, Ni, 21.7%, C, 17.86%, H, 4.07%, H_2O, 23.42%; found Ni, 20.90%, C, 17.50%, H, 4.06%, H_2O, 23.10%.

NiC_2O_4 was prepared by the reaction between $Ni(OH)_2$ and oxalic acid in hot water. The greenish yellow compound was washed repeatedly with cold distilled water and then by acetone and finally it was dried over $CaCl_2$ in vacuum. Analysis: calculated for NiC_2O_4, Ni, 39.73%, C, 16.45%. found: Ni, 38.21%, C, 15.85%.

Spectroscopic and thermal measurements

The infrared spectra of the gases evolved during the complete decomposition of the complex were recorded as described earlier [5]. The IR spectra (4000–5000 cm^{-1}, pellet is KBr) of complex and of the intermediates were recorded with a Perkin Elmer spectrophotometer. The low-frequency IR spectra (625–125 cm^{-1}) was recorded with BOMEN DA-8 FTIR spectrophotometer. Diffuse reflectance spectra were recorded with a Shimadzu UV 240 spectrophotometer using $BaSO_4$ as the reference material. A varian E-line century series ESR spectrometer was used to record the ESR spectra of the complex with TCNE as marker. The thermogravimetric analysis (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) were carried out with Perkin Elmer thermal analyser operating at a heating rate of 10°C min^{-1}. TG and DTA were carried out both in air and nitrogen media, but DSC was carried out only in nitrogen medium. For TG in air and nitrogen, the amount of the samples were 8.95 and 0.87 mg, respectively. For DTA in air and nitrogen, the amounts were 10.00 and 15.00 mg, respectively. Magnetic moment of the complex was measured through vibrating sample magnetometer Model No. 155 using cobalt mercuric thiocyanate $Co[Hg(SCN)_4]$ as reference. X-ray powder diffraction spectrum was taken using CuK_α radiation. The operation voltage was 30 kV and current 10 mA. The scattering angle was 2 to 100° with a step angle 0.05°.

Results and discussion

The greenish powdery tartrato compound was insoluble in hot water and in common organic solvents. However, it could be decomposed by strong acids and alkalis. The electronic spectrum (Fig. 1) of the solid sample showed some complex multicomponent bands centred around 20.000 cm^{-1} (33.333, 25.000, 19.230, 16.660 and 11.363 cm^{-1}). Out of these bands, the bands at 25.000, 19.230 and 11.363 cm^{-1} were assigned approximately as $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions in octahedral nickel(II) complex, respectively [12]. The spectrum is too complex to exactly fit a regular octahedral or square planar geometry. So a distorted structure for the complex may be predicted [7].

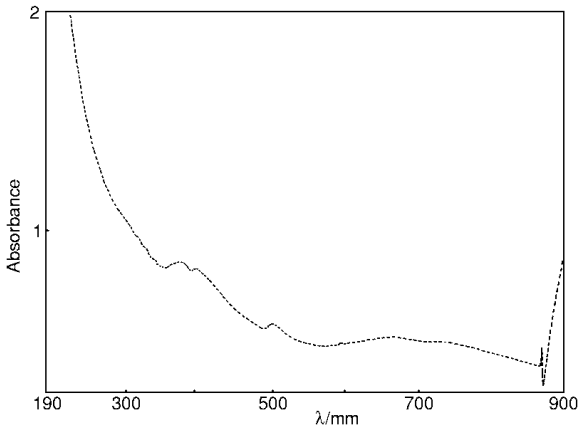

Fig. 1 Electronic spectrum (solid state) of $Ni[Ni(C_4H_4O_6)_2]\cdot 7H_2O$

Gravimetric analysis indicated the association of seven molecules of water with each molecule of the compound. The broad band observed in the region 3700–2700 cm^{-1} in the IR spectra (Table 1) of the compound was due to the symmetric and asymmetric stretching frequencies of water [13] as well as due to hydrogen bonding. The medium sharp peak around 606 cm^{-1} was due to rocking mode [14] or to coordinated water and crystal water [15]. The nickel tartrate complex showed two strong absorptions at 1600 and 1406 cm^{-1}. These two absorptions were

