

CRYSTALLOGRAPHIC CONSTANTS FOR SOME HIGH-DENSITY β -PHTHALOCYANINES*

By P. E. FIELDING† and N. C. STEPHENSON‡

The authors of a number of papers¹ dealing with the problem of electrical conduction in the various phthalocyanines assume that the compounds studied were the high-temperature β -polymorphs having the same unit cell dimensions as those given by Robertson² (Table 1). One of the present authors (P.E.F.) and his colleagues accepted these data until H. Struve observed that the activation energy for electrical

TABLE 1
UNIT CELL DIMENSIONS OF β -POLYMORPHS

Compound	Ref.	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β	<i>V</i> (Å ³)
C ₃₂ H ₁₆ N ₈	2	19.85	4.72	14.8	122.25°	1173
C ₃₂ H ₁₆ N ₈ Cu	§	19.61	4.80	14.74	121.51°	1180
C ₃₂ H ₁₆ N ₈ Cu	2	19.6	4.79	14.6	120.6°	1180
C ₃₂ H ₁₆ N ₈ Ni	§	19.48	4.70	14.82	122.33°	1147
C ₃₂ H ₁₆ N ₈ Ni	2	19.9	4.71	14.9	121.9°	1186
C ₃₂ H ₁₆ N ₈ Co	§	19.39	4.79	14.57	120.66°	1164
C ₃₂ H ₁₆ N ₈ Co	2	20.2	4.77	15.0	121.33°	1235
C ₃₂ H ₁₆ N ₈ Fe	§	19.39	4.78	14.55	120.74°	1159
C ₃₂ H ₁₆ N ₈ Fe	2	20.2	4.77	15.0	121.6°	1231
C ₃₂ H ₁₆ N ₈ Mn	§	19.17	4.77	14.43	119.4°	1148
C ₃₂ H ₁₆ N ₈ Mn	2	20.2	4.75	15.1	121.3°	1233
C ₃₂ H ₁₆ N ₈ Zn	§	19.13	4.86	14.50	120.1°	1166

§ Present work (by N.C.S.).

conduction in cobalt phthalocyanine was affected by thermal annealing.³ This has since been shown to be due to electrode and surface phenomena, but density measurements were carried out to check for possible phase changes.

A density-gradient column⁴ consisting of mixtures of 1,2-dibromoethane and carbon tetrachloride with calibrated glass markers⁵ was used to measure the densities of batches of single crystal sections prepared by vapour-phase sublimation.¹ Although

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† Department of Physical and Inorganic Chemistry, University of New England, Armidale, N.S.W.

‡ Department of Inorganic Chemistry, University of New South Wales, Kensington, N.S.W.

¹ Fielding, P. E., and MacKay, A. G., *Aust. J. Chem.*, 1964, **17**, 750, and references therein.

² Robertson, J. M., *J. Chem. Soc.*, 1935, 615; Linstead, R. P., and Robertson, J. M., *J. Chem. Soc.*, 1936, 1736.

³ Fielding, P. E., and Struve, H., unpublished data.

⁴ Oster, G., and Yamamoto, M., *Chem. Rev.*, 1963, **63**, 257.

⁵ Gordon, M., and Macnab, I. A., *Trans. Faraday Soc.*, 1953, **49**, 31.

the column could easily detect differences in densities of the order of 1 in 10^5 , it was found that a number of interesting observations could be made without recourse to its high sensitivity. These were:

- (1) Crystals prepared by vapour-phase entrainer-gas sublimation had densities distributed over a range which could extend to 5% lower than the maximum.
- (2) Many crystals contained minute voids, but others completely free of voids had densities 1-3% less than the maximum.
- (3) A number of metal-substituted phthalocyanines had maximum densities some 5-6% higher than previously reported² (Table 2).

TABLE 2
DENSITIES OF β -POLYMORPHS

Compound	Measured		X-Ray	
	Present Work	Ref. 2	Present Work	Ref. 2
$C_{32}H_{18}N_8$	1.44	1.44	—	1.445
$C_{32}H_{16}N_8Cu$	1.625	1.63	1.62	1.61
$C_{32}H_{16}N_8Ni$	1.61	1.63	1.65	1.59
$C_{32}H_{16}N_8Co$	1.632	—	1.63	1.53
$C_{32}H_{16}N_8Zn$	1.6303	—	1.63	—
$C_{32}H_{16}N_8Mn^{II}$	1.62	—	1.64	1.52
$C_{32}H_{16}N_8Fe^{II}$	1.59-1.62	—	1.62	1.52

Typical microanalyses as in Table 3 show that there is no doubt of the stoichiometry of the high-density forms studied. It should be pointed out that Robertson² did not determine the densities of the cobalt, iron, and manganese compounds by

TABLE 3
ANALYSES

		C (%)	H (%)	N (%)	Zn (%)	Co (%)
$C_{32}H_{16}N_8$	Calc.	74.7	3.5	21.8		
	Found	74.5	3.7	21.7		
$C_{32}H_{16}N_8Zn$	Calc.	66.5	2.8	19.4	11.3	
	Found	66.5	3.0	19.4	11.1	
$C_{32}H_{16}N_8Co$	Calc.	67.3	2.8	19.6		10.3
	Found	67.4	2.9	20.1		9.6

pyknometric methods, as earlier measurements on metal-free, copper, and nickel phthalocyanines had established the number of molecules per unit cell. This is unfortunate, as the present values for the latter series are in agreement with Robertson's, but the comparisons can be carried no further (Table 2). Attempts to

produce the low density forms using the sublimation apparatus described by Linstead and co-workers⁶ were unsuccessful.

Single crystals of the metal-substituted phthalocyanines are invariably elongated in a direction perpendicular to (010). This particular crystal habit greatly simplifies the photography of the reciprocal lattice. The relative orientation of the a^* and c^* axes with respect to the incident X-ray beam can be obtained from zero-level Weissenberg photographs. Direct transfer of the goniometer to a precession camera enables a^* , b^* , and c^* to be measured—once the dial settings have been calculated approximately from the Weissenberg data, and accurately adjusted using zero-level precession photography. The β angle can be measured to $\pm 0.20^\circ$ from the dial settings.

The unit cell dimensions are listed in Table 1. The estimated standard deviation in cell dimension is 0.5%, so that the standard deviation in cell volume is estimated at 10 Å³. There are no significant differences in the lengths of the b axes of the β -polymorphs and the b axes of the corresponding metal-substituted phthalocyanines measured by Robertson.² However, there are some significant changes in the remaining unit cell dimensions and in the cell volumes. Recent electron spin resonance studies⁷ on cobalt phthalocyanine have made use of Robertson's data without any independent check of the unit cell dimensions. The marked contraction in molar volumes will have to be taken into account in any discussions involving the molar polarization, a quantity of present interest as it is involved in the calculation of the position of a charge resonance state relative to the ground state of an aromatic molecule.^{3,8,9}

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⁶ Barrett, P. A., Dent, C. E., and Linstead, R. P., *J. Chem. Soc.*, 1936, 1719.

⁷ Assour, J. M., and Kahn, W. K., *J. Am. Chem. Soc.*, 1965, **87**, 207.

⁸ Lyons, L. E., in "Physics and Chemistry of the Organic Solid State." (Eds. D. Fox, M. M. Labes, and A. Weissberger.) Vol. I, p. 745. (Interscience: New York 1963.)

⁹ Choi, S., Jortner, J., Rice, S. A., and Silbey, R., *J. Chem. Phys.*, 1964, **41**, 3294.