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ALKALI HEXAMOLYBDOCHROMATES

PREPARATION, CHARACTERIZATION AND THERMAL BEHAVIOUR*

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Li, Na, K, Rb, Cs and NH_4 hexamolybdochromates have been prepared, characterized by X-ray and IR spectra, and their thermal behaviour was studied. We observed that the anion decomposition occurs only when the last 3 H_2O are eliminated. The ΔH values for this elimination decrease from the Li to the Cs salt in the same manner as the lattice energies found in other alkali salts with a common anion. The exothermic reactions in the decomposition of the complexes are interpreted by inspection of the compounds obtained.

Hexamolybdochromates have been studied by several authors: the potassium and ammonium salts by Rosenheim [1] who established their formulae and, in part, their thermal behaviour; Anderson [2] and Evans [3] suggested a structure for this type of complex; Baker et al. [4, 5] studied the behaviour in solution of these and other analogous complexes and determined the basicity of the corresponding acids; more recently in our Institute the thermal behaviour of several homologues has been studied [6, 7]. The crystal structure of sodium hexamolybdochromate was determined on a single crystal in 1966 by Perloff [8], who corroborated experimentally the structure proposed by Anderson and Evans.

In this paper we report the results obtained by studying the thermal behaviour of various alkali hexamolybdochromates, with emphasis on the role of the alkali cation on the composition, on the dehydration steps, on the complex stability, and finally on the reactivity of the compounds obtained from the thermal decomposition. By determining ΔH values for the successive dehydration steps from DTA curves, we have sought to elucidate the role of different types of water of crystallization in this class of complexes.

Several techniques have been used: DTA and TG to examine the thermal behaviour and to determine ΔH and E values for the different reactions; X-ray diffraction and IR spectra to characterize the complexes and their decomposition products.

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Experimental

Preparation. In general, the salts were prepared according to the method previously described [6], by adding the stoichiometric amount of alkali carbonate to the hexamolybdochromic acid solution (obtained by cation exchange) and by slowly evaporating solutions until separation of the corresponding hexamolybdochromates. After recrystallization the salts were analysed for Cr, Mo, alkali and H_2O; from these analyses the following compositions were obtained:

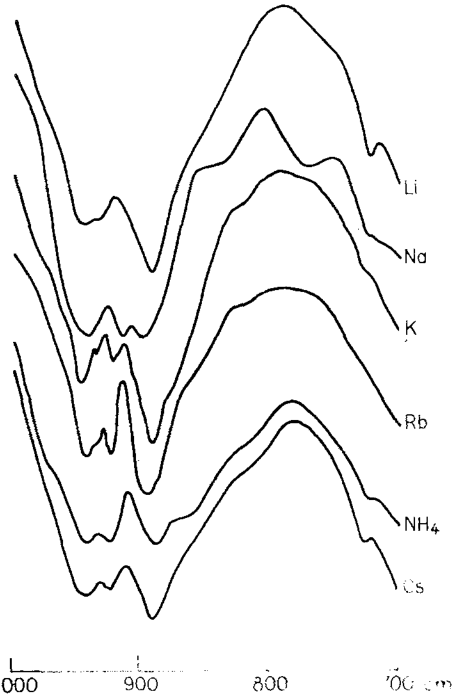


Fig. 1. IR spectra of the alkali hexamolybdochromates

$Li_3 [H_6CrMo_6O_{24}] \cdot 10 H_2O$
$Na_3 [H_6CrMo_6O_{24}] \cdot 8 H_2O$
$K_3 [H_6CrMo_6O_{24}] \cdot 7 H_2O$
$Rb_3 [H_6CrMo_6O_{24}] \cdot 7 H_2O$
$Cs_3 [H_6CrMo_6O_{24}] \cdot 5 H_2O$
$(NH_4)_3 [H_6CrMo_6O_{24}] \cdot 7 H_2O$

The sodium salt was also prepared by the Perloff method [8]; it was observed that the number of waters of crystallization varied with the ambient temperature. At room temperature the salt separated with 8 H_2O; at lower temperature it can crystallize with 13 H_2O and at 0° with 15–16 H_2O.

