

CHARACTERISATION OF SOME NEW CHROMATES $M_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O$ ($M = Li, Na$) *

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ABSTRACT

The chromates $M_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O$ were prepared as amorphous red-brown powders from mixtures of $Fe(NO_3)_3 \cdot 9H_2O$ and $M_2Cr_2O_7$ ($M = Na, Li$) fused at $65^\circ C$. Decomposition of the chromates occurred over the range 110 – $530^\circ C$ to yield the respective alkali chromate and a mixture of iron(III) and chromium(III) oxides. Infrared spectroscopy of the chromates showed the presence of coordinated water and long range $OH \cdots O$ interactions, whilst Mössbauer spectra indicate the presence of more than one iron site.

INTRODUCTION

For the preparation of iron chromates from aqueous solution, high iron and chromium concentrations are required [1–3]. This necessitates the use of concentrated solutions of chromium trioxide and iron(III) nitrate or chloride. In addition, they are not easy to make, being complicated by hydrolytic and polymerization equilibria. Careful control of conditions and patience are required to form products of definite, reproducible compositions. It is of interest, therefore, to establish whether chromates can be prepared by the use of a molten salt as the reaction medium. This method is particularly suited to a synthetic route to the chromates, in view of the existence of low-melting iron(III) salts. The method satisfies the requirement for high iron concentrations and provides manageable reaction conditions.

In previous communications, the room temperature Mössbauer parameters [4] and thermal decomposition patterns [5] for a range of chromates have been reported. In this report, the reactions of the dichromates of lithium and sodium metals with iron(III) nitrate hydrate melt [6] were studied and the reaction products analysed.

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EXPERIMENTAL

Analytical

The chemical constituents of the basic chromates were determined by conventional chemical means: lithium, sodium, iron and chromium by atomic absorption spectroscopy, and water by measuring the weight loss on dehydration.

Instrumentation

Mössbauer, X-ray powder diffraction, thermogravimetry, differential thermal analysis, magnetic measurements and atomic absorption spectrometry were all performed as described previously [4]. Infrared spectra were measured on a Perkin-Elmer 1800 Fourier Transform Infrared Spectrophotometer using the KBR disc method. Mössbauer spectra were collected by a PDP 10/11 computer and fitted by a pseudo-Lorentzian program using an iterative, non-linear least-squares method, on the basis of the chi-square (χ^2) values, consistency of parameters and convergence of the fitting process [7].

Materials

B.D.H. $\text{Li}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (96%), May and Baker $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (98%), and AJAX $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR) were all used as supplied.

Preparation of $\text{Na}_2\text{Fe}_3(\text{OH})_5(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$

An excess of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.0 g, 2.60 mmol) was placed into a silica crucible to which was added sodium dichromate (0.74 g, 2.47 mmol). The contents were mixed thoroughly and heated in an oven at 65°C for 2 h. The crucible contents were then placed in water, and a red-brown insoluble powder filtered off, washed with water (20 ml) and then acetone (20 ml). Yield 50 mg. Found (wt.%): Na, 6.65; Fe, 24.05; Cr, 22.75; H_2O , 14.63. $\text{Na}_2\text{Fe}_3(\text{OH})_5(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$ requires (wt.%) Na, 6.56; Fe, 23.82; Cr, 22.30; H_2O , 14.13. The room temperature magnetic moment measured was $\mu_{\text{eff}} = 3.4$ BM.

Preparation of $\text{Li}_2\text{Fe}_3(\text{OH})_5(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$

This was prepared similarly to the corresponding sodium salt, $\text{Li}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (0.65 g, 2.44 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.0 g, 2.60 mmol). Yield of red powder 35 mg. Found (wt.%): Li, 2.21; Fe, 25.50; Cr, 24.40; H_2O , 14.61. $\text{Li}_2\text{Fe}_3(\text{OH})_5(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$ requires (wt.%) Li, 2.10.; Fe, 25.10; Cr, 24.40; H_2O , 14.81. Magnetic moment, $\mu_{\text{eff}} = 3.3$ BM.

