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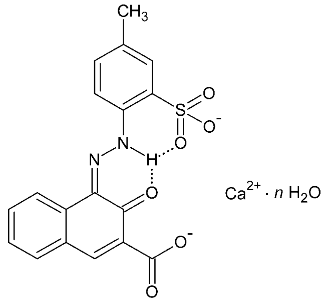
Crystal Structures of the Hydration States of Pigment Red 57:1**

*Sándor L. Bekö, Sonja M. Hammer, and Martin U. Schmidt**

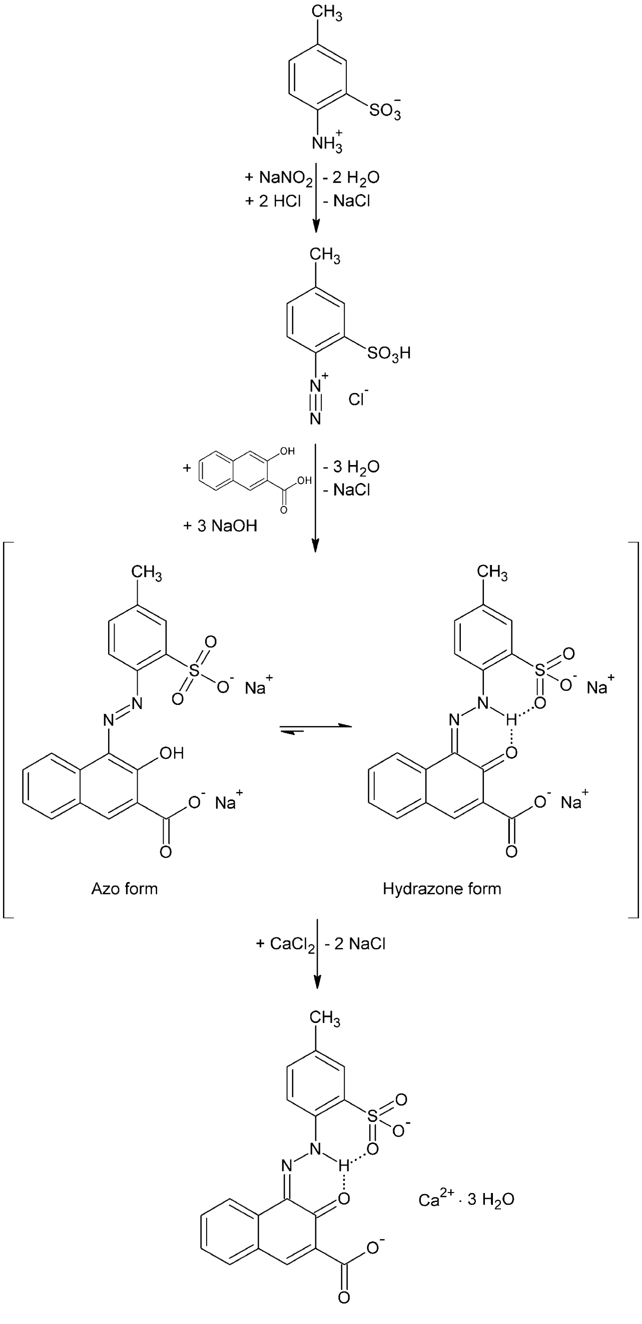
Today, most journals and newspapers are printed with Pigment Red 57:1 (P.R.57:1, **1**). This is true for scientific journals like *Angewandte Chemie* and *Zeitschrift für Kristallographie* as well as for newspapers such as *The New York Times*, *The Sun*, *Bild*, *El País*, *La Repubblica*, *Le Monde*, and *Shanghai Daily*.[1] P.R.57:1 is the most important organic red pigment with a production of more than 50000 tons per year and an annual sales volume of more than 200 million Euro.[2,3] In printing ink the pigment is not dissolved, but finely dispersed. Consequently the solid-state properties are maintained. Most pigments, including P.R.57:1, occur in different crystal phases with different colors. Although P.R.57:1 has been industrially produced for more than 100 years,[4] the crystal structures of P.R.57:1 have never been determined.[5,6] Here we report the crystal structures of three crystal phases of P.R.57:1 (Scheme 1).

