[7] a) A. R. Gordon, C. Johnstone, W. R. Kerr, *Synlett* **1995**, 1083; b) S. Shambayati, W. E. Crowe, S. L. Schreiber, *Tetrahedron Lett.* **1990**, *31*, 5289; c) N. Jeong, Y. K. Chung, B. Y. Lee, S. H. Lee, S. E. Yoo, *Synlett* **1991**, 204.
[8] V. Rautenstrauch, P. Megard, J. Conesa, W. Kuster, *Angew. Chem.* **1990**, *102*, 1441; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1413.
[9] J. A. Banister, S. M. Howdle, M. Poliakoff, *J. Chem. Soc. Chem. Commun.* **1993**, 1814.
[10] S. Beuermann, M. Buback, M. Busch in *Chemical Synthesis using Supercritical Fluids* (Eds.: P. G. Jessop, W. Leitner), Wiley-VCH, Weinheim, **1999**, pp. 326–350.
[11] **Caution!** Although no incident occurred during this study, we observed that highly purified $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ ignited spontaneously at times upon contact with air. Special precaution should be paid. Therefore, we prefer to use stable $[Co_4(CO)_{11}\{P(OPh)_3\}]$ to avoid any potential danger.
[12] J. W. Kim, Y. K. Chung, *Synthesis* **1998**, 142.
[13] K. S. Jerome, E. J. Parsons, *Organometallics* **1993**, *12*, 2991.
[14] See ref. [8]. Note that a much higher pressure of CO (100 bar at the inception) was required under their conditions.

The First Red Azo Lake Pigment whose Structure is Characterized by Single Crystal Diffraction**

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As organic pigments are used in the form of crystals dispersed throughout the media to be colored, their color characteristics depend not only on their molecular structure but also crucially upon their crystal structure. Furthermore, the crystal structure influences the stability of the pigment to solvent, heat, and light and also determines the crystal morphology which is in turn related to color strength, hiding power, stability, flow, and dispersion properties.[1] As a good pigment is, by design, highly insoluble, it is difficult to grow the large, high-quality crystals needed for conventional diffraction methods and thus little detailed structural information is available. These generalizations are true of the red azo pigments as exemplified by Ca4B toner (the calcium salt of 4-(4-methyl-2-sulfophenyl)azo-3-hydroxy-2-naphthalic acid; also known as CIPR 57:1) which is considered the worldwide standard process red for printing and its continuing industrial importance is attested to by the patent literature.[2]

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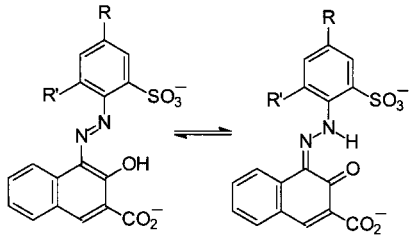
Previous work on the structure of Ca4B[3] showed that the classification "azo pigment" is actually a misnomer, as in the solid state the pigment exists largely as the keto-hydrazone tautomer (Scheme 1). Further, dideprotonation occurs at the



Scheme 1. Tautomerism in red azo pigments.

sulfonate and carboxy groups but not at the hydroxy/hydrazo group, and there is only one type of calcium binding site. Harris et al.[3a] suggested from solid-state NMR measurements that the calcium atom is complexed by sulfonate and carboxylate groups from different molecules and thus proposed a simple polymeric structure with azo molecules bridged by Ca^{2+} ions, whereas Fryer and coworkers[3c] showed evidence from electron microscopy that Ca4B exists as head-to-tail dimers.

We have now succeeded in growing, by slow evaporation of a DMF solution, small crystals of a dichloro analogue of Ca4B (**1**) suitable for characterization by synchrotron radiation.[4] Compound **1** displays a complex, supramolecular structure of a type not previously suspected for red azo pigments but which we believe to be consistent with the experimental evidence in the published work on Ca4B, and which we propose to be a suitable model structure to relate to the structure of many other red azo pigments.

The structural analysis confirms that the azo dianion is deprotonated at the sulfonate and carboxylate groups. The Ca atoms are eight coordinate through bonding to three sites (carboxylate, keto, and sulfonate) on one azo anion, to two terminal water molecules, and to three oxygen atoms supplied by bridging interactions to the carboxylate groups of neighboring azo anions (Figure 1). That the azo anion acts in such a

