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THERMAL BEHAVIOUR OF $[CoCO_3(NH_3)_4]_2SO_4 \cdot 3H_2O$*

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The thermal behaviour of $[CoCO_3(NH_3)_4]_2SO_4 \cdot 3H_2O$ was studied using X-ray diffraction diagrams, DTA, TG and heating at constant temperatures for different periods of time. The X-ray study was made in order to characterize with the powder diagrams the phases obtained and to follow the reactions of the complex when heated in air up to 800°. A parallel infrared spectral study was also made. The results obtained by the various experimental methods were compared with the theoretical weight losses.

Several techniques were used in the thermal study of the complex $[CoCO_3(NH_3)_4]_2SO_4 \cdot 3H_2O$: DTA and TG to examine the thermal behaviour; X-ray diffraction and IR spectra to characterize the phases obtained and to follow the reactions of the complex heated in air up to 800°.

The compound was prepared according to the method of "Inorganic Syntheses" [1]. The crystals were thus obtained as ruby-red needles. The crystal has been investigated by Jaeger [2] and Strock [3] in order to characterize its structural constants.

Several authors have already studied the thermal stability of cobalt(III) ammine complexes. The work of Wendlandt and Smith [4] is worth mentioning here.

Experimental

The thermal study of the complex was performed by DTA, TG and heating at constant temperatures for different periods of time.

DTA measurements were carried out in a Bolton apparatus, model DITA (chromel/alumel thermocouples). In this apparatus the two specimens (sample and reference material) are placed in separate identical wells, contained in a single Inconel block, which is inserted in an electric furnace. A heating rate of 10°/min was employed. 150 mg of sample were used. The sensitivity on the ΔT scale was 2°/inch. The reference material used was α-Al_2O_3.

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TG curves were obtained using a Staton Massflow apparatus. 505 mg of sample were used and the heating rate was 5°/min.

The X-ray spectra were obtained on a Philips apparatus, model PW 1010 and the IR spectra were made with a Perkin Elmer 457 spectrophotometer in the region 250–4000 cm^{-1}.

Results

The differential thermal analysis (Fig. 1) of the complex heated up to 800° in the air is characterized by two endothermic maxima corresponding to the dehydration and the total destruction of the complex, respectively, followed by an exothermic maximum at 350°. The other exothermic peaks are at 415° and 450°.

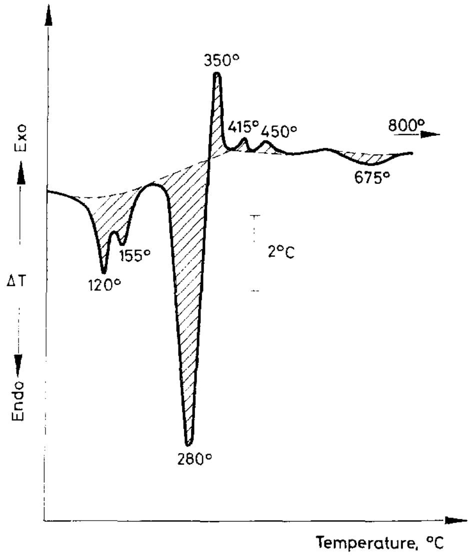

Fig. 1. DTA curve of $[CoCO_3(NH_3)_4]_2SO_4 \cdot 3H_2O$ in air atmosphere; mass of the sample: 150 mg; inert reference material: α-Al_2O_3; thermocouples: chromel/alumel; sample holder: Ni; rate of heating: 10°/min

The TG curve (Fig. 2) is characterized by three steps. The first one comes between 100° and 190°, corresponding to a 9.7% weight loss; the second, between 240° and 380°, corresponds to a loss of 40.7 wt%; and the final one, between 690° and 870°, to a loss of 16.4 wt%.

The thermal decomposition of the complex was then studied by heating it to a constant temperature for different periods of time.

The sample was heated at 120°, 300°, 400°, 500°, 700° and 800° for some seconds and during 2, 4 and 6 hours. The data obtained at 120° are summarized in Table 1.

