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X-ray single-crystal diffraction data for some azo pigments.

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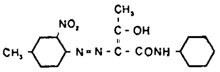
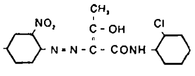
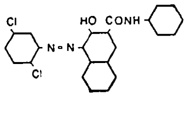
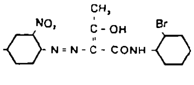
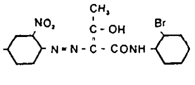
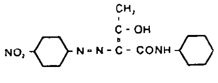
X-ray single-crystal data are reported for the following materials: C. I. Pigment Yellow 1 (Hansa Yellow *G*) C. I. Yellow 3 (Hansa Yellow 10*G*), C. I. Pigment Yellow 4, C. I. Pigment Red 2 as well as for a monobromo and a dibromo analogue of C. I. Pigment Yellow 3 (Hansa 10*G*).

As part of a programme of investigation of some printing pigments using X-rays, crystal data has been obtained on four pigments and two analogues of one particular pigment.

The Colour Index Number and/or common name of the compounds investigated are as follows: C. I. Pigment Yellow 1 (Hansa Yellow *G*), C. I. Pigment Yellow 4, C. I. Pigment Red 2, C. I. Pigment Yellow 3 (Hansa Yellow 10*G*), a monobromo analogue (Patterson, 1968) and a dibromo analogue (Chapman & Mijovic, 1970) of C. I. Pigment Yellow 3 (Hansa Yellow 10*G*). For convenience the chemical and structural formulae of the various compounds are given in Table 1.

Single crystals suitable for X-ray examination were prepared by saturating boiling xylene with the appropriate pigment and allowing the solution to cool slowly. Attempts

Table 1. *Crystal data*

Name	Chemical formula	Structural formula	Space group	Cell dimensions (Å) and volume (Å)^3		Observed and calculated densities (g.cm^{-3})	No. of molecules per unit cell
C. I. Pigment Yellow 1 Hansa Yellow *G*	$C_{17}H_{16}N_4O_4$		$P2_1/c$	$a=7{\cdot}52$ $b=20{\cdot}7$ $c=12{\cdot}0$ $\beta=120°$ $V=1620$		$\varrho_o=1{\cdot}416$ $\varrho_c=1{\cdot}392$	4
C. I. Pigment Yellow 3 Hansa Yellow 10*G*	$C_{16}H_{12}N_4O_4Cl_2$		*Pbca*	$a=13{\cdot}1$ $b=29{\cdot}9$ $c=8{\cdot}40$ $V=3291$		$\varrho_o=1{\cdot}571$ $\varrho_c=1{\cdot}594$	8
C. I. Pigment Red 2	$C_{23}H_{15}N_3O_2Cl_2$		$P2_1/c$	$a=10{\cdot}5$ $b=8{\cdot}90$ $c=21{\cdot}9$ $\beta=102°$ $V=2001$		$\varrho_o=1{\cdot}459$ $\varrho_c=1{\cdot}454$	4
Mono-bromo analogue of C. I. Pigment Yellow 3	$C_{16}H_{12}N_4O_4BrCl$		*Pbca*	$a=13{\cdot}4$ $b=30{\cdot}6$ $c=8{\cdot}36$ $V=3428$		$\varrho_o=1{\cdot}729$ $\varrho_c=1{\cdot}702$	8
Di-bromo analogue of C. I. Pigment Yellow 3	$C_{16}H_{12}N_4O_4Br_2$		*Pbca*	$a=13{\cdot}4$ $b=30{\cdot}8$ $c=8{\cdot}40$ $V=3467$		$\varrho_o=1{\cdot}884$ $\varrho_c=1{\cdot}852$	8
C. I. Pigment Yellow 4	$C_{16}H_{14}N_4O_4$		$P1$ or $P\bar{1}$	* $a=7{\cdot}54$ $b=11{\cdot}4$ $c=10{\cdot}3$ $V=764{\cdot}5$	$\alpha=106{\cdot}7°$ $\beta=111{\cdot}8°$ $\gamma=75{\cdot}3°$	$\varrho_o=1{\cdot}420$ $\varrho_c=1{\cdot}417$	2
				† $a=7{\cdot}51$ $\pm0{\cdot}06$ $b=10{\cdot}96$ $\pm0{\cdot}07$ $c=10{\cdot}32$ $\pm0{\cdot}11$ $V=757{\cdot}4$	$\alpha=105{\cdot}8$ $\pm0{\cdot}8$ $\beta=111{\cdot}0$ $\pm0{\cdot}7$ $\gamma=77{\cdot}8$ $\pm0{\cdot}8$	$\varrho_o=1{\cdot}420$ $\varrho_c=1{\cdot}428$	2

* Dimensions obtained by using Buerger's method of level offsets.

† Dimensions obtained from powder diffraction lines used in conjunction with the program *CEDI*.

to recrystallize the pigments from other solvents tended to produce multiply twinned crystals. Densities of the crystals were measured by flotation in mixtures of either carbon tetrachloride and bromoform or carbon tetrachloride and benzene. Estimated accuracy was ±0·003 g.cm^{-3}. The calculated densities are given for comparison. The crystal classes were deduced from Laue photographs. Oscillation, zero, first, second and third layer Weissenberg photographs were taken about two crystallographic axes for each crystal with filtered Cu $K\alpha$ radiation. From these photographs the systematic absences and cell dimensions were obtained. As no corrections were applied for film shrinkage, the cell dimensions, with one exception, are probably accurate to ±1% and the angles to ±2°.