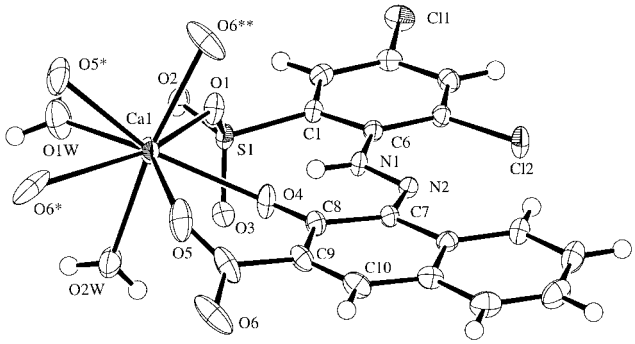


Figure 1. Molecular structure of **1** showing the coordination geometry about Ca1. Selected distances [Å]: Ca1-O1 2.542(2), Ca1-O4 2.394(2), Ca1-O5 2.385(2), Ca1-O1W 2.449(2), Ca1-O2W 2.352(2), Ca1-O5* 2.440(2), Ca1-O6* 2.881(2), Ca1-O6** 2.374(2), N1-N2 1.304(2), N1-C6 1.395(2), N2-C7 1.333(2), C8-O4 1.257(2), C7-C8 1.458(3), C8-C9 1.451(3), C9-C10 1.349(3). Symbols: * = −x + 1, y + 0.5, −z + 0.5; ** = x, y + 1, z.

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terdentate mode with the keto group binding to calcium had not previously been suspected. The Ca–O6* distance of 2.881(2) Å, corresponding to one of the bonds to the bridging, chelated carboxylate group, is considerably longer than the other Ca–O distances (2.352(2) – 2.542(2) Å). In contrast to the transition metal chemistry of simple keto-hydrazo dyes, no Ca–N bond is formed.[5] That the azo ligand exists predominately in the keto-hydrazo form is shown by the lengthening of the N1–N2, C7–C8, and C8–C9 distances and by the complimentary shortening of the C8–O4, N2–C7, and C9–C10 distances. The ligand is nearly planar (C6-N1-N2-C7, N1-N2-C7-C8, and N2-N1-C6-C1 dihedral angles are 178.4(2)°, 0.1(3)°, and 176.8(2)°, respectively), a conformation which is favored by the internal hydrogen bond between the hydrazo and keto groups. The calcium atom is significantly displaced from this ligand plane as shown in Figure 1. The geometry of the azo ligand is in good agreement with that seen in reference [6] (a sodium salt of an azo dye rotaxane, which is the only previously known structure to show complexation of a main group metal with any type of keto-hydrazo species) and also with the main group salts of orange G[7] where the hydrated metal cations are not bonded to the dye.

The extended structure of **1** is shown in Figure 2. Its salient feature is the polymeric double-chain of calcium atoms that propagate along the *b* direction by translation and the action of the 2_1 screw axis. This architecture is suggestive of the ring – ladder structures found in certain group I amides and organometallic compounds[8] and, under that system, would be described as an infinite ladder structure of alternating, fused Ca_2O_2 rhomboids and CaOCO kites.[9] (Replacing the chelating carboxylate group with a monoatomic bridge species would give a conventional ladder arrangement.) Both ring types are internally folded and, together with an angle of 122° between the two ring types, give the ladder a zig-zag conformation. This double-chain structure is germane to that of Ca4B. It is proposed from electron microscopy[3c] that Ca4B has unit cell parameters $a = 8.4$, $b = 5.8$, $c = 18$ Å, $\beta = 92°$, and $Z = 2$. Notice that both *b* and *c* are similar in **1**, indicating some relationship between the two structures, but especially that the *b* distance corresponds to the calcium – calcium separation along the chain. This must indicate that Ca4B has a similar central, polymeric, double-chain structure. Where unit cells can be derived from powder diffraction, this parameter could be used as a diagnostic feature to assign other azo red pigments to this structural type.

The water ligands on one strand of the calcium double chain all lie below the ladder plane whilst those on the other strand lie above, giving an *anti* arrangement. Figure 2 highlights other structural features. The azo ligands are parallel to their companions on the same side of the ladder, but are angled with respect to those on the opposite side. The closest contacts between parallel ligands fall just within the range usually accepted as indicating π-stacking (N1 ··· C10 3.43 and C5 ··· C12 3.46 Å). All the azo ligands in a chain run in the same head-to-tail orientation along the *b* direction and the interchain contacts in the *a* and *c* directions are also head-to-tail. The interchain contacts in the *c* direction are dominated by sulfonate – water hydrogen bonding (there is also hydrogen bonding present along the chains) but in the *a* direction the chains are separated by at least van der Waals distances. There are no significant interchain Cl ··· Cl or Cl ··· H contacts.

This highly directionalized supramolecular structure, featuring the self assembly motifs of a polydentate chelate, ligands bridging metal atoms, hydrogen bonding, and π-stacking is consistent with the poor and highly anisotropic crystal growth properties of red azo lake pigments. It is also consistent with the previous work on Ca4B, but combines the known data in a previously unsuspected manner to give a new and unsuspected outcome. Further work on a range of derivatives of both **1** and Ca4B is currently underway in an attempt to relate changes in structure to changes in color.