Table 1 Selected bands in the IR spectrum of the complex $Ni[Ni(C_4O_6H_2)_2]\cdot 7H_2O$

IR bands/cm^{-1}	Assignments
2700–3700 (b)	$\nu_{sy(O-H)} + \nu_{asy(O-H)}$ or hydrogen bonding
1600 (s) 1406 (s)	asymmetric and symmetric COO^- stretching vibration
1125 (s) 1050 (s)	alcoholic C–O stretching vibration [1]
1337 (m)	$\nu_{sy(O-C)}$ and/or $\nu_{(O-C)}$
1298 (m)	$\nu_{sy(O-C)}$ and/or $\nu_{(O-C=O)}$
815 (m)	$\delta_{(O-C=O)}$
730 (m)	coordinated water [25]
650 (ms)	$\nu_{(Ni-O)}$
600 (w)	crystal water
485 (ms)	$\nu_{(Ni-O)}$ or $\nu_{(C-C)}$ and/or $\nu_{(O-C=O)}$
317 (ms)	ring deformation
205 (ms)	$\nu_{(Ni-Ni)}$

s = sharp, m = medium, b = broad

assigned to the asymmetric and symmetric COO^- stretching frequencies, respectively [16]. These carboxylate stretchings observed for nickel tartrato complex strongly suggested that both oxygen atoms are coordinated to nickel [2]. Two other prominent absorptions for nickel tartrato complex occurred at 1125 and 1050 cm^{-1} which were assigned to stretching vibration of alcoholic hydroxyl groups [1]. These bands observed in IR spectra strongly supported the presence of coordinated tartrato group [1]. The medium sharp band at 205 cm^{-1} in the far infrared spectrum of the complex might be due to metal–metal i.e. Ni–Ni bond in the complex [7]. The presence of a very weak signal in the ESR spectrum of the complex indicated weak paramagnetic nature of the complex.

At room temperature, the magnetic moment of the complex was found to be 0.79 BM. The lowering of μ_{eff} from the spin-only magnetic moment value for isolated Ni^{2+} ion might be attributed to the presence of metal–metal bond in the complex [12, 6–8]. In absence of Ni–Ni bond, the magnetic moment would have been from 2.9 to 3.4 BM [12] and would not show the peak at 205 cm^{-1} in the far IR spectrum.

The preliminary investigation by analytical method, extreme insolubility of the compound, far IR data and magnetic moment determination indicated the possibility of existence of Ni–Ni bond, but it could not be established conclusively. The compound could be isolated only in the powder form and the isolation of the single crystal could not be achieved. So, the micro structure of the compound could not be established. However, the molecular formula of the compound was established conclusively.

The water vapour, CO, CO_2 and C_2H_4 evolved during decomposition were identified by IR spectroscopy [5].

Thermal studies

The thermal decomposition of nickel tartrate heptahydrate in air occurred in three distinct steps. The TG curve in air (Fig. 2a) showed that the complex started to lose water molecules at about 45° and this process was completed at about 150°C, 16.5% of the mass was lost which corresponded to the loss of five molecules of water (calculated mass loss 16.69%). For these two dehydration processes two overlapping DTG peaks were obtained between 50–150°C (Fig. 2b).

Two small endothermic peaks were obtained at 65 and 160°C in DTA curve in air (Fig. 4a). The overlapping DTG peaks and two endothermic peaks in DTA curve suggested that the water molecules were eliminated in two different steps. The second step of decomposition started at 160°C and continued upto 330°C. The mass loss at the end of this step was 55% which corresponded to the simultaneous dehydration and decomposition of the complex to a mixture of NiC_2O_4, NiO and C (calculated 54.55%). It was not possible to isolate the completely anhydrous form as the last traces of water got removed only during the time of further decomposition of the compound [5]. The presence of a weak band at 3400–3200 cm^{-1} in the IR spectrum of the compound preheated to 160°C indicated the presence of water molecule. The presence of the peaks indicated that the chelating character of the tartrato group was retained. The faint green compound so produced absorbed moisture immediately on

