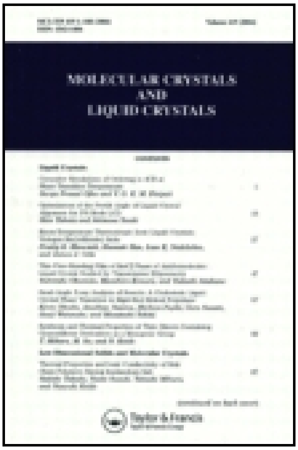

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Evidence of Liquid Crystal Phase Transitions in Mesostructured Alkyltrimethylammonium Chromates

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Evidence of Liquid Crystal Phase Transitions in Mesostructured Alkyltrimethylammonium Chromates

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Using amphiphilic molecules as templating director agents, we have recently synthesized, under soft chemistry conditions, new mesostructured bis-alkyltrimethylammonium dichromates of formula $(C_nH_{2n+1}(CH_3)_3\,N)_2\,Cr_2O_7\bullet\,x\,H_2O$ where n = 12, 14, 16, 18, and $0 \leq x \leq 2$. These layered compounds crystallise in the triclinic system, space group P-1. The structure consists of discrete dichromate anions stacking up in a layer, separated by a double layer of alkyltrimethylammonium cationic molecules lying in parallel. The d-spacing of these compounds linearly increase with the number of carbons in the alkyl chain, and depend on the number of water molecules. Phase transitions were investigated by mean of thermogravimetric analysis coupled with differential scanning calorimetry and mass spectrometry, optical microscopy and X-ray powder diffraction experiments. The hydrated bis-alkyltrimethylammonium dichromates exhibits a mesophasic behavior and the temperature domain in which the smectic A mesophase exists decreases when the length of the alkyl chains increases.

Keywords: mesostructured alkyltrimethylammoniumdichromates; liquid crystal phase transitions

INTRODUCTION

The design and synthesis of new solid materials with controlled structure is a current challenge in solid state chemistry. Recent studies have resulted in the use of liquid crystal-like arrays of main group or transition metal ions coordinated with organic molecules and clusters to form crystalline mesostructured phases. Following these guidelines, using amphiphilic molecules as templating agents, we have synthesized new mesostructured chromium oxides : $(C_nH_{2n+1}(CH_3)_3N)_2\ Cr_2O_7{\cdot}xH_2O$ (ATMACr) with $n = 12$, 14, 16, 18 and $0 \leq x \leq 2$.

The preparation , structural characterization, and phase transitions studies of hydrated and anhydrous mesostructured (*) chromium oxides were reported.

EXPERIMENTAL

A solution of $K_2Cr_2O_7$, $C_nH_{2n+1}(CH_3)_3NBr$ (ATMABr) and H_2O in a 1:2:100 molar composition was heated at 80°C for 12 hours, in a screw top tube. After cooling, the solid orange product was recovered by filtration, washed

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(*)The terms microstructured, mesostructured and macrostructured are used analogously to scale definitions for the three classes of porous materials defined by IUPAC [1]: first, microporous materials, in which the pore diameter $d_p < 2$ nm; second, mesoporous materials, in which 2 nm $< d_p < 50$ nm; and, third, macroporous materials, in which $d_p > 50$ nm.

with distilled water and dried in air at room temperature or at 100°C. The chemical reaction can be summarized as follows:

$$2C_nH_{2n+1}(CH_3)_3NBr + K_2Cr_2O_7 + yH_2O \rightarrow$$

$$(C_nH_{2n+1}(CH_3)_3N)_2Cr_2O_7 \cdot xH_2O + (y-x)H_2O + 2KBr$$

The thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) was carried out on SETARAM TG-DSC 111, by using samples of about 20 mg with heating rate of 2°C min^{-1} under a flowing argon atmosphere. Evolved Gas Analysis - Mass Spectrometry (EGA-MS) coupled with ATG and DSC was performed on Leybold H300CIS apparatus. X-ray powder diffraction (XRPD) patterns were recorded on a D5000 SIEMENS diffractometer in a Bragg-Brentano geometry using CuK$_\alpha$ radiation, with a 2θ step width of 0.03° and a step time of 1.5 s. For the structural analysis of anhydrous OTMACr by X-ray diffraction techniques, a platelike-shaped single-crystal was selected and the intensity data collection was performed with a STOE Imaging Plate Diffraction System diffractometer. SHELXTL software [2] Version 5 was used for data analysis, structure solution and refinement.

