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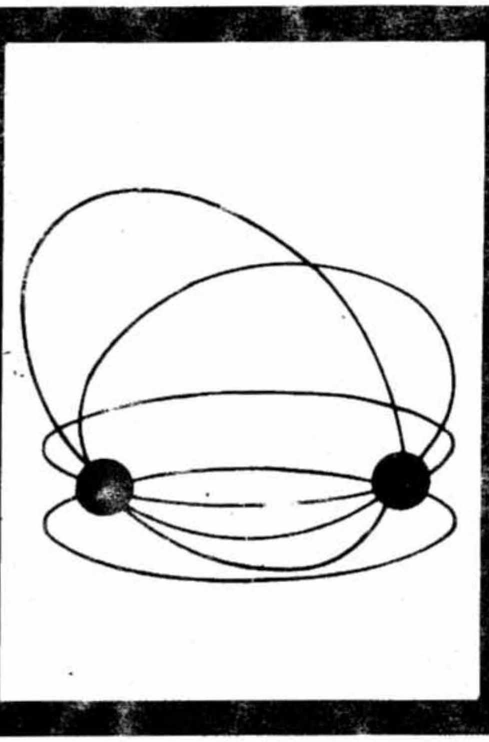

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Thermal decomposition of single hydroxychlorides of nickel, copper and cobalt.

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Abstract

The thermal decomposition reactions of $Ni(OH)Cl.1\frac{1}{2}H_2O$ in still air and in nitrogen and β-$Co_2(OH)_3Cl$ and γ-$Cu_2(OH)_3Cl$ in nitrogen atmosphere, have been studied by DTA and TG analysis, and the intermediates and final products have been characterized by x-ray diffraction and infrared spectroscopy. The thermal evolution of the above indicated compounds under dynamic vacuum conditions has been studied with the aid of an x-ray high temperature diffraction chamber. They reveals that in these conditions, the pure metallic nickel, copper and cobalt can be obtained at comparative low temperature. The infrared spectra of these hydroxychlorides have been tentatively assigned.

Experimental

The hydroxychlorides β-$Co_2(OH)_3Cl$ and γ-$Cu_2(OH)_3Cl$ were prepared in the usual way (1,2) and their chemical analyses and x-ray diffraction patterns agreed with the published data (1,3). $Ni(OH)Cl.1\frac{1}{2}H_2O$ was prepared by reacting 20 ml 4M $CoCl_2.6H_2O$ solution with 0,5 g NiO obtained from the thermal decomposition of $NiCO_3$. The product was aged in the mother liquor a) for one year at room temperature b) two moths at 343 K and, after centrifugation, the samples were washed with water, ethanol and acetone, dried under vacuum and kept on P_2O_5.

The thermograms were obtained on a 990 Dupont Thermoanalyzer an on a Mettler TA 3000 equipment, the heating rate was 10 $deg.min^{-1}$ and Al_2O_3 was used as reference. The TG curves were recorded on samples placed in open pans or in aluminium sealed cups.

The x-ray high temperature diffraction studies were made on an Anton PAAR HTK 10 attachment mounted on a Philips PW 1010 equipment, the samples were deposited on a platinum sheet placed on a tantalum strip which acts as the heating element. The temperature was measured with a Pt-Pt10%Rh thermocouple welded onto the centre of the platinum sheet. The vacuum was gauged in the usual way and it was maintained between 10^{-2} - 10^{-3} mm Hg along the experiences.

The infrared spectra were recorded on a 325 Perkin Elmer spectrophotometer, in KBr discs.

