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Neutron Diffraction at 115 K to 1·09 Å^{-1} from Cobalt Phthalocyanine

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Abstract

$[\mathrm{Co(C_{32}H_{16}N_8)}]$, $M_r = 571{\cdot}47$, monoclinic, $P2_1/c$, $a = 14{\cdot}489\,(9)$, $b = 4{\cdot}763\,(4)$, $c = 19{\cdot}156\,(16)$ Å, $\beta = 120{\cdot}76\,(4)^\circ$, $V = 1136\,(3)$ Å^3, $Z = 2$, $D_n = 1{\cdot}67$ Mg m^{-3}, neutron $\lambda = 0{\cdot}753\,(1)$ Å, $\mu = 0{\cdot}0879$ mm^{-1}, $F(000) = 46{\cdot}05 \times 10^{-14}$ m, $T = 115{\cdot}0\,(1)$ K, $R(F) = 0{\cdot}018$, $R(F^2) = 0{\cdot}030$, $S = 1{\cdot}08$ for 2789 reflections, 1008 at wavevectors above 0·7 Å^{-1}, with anharmonic Gram–Charlier expansion refinement and thermal diffuse-scattering (TDS) correction derived from theoretical intermolecular potentials. The introduction of 715 cubic and quartic anharmonic parameters reduces $R(F^2)$ by 0·011 and S by 0·11 from the values obtained in a harmonic refinement. Use of the local molecular approximate symmetry is not helpful in describing anharmonicity. Quartic parameters are more significant than cubic ones. Much of the anharmonic correction seems to result from intermolecular interaction affecting the relatively soft motion along **b**, resulting in one-particle potential wells with flat bottoms along **b**, but relatively harmonic potential in the *ac* plane. Agreement of positional parameters with the 115 K X-ray charge-density results is good, if similar refinements are made. But the neutron thermal parameters are significantly lower than X-ray, 8% on average, probably reflecting a difference in the TDS correction in the two experiments. The molecule is significantly distorted from planarity.

Introduction

Cobalt phthalocyanine (Fig. 1), CoPc, has interesting electronic properties with biological implications (Buchler, 1987; Dolphin, 1979). Both X-ray (Figgis, Kucharski & Reynolds, 1989*a*, and references therein) and polarized neutron (Williams, Figgis & Mason, 1981) diffraction experiments have been performed to examine the charge and spin densities. Reynolds & Figgis (1991) have analysed these and other metal(II) phthalocyanine diffraction and theoretical results to elucidate the ground electronic states in the crystals.

The 115 K charge-density X-ray study could not be interpreted in terms of a simple harmonic model for nuclear motion together with a valence-electron density model. This raised the question of the extent of anharmonicity and the accuracy of the positional and thermal parameters derived from the X-ray data, considerations which are critical in any modelling of valence-electron density.

In this paper we describe a neutron diffraction experiment, at the same temperature as the X-ray diffraction experiment, and which extends further in reciprocal space than is usual – up to the limit of the X-ray experiment. It allows an examination of anharmonic effects and of the reliability of X-ray-defined thermal parameters.

Experimental

Data collection

The crystal was from the same batch, grown by entrainer vacuum sublimation techniques, as used in previous diffraction experiments. The crystal was cut from that employed in the 4·3 K neutron diffraction experiment (Williams, Figgis, Mason, Mason & Fielding, 1980) and was a 6·0 mm needle along **b**, with an irregular eight-sided cross section [(100), $(10\bar{1})$, $(10\bar{2})$, $(00\bar{1})$, $(\bar{1}00)$, $(\bar{1}01)$, $(\bar{1}02)$, (001)] of maxi-

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mum dimension 1·4 mm, and volume 5·2 mm^3. We use the $P2_1/c$ setting rather than the $P2_1/n$ (which gives a preferable unit cell) to maintain comparability with past work.

