

Spectroscopic and Thermal Studies of $[\text{Cr}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$, $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ and $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ Compounds Formed by the Reactions of Urea with $\text{Cr}_2(\text{SO}_4)_3$, $\text{Cr}(\text{CH}_3\text{COO})_3$ AND $\text{Fe}_2(\text{SO}_4)_3$

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요약. 두개의 sulphato로 다리걸친 착물 $[\text{Cr}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$, 말단 3개의 isocyanato $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ 화합물과 갈철광 $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ 화합물들은 각각의 $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, $\text{Cr}(\text{CH}_3\text{COO})_3$, $\text{Fe}_2(\text{SO}_4)_3$ 과 80 °C, 수용액에서 요소와 반응으로 합성되었다. 생성물들의 IR 스펙트럼에서 요소(urea)의 띠가 나타나지 않지만, 결합된 아마이드(amide), 물, 연결된 sulphato와 isocyanato 그룹에 대해서 특징적인 띠를 보인다. 착물들에 대한 열무게분석(TG)과 시차열분석법(DTA) 측정을 기록하였다. 얻어진 데이터들은 예상했던 구조와 잘 일치한다. 형성에 대한 설명과 화합물의 열역학적 분해에 대한 일반적인 메커니즘을 제시하였다.

주제어: Bridged Disulphato Complex, Limonite, Triisocyanato Complex, TGA, Urea

ABSTRACT. The bridged disulphato complex $[\text{Cr}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$, terminal triisocyanato $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ complex and limonite, $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ compound were prepared by the reaction of $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, $\text{Cr}(\text{CH}_3\text{COO})_3$ and $\text{Fe}_2(\text{SO}_4)_3$, respectively, with urea in aqueous media at 80 °C. The infrared spectra of the products indicate that the absence of the bands of urea, but shows the characteristic bands of coordinated amide, water, bridged sulphato and isocyanato groups. Thermogravimetric (TG) and differential thermal analysis (DTA) measurements on the complexes are also recorded. The data obtained agree quite well with the expected structures. A general mechanisms describing the formation and its thermal decomposition of the complexes are suggested.

Keywords: Bridged Disulphato Complex, Limonite, Triisocyanato Complex, TGA, Urea

INTRODUCTION

The reactions between urea and d-block elements at room temperature have been studied extensively.¹⁻⁶ Most of these studies were indicate that urea coor-

dinates either via the amide nitrogen or the carbonyl oxygen atoms, depending on the type of the metal ion and the nature of such coordination can easily be identified from the shift in both the $\nu(\text{N-H})$ and $\nu(\text{C=O})$ frequencies of the coordinated urea

compared with those of free urea. Penland *et al.*⁶ studied the infrared spectra of both $[\text{Cr}(\text{urea})_6] \text{X}_3$ and $[\text{Fe}(\text{urea})_6] \text{X}_3$, and they indicate that oxygen-to-metal bonds are present in these complexes. However, detailed studies for this class of reaction at high temperature appear to be limited in the literature.⁷⁻¹² The nature of the reaction products was to be strongly dependent on the type of metal ion and the metal salt used in the reaction.

To continue our investigation in this area,^{7,10,12} we report in the present article the preparation of the related new compounds $[\text{Cr}_2(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$, $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ and $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$. The infrared spectra of the compounds as well as thermogravimetric (TG) and differential thermal (DTA) analysis were carried out.

EXPERIMENTAL

All chemicals used through out this work were Analar or extra pure grade. The dark green solid complex $[\text{Cr}_2(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$ was prepared by mixing equal volumes of aqueous solutions of 0.1 M of $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ and 0.6M of urea. The mixture was heated on a water bath to approx. 80 °C for about 4-6 h. The complex was precipitated, filtered off, washed several times with hot water and dried *in vacuo* over P_2O_5 . The two compounds $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ and $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ were prepared in a manner similar to that described above by the reaction of $\text{Cr}(\text{CH}_3\text{COO})_3$ and $\text{Fe}_2(\text{SO}_4)_3$ with urea, respectively. Its elemental analysis, infrared spectra and thermal properties DTA and TG characterized the compounds. Analysis of the products obtained:

1. $[\text{Cr}_2(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$ (400): H, 2.96 (3.00); N, 7.10 (7.00); SO_4^{2-} , 47.50 (48.00); Cr, 26.20 (26.00).