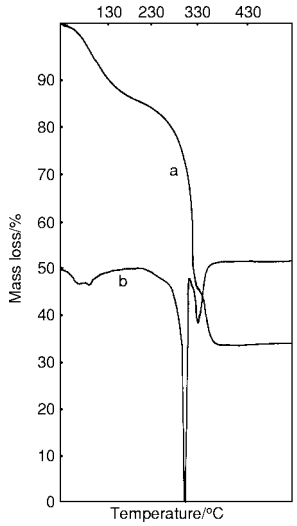

Fig. 2 TG (a), DTG curve of the complex in air medium (b)

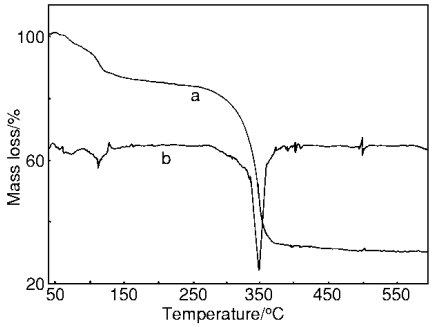

Fig. 3 TG (a), DTG curve of the complex in nitrogen medium (b)

exposure to humid atmosphere resulting in the reformation of the original compound as evidenced by the reappearance of the broad band in the region 3700–3000 cm^{-1}. The removal of water at high-temperature supported the formation of metal–oxygen coordination bond with water as well as hydrogen bonding [7].

In N_2 atmosphere, the mass loss started from 50°C (Fig. 3a) and completed at 100°C with mass loss 3.5% corresponded to the elimination of one water molecule (calcd. 3.3%). The second step of dehydration was between 100 to 150°C with mass loss 16.50% which indicated the loss of five molecules of water (calcd. 16.72%).

These two dehydration processes were confirmed by DTA in N_2 where two endothermic peaks were obtained at 100 and 150°C (Fig. 4b). For these processes, a broad peak was obtained between 90–150°C in DTG curve (Fig. 3b). In N_2 atmosphere, the partly dehydrated compound was almost stable upto 270°C. A greenish yellow mixture was obtained as intermediate in air around 330°C. The intermediate

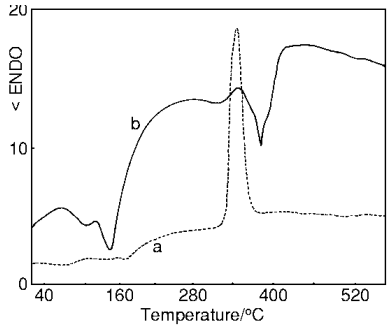

Fig. 4 DTA curve of the complex in air (a) and nitrogen medium (b)

was a mixture of NiO, NiC_2O_4 and C with mass loss 55% (calcd. 54.51%). The constituents were separated by hot water with difficulty [7]. The greenish compound was identified to be NiO analytically (Ni, found 78.32%, calcd. 78.58%) and spectroscopically with a broad band around 460 cm^{-1} in the IR spectrum [14, 7]. The X-ray powder diffraction pattern of this compound was similar to that of NiO [7]. Nickel content was estimated for the greenish yellow compound and from this it was confirmed that the compound was NiC_2O_4 (found 39.98%, calcd. 40.01%). The IR spectrum of this compound was similar to that of the compound reported by Tanaka *et al.* [18].

The XRD spectra of this compound was also similar to that of NiC_2O_4 prepared in the laboratory. Some workers also established that the thermal decomposition of tartrato complexes took place through the intermediate formation of oxalates [22, 23]. NiC_2O_4 decomposed immediately before its normal decomposition temperature was reached because of the heat produced during the decomposition process. NiO may have an accelerating effect on the rapid decomposition of NiC_2O_4 [7]. The formation of a mixture of NiO and NiC_2O_4 indicated that the outer nickel in the complex produced nickel oxide and the inner nickel, NiC_2O_4 [5]. The last decomposition step in air was completed at 360°C with mass loss 67% which indicated the formation of a stable compound NiO and C (calcd. mass loss 67.89%) or a mixture of NiO, Ni_2O_3 and C. The large exothermic peak recorded in DTA curve in air around 350°C correspond to this overall decomposition step. The black residue (Ni, 74.36%) was found to be paramagnetic in nature in the ESR spectrum. The IR spectrum showed a broad band at 462 cm^{-1} and a weak band at 650 cm^{-1} [24]. The results obtained from analytical data suggested that the residue could be a non-stoichiometric form of the oxides [6, 7]. In DTG curve, two distinct peaks were obtained between 210–330°C and 330–370°C. The last two decomposition steps were confirmed by the appearance of these peaks.