The neutron data were collected on the four-circle neutron diffractometer D9 equipped with a conventional single-wire detector, mounted on the hot source at the Institut Laue–Langevin. An erbium-filtered neutron beam of mean wavelength 0·753 (1) Å (measured by use of a germanium crystal) was employed. The beam was diffracted in transmission from a Cu(220) monochromator. The crystal under study was mounted in a closed-cycle refrigerator, with **b** approximately parallel to the φ axis, and was cooled to 115·0 (1) K. Over the 14-day collection period the maximum temperature excursions were to 114·69 and 115·27 K. Collimation was defined at the counter by a 14 mm circular aperture at 38 cm distance, subtending 2·09° at the sample. The lattice parameters and diffractometer angular offsets were obtained by least-squares fitting to the setting angles of 26 reflections spread in reciprocal space with $2\theta <$ 65°. Half-wavelength contamination was measured by setting to very strong reflections, and remeasuring at the angles appropriate for $\lambda/2$. For five reflections the maximum F^2 ratio was 0·0028, average 0·0011, and so contamination was considered to be negligible.

Neutron integrated intensities were measured by scans varying from ω–θ, *via* ω–1·5θ, to ω–2θ in three steps as 2θ increases, so as to optimize peak width. The scan width [$\delta(2\theta)$] varied from 1·2° at 2θ of 20° to 1·0° at 2θ of 42°, and to 3·0° at the highest angles. Three standard reflections were measured every 100 reflections, and did not change significantly throughout the data collection. Scaled squared structure amplitudes and their variances were estimated by the profile analysis program *COLL5N* (Lehmann & Larsen, 1974). In total 5375 reflection profiles were measured in three classes. In each case both non-Friedel equivalents were usually collected. For $2\theta <$ 50° a complete hemisphere was collected (3189 reflections). For $110 > 2\theta > 50$° approximately 1000 reflections were collected, selected pseudorandomly from the $k < l$ hemisphere. This is 5% of the available reflections in that range. Lastly a calculation of intensities, predicted from the positional and thermal parameters derived from the 115 K X-ray experiment was performed. The 500 most intense unique reflections were measured. $|h| < 32$, $|k| < 11$, $|l| < 40$ for all data.

The amplitudes measured were corrected for absorption and incoherent scattering by use of a Gaussian integration approximation (Coppens, Leiserowitz & Rabinovich, 1965). The effective absorption coefficient was estimated by adding the incoherent contribution (Kuhs, 1988*a*) to the absorption (*International Tables for X-ray Crystallography*, 1974, Vol. IV). The resulting transmission factors varied from 0·84 to 0·95. Averaging the equivalent reflections gave an agreement factor between equivalents of R_I $(=\sum|I-\langle I\rangle|/\sum I) = 0{\cdot}035$ and $\sum\sigma(I)/\sum I =$ 0·044. For the most intense reflections R_I is less than 0·02. The larger total value reflects the large number of mostly weak high-angle data required to determine anharmonicity. No evidence was found of differences in intensity of equivalents due to such factors as anisotropic extinction and thermal diffuse scattering (TDS) (see below). 2789 unique reflections resulted with 2167 $I > 3\sigma(I)$.

Thermal diffuse scattering

Correction for first- and second-order thermal diffuse scattering requires a knowledge of the crystal elastic constants and can be accomplished by use of Stevens (1974) program. This can come from experiments or, if these are not available, *via* a theoretical crystal potential model. CoPc is a large molecule with low-energy internal modes. These may mix with the acoustic modes, important in the TDS correction, at wavevector values so close to the Brillouin zone centre that use of Stevens' program may not be adequate. We have not taken this into account. In addition there are already other approximations, both in the theory, and in our particular application (for example, not all our scans are ω–2θ).

Since no experimental values are available we estimate the elastic constants from calculated phonon-dispersion curves. We assume a rigid molecule, and use the empirical atom–atom intermolecular potential for azahydrocarbons of Williams & Cox (1984), employing the program *CRASH* of Pawley (1967). We use the experimental molecular geometry, assume 2+ charge on Co, $\frac{1}{4}$− on each N, and electric dipoles on N and CH taken from the work of Williams & Cox. We ignore atom–atom interactions with Co, as by trial and error we find they have little effect on the results. Table 1 shows calculated and observed unit-cell and sublimation energies at the energy minimum for this intermolecular potential. Also shown are the three acoustic velocities in the three principal reciprocal lattice directions, calculated with the observed cell. These change little from values obtained when the minimized cell is used. We note that calculated and observed sublimation energy and cell parameters agree well, and all acoustic slopes are positive (as they must be for stability). However, further out in the $h0l$ plane imaginary phonon frequencies do occur, so this model does not in fact corrspond to a stable crystal. Removal of the electrostatic interactions significantly degrades the fit, as we would deduce from the conclusions of Williams & Cox. For example the calculated subli-