Table 1

a)		b)		c)		d)	
d Å	I_r	d, Å	I_r	d, Å	I_r	d, Å	I_r
11.66	48			10.05	8	11.63	48
5.292	42			5.24	12	5.27	30
5.122	100					5.12	50
		4.984	25	4.984	50		
4.928	28	4.928	20	4.928	45	4.928	20
4.833	42					4.822	30
4.472	62			4.496	12	4.462	60
4.280	25	4.220	3	4.226	5	4.270	30
		4.014	15	4.015	20		
3.920	100	3.951	10	3.946	15	3.917	75
3.890	57						
3.479	34					3.480	30
3.464	31	3.408	12	3.403	35		
3.125	42					3.121	30
3.069	13					3.028	20
2.915	14					2.921	20
2.550	20	2.560	8	2.560	25		
				2.512	8		
2.410	17						
2.405	17						
						2.332	65

a) Without thermal treatment
b) Thermal treatment at 120°
c) Thermal treatment at 120° (after two weeks in air)
d) Thermal treatment at 120° (re-hydrated in a moist environment at 25°)

Table 2

a)		b)		c)	
d, Å	I_r	d, Å	I_r	d, Å	I_r
3.507	35				
2.849	30	2.849	28	2.860	40
2.637	20				
2.436	100	2.436	100	2.438	100
2.019	20	2.019	32	2.021	25
1.558	35	1.558	28	1.556	35
1.429	35	1.427	40	1.429	45

a) Thermal treatment at 800°
b) Thermal treatment at 800° during 4 hours
c) Co_3O_4 powder standard diagram, ASTM: 9—418

Heating at 120° was made to examine the evolution of the 3 molecules of H_2O of the complex. In Fig. 3 are schematized three DTA curves corresponding to the initial complex (curve A), to the complex heated at 120° with loss of three molecules of H_2O (curve B) and to the complex heated at 120° and re-hydrated in a moist environment at 25° (curve C).

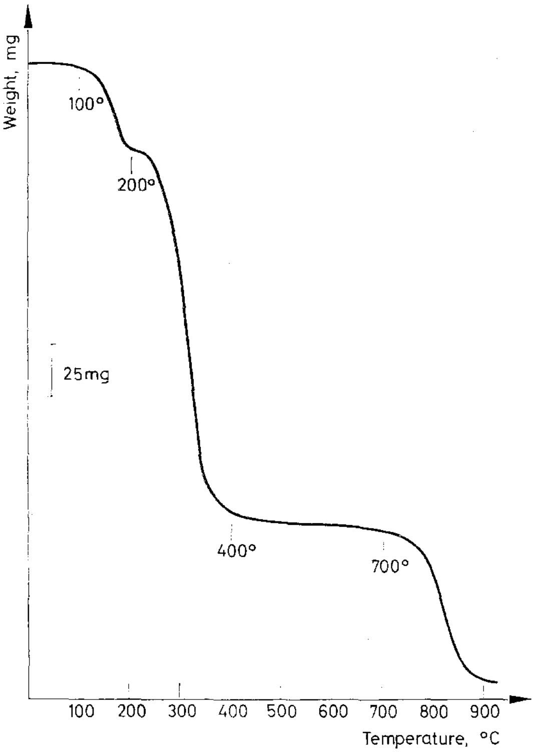

Fig. 2. Mass-loss curve of $[CoCO_3(NH_3)_4]_2SO_4 \cdot 3H_2O$ in air atmosphere; mass of the sample: 505 mg; rate of heating: 5°/min

The X-ray diagrams taken of the sample show a complete structural disorganization of the complex, and the identification is difficult. On the other hand the X-ray diagrams of the samples heated at 800°, for some seconds and during 4 hours, show the presence of lines corresponding to Co_3O_4 (Table 2).

In order to characterize the complex $[CoCO_3(NH_3)_4]_2SO_4 \cdot 3H_2O$ its spectrum was taken. In Table 3 are given the results obtained in the present work, and those obtained by Siebert [5] and Goldschmidt et al. [6].

