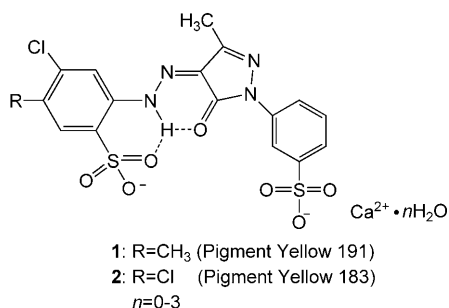


## The First Crystal Structures of Industrial Laked Yellow Pigments Determined by X-ray Powder Diffraction

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Laked pigments—that is, azo pigments containing an  $\text{SO}_3^-$  or  $\text{COO}^-$  group with a divalent metal ion as counterion—are still one of the most important pigment classes, with a production in the order of 60 000 tons per year and an annual sales volume of more than 200 million Euros.<sup>[1]</sup>

The properties of laked pigments clearly depend on their crystal structures: most laked pigments exist in different polymorphic forms showing different colors.<sup>[2]</sup> Although laked pigments have been industrially produced for more than 100 years,<sup>[3]</sup> no crystal structure of any commercial laked pigment is known hitherto.<sup>[4]</sup> Here we report the crystal structures of Pigment Yellow 191 (**1**)<sup>[5]</sup> and Pigment Yellow 183 (**2**).<sup>[6]</sup>



For all laked pigments, the growth of single crystals is hampered by the very low solubilities in water and all solvents, even at temperatures of 200 °C. Therefore, we determined the crystal structures from X-ray powder diffraction data.

Compounds **1** and **2** are commercially used for the coloration of plastics; compound **1** is also used for hot melt traffic paints in the US.<sup>[1]</sup> The compounds are synthesized in water by diazotization of the corresponding anilinesulfonic acids and coupling onto 3-methyl-1-(3-sulfophenyl)-5-pyrazolone; finally  $\text{CaCl}_2$  is added (Scheme 1). The pigments precipitate as fine powders with crystallite sizes of 0.1 to 1  $\mu\text{m}$ .

In the solid state all commercial “azo” pigments adopt the hydrazone tautomeric form shown above.<sup>[7]</sup> Thus the name “hydrazone pigments” would be more appropriate than the expression “azo pigments”. Compound **2** exhibits at least four crystal phases, and **1** exhibits at least five.<sup>[8]</sup> The  $\alpha$  and  $\beta$  phases of both pigments are commercially produced.

Crystal structure determination from powder diffraction data (for molecular compounds) is usually a three-step procedure: 1) determination of the unit-cell parameters (indexing); 2) structure solution, for example, by means of real-space methods in which the molecules are moved and rotated within the unit cell until the calculated powder pattern matches the experimental powder pattern; and 3) Rietveld refinement of the final crystal structure.

The crystallinity of **1** and **2** was limited, but nevertheless, the powder diagrams could be indexed.<sup>[9]</sup> There were two additional challenges. 1) The exact number of water molecules was unknown and 2) it was not known, if the structure contained one or two symmetrically independent  $\text{Ca}^{2+}$  ions.<sup>[10]</sup>