Table 1. *Results of the theoretical calculation of* Co*Pc* *crystal properties*

	a (Å)	b (Å)	c (Å)	β (°)	$-E_s$ (kJ mol^{-1})
Observed*	14·495 (5)	4·742 (4)	19·107 (5)	120·76 (2)	251 (12)†
Calculated	14·558	4·877	19·282	120·43	261

Lattice direction	Acoustic velocities (× 10^3 m s^{-1})		
ζ 0 0	2·03	2·42	5·30
0 ζ 0	2·16	2·81	3·57
0 0 ζ	2·36	2·68	4·20

* 4·3 K neutron cell, Williams *et al.* (1980).
† Mackay (1973).

mation energy decreases to -223 kJ mol^{-1}. Fitting the Co charge to the observed sublimation energy gives a Co charge of 1·5+, in good agreement with the X-ray results. Neglect of molecular non-rigidity is an important remaining error which we have not taken into account here.

Rather than using the complete 13-parameter monoclinic elastic-constant matrix, we have fitted the nine principal-axis acoustic velocities to only the six-diagonal elastic-constant elements. Given the approximate nature of the intermolecular potential and the other approximations, better prediction of the acoustic frequencies used in the TDS correction is unnecessary.

On use of this theory we find:

(1) The TDS correction [defined as $I_{\rm Bragg} = I_{\rm obs}/(1 + \alpha)$] varies as $\theta\sin^2(\theta)$ up to $\alpha = 0{\cdot}61$ (6) at the highest angles. The first-order correction is still more than 80% of the correction even at the highest angles. The error reflects the dispersion in the anisotropy. This θ dependence produces a mainly anharmonic component in the scattering. At low θ we see that the TDS correction varies as θ^3, not as θ^2 which harmonic variation requires. This happens because of the steady increase in experimental scan width as θ is increased. The error in the TDS α's for individual reflections is not quantifiable, depending as it does on the unknown effect of systematic errors.

(2) The TDS correction is anisotropic. For thin shells of data, $\sigma(\alpha)/\alpha$ is about 0·1. For example between 54 and 56° α varies from 0·53 to 0·75.

(3) Non-Friedel equivalents have very similar α's. Thus, in this case, averaging does not reduce the anisotropy in TDS; conversely averaging before TDS correction, as we have done, produces little error here. The symmetrical crystal mounting is the reason for this.

Refinements

Refinements were full-matrix least squares using the program *ASRED* (Figgis, Reynolds & Williams, 1980) minimizing $\sum w(F_o^2 - k^2F_c^2)^2$, with weights $w = \sigma(F_o^2)^{-2}$ and scattering lengths from Sears (1986) (C = 6·6460, H = 3·7390, N = 9·36, Co = 2·50 fm). For the 978-parameter refinement, computing facilities constrained a two-block (922 + 75) refinement, which was repeated with changed blocking until the maximum shift on e.s.d. was less than 0·1.

Initial coordinates and harmonic thermal parameters were taken from the 115 K X-ray study by Figgis, Kucharski & Reynolds (1989*a*). All reflections were included, and refinement proceeded until the maximum shift on e.s.d. was less than 0·1. Multiple scattering and extinction corrections were applied; the former as a linear correction to the observed F^2 of the form $[m_1 + m_2(1 - |s|)]$, where m_1 and m_2 are parameters and $|s|$ the modulus of the momentum transfer [$\sin(\theta)/\lambda$, Å^{-1}] (Le Page & Gabe, 1979); the latter as a two-parameter anisotropic type-I correction of the form $\{ex_1 + ex_2[3\cos^2(\nu) - 1]\}$, where ex_1 and ex_2 are parameters and ν is the angle between s and [010] (Becker & Coppens, 1974; Coppens & Hamilton, 1970; Thornley & Nelmes, 1974; Figgis, Kucharski & Reynolds, 1989*b*).

In refinements including anharmonicity we used the Gram–Charlier expansion, for the reasons summarized by Kuhs (1988*b*). For each atom in a general position this entails ten cubic and 15 quartic parameters. In Table 2 we list the agreement factors and variable numbers for refinements.