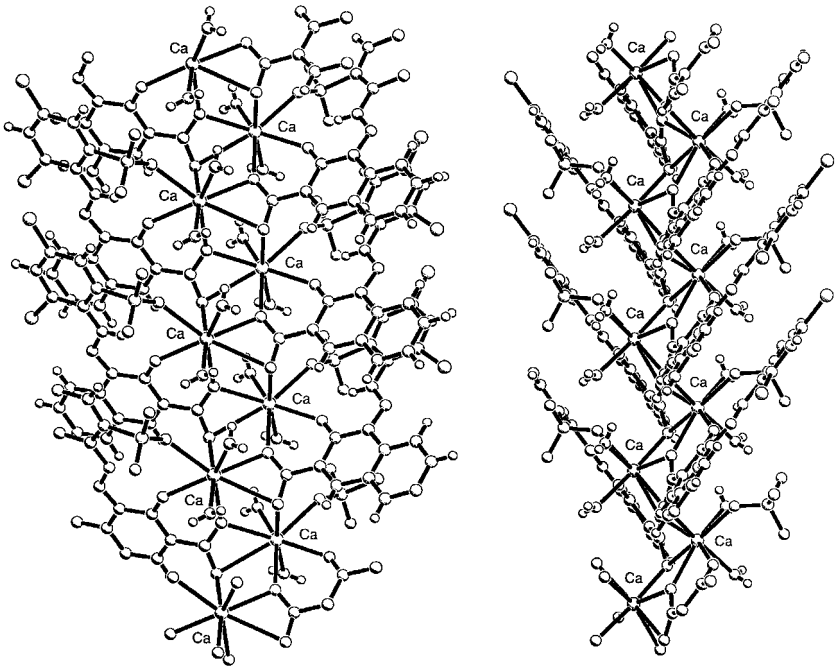

Figure 2. Two views of the polymeric structure of **1** as it extends along the *b* direction.

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[1] Z. Hao, A. Iqbal, *Chem. Soc. Rev.* **1997**, *26*, 203.
[2] For general information on Ca4B, see: a) W. Herbst, K. Hunger, *Industrial Organic Pigments: Production, Properties, Applications*, VCH, New York, **1993**; b) *Pigment Handbook*, *2nd ed.*, (Ed.: P. A. Lewis), Wiley Interscience, New York, **1988**.
[3] a) R. K. Harris, P. Jonsen, K. J. Packer, C. D. Campbell, *J. Chem. Soc. Perkin Trans. 2* **1987**, 1383; b) J. Clarkson, D. R. Armstrong, C. H. Munro, W. E. Smith, *J. Raman Spectrosc.* **1998**, *29*, 421; c) G. R. Duckett, J. R. Fryer, T. Baird, *Inst. Phys. Conf. Ser.* **1985**, *78*, 437.
[4] a) R. J. Cernik, W. Clegg, C. R. A. Catlow, G. Bushnell Wye, J. V. Flaherty, G. W. Greaves, I. Burrows, D. J. Taylor, S. J. Teat, M. Hamichi, *J. Synchrotron Radiat.* **1997**, *4*, 279; b) Crystal structure data for **1**: $C_{17}H_{12}CaCl_2N_2O_8S$, $M =$ 515.33, red needles, $150 \times 20 \times 5$μm. Si111 monochromated synchrotron radiation from Daresbury Station 9.8 ($\lambda = 0.68910$ Å), $T = 150$ K; monoclinic, space group $P2_1/c$; $a = 19.2996(8)$, $b = 5.6514(2)$, $c = 18.1528(8)$ Å; $\beta = 104.454(2)°$;

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$V = 1917.25(13)$ Å^3; $Z = 4$; $\mu = 0.768$ mm^{-1}; $\rho_{calcd} = 1.785$ Mg m^{-3}; $2\theta_{max} = 54^\circ$; 11456 reflections collected, 4540 unique used ($R_m = 0.0280$). The structure was solved and refined on F^2 using published programs and techniques [10] to convergence at $R1 = 0.0369$ (for 3848 reflections with $I > 2\sigma(I)$), $wR2 = 0.0904$, and $S = 1.061$ for 300 parameters. Maximum residual electron density 0.43 e Å^{-3}. The H atoms on N and O were treated isotropically but all other H atoms were placed in calculated positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134039. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[5] For a representative example, see: S. B. Choudhury, D. Ray, A Chakravorty, *J. Chem. Soc. Dalton Trans.* **1992**, 107.

[6] S. Anderson, W. Clegg, H. L. Anderson, *Chem. Commun.* **1998**, 2379.

[7] W. H. Ojala, L. K. Lu, K. E. Albers, W. B. Gleason, T. I. Richardson, R. E. Lovrien, E. A. Sudbeck, *Acta Crystallogr. Sect. B* **1994**, *50*, 684.

[8] R. E. Mulvey, *Chem. Soc. Rev.* **1998**, *27*, 339.

[9] P. C. Andrews, W. Clegg, R. E. Mulvey, P. A. O'Neil, H. M. M. Wilson, *J. Chem. Soc. Chem. Commun.* **1993**, 1142.

[10] a) G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, **1997**; b) W. Clegg, M. R. J. Elsegood, S. J. Teat, C. Redshaw, V. C. Gibson, *J. Chem. Soc. Dalton Trans.* **1998**, 3037.

  0570-0833/00/3903-0640 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **2000**, *39*, No. 3