The compound is industrially synthesized in water by azo coupling and subsequent laking with $CaCl_2$ (see Scheme 2). In the solid state all commercial "azo pigments" do not contain an azo group but adopt the tautomeric hydrazone form (Scheme 2).[3,7] Thus the name "hydrazone pigments" is more appropriate than the traditional expression "azo pigments". In the synthesis of P.R.57:1 the trihydrate (**1a**) precipitates, as verified by thermal gravimetry and the Karl-Fischer oven method. Gentle heating to about 50 °C generates a monohydrate (**1b**)[8] as substantiated by DTA/TG (differential thermal analysis/thermogravimetry), DSC (differential scan-



1a: $n = 3$ (red)
1b: $n = 1$ (magenta)
1c: $n = 0$ (dull dark magenta)

Scheme 1. Chemical structure of P.R.57:1 (**1**).



Scheme 2. Industrial synthesis of P.R.57:1.

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[*] S. L. Bekö, S. M. Hammer, Prof. Dr. M. U. Schmidt
Institut für Anorganische und Analytische Chemie
Goethe-Universität
Max-von-Laue-Strasse 7, 60438 Frankfurt am Main (Germany)
E-mail: m.schmidt@chemie.uni-frankfurt.de

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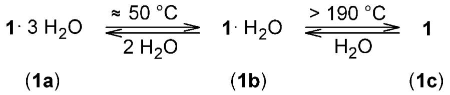
ning calorimetry), and T-XRPD (temperature-dependent X-ray powder diffraction). Suspension of the monohydrate in water leads to a full reconversion to the trihydrate (see Scheme 3). At ambient conditions both phases are kinetically stable for at least one year,[9] but at 90 % relative humidity the monohydrate converts to the trihydrate within one week.



$$\mathbf{1}\cdot 3\,H_2O \underset{2\,H_2O}{\overset{\approx 50\,°C}{\rightleftharpoons}} \mathbf{1}\cdot H_2O \underset{H_2O}{\overset{> 190\,°C}{\rightleftharpoons}} \mathbf{1}$$

(**1a**) (**1b**) (**1c**)

Scheme 3. De- and rehydration of P.R.57:1.

The monohydrate is thermally stable at temperatures higher than 190 °C before it releases water to yield a hitherto unknown anhydrous phase (**1c**). This phase is highly hygroscopic and reconverts to the monohydrate in an open vial at ambient conditions within one hour.

The phase change between the red trihydrate and the magenta monohydrate (which is used for color printing) also occurs in journals and newspapers, hence the shade of the red may depend on the weather conditions.

For all three phases the growth of single crystals is impeded by the low solubility of the pigment in most media. In high-boiling polar solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), *N*,*N*′-dimethylacetamide (DMAC), and *N*-methyl-2-pyrrolidone (NMP) the pigment is slightly soluble at 150 to 200 °C, but all crystallization experiments resulted in poorly crystalline powders only. Therefore we determined the crystal structures of all three phases from X-ray powder diffraction data. The powder diagrams could be indexed with DICVOL[10] without ambiguity. For structure solution by real-space methods the program DASH[11] was used. Subsequently, Rietveld refinements were performed with the program TOPAS,[12] using restraints for bond lengths, bond angles, and planar groups. All Rietveld refinements converged with good *R* values and very smooth difference curves (Figure 1).[13]

In the trihydrate **1a** the pigment anion acts as an η^3 ligand: the sulfonate, the keto, and the carboxylate groups coordinate to the same calcium ion (Figure 2a). The calcium ion is additionally coordinated to the carboxylate group of a neighboring anion and to four water molecules (two of which are shared by two calcium ions) leading to an eightfold coordination geometry around the calcium ion. The carboxylate groups bridge two calcium ions leading to chains, which are connected to neighboring chains through μ^2-H_2O molecules; the resulting ladder structure runs parallel to the crystallographic *b* axis (see Figure 3). Neighboring ladders are connected by hydrogen bonds.