2. $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (250): C, 14.46 (14.40); H, 3.30 (3.20); N, 16.51 (16.80); Cr, 20.64 (20.80).

3. $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ (92.45): H, 1.53 (1.51); Fe, 60.96 (60.41) the calculated values are shown in parenthesis.

The infrared spectra of the compounds obtained, $[\text{Cr}_2(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$, $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot$

$3\text{H}_2\text{O}$ and $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ and of the DTA decomposition products were recorded from KBr discs using a Genesis II FT IR Spectrophotometer. Thermogravimetric (TG) and differential thermal analysis (DTA) of the compounds were carried out using a Shimadzu DT-50H computerized thermal system.

RESULTS AND DISCUSSION

Urea reacts with chromium(III) sulphate in aqueous media at -80°C to form dark green solid complex identified as $[\text{Cr}_2(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$. The formation of this complex upon the heating of an aqueous mixture of Cr(III) sulphate and urea may be understood as follows. At room temperature the $[\text{Cr}(\text{urea})_6]^{3+}$ complex is formed⁶ where urea coordinates to Cr(III) ions via its oxygen atom. At high temperature the following reaction may take place:

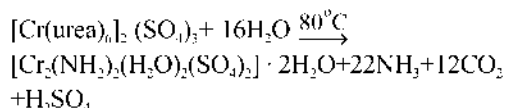
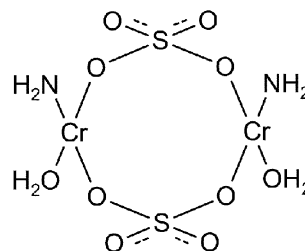


Fig. 1(a&b) shows the infrared spectra of the free urea along with spectra of the $[\text{Cr}_2(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$ product and its band assignments are given in Table 1. The most probable structure according to the complex formula and the infrared spectrum is shown in formula (I) where the complex contains two bridged sulphato ligands and possess C_2 symmetry.



Formula (I)

The infrared spectrum of the complex clearly indicates the absence of bands due to coordinated

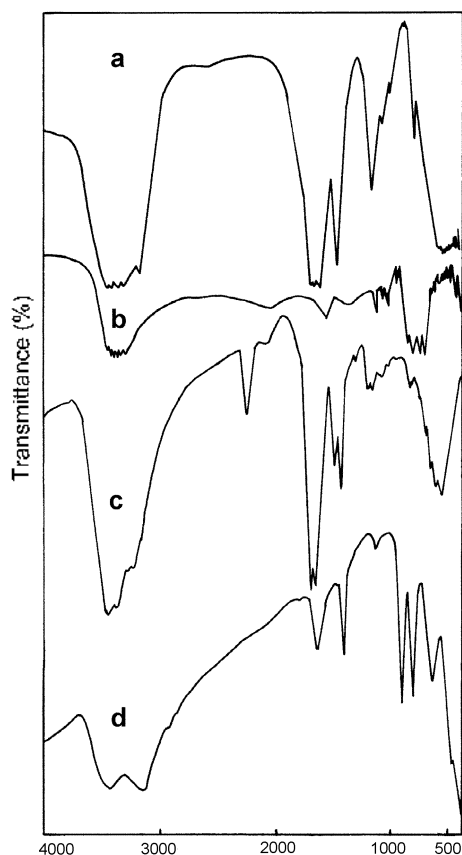


Fig. 1. Infrared spectra of: (a) urea; (b) $[\text{Cr}_2(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$; (c) $[\text{Cr}(\text{NCO})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ and (d) $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$.