In the case of C. I. Pigment Yellow 4, which crystallizes in the triclinic class, the cell dimensions were obtained using Buerger's (1942) method of level offsets.

In view of the small offsets measured, there was some doubt concerning the accuracy of some of the results.

As a consequence low-angle diffraction lines from the powder pattern of the pigment, which could be indexed unambiguously, were used in conjunction with the program *CEDI* (by courtesy of D. Williams, Dept. of Chemistry, Imperial College, London), whereby the cell dimensions and an estimate of their errors were obtained. These are given for comparison.

During the course of the work the structure of C. I. Pigment Yellow 1 (Hansa *G*) was determined independently by Mez (1968). The unit cell chosen by him is different from the one obtained in this present investigation, but the two unit cells are equivalent. In this investigation the *a* axis chosen was that giving the most prominent row of pinacoidal spots on the first layer Weissenberg photograph and for this reason the present cell is preferred.

Further work is proceeding on the crystal structure determinations of Hansa 10*G*, its mono-bromo analogue and C. I. Pigment Red 2.

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The structure of the potassium salt of μ$_4$-oxo-hexa-μ-chloro-tetra[chlorocuprate(II)], $K_4Cu_4OCl_{10}$.

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$K_4Cu_4OCl_{10}$ crystallizes in space group $C2/c$ with two molecules in the unit cell having dimensions a = 14·70 (1), b = 14·88 (1), c = 8·95 (1) Å, β = 104·74 (5)°. The structure has been refined by full-matrix least-squares techniques to a final R value of 6·8%.

Crystals of potassium μ_4-oxo-hexa-μ-chloro-tetra[chlorocuprate(II)], $K_4Cu_4OCl_{10}$, can be prepared by slowly cooling a melt of K_2CuCl_4 and CuCl under oxygen. The anion $[Cu_4OCl_{10}]^{4-}$ of this potassium salt occurs also in the tetramethylammonium salt (Bertrand & Kelley, 1969) and is analogous to the central unit in the complexes $Cu_4OCl_6L_4$ with L = triphenylphosphine (Bertrand, 1967), pyridine (Kilbourn & Dunitz, 1967) and methylpyridine (Gill & Sterns, 1970).

The crystals are irregularly shaped and orange-red. Precession photographs showed the extinction rules hkl: $h+k=2n$, $h0l$: $l=2n$; the true space group, $C2/c$, followed from the refinement. A least-squares fit for several θ, $-\theta$ values measured on a Nonius three-circle diffractometer resulted in the following cell parameters: a = 14·70 (1), b = 14·88 (1), c = 8·95 (1) Å, β = 104·74 (5)°. On the diffractometer we measured 544 unique reflexions with intensities significantly above background and with $\sin\theta/\lambda \le 0{\cdot}48$. We used a θ, 2θ scan and Zr-filtered Mo K radiation.

The structure was solved from the three-dimensional Patterson function. Scattering factors and the corrections for anomalous scattering were taken from *International Tables for X-ray Crystallography* (1962). Full-matrix least-squares refinement with isotropic vibration parameters resulted in a final conventional R value (based on F) of 6·8% the weighted R value $\{\sum w(|F_o|-|F_c|)^2/\sum|wF_o|^2\}^{1/2}$ was 8·9%.

The final atomic parameters with their estimated standard deviations are given in Table 1. A listing of $|F_o|$ and $|F_c|$ may be obtained on request. The atomic numbering scheme and the bond distances are given in Fig. 1. The other important structural parameters, together with their e.s.d.'s, are listed in Table 2. The bond distances and angles are all comparable with those in the analogous compounds mentioned above. The asymmetric unit consists of half a molecule, the second half is generated by the crystallographic twofold rotation axis which passes through Cl(3), O, Cl(4).

Table 1. $K_4Cu_4OCl_{10}$, *final least-squares parameters*

	Fractional coordinates			
	x	y	z	B
O	0	0·2168 (14)*	$-\frac{1}{4}$	1·3 (4)
Cu(1)	0·0614 (2)	0·2914 (2)	−0·3680 (3)	1·82 (7)
Cu(2)	0·0921 (2)	0·1413 (2)	−0·1149 (3)	2·08 (8)
Cl(1)	0·1956 (4)	0·2042 (5)	−0·2742 (7)	2·5 (1)
Cl(2)	−0·0521 (4)	0·2249 (5)	−0·5848 (7)	2·5 (1)
Cl(3)	0	0·4152 (7)	$-\frac{1}{4}$	2·7 (2)
Cl(4)	0	0·0198 (8)	$-\frac{1}{4}$	4·3 (3)
Cl(5)	0·1214 (4)	0·3820 (5)	−0·5196 (8)	2·5 (1)
Cl(6)	0·2061 (4)	0·0598 (5)	0·0423 (7)	2·3 (1)
K(1)	0·1590 (4)	0·1295 (4)	0·3758 (7)	2·8 (1)
K(2)	0·1315 (4)	0·4271 (4)	0·1401 (7)	3·0 (1)

[*] Numbers in parentheses here and elsewhere are the estimated standard deviations in the least significant digit. None are given for parameters fixed by symmetry.