Thermal Analysis Studies

$Ni(OH)Cl.1\frac{1}{2}H_2O$

When nickel hydroxychloride decomposes in still air on in nitrogen flow, the same TG curves are obtained; (Fig. 1) the weight losses can be fitted to the following reactions scheme

$$2\ Ni(OH)Cl.1\tfrac{1}{2}H_2O \xrightarrow{373\ -\ 573\ K} 2\ Ni(OH)Cl + 3\ H_2O \xrightarrow{573\ -\ 689\ K}$$

$$\longrightarrow NiCl_2 + NiO + H_2O \xrightarrow[+\ \frac{1}{2}\ O_2]{698\ -\ 1103\ K} 2\ NiO + Cl_2$$

according to the general equation proposed by Ramamurthy and Secco for the thermal decomposition reaction of single hydroxyhalides (5). The infrared spectrum of the compound heated at 573 K in air or nitrogen and cooled under the same atmospheres shows strong features at 3600, 680 and 385 cm^{-1} (Table 2) and the x-ray diffraction diagram shows the most intense peaks of Ni(OH)Cl (4).

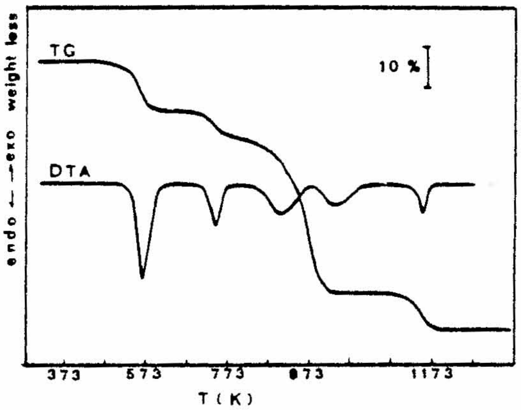

Figure 2

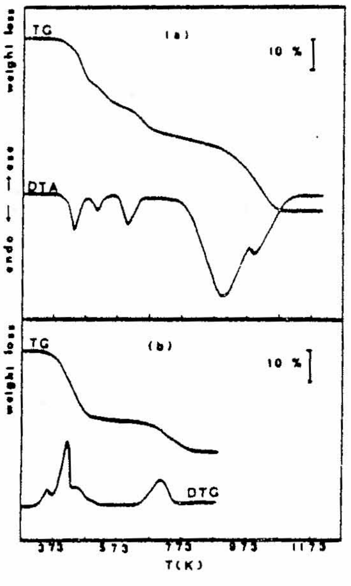

Figure 1

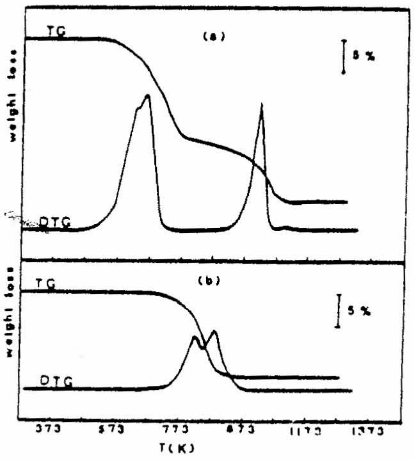

Figure 3

Thermograms of 1.- $Ni(OH)Cl.1\frac{1}{2}H_2O$, a) open pan, b) sealed cup, 2.- $Cu_2(OH)_3Cl$ in N_2; 3.- $Co_2(OH)_3Cl$ in N_2, a) open pan, b) sealed cup.

The product isolated at 698 K, being the samples either placed in open pan or enclosed in sealed cups both in air or nitrogen, consists of a mixture of anhydrous nickel chloride and the oxide, as would be expected according to the above indicated reactions scheme.

Nickel oxide was obtained as final product irrespective of the surrounding atmosphere.

The question arising is how nickel chloride decomposes to yield nickel oxide, when the reaction is carried out in a strong nitrogen flow (2 $l.min^{-1}$). Further experiences have to be done in order to obtain a reliable explanation.