RESULTS AND DISCUSSION

Thermal analysis

Weight loss (TG) and differential thermal analysis (DTA) results are shown in Tables 1 and 2 respectively. The chromates decomposed in several stages. The final weight losses were in close agreement with those calculated of 22.00% and 21.06% for the lithium and sodium complexes, respectively (eqns. (3) and (6) in Table 1). X-ray powder diffraction (XRD) patterns of the chromate residues quenched from 550 °C, showed the presence of the respective alkali metal chromate, and a mixture of iron(III) and chromium(III) oxides, further supporting eqns. (3) and (6). Decomposition of the chromates $M_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O$ confirms the general trend as proposed by Golub and Popel [8], that coordinated water is lost prior to dehydroxylation in basic chromate hydrates. The instability of the anhydrous salts $M_2Fe_3(OH)_5(CrO_4)_3$, as judged by the absence of a plateau in the TG corresponding to their formation, appears not to be dependent on the size of the monovalent cation, but rather on whether the cations form stable $M_2Cr_2O_7$ or M_2CrO_4 species. This point is clearly demonstrated for the chromates $MFe(CrO_4)_2$ ($M = NH_4, Na, K, Rb, Cs$). The cations of the ammonium and sodium salts form unstable dichromates in the region of decomposition (400 °C) [4,9], whilst the potassium, rubidium and cesium salts all form stable dichromates and decompose at much higher temperatures (500 °C) [9].

The presence of endotherms at about 500 °C (Table 2) is a characteristic feature of basic iron chromate decomposition [5]. The intermediate phase $Fe_2O(CrO_4)_2$ has been observed during the decomposition of all basic iron chromates reported thus far in the literature [5]. The occurrence of an endotherm within this temperature region is thought, therefore, to be associated with the formation of the unstable oxochromato species $Fe_2O(CrO_4)_2$. The remaining endotherms (Table 2) were assigned to dehydration processes.

X-ray powder diffraction.

The red-brown powders deposited from the melt were amorphous to X-rays. Investigations are at present underway to procure suitable crystalline material for structural analysis.

Infrared spectroscopy

The chromates exhibit free OH stretching and M–OH bending vibrations at around 3650 and 1000 cm^{-1} , respectively (Table 3). Broad absorption maxima (Fig. 1) at around 3400 cm^{-1} and sharp peaks at about 1600 cm^{-1} are assigned to the stretching and bending modes of coordinated water [10].

TABLE 1

Proposed reaction stoichiometries for the thermal decomposition of the chromates $M_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O$ at a heating rate of $10^\circ C \text{ min}^{-1}$

Reaction	Weight loss (%)		Equation
	Found	Calculated	
110-290			
$Li_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O \rightarrow Li_2Fe_3(OH)_5(CrO_4)_3 \cdot H_2O + 2H_2O$	5.88(0.35)	5.38	(1)
295-595			
$Li_2Fe_3(OH)_5(CrO_4)_3 \cdot H_2O \rightarrow Li_2CrO_4 + 3/2 Fe_2O_3 + Cr_2O_3 + 3/2 O_2 + 7/2 H_2O$	16.72(1.5)	17.56	(2)
$Li_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O \rightarrow Li_2CrO_4 + 3/2 Fe_2O_3 + Cr_2O_3 + 3/2 O_2 + 11/2 H_2O$	21.70(0.75)	22.00	(3)
108-240			
$Na_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O \rightarrow Na_2Fe_3(OH)_5(CrO_4)_3 \cdot 1/2 H_2O + 5/2 H_2O$	6.42(0.25)	6.42	(4)
245-530			
$Na_2Fe_3(OH)_5(CrO_4)_3 \cdot 1/2 H_2O \rightarrow Na_2CrO_4 + 3/2 Fe_2O_3 + Cr_2O_3 + 3/2 O_2 + 3H_2O$	22.41(0.30)	21.98	(5)
$Na_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O \rightarrow Na_2CrO_4 + 3/2 Fe_2O_3 + Cr_2O_3 + 3/2 O_2 + 11/2 H_2O$	21.82(0.30)	21.06	(6)

TABLE 2

Differential thermal analysis of the chromates $M_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O$ at a heating rate of $10^\circ C \text{ min}^{-1}$

Compound	T_i^a	T_{max}^b	T_f^c	ΔH	Reaction
$Li_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O$	120	240	270	Endo	$-H_2O$
	275	420	490	Endo	$-H_2O, -O_2$
	490	502	505	Endo	$-O_2$
$Na_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O$	115	259	275	Endo	$-H_2O$
	277	439	485	Endo	$-H_2O, -O_2$
	492	505	508	Endo	$-O_2$

^a T_i , initial departure of curve from baseline.

^b T_{max} , maximum departure from baseline.

^c T_f , return to baseline.

The position and shape of bands at 2900 cm^{-1} are consistent with long range $OH \cdots O$ hydrogen bond interactions [11,12]. Their presence explains the sequential loss of water (eqns. (1) and (4), Table 1) for the chromates, owing to some water molecules being more strongly coordinated to the iron atoms. The remainder of the assignments in Table 3 are based on those reported by Cudennec et al. for the basic chromate $KFe_3(OH)_6(CrO_4)_2$ [13].