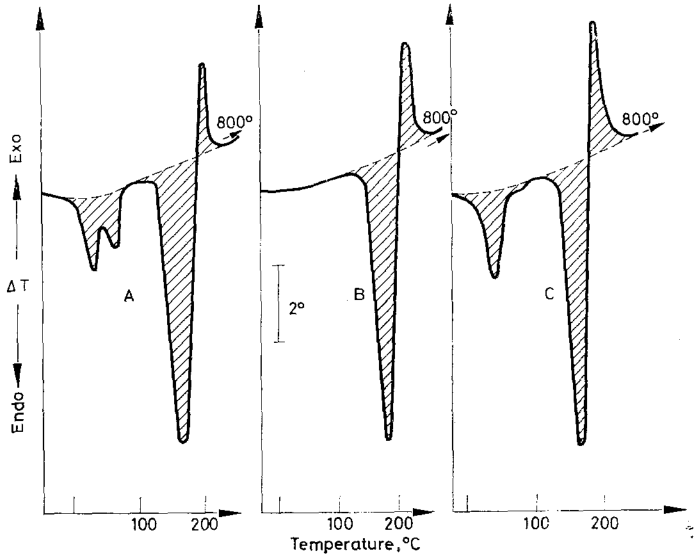

Fig. 3. Evolution of 3 molecules of H_2O of the complex. A: normal; B: dehydrated; C: rehydrated

Table 3

ν, cm⁻¹	Siebert	Goldschmidt et al.	Present work
3290	+		+
3180	+		+
1606	+		+
1320	+		+
1279	+		+
1265	+		+
846	+		+
832	+		+
764	+		+
757	+		+
673	+		+
514		+	+
484		+	+
440		+	+
430		+	+
400		+	+
336		+	
326		+	
286		+	
204		+	
142		+	
130		+	
106		+	

Similarly, due to the impossibility of following the thermal decomposition of the complex by means of X-ray examinations, a parallel infrared spectral study was made with the samples treated for different times and at different temperatures. Fig. 4 shows the variation of the properties studied. The spectra were recorded in the region 1800–250 cm^{-1}, which was most characteristic of the structure and structural changes of the complex.

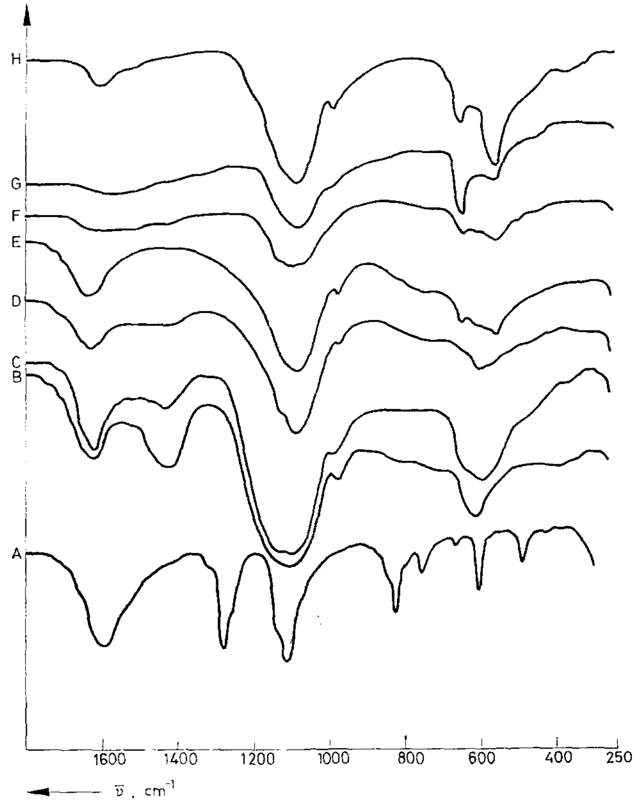

Fig. 4. IR spectra of $[CoCO_3(NH_3)_4]_2SO_4 \cdot 3H_2O$. A: without thermal treatment; B: thermal treatment at 300°; C: thermal treatment at 300° (2 hours); D: thermal treatment at 300° (6 hours); E: thermal treatment at 500° (6 hours); F: thermal treatment at 700°; G: thermal treatment at 700° (2 hours); H: thermal treatment at 700° (6 hours)

On heating at 300° the complex decomposed, that is to say, the bands due to the NH_3 and CO_3 groups as well as the skeletal vibration bands of the complex and the Co – N bands disappeared. It was the same with the bands corresponding to ionic CO_3, which disappeared on continuing the heating for some time.

At 500° and 700° the destruction of the complex continued as indicated by the appearance of the vibration band corresponding to free SO_4.

Finally, the isothermal heating at 700° made the formation of the free SO_4 even more clear as indicated by three bands at 1150, 1100 and 980 cm^{-1} [7].

Discussion

The application of all these different techniques permits us to offer an approximate explanation of the behaviour of the complex (Table 4), without making an analysis of the products of the reaction because of the limitation of equipment.