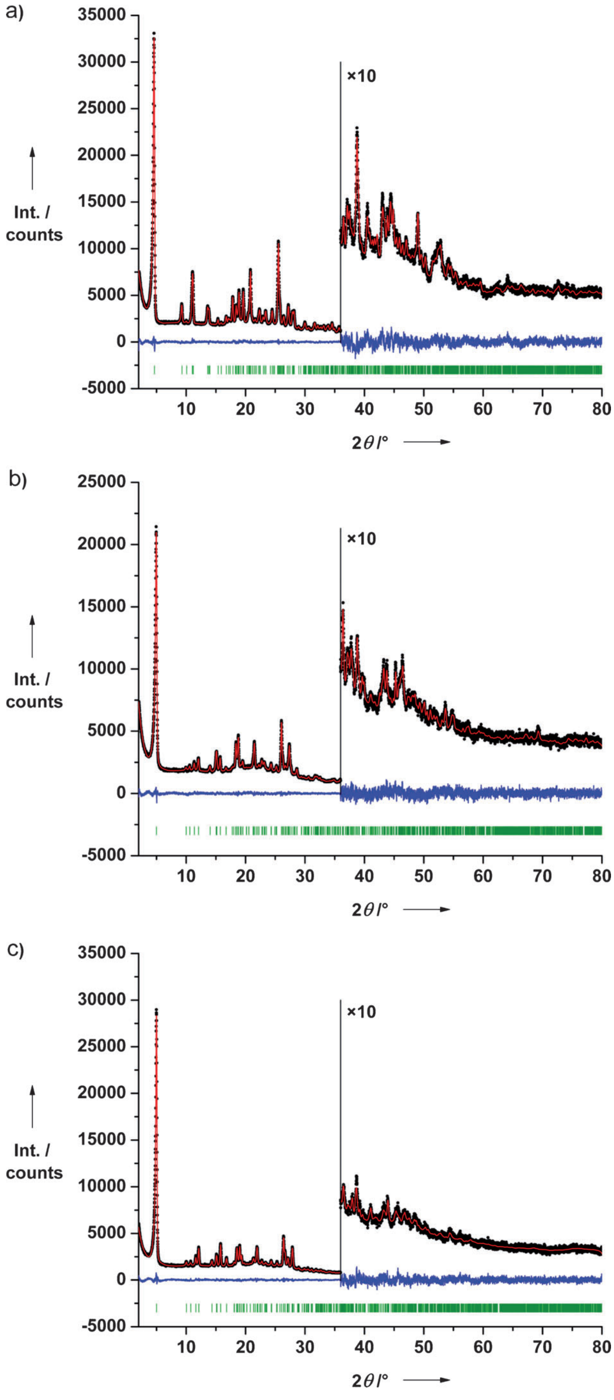


Figure 1. Rietveld refinements of a) **1a**, b) **1b**, c) **1c**. Observed powder diagram (black points), calculated diagram (red solid line), difference profiles (blue solid line below), and reflection positions (green vertical lines).

In the monohydrate **1b** the anion also acts as an η^3 ligand. However, in contrast to **1a** the calcium ion in the monohydrate **1b** is additionally coordinated to two carboxylate anions (one acting as a bidentate group), one sulfonate group, and only one water molecule. This results in an eightfold coordination geometry around the calcium ion. The loss of two water molecules of **1a** is compensated for by the pigment anions which form more bonds to the calcium ion (see Figure 2b). Pigment anions and calcium cations form a two-dimensional coordination polymer.