Room temperature Mössbauer

Table 4 lists the Mössbauer parameters for the chromates. The isomer shifts δ are normal for high spin Fe(III) compounds. Their relatively narrow

TABLE 3

Infrared band positions for the chromates (KBr disc)

Compound		Compound	
$Li_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O$		$Na_2Fe_3(OH)_5(CrO_4)_3 \cdot 3H_2O$	
$\nu (\pm 5 \text{ cm}^{-1})$	Assignment	$\nu (\pm 5 \text{ cm}^{-1})$	Assignment
3650 (sh, m)	$\nu(M-OH)$	3672 (sh, m)	$\nu(M-OH)$
3405 (s) } 2922 (vw) } 2852 (vw) } 1652 (m) } 1459 (w) } 1000 (w) } 939 (s) } 774 (m) } 713 (w) } 474 (m) }	$\nu(OH)$ δOH $\delta(M-OH)$ $\nu(Cr-O)$ $\nu(Fe-O)$ $\delta(O-Cr-O)$	3414 (s) } 2923 (vw) } 2856 (vw) } 1594 (m) } 1030 (s) } 968 (m) } 928 (m) } 893 (w) } 848 (m) } 795 (w) } 515 (m) }	$\nu(OH)$ $\delta(OH)$ $\delta(M-OH)$ $\delta(Cr-O)$ $\nu(M-O)$ $\nu(Fe-O)$ $\nu(FeO)$

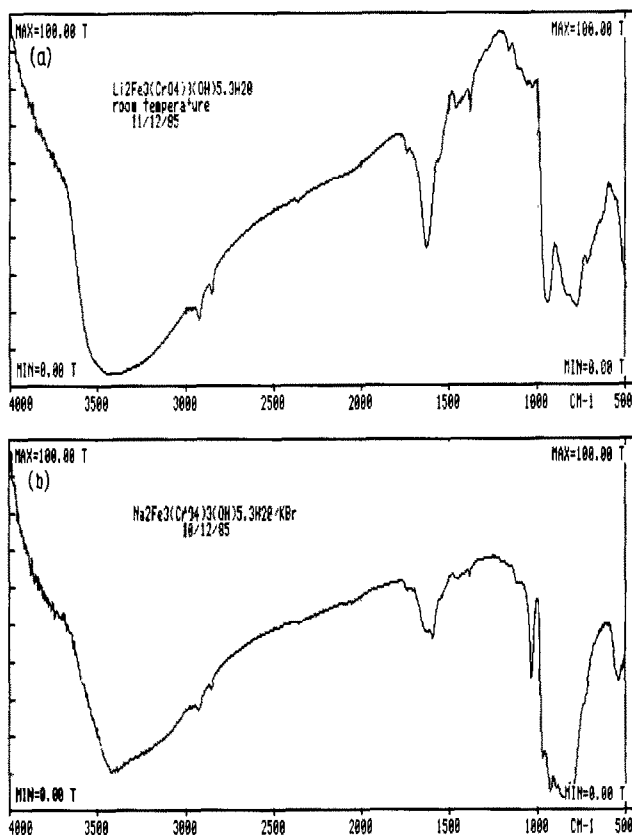


Fig. 1. Infrared spectra of chromates (a) $\text{Na}_2\text{Fe}_3(\text{OH})_5(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$; (b) $\text{Li}_2\text{Fe}_3(\text{OH})_5(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$.

TABLE 4

Mössbauer parameters for chromates $\text{M}_2\text{Fe}_3(\text{OH})_5(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$

Example	Fit ^a	Chi-squared χ^2	Mössbauer parameters (mm s^{-1})		
			δ	ΔE	Γ ^b
$\text{Li}_2\text{Fe}_3(\text{OH})_5(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$	2T2	2.51	0.392(2)	0.151(2)	0.251(3)
			0.392(2)	0.365(8)	0.371(6)
	2T3 ^c	0.92	0.392(2)	0.159(2)	0.291(2)
			0.392(2)	0.331(5)	0.280(4)
			0.392(2)	0.452(5)	0.226(1)
$\text{Na}_2\text{Fe}_3(\text{OH})_5(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$	2T2	2.45	0.392(2)	0.161(3)	0.273(2)
			0.392(2)	0.388(9)	0.345(9)
	2T3	0.95	0.391(1)	0.176(2)	0.316(6)
			0.391(1)	0.351(2)	0.278(6)
			0.389(1)	0.462(2)	0.274(4)

^a 2T2, fitted to two sets of quadrupole split doublets.