RESULTS AND DISCUSSION

Structural characterization:

The XRPD patterns of hydrated and anhydrous bis-alkyltrimethylammonium dichromates show (Fig.1) an enhancement of the *0 0 l* peaks intensities due to a preferential orientation and a characteristic d_{00l} -spacing of a lamellar structure. As shown Fig. 2, the interlayer d_{00l} both of the surfactant ATMABr, and of the anhydrous and hydrated mesostructured organochromates

$(C_nH_{2n+1}(CH_3)_3N)_2Cr_2O_7{\cdot}2H_2O$, continuously increase along with the number of carbons in the alkyl chain, with slopes equal to respectively, 1.12 Å, 0.89 Å and 1.3 Å per added carbon atom. These results are in good agreement with those published by D. F. Evans and H. Wennerström [3] where the L -length of alkyl chain- is given by the following relation L = 1.5 + 1.27 n.

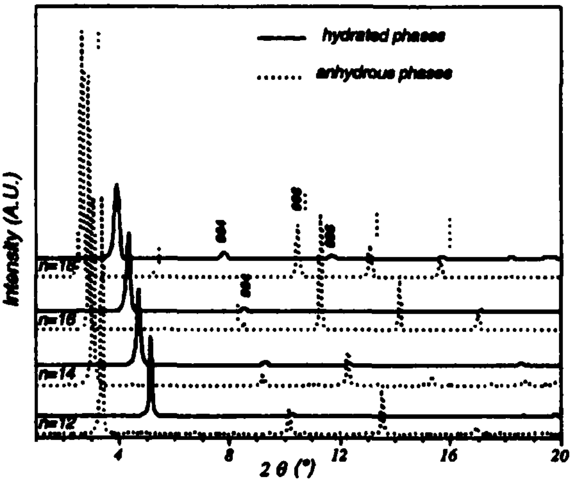

FIGURE 1 X-ray powder diffraction patterns of hydrated and anhydrous alkyltrimethylammonium dichromates.

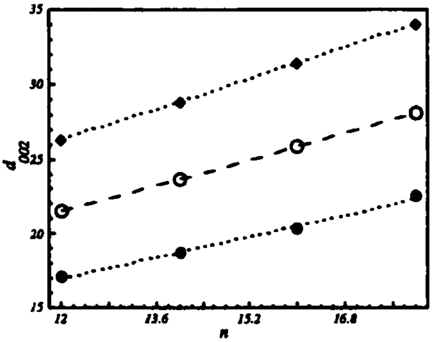

FIGURE 2 d_{00l}-spacing as a function of the number of carbon atoms in the alkyl chain of the (○) $C_nH_{2n+1}(CH_3)_3NBr$, (◆) $(C_nH_{2n+1}(CH_3)_3N)_2Cr_2O_7{\bullet}2H_2O$ and (●) $(C_nH_{2n+1}(CH_3)_3N)_2Cr_2O_7{\bullet}0H_2O$

Structure of anhydrous $(C_{12}H_{25}(CH_3)_3N)_2Cr_2O_7$ (OTMACr)

The structure of the anhydrous OTMACr compound corresponds to a large unit cell of dimensions a = 7.197(1) Å, b = 8.816(2) Å, c = 43.400(9) Å, α = 93.43(3)°, β = 90.00(3)°, γ = 113.98(3)°, similar to our early preliminary data described in a space group P-1 [4]. From the refinement results, the unit cell was found to contain isolated $(Cr_2O_7)^{2-}$ dichromate ions which consist of two CrO_4 tetrahedra sharing the bridging oxygen atom. These $(Cr_2O_7)^{2-}$ clusters are arranged in layers and their anionic charge is counter-balanced by those of alkylammonium cations. The O-H distances are longer than the sum of the Van der Waals radii. Therefore $(Cr_2O_7)^{2-}$ clusters are just in equilibrium with OTMA thanks to coulombic interactions. The surfactants pack within crystals so that the lipophilic groups of different molecules are gathered together in a lipophilic region and the hydrophilic groups are similarly arranged within polar regions.