urea and the presence of bands characteristic for coordinated water,¹³ at 3520, 3500, 3370 and 3350 cm^{-1} . The appearance of these four bands is expected for such a C_{2v} symmetry and can be assigned as follows: the first two bands are assigned to the two antisymmetric vibrations of the type, $\nu_{as}(\text{O-H})$, B_2 , while the other two bands are associated with the two symmetric vibrations of the type, $\nu_s(\text{O-H})$, A_1 . The bending motion for coordinated water in this Cr(III) complex, $\delta(\text{H}_2\text{O})$, is assigned at 1635 cm^{-1} while the rocking motion, $\delta_r(\text{H}_2\text{O})$, is assigned at 885 and 841 cm^{-1} the assignments for both the bond stretches and the angular deformations of the coordinated water molecules fall in the frequency regions reported for many related aqua complexes.¹¹⁻¹⁷

The coordinated $-\text{NH}_2$ groups show a set of bands agree quite well with those previously reported for related complexes.^{11,14,15} The two bands at 3305 and 3290 cm^{-1} are associated to the N-H stretching modes corresponding to the antisymmetric and symmetric motions, respectively. The angular deformation motions of the coordinated $-\text{NH}_2$ groups in this Cr(III) complex can be classified into three types of vibrations: δ_b (bend), δ_w (wag) and δ_t (twist). The assignments of these motions in our complex are as follows. The bending motion, $\delta_b(\text{NH}_2)$, is assigned at 1490 cm^{-1} . The wagging motion, $\delta_w(\text{NH}_2)$, is assigned at 985 cm^{-1} . The twisting motion, $\delta_t(\text{NH}_2)$, is observed at 923 cm^{-1} . The Cr-N stretching frequency is assigned at 516 cm^{-1} .

The bands of bridged coordinated sulphato group are observed at their expected values,¹⁸⁻²² three bands occur in the region above 1000 cm^{-1} at 1125, 1075 and 1060 cm^{-1} , while three bands of different intensities occupy the region below 1000 cm^{-1} at 758, 600 and 490 cm^{-1} (Table 1). The bands at 1125, 1075 and 1060 cm^{-1} are related to the stretching vibrations of $n(\text{SO}_4)^{2-}$ in agreement with the group theoretical analysis for this structure, while the other three bands which observed at 785, 600 and 490 cm^{-1} are associated with the bending vibrations of SO_4^{2-} .

Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out for the $[\text{Cr}_2(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$ complex under a N_2 flow. Fig. 2(A&B) represents the DTA and TG curves and Table 2 gives the maximum temperature values for decomposition along with the corresponding weight loss values. These data support the proposed complex structure and also indicate that the decomposition of the complex occurs in four degradation steps. The first stage of decomposition occurs at maximum temperature of 120 °C and is accompanied by a weight loss of 8.68% corresponding to the loss of the two uncoordinated water molecules. The relative low value of temperature of this step may indicate that these water molecules undergoes less H-bonding. The second step of degradation occurs at 286 °C with a weight loss of 8.79%, this associated with the loss of the two coordinated water molecules. The third decomposition stage occurs at a

Table 1. Infrared frequencies^(a) (cm^{-1}) and tentative assignments^(b) for urea, $[\text{Cr}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$, $[\text{Cr}(\text{NCO})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ and $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ compounds