Atomic coordinates and anisotropic harmonic thermal parameters from the most general refinement (11) are given in Table 3.* Extinction was important and significantly anisotropic. The extinction parameter in the $h0l$ plane, 0·38 (2), is a fraction of that along $0k0$, 1·25 (2) (arbitrary units). We note that this extinction correction affects equivalent reflections equally, and so can be applied after averaging, and will not affect the agreement of equivalents. Of course for general anisotropic extinction the equivalents are differentially affected and it is then incorrect to average the data before extinction correction. The maximum reduction in F^2 was a factor of 0·63, with five others < 0·85. This two-parameter model gave an excellent fit to the affected reflections. The multiple-scattering correction was barely significant though everywhere positive [$m_1 = 0{\cdot}09$ (6) × 10^{-28} m^2, $m_2 = 0{\cdot}00$ (1)]. Fig. 1 shows the atomic notation and the harmonic thermal motion ellipsoids from refinement (11). Use of results from the purely harmonic models gives improved e.s.d.'s, owing to the drastic reduction in parameter numbers, but must be rejected as being a result of hiding systematic inadequacies in the modelling.

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* Lists of observed and calculated F^2 values, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54435 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Results of various harmonic and anharmonic refinements*

(1) All data to 0·7 Å^{-1}, harmonic refinement. (2) All data, harmonic refinement. (3) All data, all harmonic plus cubic and quartic anharmonic parameters. (4) All data, harmonic, but assuming mirror symmetry in anharmonicity in CoPc molecular plane. (5) All data plus quartic anharmonic terms. (6) All data plus only quartic terms of the form $|s|^2h_ih_j$. (7) All data plus quartic terms of the form $|s|^4$. (8) All data plus quartic term of the form $|s|^2k^2$. (9) All data plus quartic term of the form $|k|^4$. (10) All data, harmonic and TDS correction. (11) All data, full anharmonic and TDS correction.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
No. of data	1781	2789	2789	2789	2789	2789	2789	2789	2789	2789	2789
Total No. of variables	263	263	978	692	698	437	292	292	292	263	978
Cubic/atom	0	0	10	6	0	0	0	0	0	0	10
Quartic/atom	0	0	15	9	15	6	1	1	1	0	15
$R(F^2)$ (%)	3·2	4·5	3·2	3·8	3·6	3·9	4·4	4·0	4·3	4·1	3·0
$R(F)$ $[F^2 > 3\sigma(F^2)]$ (%)	2·0	2·6	1·8	2·2	2·1	2·3	2·5	2·4	2·5	2·4	1·8
S (goodness of fit)	1·17	1·28	1·10	1·20	1·14	1·15	1·25	1·16	1·21	1·19	1·08