γ-$Cu_2(OH)_3Cl$

The TG and DTA curves obtained in nitrogen flow are shown in Figure 2. The first step observed in the TG curve between 493 and 615 K is caused by the dehydroxylation reaction to yield copper (II) oxychloride and cupric oxide, instead of cupric chloride and oxide as indicated by Ramamurthy and Secco (5). The calculated and experimental weight losses are in very good agreement and the x-ray diffraction diagram obtained on the products formed at 673 K only shows the lines of Cu_2OCl_2 and those of cupric oxide (6,7). The decomposition of Cu_2OCl_2 to yield cuprous chloride probably causes the second step observed in the TG curve and, in fact, the x-ray diffraction diagram of the product isolated at 720 K only shows the diffraction lines of Cu_2Cl_2 and cupric oxide and those of cupric chloride have never been observed.

The experimental weight loss up to 723 K agrees with the calculated for the reaction (Table 1)

$$Cu_2OCl_2 \longrightarrow Cu_2Cl_2 + \tfrac{1}{2}\,O_2$$

In the DTA curve, a very sharp endothermic peak, centered at 718 K indicates the melting of the formed cuprous chloride.

Nevertheless, if it is assumed that Cu_2Cl_2 after liquid, volatilizes and no other reaction occurs, the calculated weigh loss in the temperature range 493 - 1073 K (62,75 %) does not agree with the experimental one (53,79 %). White Cu_2Cl_2 condenses in the cold part of the Dupont Thermobalance tube and if some Cu_2Cl_2 would not be evolved, it could explain the discrepancy between the experimental and calculated weight losses.

On the other hand, if we have in mind the reaction scheme proposed by Walter-Levy et al. (8) and that suggested by Ramamurthy and Secco (5) the overall thermal decomposition reactions could be as follows:

$$4\,Cu_2(OH)_3Cl \xrightarrow{493-615\ K} 2\,Cu_2OCl_2 + 4\,CuO + 6\,H_2O \xrightarrow{693-1073\ K}$$

$$\longrightarrow [Cu_2Cl_2 + \underset{\underset{[\frac{1}{2}Cu_2Cl_2 + \frac{1}{2}\,Cl_2]}{\downarrow}}{CuCl_2} + CuO + \tfrac{1}{2}\,O_2 + 4\,CuO] \longrightarrow 3/2\,Cu_2Cl_2 + 5\,CuO + \tfrac{1}{2}\,O_2 + \tfrac{1}{2}\,Cl_2$$

The calculated weight loss agrees quite well with the experimental one (53,97 % and 53,45 % respectively) as it does the calculated and found for the reaction (Table 1)

$$5\,CuO \xrightarrow{1163\ -\ 1198\ K} 5/2\,Cu_2O + 5/4\,O_2$$

TABLE 1

Experimental and calculated weight losses for the thermal decomposition of $Cu_2(OH)_3Cl$ in nitrogen atmosphere.

TEMPERATURE RANGE (K)	Partial weight loss (%) calc.	Partial weight loss (%) found	Reactions
493 - 615	12,64	12,64	$4Cu_2(OH)_3Cl$ — $2Cu_2OCl_2+4CuO+6H_2O$
693 - 723	4,28	4,16	$2Cu_2OCl_2+4CuO$ — $2Cu_2Cl_2+4CuO+O_2$
723 - 1073	55,46	44,80	$2Cu_2Cl_2+4CuO$ — $4CuO+2Cu_2Cl_2$
693 - 1073	46,71	47,10	$2Cu_2Cl_2+4CuO$ — $3/2Cu_2Cl_2+5CuO+\frac{1}{2}Cl_2+\frac{1}{2}O_2$
1163 - 1198	10,05	9,69	$5CuO$ — $5/2Cu_2O+5/4O_2$

β-$Co_2(OH)_3Cl$

The thermal decomposition of this compound in air and nitrogen, has been studied by Rasines et al. (7). We have undertaken again the study of the thermal behaviour of this compound in nitrogen and we have arrived to some slightly different conclusions.