^b Γ , linewidth at half peak height.

^c 2T3, fitted to three sets of quadrupole split doublets.

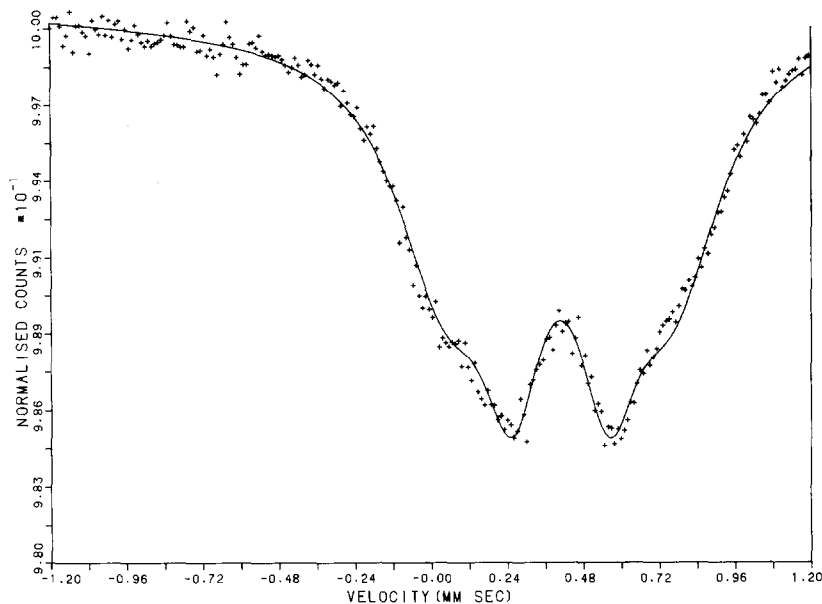


Fig. 2. Representative Mössbauer spectrum of the basic chromates $\text{Li}_2\text{Fe}_3(\text{OH})_5(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$.

line widths ($0.22\text{--}0.31 \text{ mm s}^{-1}$), indicate that line broadening due to the presence of coupling is not of much importance. Initial fitting of each spectrum (Figure 2) to two sets of quadrupole split doublets (ΔE) gave χ^2 values of about 2.5—a fair fit. It was felt that the fits could be improved by incorporating the outer doublet ($\Delta E \approx 0.37 \text{ mm s}^{-1}$) as two overlapping doublets. On doing so the χ^2 values were reduced to about 1.0, an excellent fit, and the parameters obtained were within acceptable limits. Assignment of spectra are shown in Table 4. The outer doublet ($\Delta E \approx 0.46 \text{ mm s}^{-1}$) was assigned to the presence of iron–oxygen polyhedra containing hydroxyl ions, $\text{Fe}(\text{OH})_x\text{O}_{6-x}$, based on the reported trend [4] that the replacement of oxygen atoms by hydroxyl or water groups results in an increase in ΔE . The order of increase in quadrupole splitting on incorporation is $\text{OH}^- > \text{H}_2\text{O} > \text{O}^{2-}$. The measured ΔE of this doublet is consistent with those reported for $\text{Fe}(\text{OH})_x\text{O}_{6-x}$ containing chromates [4,5] of between 0.46 and 0.49 mm s^{-1} . A similar argument sees the two inner doublets, ΔE 0.16 and 0.33 mm s^{-1} , being assigned to $\text{Fe}(\text{OH}_2)_x\text{O}_{6-x}$ polyhedra. The presence of more than one water environment is consistent with the infrared spectra (Fig. 1) which show the presence of coordinated water of varying strengths.

CONCLUSION

Synthetic routes to iron chromates using low melting iron(III) salt hydrates, has the potential for the preparation of a range of new chromates,

containing more than one iron site as indicated by Mössbauer spectroscopy. The synthesis of iron chromates containing multi-iron sites should further aid the development of structural correlation, reported thus far [4] by the compilation of isomer shifts and quadrupole splittings for iron chromates. The magnetic moments of both chromates of around 3.4 BM, are considerably reduced from the spin-only value for an uncoupled $S = 5/2$ Fe(III) state (viz. $\mu_{\text{eff}} = 5.92$). The μ_{eff} values are comparable to those reported for chromates FeOHCrO_4 and $\text{KFe}_3(\text{OH})_6(\text{CrO}_4)_2$, and must be presumed to arise from similar antiferromagnetic coupling [13]. A more detailed magnetic investigation is however required for the compounds. Decomposition of the basic chromate hydrates follows a similar pathway to those basic chromates reported previously [5], with dehydroxylation occurring at higher temperatures than the loss of coordinated water.

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