It was also observed that the normal sodium salt, if maintained in not well-closed containers, loses some 3 to 4 moles of H_2O in a few weeks, and consequently has a different X-ray spectrum and quite different thermal dehydration steps, at least in the initial part of the curves.

Characterization of compounds. X-ray spectra obtained on a Philips apparatus (CuKα rad.; 114.6 mm diam. camera) are reported in Table 1.

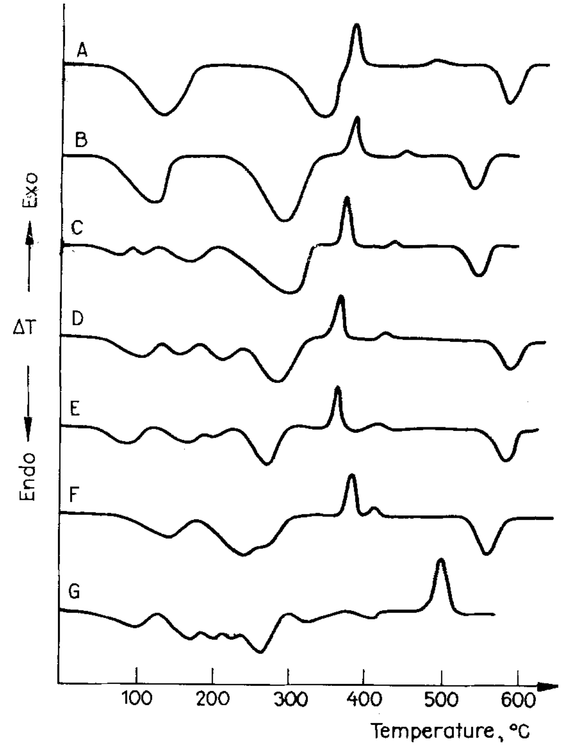


Fig. 2. DTA curves of the alkali hexamolybdochromates. A: Li(HMC) · 10 H_2O; B: Na(HMC) · 8 H_2O; C: Na(HMC) · 5 H_2O; D: K(HMC) · 7 H_2O; E: Rb(HMC) · 7 H_2O; F: Cs(HMC) · 5 H_2O; G: NH_4(HMC) · 7 H_2O

Similar spectra are shown by the K, NH_4 and Rb salts only. It is not very strange that the other salts have different spectra because they differ in their water content.

The IR spectra, run on a Beckman IR 7 apparatus as Nujol mulls (700 – 1000 cm^{-1}), are reported in Fig. 1, and the frequency maxima with corresponding intensities are reported in Table 2. Quite similar spectra are given by all complexes, except for the Na salt, particularly in the Mo – O and Cr – O stretching region between 700 – 1000 cm^{-1}.

Thermal behaviour. In order to follow the dehydration steps and the successive transformations of the salts differential thermal analysis and thermogravimetric

Table 1

X-ray diffraction spectra of the alkali hexamolybdochromates

Li(HMC) · 10 H_2O		Na(HMC) · 8 H_2O		K(HMC) · 7 H_2O		NH_4(HMC) · 7 H_2O		Rb(HMC) · 7 H_2O		Cs(HMC) · 5 H_2O	
d Å	*i*	*d* Å	*i*	*d* Å	*i*	*d* Å	*i*	*d* Å	*i*	*d* Å	*i*
				12.44	w	12.62	ms	12.44	m		
11.88	vs			11.25	s	11.20	vs	11.25	vs	11.18	m
		10.88	m	10.84	m						
		10.15	s								
		9.82	vs								
		8.88	mw	8.97	mw	8.88	w				
7.96	vs			8.11	vs	8.00	ms	7.99	m	7.86	w
										7.59	w
		6.86	w								
		6.19	ms	6.14	vw	6.21	w	6.23	m	6.21	mw
5.90	s	5.98	vw			5.82	m	5.82	w	5.90	w
5.58	w	5.78	vw	5.62	ms	5.62	s	5.62	vs	5.61	s
				5.53	ms						
5.45	vw	5.38	m	5.45	m						
5.06	vs	5.21	ms	5.09	m	5.14	ms	5.15	m	5.15	mv
				5.02	m	4.96	ms			4.95	m
4.88	w			4.92	m	4.89	ms	4.94	s	4.96	m
		4.75	w	4.74	mw					4.66	m
4.57	w	4.65	s	4.53	w						
4.25	vw	4.34	mw			4.43	w				
4.02	mw	3.92	mw								
		3.85	mw								
		3.72	w			3.73	w			3.75	ms
3.69	ms	3.68	w								
		3.62	vw	3.59	mw	3.58	w	3.66	w		
		3.49	w			3.52	w	3.55	w		
3.37	s	3.36	ms	3.39	w	3.43	m	3.44	ms		