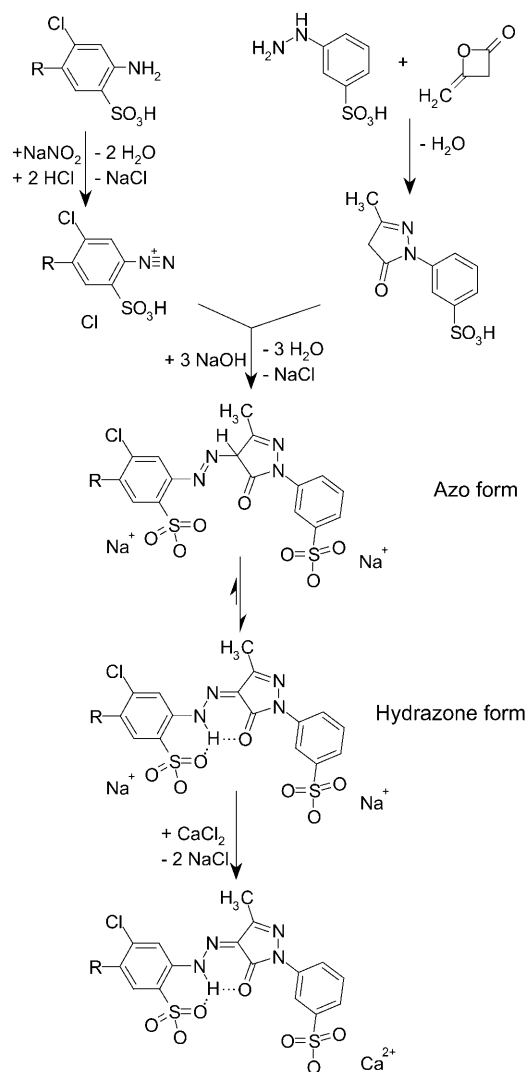
These problems were overcome by alternating the structure solution (step 2) with partial Rietveld refinements of the intermediate solutions (step 3). First the organic anion and a calcium cation were used for structure solution and the best structure thus obtained was refined using Rietveld methods. The positions of the organic anion and the calcium cation were then fixed, and structure solution (step 2) was

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Scheme 1. Industrial synthesis of **1** (R = Cl) and **2** (R = CH<sub>3</sub>).

repeated with an additional water molecule, followed by another Rietveld refinement again. From that point on, the crystal structure was complete enough that further missing water molecules in the  $\beta$  phase could be determined straight from Rietveld refinement. Two additional water molecules were found. In the  $\alpha$  phase, no additional water molecules were found, but it turned out that there were two symmetrically independent calcium atoms, both on inversion centers. Laboratory X-ray powder diffraction data measured in routine manner turned out to be fully sufficient for structure solution and Rietveld refinement. For  $\beta$ -**1** a final Rietveld refinement was made with synchrotron data, but no significant changes occurred (Figure 1).<sup>[11]</sup>

The phases  $\alpha$ -**1** and  $\alpha$ -**2** are monohydrates and isostructural. They have very similar lattice parameters; the volume of  $\alpha$ -**1** is about 0.2% larger, which reflects the slightly larger size of a methyl group compared with a chlorine atom. The crystal structure of  $\alpha$ -**1** and  $\alpha$ -**2** contains two crystallographi-

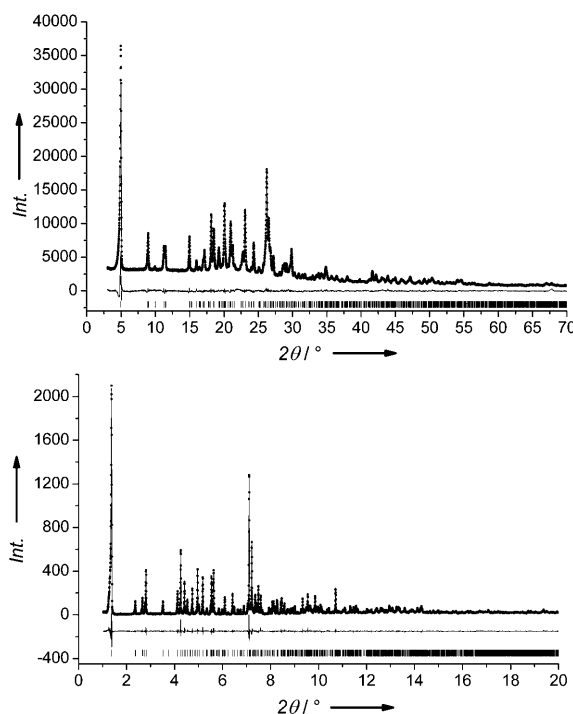


Figure 1. Rietveld refinements of  $\alpha$ -**1** ( $\lambda = 1.5406 \text{ \AA}$ ) (top) and  $\beta$ -**1** ( $\lambda = 0.64982 \text{ \AA}$ ) (bottom). Experimental powder diagrams shown as points, simulated diagrams as a solid line, difference curves at the bottom.