Urea	$[\text{Cr}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$	$[\text{Cr}(\text{NCO})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$	$[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$	Assignments
	3520 m, 3500 m	3360 w		$\nu_{\text{as}}(\text{O-H})$; H_2O
3460 br	3400 w	3435 ms	3410 m,br	$\nu(\text{O-H})$; uncoord. H_2O
3386w	3370 m, 3350 m	3270w,sh, 3220w,sh	3170 m,br	$\nu_{\text{t}}(\text{O-H})$; H_2O
3342 w	3305 m			$\nu(\text{N-H})$
3180 w	3290 w			
		2190 s		$\nu_{\text{as}}(\text{N}\equiv\text{C})$
		2044 ms		$\nu_{\text{t}}(\text{N}\equiv\text{C})$
1682 vs				$\nu(\text{C-O})$
	1635 ms	1667 vs, 1635 vs	1642 s	$\delta_{\text{t}}(\text{H}_2\text{O})$
1630 vs	1490 m,br			$\delta_{\text{t}}(\text{NH}_2)$
1460 vs				$\nu_{\text{as}}(\text{CN})$
		1458 s		$\nu(\text{C-O})$; NCO^-
		1416 w		
1164 s				$\delta_{\text{t}}(\text{NH}_2)$
	1125 s			
	1075 ms			$\nu(\text{SO}_4)^{2-}$
	1060 ms			
1070 m				$\nu_{\text{t}}(\text{CN})$
		1155 w, 1050 w		$\delta_{\text{t}}(\text{H}_2\text{O})$
1000 m	985 w			$\delta_{\text{t}}(\text{NH}_2)$
	923 w			$\delta_{\text{t}}(\text{NH}_2)$
			1285 ms	
			1027 ms	$\delta(\text{M-OH})$
			900 vs, 800 vs	$\nu(\text{Fe-O})$
790 m	885 w, 841 w	990 vw, 908 vw		$\delta_{\text{t}}(\text{H}_2\text{O})$
		795 vw, 788 vw		$\delta_{\text{t}}(\text{NH}_2)$
				$\delta_{\text{t}}(\text{H}_2\text{O})$
	758 w, 600 m			$\delta(\text{SO}_4)^{2-}$
590 w		588 mw, 530 ms		$\delta(\text{NCO})^-$
540 w				$\delta(\text{NCN})$
			621 ms	$\nu(\text{Fe-O})$
	516 m			$\nu(\text{Cr-N})$
	490 m			$\delta(\text{SO}_4)^{2-}$

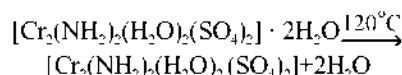
(a): s=strong, w=weak, m=medium, sh=shoulder, v=very, br=broad.

(b): ν , stretching; δ_{t} , δ_{r} , δ_{t} and δ_{w} correspond to bending, rocking, twist and wagging motions, respectively.

maximum temperature 352 °C and is accompanied by a weight loss of 7.89%, this is associated with the loss of the two amide groups. The final step occurs at 416 °C without loss weight, this stage should be attributed to the rupture of the Cr-O bonds (O of sulphato). No weight loss in this step is related to the fact that SO_4^{2-} is still associated with Cr(III) but in ionic form. The infrared spectra of the different decomposition steps (Fig. 3), were supported these

conclusions which shows the absence of any bands associated to the amido and bridged sulphato groups, but shows a group of bands characteristic of ionic sulphate, $\text{Cr}_2(\text{SO}_4)_3$ at 1085, 940 and 885 cm^{-1} .

Accordingly to these conclusions, the decomposition mechanism for this complex is as follows:



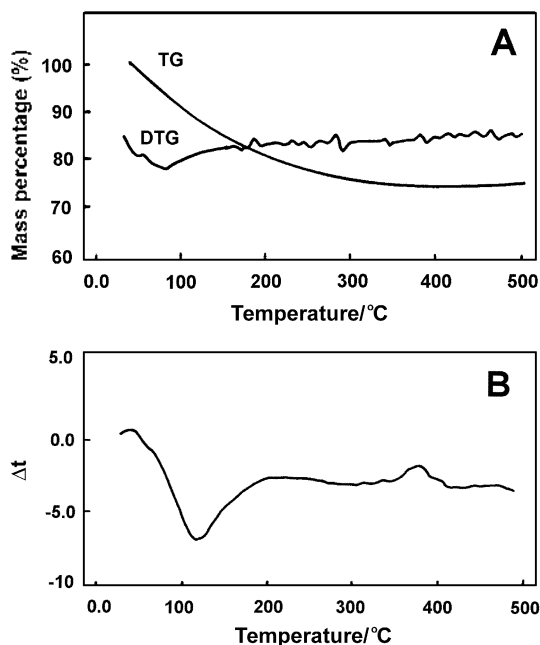
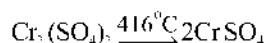
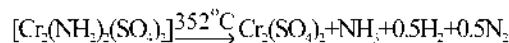
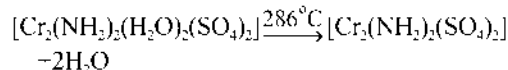


Fig. 2. Thermal analysis diagrams of $[\text{Cr}_3(\text{NH}_3)_3(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$. (a) TG and DTG, (b) DTA.