		3.29	w			3.27	m	3.32	w		
		3.24	w	3.24	vw	3.24	mw	3.26	m	3.19	ms
3.06	vs	3.13	w	3.12	m	3.10	s	3.10	vs	3.11	ms
		3.01	m	3.06	w					3.01	w
		2.97	mw	3.01	vw					2.97	ms
		2.95	m								
		2.86	mw					2.84	w		
2.82	w	2.83	m	2.81	vw	2.83	w	2.82	w	2.81	ws
		2.80	mw								
2.72	ms	2.70	w	2.68	w			2.73	vw		
2.66	mw					2.66	w			2.66	vw
2.62	mw	2.60	w								
2.58	mw					2.58	w				
2.53	mw	2.52	w	2.52	vw	2.50	m	2.50	w		
2.48	mw										
		2.44	mw								
2.40	w	2.41	mw								
2.27	w	2.26	mw	2.27	w	2.29	w	2.29	w		
2.21	s					2.25	w			2.24	vw
2.16	mw	2.18	m			2.18	w	2.19	w		
				2.12	vw						
2.02	mw					2.06	w	2.07	w	2.08	vw
1.97	s			1.95	vw	1.99	w	2.00	vw	2.00	vw
1.93	w	1.92	w								
		1.90	w			1.87	w	1.88	w	1.88	w
1.85	m	1.79	w			1.85	vw	1.85	w		
1.76	mw	1.76	vw								
1.73	w	1.73	vw								
1.71	w										
		1.61	vw			1.61	mw	1.61	w		

Table 2

IR spectra of the alkali hexamolybdochromates

Li(HMC) · 10 H_2O		Na(HMC) · 8 H_2O		K(HMC) · 7 H_2O		NH_4(HMC) · 7 H_2O		Rb(HMC) · 7 H_2O		Cs(HMC) · 5 H_2O	
ν(cm^{-1})	i	ν(cm^{-1})	i	ν(cm^{-1})	i	ν(cm^{-1})	i	ν(cm^{-1})	i	ν(cm^{-1})	i
		777	m								
				820	vw	818	vw	820	vw	815	vw
		848	m							848	m
866	m			875	ms	870	mw	868	m		
893	s	887	ms	890	s	888	s	893	s	891	s
		902	s			897	ms				
915	ms	917	s	920	m	922	s	923	ms	925	ms
935	ms			932	m			935	ms	938	ms
950	ms	945	s	947	ms	943	s	941	ms	945	ms
		957	ms								
975	m			975	mw	970	w	975	mw	970	m
		1010	mw								
		1110	vw	1085	vw	1085	vw	1090	vw	1078	w
						1412	mw				
1615	mw	1615	m	1612	mw	1607	mw	1614	w	1612	mw
1635	mw	1637	m	1650	w	1635	mw	1640	vw	1630	mw
		1645	mw			1675	w				
				3200	m	3170		3200	ms	3190	m
3350	m	3340	ms			3350		3310	ms	3350	mw
3470	m	3460	m	3475	ms	3475		3425	mw	3465	mw
3580	m	3550	mw	3550	m	3550		3550	m	3550	w
				3600	mw						

