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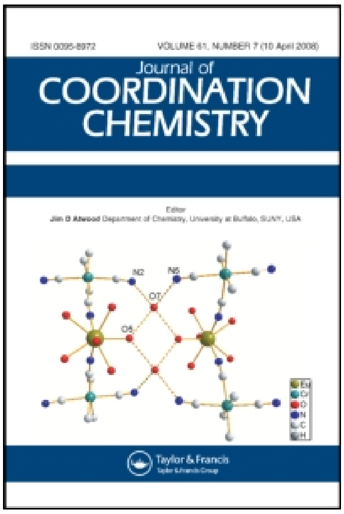

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SYNTHESIS AND CHARACTERIZATION OF A CHROMIUM(III) PHTHALATE

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A chromium(III) phthalate (CP) of composition $[Cr(pht)_{1-x}(Hpht)_x(OH)_{1+x}(H_2O)_{1-x}]$ ($x < 0.5$; pht = phthalate ion, $C_8H_4O_4{}^{2-}$; Hpht = hydrogen phthalate ion) has been prepared by aerial oxidation of a chromium(II) phthalate. TG analysis shows that CP loses its water content at 110°C in an essentially reversible manner, while the bulk of the organic component is lost in the 300–520°C range. A least-squares analysis of the electronic spectrum of CP reveals three d–d transitions consistent with an octahedral environment around the Cr(III) sites, together with a high energy charge transfer band.

Keywords: Chromium(III), double salts, phthalate, thermal studies, spectral properties

INTRODUCTION

A variety of chromium(III) phthalates have been reported, their composition primarily depending on the synthetic conditions used. Thus the reaction of potassium hydrogen phthalate with chromium(III) chloride in an alkaline medium yielded a solid described[1] as $Cr_3(OH)_{12}(pht)$ (*sic*). By treating phthalic acid with chromium(III) perchlorate[2] or nitrate[3] the compounds $K_3[Cr_3(OH)_6(pht)_3(H_2O)_6]$ and $H[Cr(pht)_2(H_2O)_2]\cdot H_2O$ were obtained, respectively, while $K_3[Cr(pht)_3]\cdot 2H_2O$ was prepared by the reaction of chromium(III) hydroxide with phthalic acid and subsequent precipitation using potassium carbonate.[4] Still another material, characterized as $H_2[Cr_2(OH)_2(pht)_3(H_2O)_2]\cdot H_2O$, resulted when phthalic acid was reacted with dihydroxochromium(III) sulphate.[3] Furthermore, the presence of the bidentate phthalate ligand has been observed when nitrilotriacetatochromate(III) was kept in a phthalate buffer, but no solid complex was isolated.[5]

Our aim in the present work has been to prepare a chromium(III) phthalate by a synthetic procedure fairly common in obtaining chromium(III) complexes, that is by temporarily reducing Cr(III) to Cr(II), reacting the latter with the appropriate ligand, and reoxidizing chromium in the product to Cr(III).

EXPERIMENTAL

Reagents

Phthalic acid and 25% aqueous ammonia were of p.a. grade, whereas chromium(III) chloride hexahydrate (Merck) was of 95% min. purity.

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Instrumentation

X-ray powder diffraction analysis was performed on a Philips PW 1051 Diffractometer using CuK_α radiation and a graphite monochromator, in the 2θ range of 4–50°. TG analysis was carried out on a Perkin-Elmer thermal analysis LAB 1, TGS-2, Model FDC-1 instrument; heating rate 5°C/min, N_2-flow rate 60 cm^3/min, temperature range 30–750°C. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the 4000–250 cm^{-1} range, with samples in KBr pellets. Diffuse reflectance spectra were recorded on a Beckman 5240 UV spectrophotometer in the 750–300 nm range.