The green solid complex, $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$, formed by the reaction of urea with chromium(III) acetate in aqueous media at $\sim 80^\circ\text{C}$. The infrared spectrum of this complex is given in Fig. 1c and its vibrational assignments are listed in Table 1. The i.r. spectrum also clearly indicates the absence of bands due to coordinated urea and the presence of bands characteristic for isocyanate ions²¹ at 2190 and 2044 cm^{-1} and for coordinated water¹³ in the 3360-3220 cm^{-1} region. The complex is well characterized through the elemental analysis, infrared spectra and thermal analysis TG and DTA. The $\nu_{\text{as}}(\text{N}=\text{C})$ and $\nu_{\text{s}}(\text{N}=\text{C})$ are observed as expected at 2190 and 2044 cm^{-1} , respectively, while the $\nu(\text{C}-\text{O})$ and $\delta(\text{NCO})$ are assigned at 1458, 1416 and 588, 530 cm^{-1} , respectively. These results for the NCO^- ions agree quite well with those known for isocyanato complexes.^{21,23} The various $\nu(\text{O}-\text{H})$ vibrations characteristic of coordinated water and uncoordinated water in the 3435-3220 cm^{-1} region. These bands can be assigned as follows, the first band at 3360 cm^{-1} is assigned to the antisymmetric vibration of the type $\nu_{\text{as}}(\text{O}-\text{H})$, B_2 while the other two bands at 3270 and 3220 cm^{-1} are associated with two symmetric vibration of the type $\nu(\text{O}-\text{H})$; A_1 , and exhibit intensities expected from their symmetry characteristic (A_1 & B_2) under C_3 symme-

Table 2. The maximum temperature, $T_{\text{max}}/^\circ\text{C}$, and weight loss values of the decomposition stages for the $[\text{Cr}_3(\text{NH}_3)_3(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$, $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ and $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ compounds

Compounds	Decomposition	$T_{\text{max}}/^\circ\text{C}$	Lost species	%weight losses	
				Found	Calc.
$[\text{Cr}_3(\text{NH}_3)_3(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$	First stage	120°C	$2\text{H}_2\text{O}$	8.68%	9.0%
	Second stage	286°C	$2\text{H}_2\text{O}$	8.79%	9.0%
	Third stage	352°C	$\text{NH}_3 - 0.5\text{H}_2 + 0.5\text{N}_2$	7.89%	8.0%
	Fourth stage	416°C	No weight loss	--	--
	Total loss			25.36%	26.00%
	Residue			74.64%	74.00%
$[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$	First stage	195°C	$3\text{H}_2\text{O}$	22.07%	21.60%
	Second stage	>350°C	$2\text{CO} + 3/2\text{N}_2 - 1/2\text{H}_2\text{O} + 1/2\text{H}_2$	43.13%	43.20%
	Total loss			65.20%	64.80%
	Residue			34.80%	35.20%
$[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$	First stage	30-163°C	$0.2\text{H}_2\text{O}$	3.91%	3.88%
	Second stage	330°C	$1/2\text{H}_2\text{O}$	9.37%	9.70%
	Total loss			13.28%	13.58%
	Residue			86.72%	86.42%