Table 3

$Li_3[CrH_6Mo_6O_{24}] \cdot 10 H_2O$	*T*	45—200°			210°		365°	485°	565°
	Reaction	—10 H_2O			—3 H_2O		tetramol. crystallization	exothermic reaction	melting
	E								
	ΔH/salt mole	80			59		(9)	1	
	ΔH/H_2O mole	8			19.7				
$Na_3[CrH_6Mo_6O_{24}] \cdot 8 H_2O$	*T*	45—110°		130—250°			370°	470°	515°
	Reaction	—6 H_2O		—5 H_2O			tetramol. crystallization	exothermic reaction	melting
	E			42					
	ΔH/salt mole	54		78.7			13	1.34	24
	ΔH/H_2O mole	9		15.7					
$K_3[CrH_6Mo_6O_{24}] \cdot 7 H_2O$	*T*	40°	100°	120°	200°		340°	420°	540—590°
	Reaction	—4 H_2O	—1.5 H_2O	—1.5 H_2O	—3 H_2O		$K_2O \cdot 4 MoO_3$ crystall.	exothermic reaction	melting
	E	25		33	40.3				
	ΔH/salt mole	27	20	30	34.5		12.5	3.96	23.8
	ΔH/H_2O mole	6.7	13.3	20	11.5				
$Rb_3[CrH_6Mo_6O_{24}] \cdot 7 H_2O$	*T*	35°	70°	110°	170°		350°	420°	550°
	Reaction	—4 H_2O	—1.5 H_2O	—1.5 H_2O	—3 H_2O		$Rb_2O \cdot 4 MoO_3$ crystall.	exothermic reaction	melting
	E				30.1				
	ΔH/salt mole	22	21	12	27		13.4	2	
	ΔH/H_2O mole	5.5	14	8	9				
$Cs_3[CrH_6Mo_6O_{24}] \cdot 5 H_2O$	*T*	30—100°	105°		160°		375°	405°	570°
	Reaction	—3.5 H_2O	—1.5 H_2O		—3 H_2O		$Cs_2O \cdot 4 MoO_3$ crystall.	exothermic reaction	melting
	E				19.7				
	ΔH/salt mole	35	29		22		9.2	3.45	21.2
	ΔH/H_2O mole	10	19.3		7.66				
$(NH_4)_3[CrH_6Mo_6O_{24}] \cdot 7 H_2O$	*T*	40°	85°	100°	140°	200—270°	300—350°	480°	
	Reaction	—3 H_2O	—2.5 H_2O	—1.5 H_2O	—3 H_2O	—NH_3—H_2O	—NH_3—H_2O	exothermic reaction $Cr_2(MoO_4)_3$ and MoO_3 crystall.	
	E				26.3				
	ΔH/salt mole	23	30.2	16	24	28	21	13	
	ΔH/H_2O mole	7.7	12.1	10.6	8				

analysis were performed. The compounds obtained by heating the alkali complexes have been identified by X-ray and IR spectra.

A Netzsch apparatus Model 404 (Pt-PtRh 10% thermocouples) was used for DTA; a special DDK measuring head, calibrated with compounds of known heat of reaction [9], was used for ΔH measurements; the heating rate giving the best results was 5°/min.

A Stanton thermobalance Model TR 01, heating rate 2°/min, was used for TG.

In order to differentiate the different dehydration steps, operations were done in a wet nitrogen atmosphere [6]; the Coats–Redfern method [10] was used for the activation energy determinations.

The results obtained are reported in Figs 2 and 3; in Table 3 are reported the reactions and transformations corresponding to the various endo- and exothermic peaks, with the relative ΔH and E values determined, where possible, from DTA and TG curves.

It is evident that the endothermic reactions below 340° correspond to the different dehydration and deammoniation steps.