The anhydrate **1c** is isostructural to the monohydrate **1b**; only the water molecule is absent and accordingly the coordination number of the calcium ion drops from eight to seven (see Figure 2c). Generally, calcium ions prefer eightfold rather than sevenfold coordination. The uptake of a water molecule does not require a reconstruction of the

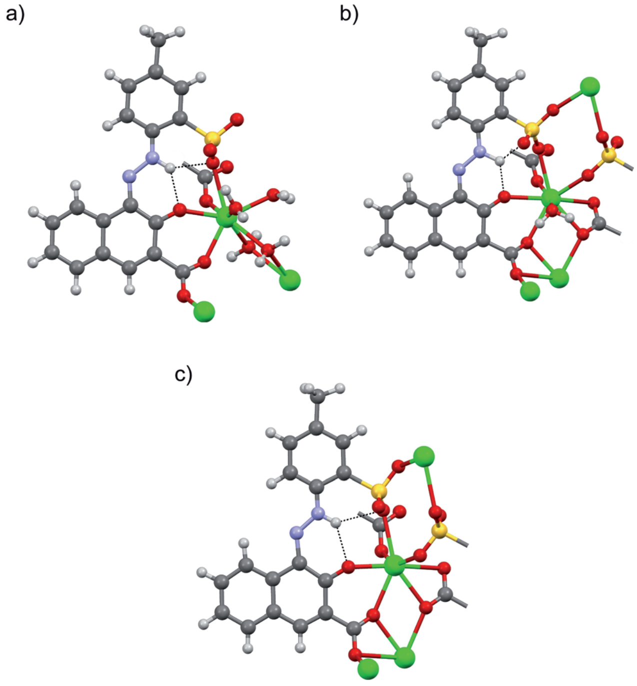


Figure 2. Molecular structure and coordination geometry in the a) trihydrate **1a**, b) monohydrate **1b**, c) anhydrate **1c.** The intermolecular hydrogen bonds are omitted for clarity.

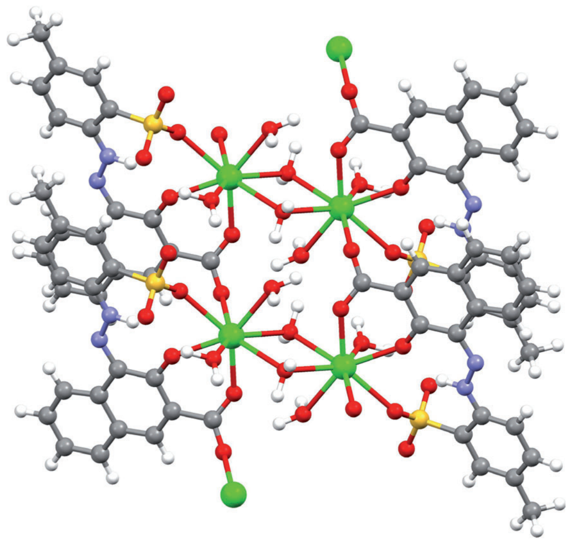


Figure 3. Ladder structure of the trihydrate **1a**.

crystal. This might explain the high hygroscopicity of the anhydrate.

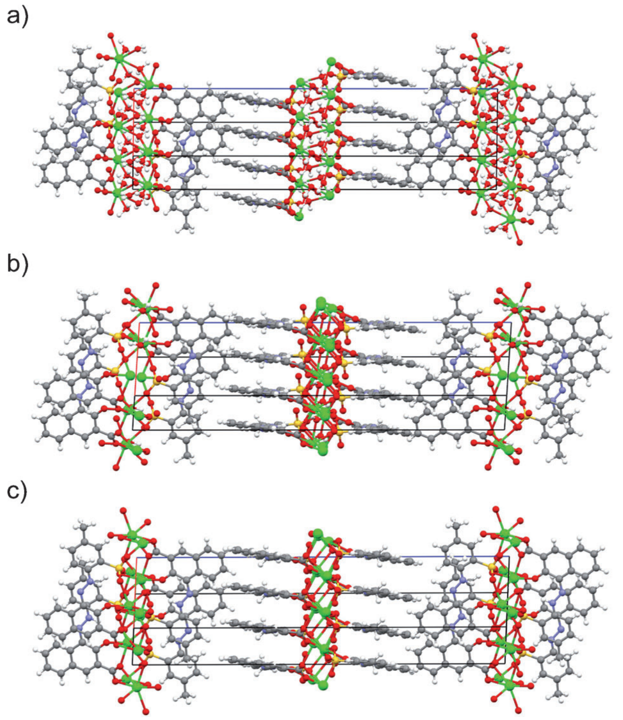


Figure 4. Packing diagrams of a) **1a**, b) **1b**, c) **1c**. View direction approximately [210].