Preparation of Chromium(III) Phthalate

13.3 g (0.05 mol) of chromium(III)chloride hexahydrate were dissolved in 18 cm^3 of water plus 5 cm^3 of 1 mol dm^{-3} sulphuric acid, and the solution was reduced in a Jones reductor by granulated zinc. This yielded a light-blue solution of the chromium (II) salt (solution A). A solution of ammonium phthalate was prepared by dissolving 24.9 g of phthalic acid (0.15 mol) in 25 cm^3 of 25% aqueous ammonia (0.335 mol), (solution B). The solution B was then added to the stirred solution A under a nitrogen atmosphere at room temperature. A bulky red-violet precipitate formed immediately. It was washed under an N_2 atmosphere with water, ethanol and ether, and then dried in a stream of nitrogen at room temperature. The dry red-violet solid was then exposed to air at room temperature, whereupon its colour began gradually to change. After 4 days, the solid was washed with methanol (to remove any free phthalic acid that might have been liberated in the course of aerial oxidation of the chromium(II) complex), then dried in air at room temperature to yield 6.06 g of a blue-green product (CP). Anal.; Calcd. for $CrC_8H_7O_6$: Cr, 20.7; C, 38.28; H, 2.79; H_2O, 7.17%; mass loss for conversion to Cr_2O_3: 69.7%. Found: Cr, 20.91; C, 38.13; H, 3.78%; mass loss at 110°C: 7.0%; mass loss at 1000°C: 69.77%. Thus the yield in the preparation is 48.4% (based on Cr). The X-ray powder diffraction pattern of CP has only one peak (at $2\theta = 6.8°$), that could be measured.

Infrared spectral data (cm^{-1}): 365(vw), 400(vw), 535(m), 595(vw), 665(m), 705(m), 760(m), 835(vw), 865(vw), 965(vw), 1030(s), 1080(vw), 1090(w), 1160(w), 1175(vw), 1235(vw), 1250(vw), 1270(vw), 1300(vw), 1410(vs), 1445(vw), 1490(s), 1540(vs), 1695(sh), 2830(vw), 2940(vw), 3370(s,b) (vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder; b = broad).

RESULTS AND DISCUSSION

A chromium(III) phthalate of the approximate formula Cr(pht)(OH)(H_2O) (CP) is obtained by the reaction of aqueous Cr^{2+} and ammonium phthalate in an inert atmosphere at room temperature, and the subsequent aerial oxidation of the resulting red-violet solid into a blue-green powder. CP has a homogenous appearance under the microscope and is essentially amorphous, although its X-ray powder diffraction pattern indicates incipient crystallization. It is entirely insoluble in water and in common organic solvents, which suggests a polymeric nature. The intermediate red-violet solid is probably chromium(II) phthalate. It too is quite insoluble, which is not surprising since chromium(II) carboxylates are typically dimeric and poorly soluble species.[6] The oxidative conversion of chromium(II) phthalate into CP necessarily involves the formation of Cr–OH–Cr or Cr–O–Cr bridges that are so characteristic of chromium(III) chemistry.[7]

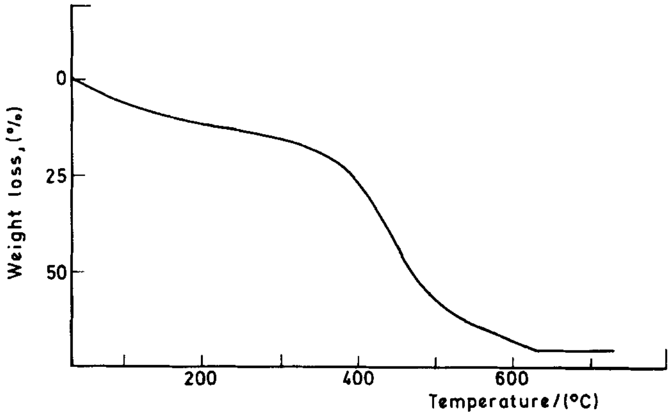

FIGURE 1 Thermogravimetric curve for CP.