The TG curve, as obtained under a nitrogen flow of about 180 $ml.min^{-1}$, is shown in Fig. 3a. The first step occurs in the temperature range 573 - 793 and correspond to the dehydroxylation to yield cobalt (II) chloride and oxide. The experimental weight loss (16,60 %) is higher than the calculated according to

$$2\ Co_2(OH)_3Cl \longrightarrow 2\ Co(OH)Cl + 2CoO + 2\ H_2O \longrightarrow CoCl_2 + 3\ CoO + 3\ H_2O$$

but if the TG runs are made on samples enclosed in sealed cups (Fig. 3.b), the experimental and calculated weight losses perfectly agrees (13,21 %) and the DTG curve clearly shows the two intermediates processes through which the reaction probably occurs. However, the x-ray diagram obtained on samples heated in sealed pans up to 873 K only shows the x-ray diffraction lines of CoO, but after a short standing in open air, the most intense peaks of $CoCl_2.2H_2O$ appears; the infrared spectrum shows a very sharp and strong feature at 1600 cm^{-1}, as well as those of CoO; this strong band is observed in the i.r. spectrum of $CoCl_2.2H_2O$ and $CoCl_2.6H_2O$ (10).

The partial weight loss obtained for the steps appearing in the temperature range 773 - 1073 K (16,03 %) cannot be explained by assuming that the formed $CoCl_2$, after melted, is removed from the sample; on this basis the partial calculated weight loss (36,63 %) is considerably higher than the experimental one and no condensation of $CoCl_2$ was observed. On the other hand, the i.r. spectrum and x-ray diagram of the residue (1193 K) correspond to that of CoO.

If $CoCl_2$ would decomposes according to

$$CoCl_2 + 3\ CoO \xrightarrow[+\frac{1}{2}\ O_2]{773\ -\ 1073\ K} 4\ CoO + Cl_2$$

the calculated (16,09 %) and experimental (16,03 %) weight losses agree quite well.

As it has been indicated before, further investigations on the thermal decomposition of cobalt and nickel chloride, in the same experimental conditions under which cobalt and nickel hydroxychlorides have been studied, will be undertaken.

X-ray high temperature diffraction studies

The evolution of nickel, copper and cobalt hydroxychlorides in the temperature range 298 - 1073 K under vacuum (10^{-2} - 10^{-3} mm Hg) can be summarized as follows (Figs. 4, 5).

$Ni(OH)Cl.1\frac{1}{2}H_2O$

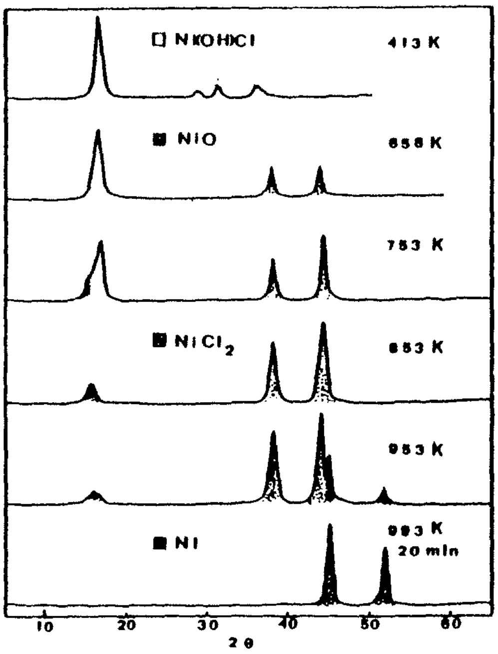

Figure 4

The initial x-ray diffraction pattern is not modify until the temperature reaches 413 K, from this one up to 523 K the most intense lines of Ni(OH)Cl are observed. At 658 K NiO appears and at 853 the (003) $NiCl_2$ diffraction line is observed.

At 953 K nickel metal appears and from this temperature up to 993 K nickel oxide progressively transforms into the metal. Finally, when the latest temperature is maintained for about 20 minutes, the pure metal is obtained.