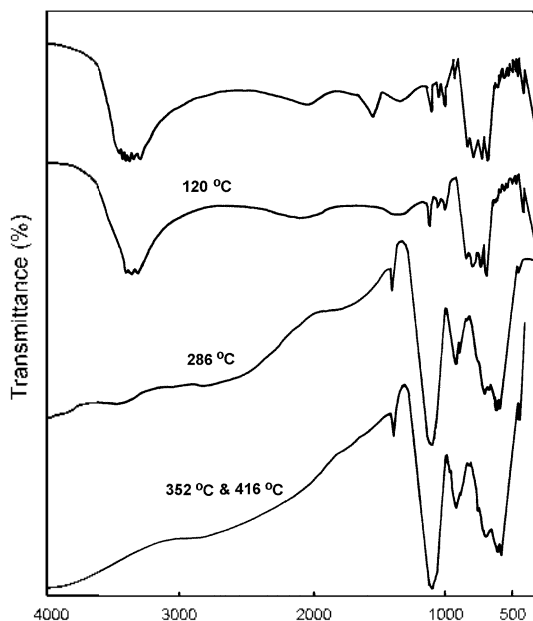
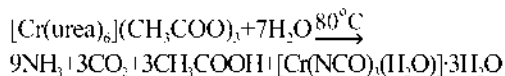


Fig. 3. Infrared spectra of the different decomposition steps for $[\text{Cr}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$.

try. The bending vibration, $\delta(\text{H}_2\text{O})$ is assigned at about 1645 cm^{-1} . The stretching and angular deformations (δ , δ_t and δ_w) of coordinated water molecules fall in their expected frequency values, Table 1 like many other compounds.¹¹⁻¹⁷

It is well known that urea coordinates to Cr(III) ions at room temperature via its oxygen atom.⁶ Forming the $[\text{Cr}(\text{urea})_6]^{3+}$ ion complex. At high temperature the following reaction may take place:



To make sure about the proposed formula and structure of the formed complex, $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$, thermogravimetric (TG) and differential thermal analysis (DTA) were carried out under N_2 flow. DTA and TG thermograms are shown in Figs. 4 (A&B). Tables 2 gives the maximum temperature values, T_{max} , together with the corresponding weight loss for each step of the decomposition reaction. The data obtained support the proposed structure and indicate that, the thermal decomposition of these complex proceeds with two main degradation steps. The first stage of decomposition occurs at a

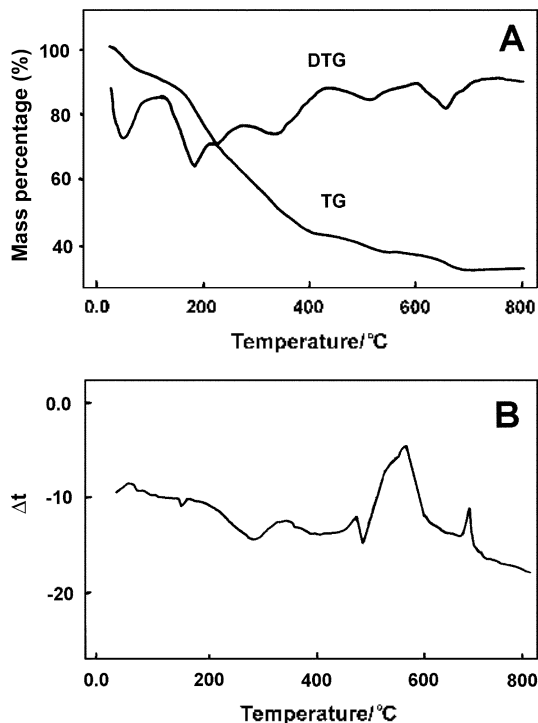


Fig. 4. Thermal analysis diagrams of $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$. (a) TG and DTG, (b) DTA.

temperature maximum of 195°C . The found weight loss associated with step is 22.07% and may be attributed to the loss of the three uncoordinated water molecules which is in good agreement with the calculated values of 21.60% . The second stage of decomposition occurs at a temperature maximum of $\geq 350^\circ\text{C}$. The weight loss found at this stage equals to 43.13% corresponds to loss of $2\text{CO} + 3/2\text{N}_2 + 1/2\text{H}_2\text{O} + 1/2\text{H}_2$. To supporting our conclusion of the absence of NCO and H_2O , we make infrared spectra for the residue of ignition at different temperatures ($200, 350, 500, 650$ and 800°C), Fig. 5, which clearly indicate that the NCO group disappeared at 350°C and the characteristic stretching vibration of Cr_2O_3 which containing the Cr=O groups that exhibit the Cr=O vibration bands in the $1050\text{--}800 \text{ cm}^{-1}$ region^{21,25} the stretching frequency of the type $\nu(\text{Cr}=\text{O})$ in our complex is assigned at $1133, 892 \text{ cm}^{-1}$ and doublet bands observed at 619 and 572 cm^{-1} . The agrees with the elemental analysis of the existence of no nitrogen or carbon elements.