Table 3. *Positional parameters* ($\times 10^5$, $\times 10^4$ *for* H *atoms; anharmonic refinement) and anisotropic harmonic thermal parameters* ($\times 10^4$ Å^2), *defined as* $T = exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}...)]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0	0	0	143 (33)	157 (33)	81 (24)	49 (28)	70 (24)	12 (25)
N(1)	25310 (9)	2820 (27)	16116 (7)	100 (5)	154 (7)	111 (5)	7 (6)	43 (4)	−12 (5)
N(2)	7324 (9)	21942 (28)	9731 (7)	114 (6)	148 (7)	114 (5)	−8 (5)	58 (5)	−18 (5)
N(3)	7134 (9)	52272 (29)	7863 (7)	119 (6)	170 (7)	126 (6)	14 (5)	64 (5)	−11 (5)
N(4)	13131 (9)	19680 (28)	−3307 (7)	102 (5)	146 (7)	116 (5)	14 (5)	55 (5)	5 (6)
C(1)	17913 (13)	19677 (37)	15813 (9)	111 (8)	129 (8)	105 (7)	0 (7)	52 (6)	−6 (7)
C(2)	20177 (12)	39635 (40)	22627 (9)	105 (8)	171 (10)	108 (8)	11 (7)	49 (7)	−20 (7)
C(3)	29369 (15)	45257 (45)	29710 (10)	122 (9)	206 (11)	117 (8)	−6 (8)	41 (7)	−17 (8)
C(4)	28584 (1)	65898 (45)	34527 (10)	144 (8)	217 (11)	133 (8)	−32 (8)	70 (7)	−35 (8)
C(5)	19022 (15)	80506 (47)	32025 (12)	171 (10)	192 (11)	151 (9)	31 (8)	103 (8)	−53 (9)
C(6)	9824 (15)	74939 (40)	24537 (11)	149 (9)	170 (9)	146 (8)	−9 (8)	83 (8)	−22 (7)
C(7)	10640 (13)	54139 (40)	19756 (9)	127 (8)	156 (9)	116 (8)	6 (7)	76 (7)	−14 (7)
C(8)	2819 (13)	42925 (38)	11920 (9)	110 (8)	150 (9)	107 (7)	9 (7)	56 (6)	−18 (6)
C(9)	−14434 (12)	40948 (38)	934 (9)	100 (8)	142 (9)	106 (8)	9 (7)	47 (7)	2 (7)
C(10)	−25533 (12)	50128 (39)	−3253 (9)	102 (7)	152 (9)	113 (8)	4 (7)	55 (6)	−9 (7)
C(11)	−30770 (13)	70336 (44)	−1323 (10)	126 (8)	182 (10)	140 (8)	33 (8)	62 (7)	−9 (8)
C(12)	−41761 (16)	73548 (54)	−6654 (11)	122 (10)	240 (14)	165 (9)	32 (10)	64 (8)	8 (9)
C(13)	−47211 (15)	57175 (46)	−13691 (11)	101 (9)	227 (11)	188 (9)	39 (8)	64 (8)	14 (9)
C(14)	−41879 (13)	36959 (43)	−15605 (11)	90 (7)	205 (10)	146 (9)	41 (8)	43 (7)	17 (8)
C(15)	30921 (12)	33901 (39)	−10245 (9)	100 (8)	151 (9)	117 (7)	7 (7)	56 (6)	6 (7)
C(16)	−22974 (12)	15110 (39)	−10224 (9)	102 (7)	141 (9)	117 (8)	16 (7)	56 (6)	−3 (7)
H(1)	3679 (4)	3390 (12)	3168 (3)	206 (21)	398 (28)	379 (26)	53 (22)	127 (20)	−47 (24)
H(2)	3557 (4)	7092 (14)	4047 (3)	252 (23)	549 (41)	220 (21)	−45 (24)	42 (20)	−176 (25)
H(3)	1870 (4)	9618 (12)	3590 (3)	429 (30)	392 (31)	250 (19)	−46 (25)	186 (21)	−106 (23)
H(4)	238 (4)	8584 (12)	2254 (3)	254 (24)	372 (30)	368 (24)	19 (22)	169 (20)	127 (23)
H(5)	−2644 (4)	8298 (12)	412 (3)	318 (23)	375 (32)	285 (21)	11 (22)	146 (19)	−127 (22)
H(6)	−4615 (4)	8879 (13)	−542 (3)	265 (22)	425 (34)	361 (23)	142 (23)	157 (20)	−4 (23)
H(7)	5584 (3)	6018 (11)	−1780 (3)	185 (21)	438 (31)	366 (24)	117 (21)	84 (19)	31 (23)
H(8)	−4616 (4)	2439 (12)	−2109 (3)	259 (21)	419 (33)	234 (19)	24 (21)	67 (17)	107 (22)

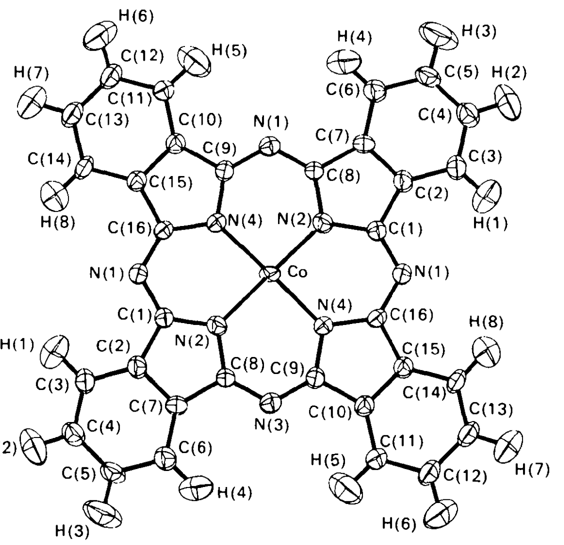

Fig. 1. The numbering of atoms in CoPc and the thermal motion ellipsoids, probability level 90%.