All three phases of P.R.57:1 crystallize within a similar molecular arrangement in a double-layer structure. The polar/ionic layers contain the calcium ions, carboxylate, keto, and sulfonate groups and the water molecules, whereas the nonpolar layer consists of the naphthalene and toluene moieties (see Figure 4). Within the polar layers, Coulomb interactions and hydrogen bonds are dominant. In contrast, the fragments of the nonpolar layers are connected by van der Waals interactions only. In all structures the pigment anions are not planar; the phenyl ring is inclined against the naphthalene fragment with dihedral angles of 12.23(14)°, 14.3(2)°, and 5.3(7)° for **1a**, **1b**, and **1c**, respectively.

The colors of the three phases differ: The trihydrate is carmine red, the monohydrate magenta, and the anhydrate a dull dark magenta. In the trihydrate the pigment anion coordinates to two calcium cations through four oxygen atoms, in the monohydrate and in the anhydrate to four calcium ions through five oxygen atoms; the coordination in the anhydrate is even stronger because of the missing water molecule. Apparently the increased anion–cation interactions lead to the observed color shift. We observed a similar effect in the orange dihydrate and the red anhydrate phases of Pigment Red 53:2.[6d,14]

Experimental Section

Trihydrate of P.R.57:1: 2-Ammonio-4-methylbenzene-1-sulfonate hemihydrate[15] (**1a**; 3.93 g, 20 mmol) was diazotized in water at pH ≈ 1 and coupled to 3-hydroxy-2-naphthoic acid (3.91 g, 20.8 mmol) in aqueous NaOH to obtain the sodium salt of P.R.57 as a fine precipitate. This intermediate was isolated by filtration, washed with water, suspended in 1000 mL of water, and treated with $5\,\mathrm{M}$ aqueous $CaCl_2$ (22 mL) at ambient temperature. The suspension was heated to 80 °C at pH ≈ 5, stirred for 60 min, and filtered. The press cake was washed with 1000 mL of water and allowed to dry on air at ambient conditions. The trihydrate of P.R.57:1 was obtained as a fine, carmine red powder (81 % yield). This sample was used for the crystal structure determination without further treatment.

Monohydrate of P.R.57:1 (**1b**): The monohydrate of P.R.57:1 can be obtained by heating the trihydrate to temperatures above approximately 50 °C to yield a fine, magenta, poorly crystalline powder. For the crystal structure determination we used a sample with improved crystallinity, which was obtained by stirring a suspension of 30 mg of the trihydrate in 3 mL of ethyl acetate for one day at ambient conditions.

Anhydrate of P.R.57:1 (**1c**): The anhydrous form of P.R.57:1 was obtained by heating a sample of the tri- or monohydrate to more than 220 °C. The anhydrate is obtained as a fine, dull, dark magenta powder.

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-$K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å) was used. For the anhydrate a capillary with a diameter of 0.7 mm was filled with the trihydrate, heated to 227 °C, and measured at this temperature for one day.

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[1] The pigments were identified directly from the printed journals and newspapers by mass spectrometry using the laser desorption ionization technique. The pigment composition may depend on the printing site and may change with time.

[2] Trade names are, for example, Lithol Rubine B and Lithol Rubine BK (both from various producers), Irgalite Magenta D4200 (BASF), Pigment Red 57:1 (various Chinese manufacturers), and Graphtol Rubine L6B, Permanent Rubine L4BT, and Permanent Toner Magenta 6B (all from Clariant).

