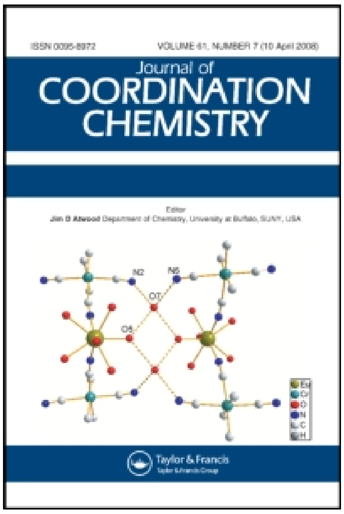

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PREPARATION OF CHROMIUM(III) PHTHALATE AND CHROMIUM(III) PYROMELLITATE *VIA* CHROMIUM(VI) OXIDE

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Reduction of CrO_3 at room temperature by ethanol in the presence of phthalic acid (H_2pht) and pyromellitic acid (H_4pyr) yields solutions that contain monomeric and low oligomeric (dimeric) Cr(III) complexes. A solution with an H_4pyr/Cr mol ratio of 1.5 : 1 is indefinitely stable toward precipitation, whereas the corresponding solution having a H_2pht/Cr mol ratio of 3 : 1 gives a precipitate in the course of ≈ 5 weeks; the difference in stability can be attributed to differences of acidity in the two systems. The solid from the H_2pht/Cr solution contains both the $Hpht^-$ and OH^- species and is probably a trimeric OH^--bridged Cr(III) complex. The solid obtained on evaporation of the stable H_4pyr/Cr solution does not contain OH^- species, its polymeric (trimeric) character being based on Cr–H_2pyr–Cr bridges. If the reaction in the H_2pht/Cr system is carried out under reflux, precipitation occurs immediately; the solid exhibits a higher degree of condensation than that obtained at room temperature.

Keywords: Chromium(VI) oxide, phthalic acid, pyromellitic acid, chromium(III) complexes

INTRODUCTION

One of the synthetic routes for the preparation of chromium(III) compounds is the reduction of CrO_3 by ethanol in the presence of various appropriate species. It has two advantages over preparations that start from a Cr(III) system: the presence of potentially undesired anions may be avoided, and synthetic problems associated with the kinetic inertness of Cr(III) complexes can sometimes be circumvented. In this manner, for example, a mixed hydrous chromium(III) oxide[1] and amorphous hydrous chromium(III) phosphates[2] have been prepared. The present paper investigates the applicability of the method for the synthesis of Cr(III) salts of 1,2-benzenedicarboxylic acid (phthalic acid) and 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid); anions of these acids have been known to act as bridging ligands in transition metal complexes.[3,4]

EXPERIMENTAL

All reagents were of *pro analysi* purity. Electronic spectra were recorded with a Superscan 3 spectrophotometer, while infrared spectra (KBr pellets) were obtained on a Perkin-Elmer 457 spectrophotometer. TG analysis was performed using a Du Pont Instruments 1090B Thermal Analyzer with a 951 Thermogravimetric Analyzer.

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The TG measurements were carried out either in air under stationary conditions or under nitrogen, at a N_2 flow rate of 50 cm^3/min; the sample size was 10–20 mg, and the heating rate 5°C/min (in N_2) or 10°C/min (in air). X-ray powder diffraction analysis was performed on a Philips PW 1051 Diffractometer using CuK$_\alpha$ radiation and a graphite monochromator, in the 2θ range 4–50°.

Reduction of CrO_3 by ethanol in the presence of phthalic acid

Two sets of reaction conditions were investigated.