Discussion

Molecular structure and harmonic motion

Intermolecular contacts suggest that the free molecule of 4/*mmm* symmetry should distort to 2/*m*, with Co—N(3) and the molecular normal defining the mirror plane (Figgis, Kucharski & Reynolds, 1989*a*). The molecule in the crystal is very close to 2/*m*, with significant distortion from 4/*mmm*. The extent, and significance, of the symmetry lowering increases from bond lengths to bond angles (Table 4) to deviations from planarity (Fig. 2), as we might expect from relative force constants. The molecular bowing is clear in Fig. 2. There is an angle of *ca* 6° between the normals to the two groups of two parallel molecular fused rings, which themselves remain fairly planar.

The harmonic thermal parameters also reflect the local molecular symmetry. In particular the molecular normal is close to the largest principal axis of motion for nearly all atoms, and this is most marked for the peripheral atoms. The TDS correction does increase the harmonic thermal parameters resulting from the anharmonic refinements [comparing refinements (3) and (11)], but the increase in U is very uneven over the diagonal elements of the thermal tensor; it averages only 0·0009 Å^2 with an e.s.d. of 0·0014 Å^2. This reflects the fact that much of the TDS correction appears in the anharmonic parameters.

Comparison with 115 K *X-ray results*

Figgis, Kucharski & Reynolds (1989*a*) use a harmonic model to analyse their X-ray diffraction results to 0·82 Å^{-1} only. We should thus compare the results of refinement (1) (to 0·7 Å^{-1}) with the X-ray results. The positional parameters differ little. The mean value of $|(x_n - x_x)/[\sigma(x_n)^2 + \sigma(x_x)^2]^{1/2}|$ for the C and N atoms is 1·13, the maximum value 4·0. The use of a valence model for the total bonded charge density has reduced the differences expected in spherical theoretical atom models (Allen, 1986). For example we note a 0·000 (2) Å shift towards the benzene ring centre of the charge density compared with 0·005 (1) Å observed elsewhere with spherical atom models. The only noticeable differences are in the N atoms where we see a shift of charge 0·0035 (12) Å towards the lone pair for N(1)–N(4), indicating the valence model does not account fully for asphericity around the N atoms. The C—H bond lengths are foreshortened in the X-ray experiment by 0·13 Å compared with the neutron diffraction values, as expected. For the thermal parameters the mean value of U^n_{11}/U^x_{11} for the 20 C and N atoms is 0·90 (5), for U_{22} 0·97 (5) and for U_{33} 0·90 (5). This corresponds to the X-ray thermal parameter exceeding that of the neutron on average by 0·0012, 0·0005 and 0·0011 Å^2, respectively. This difference, while small, is consistent over all atoms and suggests a difference in TDS correction between X-ray and neutron experiments. If a purely harmonic model is used TDS causes a 0·0025 Å^2 increase in the diagonal elements of the U tensor for the neutron data, even though, as we have noted, the correction is actually much better simulated by anharmonic parameters.

Anharmonicity

Introduction of all cubic and quartic anharmonic parameters produces a significant improvement in the fit (Table 2) but at the expense of reducing the observation to parameter ratio from 10·6 to 2·85. The values of only 14 parameters exceed three times their standard deviation; all are k^4 terms, and they are associated with no obvious class of atom. Assumption of a mirror plane of symmetry in the molecular plane for the anharmonic parameters significantly degrades the fit, implying that the intermolecular rather than intramolecular interactions are important for anharmonicity. The cubic parameters,

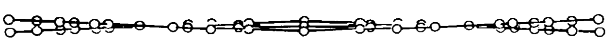

Fig. 2. Molecular geometry of CoPc. Least-squares molecular plane horizontal, Co—N(3) perpendicular to plane of diagram.

Table 4. *Bond lengths* (Å) *and angles* (°) *for* Co*Pc*

The bonds and angles are grouped in 4 *mmm* symmetry, the symmetry of an isolated molecule, with a blank between each group. The symmetry of the molecule in the crystal is inversion only, but the observed, almost 2/*m* symmetry is emphasized by grouping the values which are identical in 2 *m* on the left or the right.