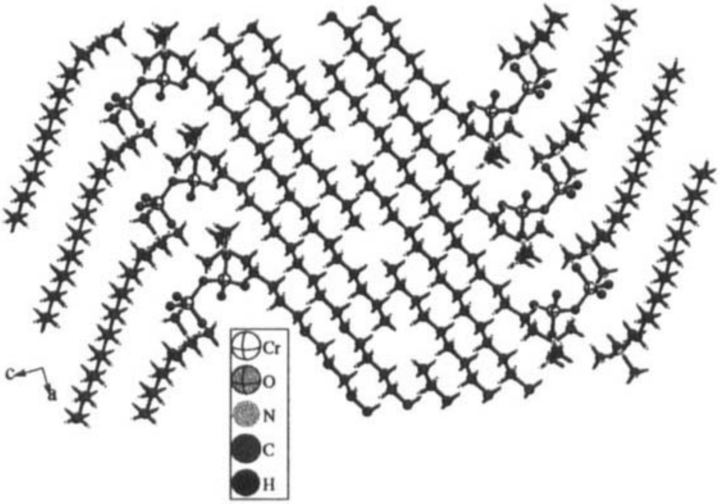

FIGURE 3 Packing of the dichromate clusters and octyltrimethylammonium cations viewed in projection along the b axis. The OTMA chains are parallel to one another, with their trimethylammonium head groups oriented in opposite directions lay between the $(Cr_2O_7)^{2-}$ layers.

As the most common packing structure observed in surfactant-water system, the octadecyltrimethylammonium chromate adopts a bilayer configuration in which the OTMA hydrocarbon chains are extended away from the planes containing the dichromate groups (Fig.3). Therefore layered structure is composed of an alternating arrangement of an inorganic wall, $(Cr_2O_7)^{2-}$ and organic bilayer. The alkyl chains, constitutive of the bilayer, alternate along the c axis, with a rotation of about 90° (Fig.3). In the OTMACr, the interlayer spacing of 43.4Å, smaller than the expected value for the fully extended molecular model is achieved through a tilting of the surfactant chains of about 70.5° from the normal to the $(Cr_2O_7)^{2-}$ plane. Moreover, adjacent OTMA molecules adopt a chevron conformational structure, as shown in Fig.4 with an angle of 84.5° in between.

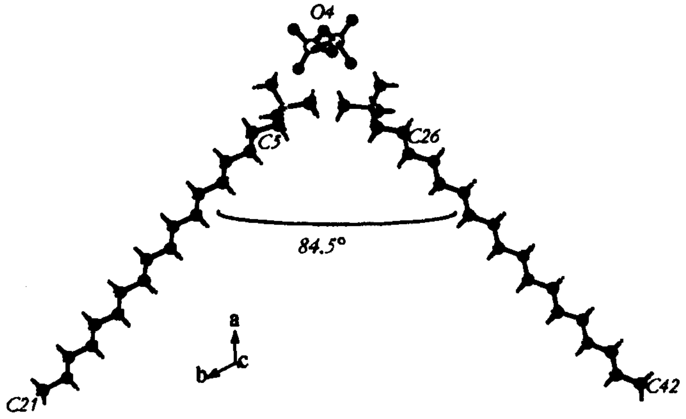

FIGURE 4 View of OTMACr showing the chevron conformational structure of the OTMA chains.

Thermal analysis

The thermal stability of the compounds n = 18, dried either at room temperature or at 100°C, was investigated by mean of TGA coupled with DSC. The results are shown in Fig.5 and 6 respectively. Between 180 and 460°C, the sample dried at room temperature exhibits three weight losses (marked A, B, C) while the other dried at 100°C, shows only two (D, E). In both cases, the last weight loss (≈ 460°C) leads to Cr_2O_3 (Eskolaïte) identified from the X-ray Powder Diffraction pattern. The total mass loss of bis-octadecyltrimethylammonium dichromates dried at room temperature and at 100°C is 75.75 % and 73.70 %, respectively.

The self combustion completely occurs only under air, and in that case the observed values are in good agreement with the expected stoichiometry $(C_{18}H_{37}(CH_3)_3N)_2Cr_2O_7{\cdot}xH_2O$, x = 2 hydrated (82.67%) and x = 0 anhydrous compounds (81.93%), respectively. Between 180 and 250°C and for x = 2, the two weight losses, noted (A) and (B) are related to water loss and to surfactant decomposition by a self-combustion process (Fig.5). The second thermal phenomenon is also observed when x = 0 and is marked (D) on Fig.6. In that way, the DSC curves (Fig.5 and 6) for both hydrated and anhydrous phases exhibit an important exothermic peak, in this temperature range, suggesting an oxidation-reduction phenomenon through which gaseous products are formed. The exothermic character excludes some interpretations. However, the EGA curves of $(C_{18}H_{37}(CH_3)_3N)_2Cr_2O_7$, showed that the weight losses correspond to the decomposition of $(C_{18}H_{37}(CH_3)_3N)_2Cr_2O_7$ by self-combustion process during which H_2O, C_nH_{2n+2}, H_2 and a minor part N_2 gas are produced around 230°C. The simplified thermal decomposition of $(C_nH_{2n+1}(CH_3)_3N)_2Cr_2O_7$ has often been represented by the equation :

$$(C_nH_{2n+1}(CH_3)_3N)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + 4H_2 + 2C_nH_{2n+2} + 6C + Cr_2O_3$$