The partly dehydrated complex was stable upto 270°C in nitrogen medium and it could be separated by temperature arrest technique. The analytical data and IR spectrum indicated the existence of chelated tartrato group and two molecules of water. The remaining water molecules were removed from 270°C in nitrogen atmosphere

Table 2 Results of decomposition processes of nickel(II) bis(tartrato) nickelate(II) heptahydrate from TG and DTA

Medium	Step No.	T_{range}/ °C	Mass loss/%		DTA peak/ °C	Loss of molecules in the step	Reaction
			observed	calculated			
Air	1	45–150	16.50	16.69	65 (endo) 160 (endo)	$5H_2O$	dehydration
	2	160–330	55.00	54.55	350 (exo)	$2CO_2$, CO, $3H_2O$, $0.5C_2H_4$	dehydration + decomposition
	3	330–360	67.00	67.89		CO, CO_2	
Nitrogen	1	50–150	16.50	16.72	100 (endo) 150 (endo)	$5H_2O$	dehydration
	2	270–330	36.25	35.25	330 (endo)	CO, $2H_2O$	dehydration + decomposition
	3	330–380	68.00	67.91	385 (endo) 420 (exo)	4CO, CO_2, $2H_2O$	

and with the elimination of water molecules, the complex decomposed. At 330°C an intermediate of the type $Ni(C_4H_4O_6)\cdot NiCO_3$ was formed (observed mass loss 36%, calculated 35.25%). The intermediate of this type was reported earlier for some tartrato compounds [19]. The intermediate could not be isolated as it decomposed beyond 330°C. The continuous mass loss from 330 to 380°C with a mass loss 68% might be due to the formation of mixture of NiO and carbon (calculated mass loss 67.91%). In DTA in nitrogen, an endothermic peak was obtained at 330°C corresponding to the formation of the intermediate $Ni(C_4H_4O_6)\cdot NiCO_3$. Another endothermic peak at 385°C corresponded to the final decomposition of the complex. Two overlapping DTG peaks (Fig. 3b) were obtained between 265–380°C in nitrogen for this two-step decomposition of the complex. The exothermic peak recorded in DTA at 420°C without any mass loss in TG curve might be ascribed to some phase transformation with the formation of a mixture of the oxides of nickel [20] or due to the interaction or the solid–solid reaction of the products [7]. The thermal analysis results are summarized in Table 2.

Depending upon the results outlined above, a tentative mechanism may be proposed for thermal decomposition of the complex.

In air

$$Ni[Ni(C_4H_4O_6)_2]\cdot 7H_2O \xrightarrow[-5H_2O]{45-150^\circ C} Ni[Ni(C_4H_4O_6)_2]\cdot 2H_2O \xrightarrow[-(CO,\ 0.5C_2H_4,\ 3H_2O,\ 2CO_2)]{160-330^\circ C}$$

$$NiC_2O_4 + NiO + 2C \xrightarrow[-(CO,\ CO_2)]{330-360^\circ C} 2NiO \text{ or } (NiO + 0.5Ni_2O_3) + 2C$$

In nitrogen

$$Ni[Ni(C_4H_4O_6)_2]\cdot 7H_2O \xrightarrow[-H_2O]{50-100^\circ C} Ni[Ni(C_4H_4O_6)_2]\cdot 6H_2O \xrightarrow[-4H_2O]{100-150^\circ C}$$

$$Ni[Ni(C_4H_4O_6)_2]\cdot 2H_2O \xrightarrow[-(2H_2O,\ CO)]{270-330^\circ C} Ni(C_4H_4O_6)\cdot NiCO_3 + 2C \xrightarrow[-(CO_2,\ 4CO,\ 2H_2O)]{330-380^\circ C}$$

$$2NiO + 2C$$

* * *

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