TG analysis showed that CP loses all its water up to 110°C [mass loss *ca* 7% (Fig. 1); calcd. 7.17%]. Above 300°C there is a steep change in the TG curve extending to *ca* 520°C. The mass loss in this region corresponds to the loss of about 80% of phthalic anhydride from the system (*ca* 46% loss; calcd. for $C_8H_4O_3$, 58.96%). In the final decomposition stage, the remaining phthalic anhydride together with the H_2O resulting from the condensation of OH-groups is liberated. The degradation of CP is complete by 630°C, the remaining solid being Cr_2O_3 (the total mass loss is 70%; calcd. for Cr_2O_3 as the end product, 69.72%). If CP is left standing in air after having being dehydrated at 110°C, it takes up water from the air (in the course of 24 h) to the extent of 93% relative to its mass before dehydration. This reversibility suggests that no structural change occurs in CP when it is heated to 110°C.

Infrared spectroscopy offers further insight as to the nature of the phthalate groups present in CP. In that context IR spectra of the phthalate and hydrogen phthalate ions have to be included in the analysis. The spectrum of the *Hpht*$^-$ ion (*e.g.*, in KHpht, Fig. 2a) shows a strong absorption at 1675 cm^{-1} which can be assigned to the C=O stretching mode of the –C(O)OH group. No such feature exists in the spectrum of the phthalate ion (*e.g.*, in Na_2pht, Fig. 2b). The IR spectrum of CP (Fig. 2c) shows a shoulder of weak intensity at 1695 cm^{-1} which suggests that a fraction of the phthalate group in CP is actually present in the form of hydrogen phthalate ions. The true composition of CP then probably corresponds to the formula $[Cr(pht)_{1-x}(Hpht)_x(OH)_{1+x}(H_2O)_{1-x}]$, where $x < 0.5$. No additional information can be obtained from infrared spectroscopy regarding the manner of coordination of phthalate groups to Cr(III). Although the phthalate ion is known to act as a monodentate, bidentate, tridentate and tetradentate ligand,[8] no reliable correlation can be ascertained between the frequency of the phthalate C=O vibrations and the denticity. Therefore, in the absence of X-ray structural data for CP one can only speculate that the latter is a polymeric substance containing OH and one or several kinds of phthalate bridges. On stoichiometric grounds it also follows that the majority of the Cr(III) sites contain one coordinated H_2O molecule, the remaining fraction being H_2O-free.

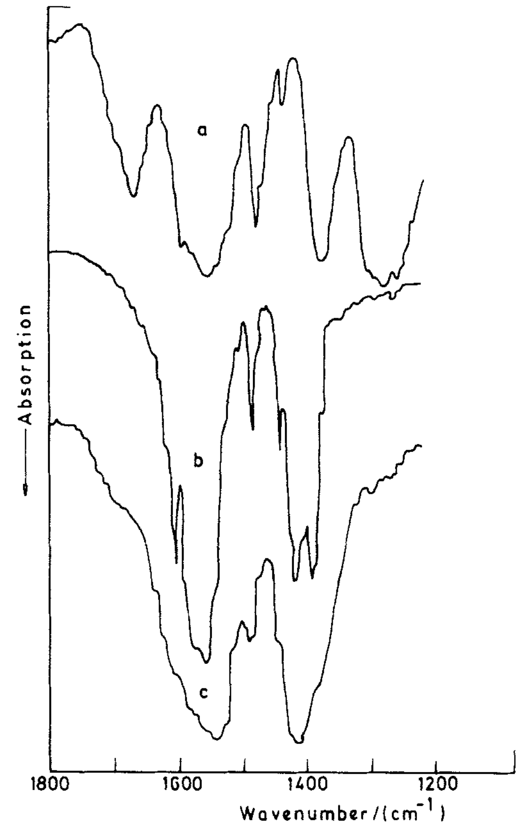

FIGURE 2 Infrared spectra in the 1800–1200 cm^{-1} range. a: KHpht; b: Na_2pht; c: CP.