cally independent Ca<sup>2+</sup> ions, both with coordination number six. Interestingly, one of the calcium ions (Ca1, see Figure 2, top) is surrounded by two water molecules and four sulfonate groups, resulting in two molecular helices; these helices

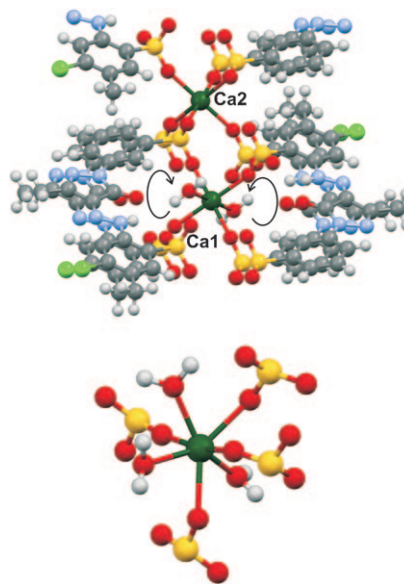


Figure 2. Top: Two molecular helices around calcium ions (Ca1) in  $\alpha$ -**1**. The helices are indicated by arrows. These moieties are connected by further calcium ions (Ca2) to form a layer. The same arrangement is found in  $\alpha$ -**2**. Bottom: Sevenfold coordination of Ca<sup>2+</sup> by water molecules and sulfonate groups in  $\beta$ -**1**.

are connected by additional calcium ions (Ca<sup>2+</sup>) that coordinate to the sulfonate groups of six different organic molecules. Consequently all oxygen atoms of the organic molecules are either involved in intramolecular hydrogen bonds with the N–H group or connected to a calcium ion.

This arrangement results in sandwich-like layers with the SO<sub>3</sub><sup>−</sup> groups, the Ca<sup>2+</sup> cations, and the water molecules as the central part, separated from the neighboring layers by the rest of the organic compound. Alternatively the structure may be regarded as a double-layer structure with polar layers containing the calcium ions, the water molecules and the sulfonate groups, and nonpolar layers containing the C/N backbone of the organic molecules and the chlorine substituents (Figure 3, top). Within the polar layers, Cou-

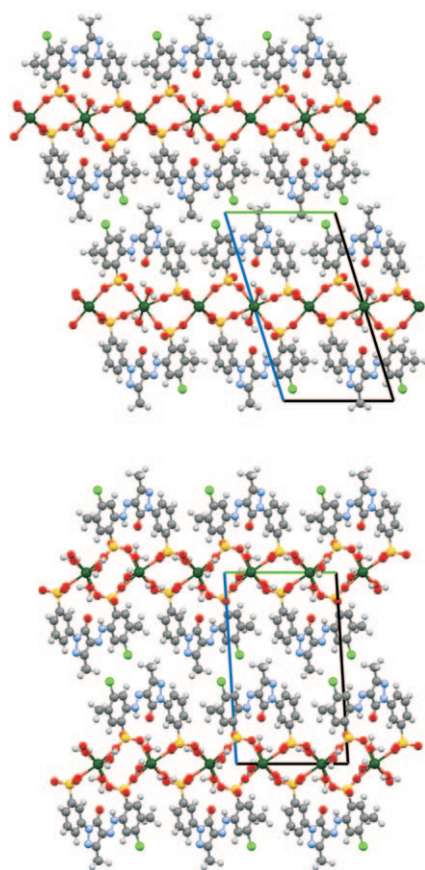


Figure 3. Crystal structures of  $\alpha$ -1 (top) and  $\beta$ -1 (bottom). For both drawings: view directions [100]; *b* axes horizontal, *c* axes vertical. The structure of  $\alpha$ -2 is isostructural to the structure of  $\alpha$ -1.