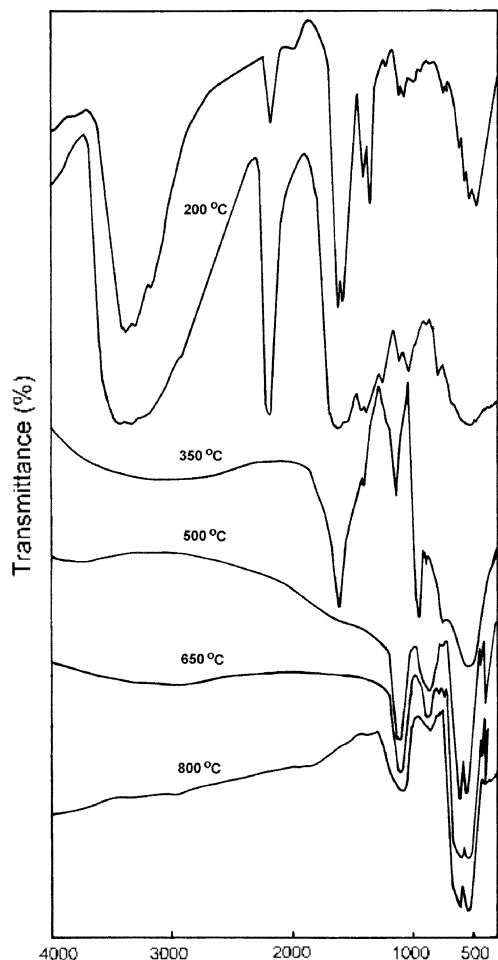
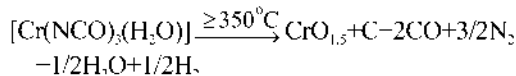
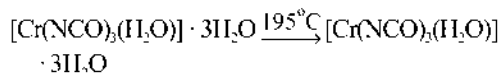


Fig. 5. Infrared spectra of the different decomposition steps for $[\text{Cr}(\text{NCO})_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$.

The weight found for the residue after decomposition is 34.80% giving an actual total weight loss of 65.20%. However the calculated total weight loss of is 64.80%.

Finally, The thermal decomposition reactions of the complex can be summarized as follows:



Urea reacts with iron(III) sulphate in aqueous media at $\sim 85^\circ\text{C}$ to form ferric hydroxide oxide

(Limonite), $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$. The infrared spectrum obtained for this compound, Fig. 1d clearly indicates the absence of any bands due to coordinated urea and the presence of bands characteristic for hydroxide ion²⁶ at 3170 and 1285, 1027 cm^{-1} . The bands associated for the stretching of Fe-O [27] is observed at 900 and 800 cm^{-1} (Table 1). Based on these facts, and with the elemental analysis, the compound $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ is formed. The formation of ferric hydroxide oxide is greatly supported by measuring the infrared spectrum of the commercially obtained ferric hydroxide oxide, $[\text{FeO}(\text{OH})] \cdot n\text{H}_2\text{O}$.²⁸ We noted that the two spectra are typically (fingerprint) indicating that, the obtained product is $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$.