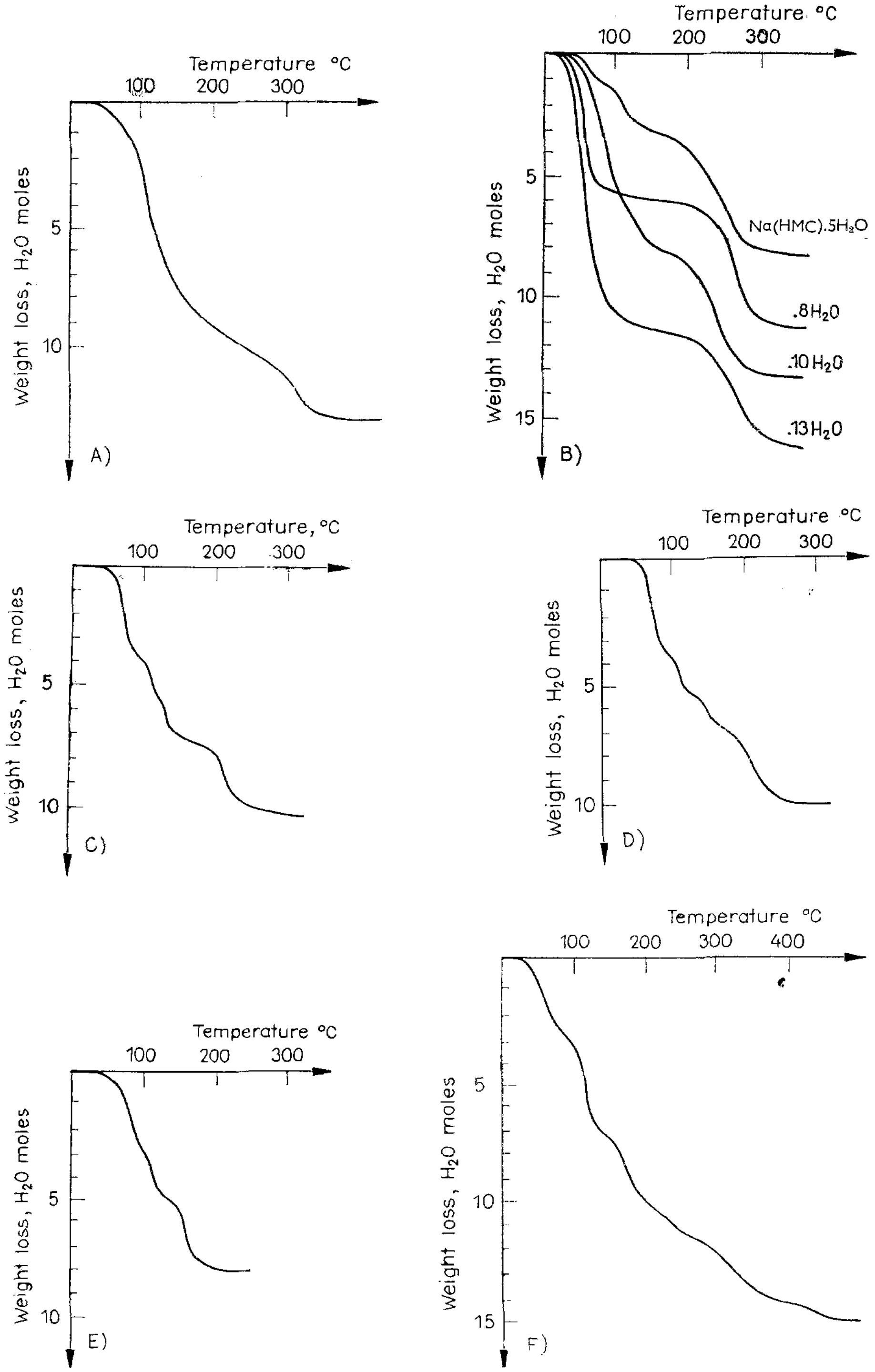
The K and Rb salts show a quite similar behaviour. Only in the last two steps do the NH_4 and Cs salts behave similarly to the K complex. The Li and Na salts, having more water of crystallization, show only two weight losses, and all attempts at differentiating the first one have been unsuccessful.

The dehydration curves for the Na salt are different when the examined salt has a different crystallization water content. The complex $Na_3[H_6CrMo_6O_{24}] \cdot 11\ H_2O$ easily obtainable by Baker's or Perloff's method, dehydrates in two steps of 6 and 5 H_2O respectively. The complex with 8 H_2O, obtained by leaving the previous salt in a not well closed container, has a different X-ray spectrum, and dehydrates in four steps. After the first three steps the compound has lost 3 H_2O; at this point it is probably equivalent to the initial product of the "11 H_2O" salt, since in the last step it also loses 5 H_2O. This last 5 H_2O weight loss was also observed for the salts with 13 and 16 H_2O. It is presumable, therefore, that the different water contents observed in the various salts obtained reflect only a varying tendency to acquire less strongly bonded waters, slowly removable at room temperature.