a) A solution of 3.0 g of phthalic acid (1.8×10^{-2} mol) in 60 cm^3 of absolute ethanol was slowly added with stirring to a solution of 0.6 g of CrO_3 (6×10^{-3} mol) in a minimum quantity (several drops) of water. After a few hours a dark-blue solution had formed, its colour in transmitted light being dark-red. The solution was left standing in a closed flask at room temperature. After 6 days, a light-green precipitate began to separate from the solution. The process continued for about 5 weeks, after which time no further precipitation was observed; the system remained unaltered during one year. The stable suspension was filtered, yielding an emerald-green filtrate (filtrate A) and a blue-green solid. The solid was washed with ethanol and dried in air at room temperature, giving 1.1 g of a powdered product (solid S1a). X-ray powder diffraction analysis showed S1a to be amorphous. Anal.: found: C, 38.01; H, 3.79; Cr, 15.43%. Calcd. for $Cr_3(Hpht)_4(OH)_5(H_2O)_6$: C, 38.06; H, 3.69; Cr, 15.45%. The yield was ≈55% (based on Cr). Mass loss at 105°C: 10.7%. Infrared (cm^{-1}): 405(vw), 535(m), 665(m), 710(m), 760(m), 800(sh), 835(sh), 865(sh), 965(vw), 1045(w), 1090(m), 1145(m,b), 1170(m), 1260(w), 1290(m), 1410(vs), 1475(sh), 1490(m), 1510(sh), 1535(s), 1580(vs,b), 1620(s), 1695(s), 2325(w), 2920(sh), 3320(vs,b); (vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, b = broad).

The filtrate had the following maxima in the visible region: 587 nm (ε ≈ 47) and 436 nm (ε ≈ 43 M cm^{-1}).

b) A solution of 9.96 g phthalic acid (6×10^{-2} mol) in 100 cm^3 of ethanol was slowly added with stirring to a solution of 2.5 g CrO_3 (2.5×10^{-2} mol) in 40 cm^3 water. The resulting solution was refluxed for 30 min after which time a blue-green suspension had formed. It was filtered and the solid was washed with ethanol and dried in air. This yielded 5.3 g of a fine, blue-green powdered product (solid S1b). X-ray powder diffraction analysis showed S1b to be amorphous.

Anal.: found C, 37.5; H, 3.75; Cr, 16.9%. Calcd. for $Cr_5(Hpht)_6(OH)_9(H_2O)_8$: C, 37.2; H, 3,32; Cr, 16.8%. The yield was ≈70% (based on Cr). Mass loss at 105°C: 9.3%; at 1000°C: 75.3%. Infrared (cm^{-1}): 410(vw), 540(m), 665(m), 710(m), 760(m), 800(sh), 835(sh), 865(vw), 970(vw), 1045(w), 1095(m), 1155(m), 1175(m), 1260(w), 1290(w), 1415(vs), 1450(sh), 1495(m), 1515(sh), 1545(s), 1560(vs,b) 1620(s), 1695(s), 2325(w), 2930(sh), 3320(vs,b).

Reduction of CrO_3 by ethanol in the presence of pyromellitic acid

A solution of 2.29 g of pyromellitic acid (9×10^{-3} mol) in 60 cm^3 of absolute ethanol was slowly added into a solution of 0.6 g of CrO_3 (6×10^{-3} mol) in several drops of water. The resulting red-brown solution was left standing at room temperature. After 24 h a deep, blue-green solution (solution I) had formed, its colour in transmitted light being dark-red. Solution I is stable, and no precipitation was observed even after several months.

10 cm^3 of solution I was poured into a Petri dish and allowed to evaporate to dryness at room temperature. The residue was a blue-green solid which could not be redissolved in ethanol. It was thoroughly washed with ethanol and dried in air at room temperature. The yield was 0.47 g of a blue-green powder (solid S2). Anal.: found C, 36.02; H, 3.49; Cr, 9.36%. Calcd. for $Cr_3(H_3pyr)(H_2pyr)_4(H_2O)_{14}$: C, 35.96; H, 2.96; Cr, 9.34%. The yield was ≈94% (based on H_4pyr). Mass loss at 105°C: 7.5%. Mass loss at 1000°C: 86.3%. X-ray powder diffraction analysis showed S2 to be amorphous. Infrared (cm^{-1}): 575(m), 720(vw), 770(m), 795(m), 845(vw), 915(w), 1025(w), 2010(m), 1245(s,b), 1375(s,b), 1415(s), 1490(w), 1520(w), 1570(s,b), 1700(s), 2300(sh), 3140(s,b).

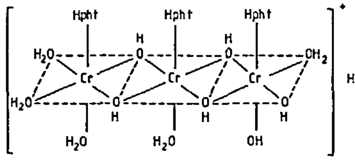
Solution I was diluted with ethanol (1 : 2) and the electronic spectrum of the resulting solution showed absorption maxima at 575 nm ($\varepsilon \approx 26\ M\ cm^{-1}$) and 410 nm. The latter absorption is partly masked by a strong Cr(VI) band at 350 nm which is due to small amounts of unreacted Cr(VI).