The formation of $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ compound upon the heating of an aqueous mixture of the ferric(III) sulphate and urea may be understood as follows at room temperature, ferric(III) ions react with urea to give the parent complex⁶ of the type $[\text{Fe}(\text{urea})_6] \text{X}_3$ where $(\text{X}=\text{SO}_4^-)$. At higher temper-

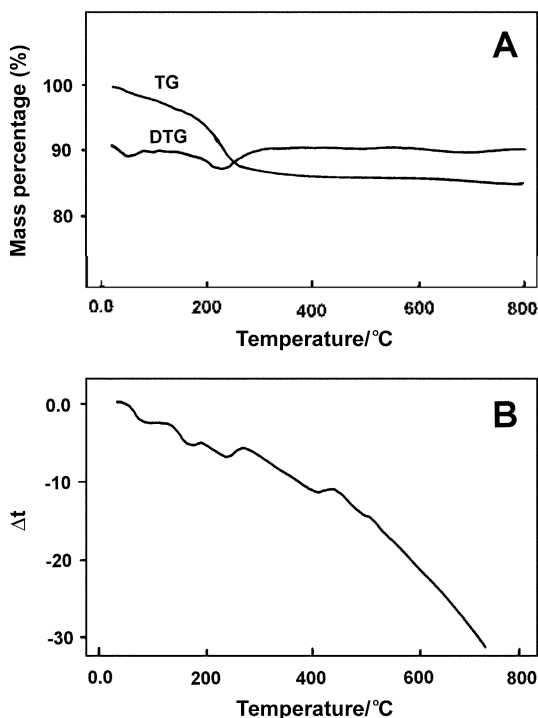
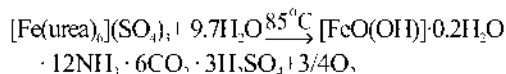


Fig. 6. Thermal analysis diagrams of $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$. (a) TG and DTG, (b) DTA.

ature, the following reaction may take place:



The thermal decomposition DTA and TGA Fig. 6 (A&B) of the compound $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ exhibits two main degradation steps. The first step of decomposition occurs from 30 to 163 °C is accompanied by a weight loss of 3.91% in agreement with the theoretical values 3.88% for the loss of $0.2\text{H}_2\text{O}$. The second step of decomposition occurs at a maximum temperature 230 °C with a weight loss of 9.37%. This step is associated with the loss of $1/2\text{H}_2\text{O}$ giving the oxide product, $\text{FeO}_{1.5}$. The infrared spectrum of the final product (Fig. 7) supports the above discussion. It only shows the bands associated with the ferric oxide, Fe_2O_3 .

Accordingly, the following mechanism is proposed for the thermal decomposition of the $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$ compound as follows:

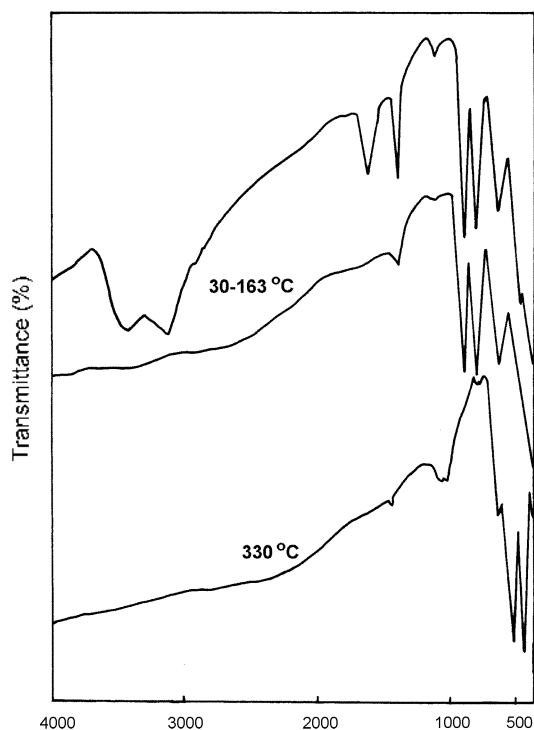
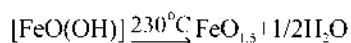
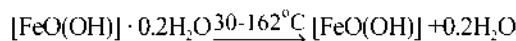


Fig. 7. Infrared spectra of the different decomposition steps for $[\text{FeO}(\text{OH})] \cdot 0.2\text{H}_2\text{O}$.



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