Phase transitions study

According to the hydrated or anhydrous nature of the compounds and for T<180°C, the D.S.C. curves (Fig.5 and 6) exhibit two (A', B') or one (E') endothermic transitions. The transition (E') can be attributed to a fusion phenomenon while the A' and B' result from solid-mesophase and mesophase-Isotrope liquid transitions, respectively. The crystal to liquid-crystal phase transition corresponding to the A' endothermic peak in Fig.5 was directly

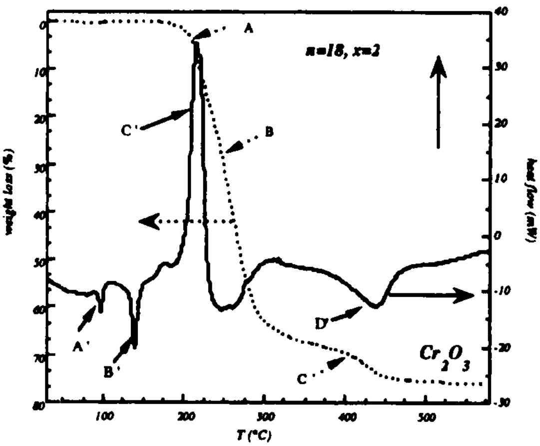

FIGURE 5 TG and DSC curves of hydrated $(C_{18}H_{37}(CH_3)_3N)_2Cr_2O_7{\cdot}2H_2O$ showing three endothermic transitions (A' B' and D') and one exothermic peak (C'). According to the TG analysis, the C' transition can be attributed to the thermal decomposition of the surfactant.

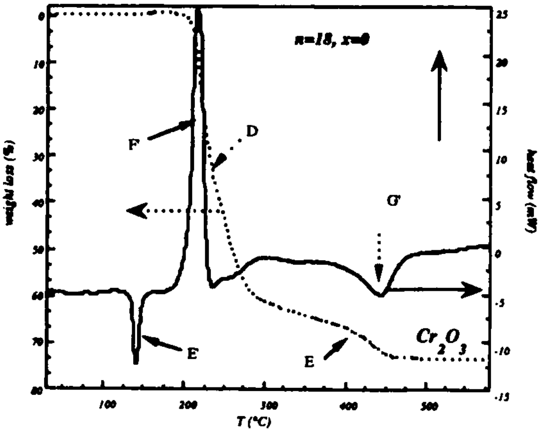

FIGURE 6 TG and DSC curves of anhydrous $(C_{18}H_{37}(CH_3)_3N)_2Cr_2O_7$ showing only one endothermic peak (E') below T=180°C.

observed in polarized light microscopy, as well. Between 75° and 140°C, the polarizing microscope images of the hydrated bis-octadecyltrimethylammonium dichromate, clearly exhibit common textures encountered in liquid crystal phases (Fig.7 (a) and (b)) [5]. The bright oily streaks (a) and the mosaic texture in complex network of positive and negative units (b), are characteristic of a smectic A mesophase.

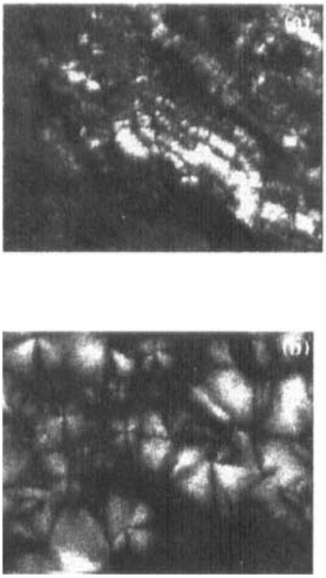

FIGURE 7 Typical appearance in the polarising microscope of lamellar mesophase (smectic A) of $(C_{18}H_{37}(CH_3)_3N)_2Cr_2O_7$ $2H_2O$, showing (a) oily streaks and (b) a mosaic texture. (See Color Plate I at the back of this issue)

The crystal to liquid-crystal phase transitions was also observed during the in situ X-ray Powder Diffraction study. Unfortunately, under the experimental conditions used, an anhydrous bis-octadecyltrimethylammonium-dichromate chains in the layer and the increase of the coherence length is consistent with a relaxation of the alkyl chain during the rotational motion or melting chain phenomenon. To clarify this end point, N.M.R. and IR experiments are actually in progress.