[3] W. Herbst, K. Hunger, *Industrial Organic Pigments*, 3rd ed., Wiley-VCH, Weinheim, **2004**.

[4] P.R.57:1 was first described and patented in 1903 (R. Gley, O. Siebert, Deutsches Reichspatent DRP 151205, **1903**). As early as 1911, the *Konstitutionstabellen neuerer Konkurrenzfarbstoffe* (Constitutional tables of new competitors' dyestuffs) [sic!], which was a "strictly confidential", internal publication of Meister Lucius & Brüning in Höchst a. M., (later, Hoechst AG), described the commercial product "Permanentrot 6R", manufactured by the Aktiengesellschaft für Anilinfabrikation in Berlin. The products "Litholrubin B Ca" and "Permanentrot 4B" were mentioned in 1914 in G. Schultz, *Farbstofftabellen*, 5th ed., Leipzig, **1914**.

[5] Harris et al. (R. K. Harris, P. Jonsen, J. Packer, C. D. Campbell, *J. Chem. Soc. Perkin Trans. 2* **1987**, 1383–1390) suggested from solid-state NMR investigations on P.R.57:1 that the calcium ion is complexed to sulfonate and carboxylate groups of different molecules, and thus they proposed a chain structure with pigment anions bridged by calcium ions. In contrast, Duckett et al. (G. R. Duckett, J. R. Fryer, T. Baird, *Inst. Phys. Conf. Ser.* **1987**, *78*, 437–440) have used electron diffraction data to propose a dimeric structure consisting of two calcium cations and two pigment anions.

[6] Apart from P.R.57:1, very few crystal structures of laked red pigments have been determined. Examples include the lakes of P.R.49: a) A. R. Kennedy, P. C. Andrikopoulos, J.-B. Arlin, D. R. Armstrong, N. Duxbury, D. V. Graham, J. B. A. Kirkhouse, *Chem. Eur. J.* **2009**, *15*, 9494–9504; b) J. Stenger, E. E. Kwan, K. Eremin, S. Speakman, D. Kirby, H. Stewart, S. G. Huang, A. R. Kennedy, R. Newman, N. Khandekar, *e-Preservations Sci.* **2010**, *7*, 147–157; and a series of noncommercial compounds: c) A. R. Kennedy, C. McNair, W. E. Smith, G. Chisholm, S. J. Teat, *Angew. Chem.* **2000**, *112*, 652–654; *Angew. Chem. Int. Ed.* **2000**, *39*, 638–640; d) T. Gorelik, M. U. Schmidt, J. Brüning, S. Bekö, U. Kolb, *Cryst. Growth Des.* **2009**, *9*, 3898–3903 (from electron-diffraction data).

[7] See, for example, a) D. Kobelt, E. F. Paulus, W. Kunstmann, *Acta Crystallogr. Sect. B* **1972**, *28*, 1319–1324; b) E. F. Paulus, *Z. Kristallogr.* **1982**, *160*, 235–243; c) H. Mustroph, *Z. Chem.* **1987**, *27*, 281–289 (review with 100 references); d) A. Whitaker, *J. Soc. Dyers Colour.* **1995**, *111*, 66–72; e) M. J. Barrow, R. M. Christie, T. D. Badcock, *Dyes Pigm.* **2003**, *57*, 99–106; f) H. Zollinger, *Color Chemistry*, 3rd ed., Wiley-VCH, Weinheim, **2003**; g) P. Gilli, V. Bertolasi, L. Pretto, L. Antonov, G. Gilli, *J. Am. Chem. Soc.* **2005**, *127*, 4943–4953.

[8] Phases **1a** and **1b** (without determination of the water content and of the crystal structures) were previously mentioned: X. Chen, P. Zhuang, R. Shengwu, *Huadong Huagong Xueyuan Xuebao* **1990**, *16*, 434–439.

[9] No phase changes were observed after one year of storage at 20 to 25 °C and about 50 % relative humidity.