In contrast, for all other alkali hexamolybdochromates the last dehydration step corresponds to 3 H_2O, which must be considered as "constitution water", as demonstrated in different ways for the K salt [6]. This last weight loss is well differentiable in the Li, K, Rb, Cs salts, but not very well in the NH_4 complex, because of the successive deammoniation reaction. In the Na salts it was impossible to find evidence for the constitution 3 H_2O, even when operating under different conditions of heating rate and water vapour pressure.

It is interesting to point out that the temperature value for onset of the last dehydration decreases from the Li to the Cs salt. If we consider the thermodynamic functions determined by DTA and TG curves, we can observe that the ΔH value corresponding to the last 3 H_2O decreases from the Li to the Cs salt.

The observed ΔH value for the NH_4 salt is an intermediate between the Rb and


Temperature °C
100
200
300
Weight loss, H_2O moles
5
10
A)
Temperature °C
100
200
300
Weight loss, H_2O moles
5
10
15
Na(HMC).5H₂O
.8H₂O
.10H₂O
.13H₂O
B)
Temperature, °C
100
200
300
Weight loss, H_2O moles
5
10
C)
Temperature °C
100
200
300
Weight loss, H_2O moles
5
10
D)
Temperature °C
100
200
300
Weight loss, H_2O moles
5
10
E)
Temperature °C
100
200
300
400
Weight loss, H_2O moles
5
10
15
F)

Cs salts. The activation energy values too decrease from the Na to the Cs salt, and have about the same order of magnitude as the corresponding ΔH values; the E relating to the Li salt is an exception.

All the alkali hexamolybdochromates show a sharp exothermic reaction corresponding to alkali tetramolybdate crystallization in the range 360–400°, as we have verified from X-ray and IR spectra of samples heated to 370°.

All ΔH values corresponding to that exothermic reaction are quite similar, except those of the Li and Cs salts, where the peak areas are affected by overlapping preceding or successive reactions.

A second less intense exothermic reaction is shown by these compounds between 405° and 480° where, in contrast to the first step, the temperature varies inversely as the ionic radius of the alkali metal. After this reaction the X-ray spectra indicate, in addition to the patterns of the alkali tetramolybdates, a very intense reflection at d values between 4.06 and 3.83, depending on the alkali salt. The most intense reflection ($Cr_2(MoO_4)_3$) has a $d = 3.86$, but the presence of this compound could be excluded, either from the absence of other characteristic reflections of this species in the compounds examined, or from the fact that this value varies greatly according to the alkali counter-ion. The formation of $Cr_2(MoO_4)_3$ was observed unequivocally by heating the ammonium hexamolybdochromate above 500°, after the intense exothermic reaction between 470 and 520°.

In the case of alkali salts, the weak exothermic reaction between 405° and 480° can probably be ascribed to a solid state reaction between the alkali tetramolybdate present and chromium oxide, giving an unknown compound. More accurate examination is necessary to elucidate its nature. The increase of the reaction temperature from the Li to the Cs salts seems to indicate that in this reaction the lattice energies of the alkali tetramolybdates are involved, because as is well known for other alkali salts with a common anion, these gradually decrease from Li to Cs.

This second exothermic reaction virtually renders the calcined products insoluble. Consequently these lose the ability to re-form the hexamolybdochromate anion when suspended in aqueous solution. However, when calcined below 400° they can give in solution a light pink colour after a few days. It is evident that the chromium, not yet insoluble, can give again the complex anion.

For the ammonium salt, several endothermic reactions have been observed between 200° and 380°, caused by several deammoniation and dehydration steps of the ammonium molybdates formed from decomposed complexes. In that range, reduction of the oxides by the NH_3 with successive reoxidation by air should not be excluded.

After the strong exothermic peak at 480°, the X-ray spectrum shows MoO_3 and $Cr_2(MoO_4)_3$ also to be present.

Fig. 3. TG curves of the alkali hexamolybdochromates. A: Li(HMC) · 10 H_2O; B: Na(HMC) · · x H_2O; C: K(HMC) · 7 H_2O; D: Rb(HMC) · 7 H_2O; E: Cs(HMC) · 5 H_2O; F: NH_4(HMC) · 7 H_2O

Discussion and conclusions

From an examination of the results obtained above for the alkali hexamolybdochromates, we suggest that alkali cation substitution in the salts may be considered only as a perturbation of the primary characteristics (such as affecting the water content or shifting of certain IR frequencies), but does not alter the principal characteristics of the complex anion structure. In fact both the solid reflectance spectra and the aqueous solution absorption spectra, in the range of $1000-250$ mμ are quite similar. The complete structural analogy of the complexes is therefore evident even on change of alkali cation.