γ-$Cu_2(OH)_3Cl$

The diffraction peaks corresponding to Cu_2Cl_2 are clearly observed in the x-ray diffraction diagram scanned at 483 K and at 513 K the diagram shows that copper hydroxychloride, cuprous chloride and copper (II) oxide are the compounds existing at this temperature. A diffractogram runned 40 minutes later in the same conditions (513 K and 10^{-3} mm Hg) only showed the Cu_2Cl_2 and CuO peaks and almost the same diagram is recorded up to 685 K. The intensity of the CuO peaks increase and those of Cu_2Cl_2 have desappeared, and at 833 K the CuO x-ray diagram is obtained. When the temperature reaches 893 K, Cu_2O, CuO and metallic copper were identified. If the temperature is increased and maintained at 993 K for about 20 minutes, pure metallic copper is obtained.

β-$Co_2(OH)_3Cl$

Cobalt hydroxychloride is stable up to 638 K and at this temperature gradually decomposes into CoO, that remains as a single compound up to 1013 K when the (111) diffraction line of cubic cobalt is observed, being this the more stable form above 723 K; cubic cobalt is obtained as a single compound at 1043 K and, this crystallographic modification is maintained after cooling the sample at room temperature, and no transformation into the hexagonal α-Co has been observed.

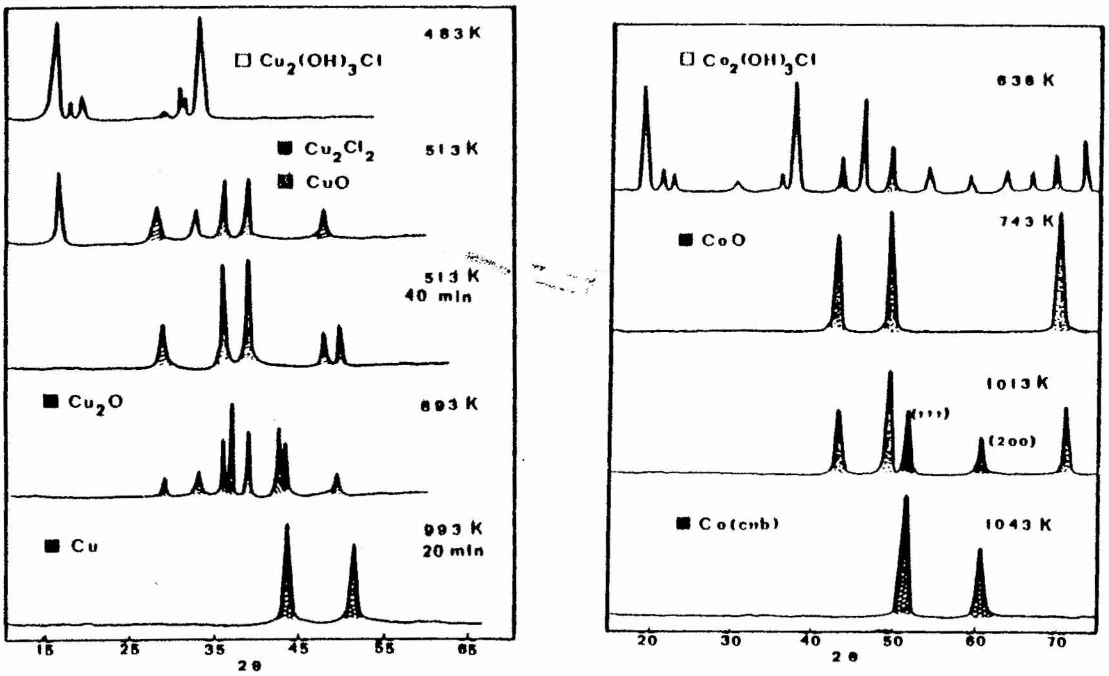

Figure 5

It must be noticed that no other intermediates such as Co(OH)Cl or Cl_2Co could be detected by x-ray diffraction, during the heating process.