RESULTS AND DISCUSSION

When aqueous CrO_3 is mixed at room temperature with an ethanolic solution of phthalic or pyromellitic acid, reduction of Cr(VI) by ethanol takes place yielding solutions of chromium(III). The reason that the Cr(III) formed remains in solution (at least temporarily, *vide infra*) is because of the acidity of the system. By comparison, if the reduction of CrO_3 by ethanol is carried out in the absence of other reagents (*i.e.* acids) a precipitate is formed; the product is "$Cr_2O_3 \cdot xH_2O$", a markedly reactive hydrous oxide gel that, as well as Cr(III), contains some chromium in higher oxidation states.[5]

Chromium(III) solutions that are obtained in such reactions when H_2pht or H_4pyr are present differ in their stabilities toward precipitation, the H_2pht/Cr system being the less stable of the two. The study involved solutions that were 6×10^{-3} mol dm^{-3} in chromium and that had H_2pht/Cr and H_4pyr/Cr mol ratios (of reactants) equal to 3:1 and 1.5:1, respectively. In this manner, both systems had the same mol ratio of acidic hydrogens to chromium (6:1). In addition, the solutions were prepared so that their water content was as low as the solubility of CrO_3 would permit. Since no precipitate appeared (at room temperature) in either system soon upon formation of the Cr(III) solutions, the latter probably contain initially only monomeric and low oligomeric (mostly dimeric) complex Cr(III) species. The H_4pyr/Cr solution does not give a precipitate even on prolonged standing, indicating that its composition probably does not change significantly with time (in any case, no change in electronic spectrum could be observed). This fact can be attributed to the relatively high acidity of pyromellitic acid (for example, in aqueous solution, at 25°C $pK_1 = 1.92$, $pK_2 = 2.87$, $pK_3 = 4.49$, $pK_4 = 5.63$)[6] and the resulting unavailability of OH groups at chromium such as are necessary to effect condensation.

The H_2pht/Cr solution, however, gives a precipitate after 6 days at room temperature. Acidity of phthalic acid (at 25°C, in aqueous solution $pK_1 = 2.89$, $pK_2 = 5.4$)[7] is obviously not high enough to prevent gradual oligomerization of complex Cr(III) species. The oligomerization occurs through formation of OH bridges between Cr(III) centres, and is rather slow due to the kinetic inertness of Cr(III). It eventually yields a species that, due to its size, no longer is soluble in ethanol; the chemical composition of the precipitate closely agrees with the trimeric species S1a featuring monodentate $Hpht^-$ ligands.



S1a

However, one can not entirely preclude the possibility that the product is actually a mixture of oligomeric complexes whose average composition corresponds to that of S1a; some indications have been obtained earlier[8] from electrical conductivity measurements that H_2pht/Cr solutions in ethanol might contain several complex species.

The presence of $Hpht^-$ species in S1 is evidenced by a strong ν(C=O) band at $1695\,cm^{-1}$ and a ν(C–O) band at $1290\,cm^{-1}$ in the IR spectrum; these bands are, for example, also found in the IR spectra of H_2pht[9] and KHpht, but are absent in the spectrum of Na_2pht. The IR spectrum of S1 also exhibits, as expected, the stretching vibrations at 1535 and $1410\,cm^{-1}$ due to the $-COO^-$ group. The same bands, found earlier[10] in the IR spectrum of a basic chromium phthalate obtained by precipitating Cr(III) by KHpht + NaOH, are also visible in the spectra of KHpht and Na_2pht, but not in that of H_2pht. TG analysis shows (Fig. 1, curve 1) that S1a loses all six H_2O molecules at 105°C (mass loss 10.7%; calcd. for $6H_2O$: 10.7%). At around 300°C begins a rather steep decline on the TG curve, extending to 520°C (b.p. of phthalic anhydride is 295°C). By 520°C, 3 out of the 4 moles of the aromatic component have been lost. Complete decomposition, yielding Cr_2O_3, occurs above 770°C, under nitrogen; in air, however, the TG curve (Fig. 1, curve 1′) indicates a sharp conversion above 350°C to Cr_2O_3, obviously caused by the combustion of organic constituents. It should be mentioned that the thermal properties of S1a are quite analogous to those of an earlier reported[11] Cr(III)-phthalate prepared by aerial oxidation of a Cr(II)-phthalate.