In the IR spectra too, one can observe a group of quite similar bands for all the salts except that of Na.

From X-ray powder spectra it is certain that all salts with the same water content are isostructural (that is, the K, Rb, and NH_4 complexes).

From the thermal behaviour too we can confirm the similarity of their structures; only in the first dehydration steps does one see variations because of their different degrees of hydration.

In fact, except for the Na salt, all compounds show a characteristic weight loss between 140° and 250° corresponding to 3 moles of constitution water, after which we can observe the irreversible decomposition of the complexes with the formation of the alkali tetramolybdate.

The dehydration ΔH determinations obtained from DTA curves showed that the values corresponding to the last 3 H_2O decrease regularly from the Li to the Cs salt in the same manner as lattice energy in different series of alkali salts with a common anion. The value observed for the NH_4 salt, intermediate between those of Rb and Cs salts, is in the same position as in other salt series.

This observation emphasizes the importance of the constitution 3 H_2O in the structure of these complexes, since the energy necessary for its elimination can be indicative of the thermal stability of these complexes in the same manner as are their respective lattice energies.

Examination of the DTA curves of the different alkali hexamolybdochromates permits a reasonable explanation of the various endo- and exothermic reactions observed during the decomposition of the complexes.

At about $300-350°$ all salts show an exothermic peak corresponding to alkali tetramolybdate crystallization; while between 405° and 480° exothermic reactions attributable to solid state reactions between the alkali tetramolybdates and the chromium oxide are evident, with the formation of as yet unknown compounds. This is also demonstrated by the fact that the chromium, after this reaction, becomes completely insoluble and cannot re-form the hexamolybdochromate anion even when left in water for extended periods, in contrast to the behaviour of the salts heated to $\lesssim 400°$.

The endothermic reactions between 500° and 600° correspond to the melting of the tetramolybdates.

This work has demonstrated the analogies of the different alkali hexamolybdochromates but has also shown that the Na salt, whose structure is the only known one [8], is something of a curiosity; it behaves quite differently during thermal dehydration and has distinctive IR and X-ray powder spectra, and therefore we believe that a structural study of another more representative salt of this series would be most interesting.

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Résumé — Examen du comportement thermique des hexamolybdochromates de Li, Na, K, Rb, Cs et NH_4 caracterisés par leurs spectres de rayons X et infrarouges. La décomposition de l'anion ne commence qu'après l'élimination des 3 dernières molécules d'eau. Les valeurs ΔH de ce processus décroissent du sel de lithium à celui de césium de la même manière que les valeurs des énergies de réseau d'autres sels alcalins contenant le même anion. Interprétation des réactions exothermiques relatives à la décomposition des complexes par examen des composés obtenus.

Zusammenfassung — Die dargestellten Hexamolybdochromate von Li, Na, K, Rb, Cs und NH_4 wurden durch ihre Röntgen- und Infrarotspektren charakterisiert und ihr thermisches Verhalten studiert. Die Zersetzung des Anions begann erst nach Entweichen der letzten 3 H_2O. Die ΔH-Werte dieses Vorganges sinken in derselben Weise vom Li zum Cs wie die Gitterenergien anderer Alkalisalze mit gleichem Anion. Die auf die Zersetzung folgenden exothermischen Reaktionen wurden durch Untersuchung der erhaltenen Verbindungen gedeutet.

Резюме — Синтезированы гексамолибдохроматы Li, Na, K, Rb, Cs и NH_4, охарактеризованные ИК-спектрами и рентгеноструктурным анализом, и исследовано их термическое поведение. Установлено, что разложение аниона происходит только после удаления последних 3 молекул H_2O. Величина ΔH при этом процессе уменьшается в ряду от Li- до Cs-солей таким же образом, как и величина энергии решетки, установленная для других солей щелочных металлов с общим анионом. Экзотермическая реакция, происходящая при распаде комплексов, обясняется с позиций структуры полученных соединений.