TABLE I Thermal evolution of d_{002}-spacing and of Full Width at Half-Maximum (FWHM) of $(C_{18}H_{37}(CH_3)_3N)_2Cr_2O_7{\cdot}2H_2O$.

Temperature (°C)	d_{002} (Å)	FWHM of *002* (Å)
30	33.19	0.108
65	33.41	0.126
75	37.05	0.096
80	37.32	0.162

The correlation between the transition temperatures and alkyl chain length (n) was evidence during the DSC experiments (Fig. 9 (a) and (b)). For the hydrated bis-alkyltrimethylammonium dichromate (Fig. 9 (a)), it clearly appears that the temperature domain in which the Sm phase exists decreases when the alkyl chain increases. Since the van der Waals interactions between the chains increases with their length, the rotation of the molecules becomes more difficult and the temperature of the S/Sm transition increases when n increases. Inversely, the temperatures of the Sm/I transitions decrease when n increases since the correlation length of the alkyl chains diminish as n increases for hydrated bis-alkyltrimethylammonium dichromates. The same thermal behavior is also observed in the case of C/L transitions of anhydrous bis-alkyltrimethylammonium-dichromate (Fig.9(b)).

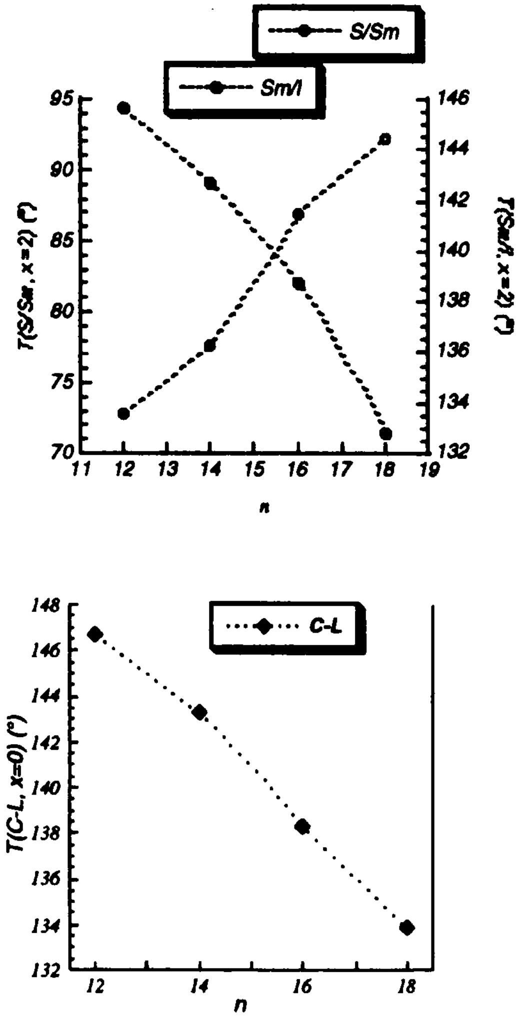

FIGURE 9 Effect of alkyl chain length, n, on the transition temperatures: (a) S/Sm and Sm/I transitions in hydrated ATMACr (b) Crystal/liquid transition of anhydrous ATMACr

CONCLUSION

A soft chemistry route has been successfully used to prepare hydrated and anhydrous mesostructured bis-alkyltrimethylammonium dichromates. Obviously, the stacking parameter of these lamellar compounds linearly increases with the increase of the alkyl chain length and also depends on their hydration level. The interlayer spacing of the anhydrous phases is smaller than those of the hydrated phases and is inconsistent with the value expected for the fully extended alkyl chain molecule.

The crystal structure of the bis-octyltrimethylammonium dichromate was determined : it consists of isolated dichromate entities stacking in a layered order, separated by a double layer of octyltrimethylammonium chains. The remarkable contraction of the stacking parameter is essentially due to the tilt of the alkyl chains towards the plan containing the polar head groups.

The DSC studies reveal phase transitions, with the formation of a mesophase in the case of the hydrated $(C_nH_{2n+1}(CH_3)_3N)_2Cr_2O_7.2H_2O$ compounds. It has been shown that the temperature domain in which the Sm phase exists decreases when the length of the alkyl chains increases. These mesophases (smectic A) were directly observed by optical microscopy and X-rays Powder Diffraction, as well. During the solid-mesophase transition, the increase in d_{002} probably results from a lower tilt of the alkyl chains in the layer

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