[10] *DICVOL91*: A. Boultif, D. Louër, *J. Appl. Crystallogr.* **1991**, *24*, 987–993.

[11] *DASH 3.2*: W. I. F. David, K. Shankland, J. van de Streek, E. Pidcock, W. D. S. Motherwell, J. C. Cole, *J. Appl. Crystallogr.* **2006**, *39*, 910–915.

[12] *TOPAS 4.1*: A. A. Coelho, *TOPAS Academic User Manual.* Version 4.1. Coelho Software, Brisbane, Australia, **2007**.

[13] Trihydrate of P.R.57:1 (**1a**): Carmine red powder, $C_{18}H_{12}CaN_2O_6S{\cdot}3H_2O$, $M_r = 478.49$, monoclinic, $P2_1/c$, $a = 8.7613(5)$, $b = 5.8155(3)$, $c = 37.943(2)$ Å, $\beta = 90.883(3)°$, $V = 1933.03(18)$ Å^3, $Z = 4$, $\rho_{calc} = 1.644$ g cm^{-3}, Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å), $2\theta = 2$–$80°$, measurement at ambient temperature, $R_{wp} = 3.132$ %, $R_p = 2.384$ %, $R_{exp} = 2.478$ % (before background subtraction), $R'_{wp} = 8.660$ %, $R'_p = 7.889$ %, $R'_{exp} = 6.852$ % (after background subtraction), $\chi^2 = 1.264$. Monohydrate of P.R.57:1 (**1b**): Magenta powder, $C_{18}H_{12}CaN_2O_6S{\cdot}H_2O$, $M_r = 442.46$, monoclinic, $P2_1/c$, $a = 8.3597(6)$, $b = 5.9307(5)$, $c = 35.359(3)$ Å, $\beta = 94.462(5)°$, $V = 1747.7(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.682$ g cm^{-3}, Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å), $2\theta = 2$–$80°$, measurement at ambient temperature, $R_{wp} = 3.055$ %, $R_p = 2.359$ %, $R_{exp} = 2.745$ % (before background subtraction), $R'_{wp} = 10.949$ %, $R'_p = 11.784$ %, $R'_{exp} = 9.839$ % (after background subtraction), $\chi^2 = 1.113$. Anhydrate of P.R.57:1 (**1c**): Dull dark magenta powder, $C_{18}H_{12}CaN_2O_6S$, $M_r = 424.44$, monoclinic, $P2_1/c$, $a = 8.2226(6)$, $b = 5.9076(5)$, $c = 35.181(4)$ Å, $\beta = 93.109(6)°$, $V = 1706(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.652$ g cm^{-3}, Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å), $2\theta = 2$–$80°$, measurement at 227 °C, $R_{wp} = 3.663$ %, $R_p = 2.796$ %, $R_{exp} = 2.967$ % (before background subtraction), $R'_{wp} = 12.421$ %, $R'_p = 12.987$ %, $R'_{exp} = 10.059$ % (after background subtraction), $\chi^2 = 1.235$. No preferred orientations were observed for all three phases. CCDC 851322 (**1a**), 851323 (**1b**) and 851324 (**1c**) contains 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. All crystal structure drawings were made with Mercury 2.4 (C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.* **2008**, *41*, 466–470).

[14] a) M. U. Schmidt, H. J. Metz, European Patent EP 965617, **1999**; b) M. U. Schmidt, H. J. Metz, European Patent EP 965616, **1999**; c) M. U. Schmidt, European Patent EP 1010732, **1999**.

[15] The zwitterionic form is preferred in solution and solid state, see a) M. A. Leonard, P. J. Squattrito, *Acta Crystallogr. Sect. C* **1997**, *53*, 648–651; b) S. L. Bekö, S. D. Thoms, J. Brüning, E. Alig, J. van de Streek, A. Lakatos, C. Glaubitz, M. U. Schmidt, *Z. Kristallogr.* **2010**, *225*, 382–387.