Table 4

		Losses of weight, %	
		Theoretical	Experimental
$[CoCO_3(NH_3)_4]_2 SO_4 \cdot 3H_2O$			
100° ↓	↗		
200° ↓	$3H_2O$ ↗	10.3	9.7
$[CoCO_3(NH_3)_4]_2 SO_4$	↗		
240° ↓	$8NH_3$ ↗		
380° ↓	$2CO_2$ ↗	42.7	40.7
Unknown compound	↗		
690° ↓	SO_3 ↗		
870° ↓	1/3O ↗	14.4	16.4
Co_3O_4	Total	67.4	66.8

As indicated by the TG curve, a weight loss of 9.7% occurred between 100 and 190° (Fig. 2). This corresponds to the loss of 3 molecules of H_2O. Theoretically the loss of 3 molecules of H_2O corresponds to a loss of weight of 10.3%. Two endothermic maxima in the DTA curve at 120° and 155° are due to the loss of the 3 molecules of H_2O (Fig. 1).

From a study of the region 100–200°, it was observed that the three water molecules are recovered by the complex. This indicates that the water loss in this complex is a reversible process (Fig. 3); this leads to an important retardation which allows one to follow the transformation by X-ray diffraction (Table 1).

The X-ray diagram of the complex at room temperature differs from that of the compound present at 120° (Table 1). The possible variation of the unit cell parameters as a result of the evolution of the 3 molecules of H_2O is a problem for further consideration.

Between 240 and 380° a loss of weight of 40.7% was found (Fig. 2). In this region the differential thermal analysis curve (Fig. 1) is characterized by a very intense exothermic maximum followed by an exothermic maximum at 350°.

It was found from the infrared spectra (Fig. 4) that in these reactions NH_3 and CO_2 are lost. Theoretically we presume that $8NH_3$ molecules and $2CO_2$ molecules are lost. This lost has a value of 42.7%.

Between 690 and 870° the mechanism of the decomposition of the complex is rather complicated (Fig. 1).

The final product of heating up to 800°, determined by X-ray diffraction, is Co_3O_4 (Table 2). The formation of Co_3O_4 is probably due to air oxidation [8]. In order to form this oxide the complex loses 1 molecule of SO_3 and 1/3 molecule of O. This corresponds to a loss of weight of 16.4% (Fig. 2).

X-ray diffraction and infrared studies supported the theoretical reaction scheme constructed on the basis of the experimental weight losses.

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Résumé — On a étudié le comportement thermique de $[CoCO_3(NH_3)_4]_2SO_4 \cdot 3H_2O$ par diffraction de rayons X, ATD et ATG avec maintien en thermostat. L'étude par rayons X a été menée dans le but de caractériser les phases obtenues par leur diagramme de poudre et de suivre les réactions données par le complexe chauffé dans l'air jusqu'à 800°. En raison de l'impossibilité de suivre l'évolution thermique par rayons X, une étude parallèle a été effectuée par spectrographie infrarouge. On a essayé de rapprocher les résultats obtenus à l'aide de ces différentes méthodes.

Zusammenfassung — Das thermische Verhalten von $[CoCO_3(NH_3)_4]_2SO_4 \cdot 3H_2O$ wurde durch Röntgendiffraktion, DTA, TG und Erhitzen auf gleiche Temperatur in verschiedenen Zeiten, untersucht. Die röntgenographische Prüfung diente zum Kennzeichnen der erhaltenen Phasen durch Pulverdiagramme und zur Verfolgung der in Luft bis 800° im Komplex verlaufenden Reaktionen. Es wurde parallel auch eine Prüfung durch infrarote Spektroskopie unternommen. Die auf verschiedene Weise erhaltenen Ergebnisse wurden miteinander in Einklang gebracht.

Резюме — Исследовано термическое поведение $[CoCO_3(NH_3)_4]_2SO_4 \cdot 3H_2O$ с помощью методов диффракции рентгеновских лучей, ДТА, ТГ, и нагревания при высокой температуре различной продолжительности. Проведено изучение образца методом диффракции рентгеновских лучей для получения сведений о возникающих фазах и сопровождающих реакций при нагревании комплексного соединения на воздухе до 800°. Параллельно исследован инфракрасный спектр этого соединения. Результаты, полученные разными экспериментальными методами, сравнимы с потерей веса, установленной теоретическим путем.