The mother liquor remaining after the precipitation of S1a is complete (≈ 5 weeks) has a higher H_2pht/Cr molar ratio (5:1) than the initial solution (3:1). The excess phthalic acid now renders the mother solution indefinitely stable toward precipitation; the electronic spectrum of the solution has absorption maxima at 587 and 436 nm. The two maxima lie in the region of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions characteristic of octahedrally coordinated Cr(III). The same properties were reported[8] for solutions prepared by dissolving active Cr(III)-hydroxide in ethanolic solutions of H_2pht, provided that the H_2pht/Cr mol ratio is $>3:1$. It was suggested that these solutions contain a mixture of low oligomeric Cr(III) complexes in the form of ions and ionic associates. Furthermore, the Hpht/Cr molar ratio of 1.33:1 found for S1 is consistent with the earlier observed[8] fact that solid materials which can be isolated from the Cr(III)-hydroxide/H_2pht systems never have Hpht/Cr ratios exceeding 1.5. This essentially means that, due to the relatively low acidity of phthalic acid, they contain numerous OH groups (bridging as well as non-bridging). The origin of OH groups as well as of H_2O molecules in S1 is twofold: (a) water introduced into the reaction system with the CrO_3 solution and (b) water produced in the reduction of CrO_3 by ethanol.

The H_4pyr/Cr solution has its ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ bands in the electronic spectrum shifted to lower wavelengths by 13 and 26 nm, respectively, relative to the spectrum of the above H_2pht/Cr solution; this indicates that the pyromellitate anions have somewhat greater ligand field strength than $Hpht^-$. Although the

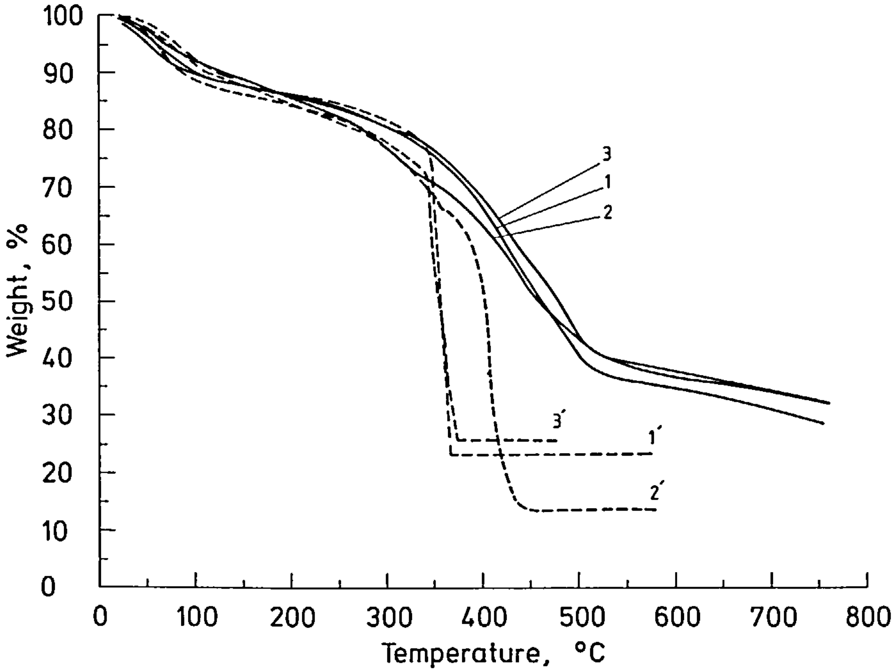
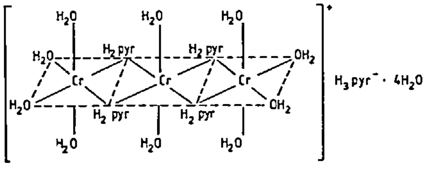


FIGURE 1 Thermogravimetric curves for S1a [under N_2 (1) and in air (1')], for S2 (2 and 2'), and for S1b (3 and 3').