lomb interactions and hydrogen bonds are dominant, whereas the nonpolar layers are held together by van der Waals (and additionally electrostatic) interactions. The water is bonded so tightly, that the structure is stable to about 250 °C without loss of water.<sup>[12]</sup> Interestingly, the organic calcium sulfonate hydrates investigated here are even more stable than their inorganic counterpart calcium sulphate: CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum) and CaSO<sub>4</sub>·<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O (hemihydrate)

lose their water molecules at lower temperatures (before 160 °C).

A similar double-layer structure is also found for  $\beta$ -1, but here, the calcium ions show a less-frequently observed sevenfold coordination, with three water molecules and four sulfonate groups of four different organic molecules (Figure 2, bottom). The  $\beta$  phase is a trihydrate. The water molecules generate an extensive hydrogen-bond network within the polar layer. As in the  $\alpha$  phases, the polar layers are separated by nonpolar layers that are connected by van der Waals (and additionally electrostatic) interactions (Figure 3, bottom).

The laked pigments investigated here are neither “molecular complexes”, nor do they show a classical ionic lattice, but they form a polymeric coordination network. The tight bonding within this network might explain the observed high temperature stability of these compounds. Non-laked yellow azo pigments, for example, of the “Hansa Yellow” type, have a considerably lower temperature stability, which generally prevents them from being used for plastics coloration).

The present work shows that crystal structures, even of molecular salts with unknown water content, can be solved from a laboratory X-ray powder pattern measured in a routine manner. The complexity of the crystal structure of  $\beta$ -1, containing five independent molecules (a flexible organic anion, a calcium cation, and three water molecules) was a challenge for structure determination from powder diffraction data.

## Experimental Section

**$\alpha$ -Pigment Yellow 191 ( $\alpha$ -1):** 2-Amino-4-chloro-5-methylbenzene-1-sulfonic acid (112.8 g, 0.5 mol) was diazotized, then coupled with 1-(3'-sulfo-phenyl)-3-methyl-5-pyrazolone (127 g) and finally treated with an aqueous solution of calcium chloride (167 g, 1.5 mol) at 80 °C as described by Deucker.<sup>[4]</sup> For improving the crystallinity, 5 g of the obtained product (the yield of the synthesis is 270 g, but only 5 g are used for the second step) is suspended in glycerol (100 mL) and heated in suspension to 180 °C for 15 min. The  $\alpha$ -phase is obtained as a fine yellow powder.

**$\beta$ -Pigment Yellow 191 ( $\beta$ -1):** Compound  $\alpha$ -1 (300 mg) was dissolved in hot dimethylacetamide (30 mL). The solution was cooled to room temperature, and water (50 mL) was added. The  $\beta$ -phase was obtained as a fine yellow powder.

**$\alpha$ -Pigment Yellow 183 ( $\alpha$ -2):** A sample of commercial Pigment Yellow 183 (Paliotol Yellow K2270 from BASF) was heated as a suspension in a water/isobutanol mixture at reflux for 1 h in order to improve the crystallinity. The  $\alpha$ -phase was obtained as a fine yellow powder.

**X-ray measurements:** Laboratory X-ray powder data were recorded in transmission geometry on a STOE-STADI-P diffractometer equipped with a curved Ge (111) primary monochromator and a linear position-sensitive detector. Cu-K <sub>$\alpha$ 1</sub> radiation ( $\lambda$  = 1.5406 Å) was used. For  $\beta$ -1, high-resolution data were also recorded with synchrotron radiation at NLS Brookhaven, using a wavelength of 0.64982 Å. For the structure solution the program DASH<sup>[13]</sup> was used. Rietveld refinements were carried out with the program TOPAS<sup>[14]</sup>, using restraints for bond lengths, bond angles, and planar groups. For  $\beta$ -1, the final Rietveld refinement was done with synchrotron data. Crystal structure drawings were made with Mercury 2.0.<sup>[15]</sup>