The electronic spectrum of CP is shown in Fig. 3 and has been obtained from the corresponding diffuse reflectance data by converting them into $f(R_\infty)$ values using the Kubelka-Munk relationship.[9] In order to gain more insight into the electronic structure of CP the spectrum has been analysed by a least-squares method,[10] analysis consisting of resolving the spectrum into its constituent Gaussian maxima. It has been shown that the spectrum in Fig. 3 can be described as a superimposition of four bands of the type

$$\varepsilon = \varepsilon_0 \cdot 2^{-(\bar{v}-\bar{v}_0)^2/\delta^2}$$

where ε is the $f(R_\infty)$ value at wavenumber $\bar{v}$, ε_0 is the $f(R_\infty)$ value of the maximum (at $\bar{v}_0$), and δ is the half-width of the maximum at half-height. The four components (shown also in Fig. 3) have the parameters shown below for their maxima ($\bar{v}_0$ values being converted here into wavelengths). The goodness-of-fit so obtained as measured by the Hamilton R-factor[11] is R = 1.87%.

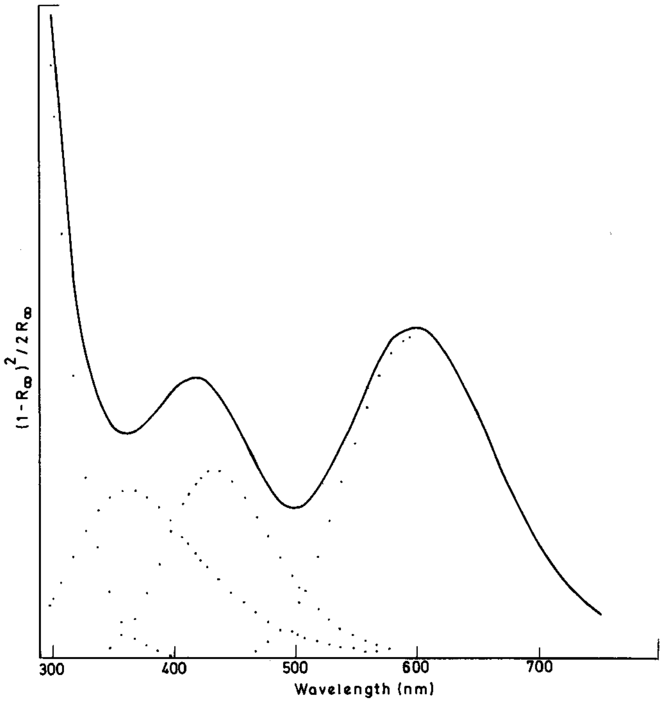

FIGURE 3 Analysis of the diffuse reflectance data [converted into $f(R_\infty)$ values] for CP. The solid line is the experimental curve and the dotted lines are its Gaussian components. Since the fit is good and the scale of the diagram is small, the sum of the four components essentially coincides with the experimental curve.

	I	II	III	IV
Wavelength, (nm)	270	361	432	598
δ, (cm^{-1})	4180	4560	2760	2010
ε_0	2.88	0.513	0.570	1.00

Such an electronic spectrum is consistent with the presence of octahedrally coordinated metal sites in CP, as expected for a chromium(III) complex. The maxima II to IV listed above correspond[12] to the d–d transitions, respectively: $^4A_{2g} \rightarrow {}^4T_{1g}(P)$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$, and $^4A_{2g} \rightarrow {}^4T_{2g}$, and their parameters are well within the values typically encountered for octahedral Cr(III) complexes.[13] The 270 nm maximum (only partly visible in Fig. 3 due to the wavelength range recorded) has a much higher intensity than the peaks II–IV, which suggests that it is not due to d–d transitions but should be classified as a charge transfer band.

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