H_4pyr/Cr solution is indefinitely stable toward precipitation, the solid that remains when the solution is evaporated at room temperature cannot be redissolved in ethanol. After removing (by washing with ethanol) any remaining H_4pyr, an amorphous solid is obtained, its chemical composition corresponding to the trimeric species S2 that contains bridging H_2pyr^{2-} ligands (again, one cannot completely preclude the possibility of S2 being in fact a mixture of oligomeric species).

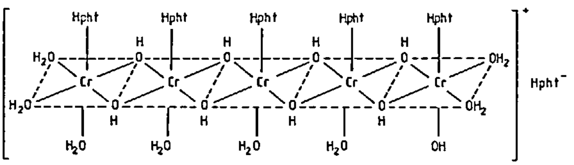


S2

The IR spectrum of S2 has rather poor resolution, indicating that the solid-state effects in this amorphous material are significant. The resolution, however, is sufficient to suggest the presence of both dissociated and undissociated carboxylic groups. Thus, the spectrum shows a strong ν(C=O) band at 1700 cm^{-1} due to undissociated —COOH groups; the same band is found in the spectrum of H_4pyr, but is absent in the spectrum of Na_4pyr. The spectrum of S2 also contains $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ at 1570 and 1375 cm^{-1}, respectively, which agrees fairly with the positions these bands have in the spectrum of Na_4pyr (1580 and 1380 cm^{-1}, respectively). TG measurements show that 4 water molecules are lost from S2 by 75°C, while the remaining water is lost gradually in the 75–220°C range (Fig. 1, curve 2). This indicates that 4 water molecules are rather loosely bound in the interstices of S2, whereas the rest are coordinated to the Cr(III) sites (similar behaviour was found[12] for $Co_2pyr \cdot 16H_2O$, where 4 water molecules are lost if the product was left standing at room temperature). In the 270–500°C range (under N_2), S2 loses nearly 3 of its 5 molecules of the aromatic component. Further decomposition occurs less quickly, so that complete conversion to Cr_2O_3 is achieved only above 760°C. In air, there is a sharp decline on the TG curve above 400°C (Fig. 1, curve 2′) so that by 430°C complete conversion to Cr_2O_3 occurs (mass loss 86.3%).

Even though it is not possible to differentiate analytically or by IR spectroscopy between the formula for S2 proposed above and "isomeric" forms containing OH^- groups, *i.e.*, $Cr_3(H_3pyr)_x(H_2pyr)_{5-x}(OH)_{x-1}(H_2O)_{15-x}$ ($x = 2$–5), such forms are not likely because of the substantial acidity of the H_3pyr^- group. The acidity strongly reduces the possibility of a simultaneous existence of both the H_3pyr^- and OH^- species in the solid product. By comparison, the acidity of $Hpht^-$ is much lower than that of H_3pyr^-, so that, in contrast, S1a *can* contain both $Hpht^-$ and OH^- groups. For the same reason, the two solids, although having the same degree of oligomerization, differ in the manner their polymeric (trimeric) nature is attained; chromium atoms are bridged by OH^- groups in S1a, and by bidentate H_2pyr^{2-} groups in S2.

It should be noticed that variations in reaction conditions in the H_2pht/Cr system affect not only the speed at which the oligomerization and separation of a precipitate takes place but also the degree of oligomerization in the solid that can be eventually isolated. Thus, when reaction conditions are altered as given in the Experimental section (reaction under reflux; presence of a substantial amount of water; concentration of CrO_3 and H_2pht/Cr mol ratio differing), precipitation begins very early under reflux. The solid that is obtained has a chemical composition that agrees with the pentameric formulation S1b, as compared with the trimeric structure of S1a. The solid S1b otherwise closely resembles S1 both in its IR spectrum and its thermal behaviour (Fig. 1, curves 3 and 3′). For example, it loses all eight H_2O molecules at 105°C, and by 520°C (under N_2) five of six molecules of the aromatic component have been lost.



S1b

Reduction of CrO_3 by ethanol in the presence of phthalic or pyromellitic acid represents a feasible route to Cr(III)/dicarboxylic acid systems either in solution or as solid phases. For example, reduction of CrO_3 by ethanol in the presence of isophthalic acid yields at room temperature a system similar to that formed in the case of phthalic acid; the system is presently under investigation.

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