The formation of metallic Ni, Cu or Co, by thermal decomposition of the hydroxychlorides are easily expected if the Ellingham diagram is taken into account (11). Under dynamic vacuum, the gaseous and volatile products are removed as they are formed, and the tendency to form the pure metals will be favoured.

The mechanism through which the metal formation occurs, has not been yet studied in detail, but an electron transfer process must be involved.

Infrared spectroscopy studies

The infrared absorption spectra have been recorded in the 4000 - 200 cm^{-1} range and the observed bands have been tentatively assigned (Table 2). The assignations have been made on the basis of the previous studies of Tartre and Pastrniak (12,13) as well as on the available structural data of paratacamite (14) and β-$Co_2(OH)_3Cl$ (15). Because of the number of different Cu-O and Cu-Cl bond lengths in the paratacamite structure, a greater number of absorption band can be expected in the i.r. spectrum of $Cu_2(OH)_3Cl$. In both Cu and Co hydroxychlorides, the metal atoms are in distorted octahedra enviroments, hydrogen bonds of different lenghts could exist and several O-H stretching frequencies will be justified.

3500-3000 cm^{-1} region. The ν(O-H) stretching frequencies are observed as very strong bands; in the i.r. spectrum of Ni(OH)Cl.1½H_2O, the broad band observed at 3250 cm^{-1} is assigned to the ν(O-H) of the water molecules. The weak features observed in the 1900-1600 cm^{-1} region have been assigned to the armonics or (O-H) bending combinations bands and that one observed at 1610 cm^{-1} in the i.r. spectrum of

TABLE 2

INFRARED ABSORPTION BANDS OF HYDROXYCLORIDES, OXIDES AND HYDROXYDES OF COPPER, COBALT AND NICKEL (νcm^{-1})

Assignment	$\gamma Cu_2(OH)_3Cl$	$Cu(OH)_2$	CuO	Cu_2O	$\beta Co_2(OH)_3Cl$	$Co(OH)_2$	Co_3O_4	CoO	$Ni(OH)Cl.1\frac{1}{2}H_2O$	Ni(OH)Cl	$Ni(OH)_2$	NiO
ν(OH)	3440 s	3570 s			3560 s	3620 s			3620 sh	3580 s	3620 s	
	3358 s	3300 s			3540 s				3580 s			
	3310 s								3500 s			
									3250 sbd, $\nu(H_2O)$			
Armonic combination	1940 w								1610 m, $\delta(H_2O)$			
	1740 w											
	1650 w											
δ(OH)	984 s	930 s			840 s	680 m			810 s	680 s	810 w	
	945 m	680 s			730 s				780 s		675 w	
	920 s	600 mbd			700 s				720 s		515 s	
	890 m								675 s, $\rho(H_2O)$			
	860 s								605 s			
	842 s											
	822 s											
	575 s											
ν(MeO)	510 s	510 m	580 sbd	662 s	425 s	500 sbd	667 sh	480 sbd	450 m	460 m	450 m	450 sbd
	470 sh	460 m	528 sbd	610 s	380 sbd	425 sbd	658 s	360 sbd	450 s	380 s	335 m	400 sbd
	450 s	410 s	480 s		340 sbd	300 s	560 s		354 s			
	400 s						388 m					
	320 m											
	270 m											
	245 w											

s = strong, m = medium, w = weak, bd = broad.

$Ni(OH)Cl.1\frac{1}{2}H_2O$ is assigned to δ(O-H) of the water molecule.

900-600 cm^{-1} region. The bands observed in this region were assigned to δ(O-H) and its number is higher than the observed ν(O-H).

500-300 cm^{-1} region. In this region, the ν(M-O) or ν(M-Cl) would appear. The weak bands observed at 270 and 240 cm^{-1} could correspond to the (Cu-Cl) stretching vibration, but as they are not observed in the i.r. spectra of the hydroxychlorides of nickel and cobalt, they cannot be interpreted for the present.

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