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**Keywords:** dyes/pigments • Rietveld refinement • structure elucidation • X-ray diffraction • X-ray powder diffraction

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- [11]  **$\alpha$ -Pigment Yellow 191 ( $\alpha$ -1):** Yellow powder, C<sub>17</sub>H<sub>13</sub>CaClN<sub>4</sub>O<sub>7</sub>S<sub>2</sub>·H<sub>2</sub>O,  $M_r = 543.00$ , Cu-K $\alpha_1$  radiation,  $2\theta = 3\text{--}70^\circ$ , RT, triclinic, space group P $\bar{1}$ ,  $Z = 2$ ,  $a = 5.6915(2)$ ,  $b = 10.6053(3)$ ,  $c = 18.5569(6)$  Å,  $\alpha = 72.828(2)$ ,  $\beta = 88.271(2)$ ,  $\gamma = 76.423(1)^\circ$ ,  $V = 1039.37(5)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.735$  g cm<sup>-3</sup>,  $R_{\text{wp}} = 3.67\%$ ,  $R_p = 2.74\%$  (before background subtraction),  $R'_{\text{wp}} = 10.03\%$ ,  $R'_p = 9.08\%$  (after background subtraction),  $\chi^2 = 1.84$ .  **$\beta$ -Pigment Yellow 191 ( $\beta$ -1):** Yellow powder, C<sub>17</sub>H<sub>13</sub>CaClN<sub>4</sub>O<sub>7</sub>S<sub>2</sub>·3H<sub>2</sub>O,  $M_r = 579.03$ ,  $\lambda = 0.64982$  Å,  $2\theta = 1\text{--}30^\circ$ , RT, triclinic, space group P $\bar{1}$ ,  $Z = 2$ ,  $a = 6.0140(1)$ ,  $b = 10.8169(2)$ ,  $c = 18.0938(3)$  Å,  $\alpha = 85.677(1)$ ,  $\beta = 86.392(1)$ ,  $\gamma = 75.783(1)^\circ$ ,  $V = 1136.55(3)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.692$  g cm<sup>-3</sup>,  $R_{\text{wp}} = 9.20\%$ ,  $R_p = 6.60\%$  (before background subtraction),  $R'_{\text{wp}} = 20.63\%$ ,  $R'_p = 9.91\%$ , (after background subtraction),  $\chi^2 = 0.59$ .  **$\alpha$ -Pigment Yellow 183 ( $\alpha$ -2):** Yellow powder, C<sub>16</sub>H<sub>10</sub>CaCl<sub>2</sub>N<sub>4</sub>O<sub>7</sub>S<sub>2</sub>·H<sub>2</sub>O,  $M_r = 563.41$ , Cu-K $\alpha_1$  radiation,  $2\theta = 3\text{--}34^\circ$ , RT, triclinic, space group P $\bar{1}$ ,  $Z = 2$ ,  $a = 5.6894(3)$ ,  $b = 10.5943(6)$ ,  $c = 18.526(1)$  Å,  $\alpha = 73.316(5)$ ,  $\beta = 87.842(3)$ ,  $\gamma = 76.127(3)^\circ$ ,  $V = 1037.8(1)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.803$  g cm<sup>-3</sup>,  $R_{\text{wp}} = 4.55\%$ ,  $R_p = 3.35\%$  (before background subtraction),  $R'_{\text{wp}} = 6.79\%$ ,  $R'_p = 7.07\%$  (after background subtraction),  $\chi^2 = 1.04$ .  $\alpha$ -2 is isostructural to  $\alpha$ -1. For all phases: restraints for planar groups were applied for both phenyl rings as well as for the pyrazolone fragment. Anisotropic peak broadening was included. No preferred orientation was observed. CCDC 692222 ( $\alpha$ -1), 692223 ( $\beta$ -1) and 692221 ( $\alpha$ -2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)
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