Co—N(2)	1·916 (2)	Co—N(4)	1·915 (1)
N(2)—C(1) N(4)—C(16)	1·376 (2) 1·380 (2)	N(2)—C(8) N(4)—C(9)	1·371 (3) 1·371 (3)
N(1)—C(1) N(1)—C(16)	1·316 (3) 1·314 (2)	N(3)—C(8) N(3)—C(9)	1·317 (2) 1·317 (2)
C(1)—C(2) C(15)—C(16)	1·458 (3) 1·457 (3)	C(7)—C(8) C(9)—C(10)	1·443 (2) 1·450 (2)
C(2)—C(7) C(10)—C(15)	1·392 (3) 1·390 (2)		
C(2)—C(3) C(14)—C(15)	1·391 (2) 1·389 (2)	C(6)—C(7) C(10)—C(11)	1·395 (3) 1·388 (3)
C(3)—C(4) C(13)—C(14)	1·392 (3) 1·396 (3)	C(5)—C(6) C(11)—C(12)	1·396 (2) 1·392 (3)
C(4)—C(5) C(12)—C(13)	1·398 (3) 1·400 (3)		
C(3)—H(1) C(14)—H(8)	1·085 (6) 1·087 (5)	C(6)—H(4) C(11)—H(5)	1·076 (6) 1·084 (5)
C(4)—H(2) C(13)—H(7)	1·094 (4) 1·094 (4)	C(5)—H(3) C(12)—H(6)	1·070 (6) 1·068 (7)
N(2)—Co—N(4)	90·98 (7)	N(2)—Co—N(4′)	89·02 (7)
Co—N(2)—C(1) Co—N(4)—C(16)	127·2 (1) 127·2 (1)	Co—N(2)—C(8) Co—N(4)—C(9)	125·6 (1) 125·5 (1)
C(1)—N(1)—C(16′)	120·8 (1)	C(8)—N(3)—C(9)	121·9 (2)
C(8)—N(2)—C(1) C(16)—N(4)—C(9)	107·3 (1) 107·3 (1)		
N(1)—C(1)—N(2) N(1′)—C(16)—N(4)	128·0 (2) 127·8 (2)	N(3)—C(9)—N(4) N(3)—C(8)—N(2)	128·1 (2) 127·9 (1)
N(1)—C(1)—C(2) N(1′)—C(16)—C(15)	122·4 (1) 122·7 (1)	N(3)—C(8)—C(7) N(3)—C(9)—C(10)	121·9 (2) 121·7 (2)
N(2)—C(1)—C(2) N(4)—C(16)—C(15)	109·7 (2) 109·5 (2)	N(2)—C(8)—C(7) N(4)—C(9)—C(10)	110·1 (1) 110·2 (1)
C(1)—C(2)—C(3) C(16)—C(15)—C(14)	132·6 (2) 132·0 (2)	C(8)—C(7)—C(6) C(9)—C(10)—C(11)	131·4 (2) 131·7 (1)
C(1)—C(2)—C(7) C(16)—C(15)—C(10)	106·1 (1) 106·6 (1)	C(8)—C(7)—C(2) C(9)—C(10)—C(15)	106·8 (2) 106·4 (2)
C(3)—C(2)—C(7) C(14)—C(15)—C(10)	121·3 (2) 121·4 (2)	C(6)—C(7)—C(2) C(11)—C(10)—C(15)	121·9 (1) 121·9 (1)
C(2)—C(3)—C(4) C(15)—C(14)—C(13)	117·1 (2) 117·1 (2)	C(7)—C(6)—C(5) C(10)—C(11)—C(12)	116·9 (2) 117·2 (2)
C(3)—C(4)—C(5) C(14)—C(13)—C(12)	121·8 (2) 121·5 (1)	C(6)—C(5)—C(4) C(11)—C(12)—C(13)	121·0 (2) 121·0 (2)
C(2)—C(3)—H(1) C(15)—C(14)—H(8)	121·3 (3) 122·0 (3)	C(7)—C(6)—H(4) C(10)—C(11)—H(5)	121·1 (3) 121·0 (3)
C(4)—C(3)—H(1) C(13)—C(14)—H(8)	121·6 (3) 121·0 (2)	C(5)—C(6)—H(4) C(12)—C(11)—H(5)	122·0 (3) 121·8 (4)
C(3)—C(4)—H(2) C(14)—C(13)—H(7)	119·9 (4) 119·0 (3)	C(6)—C(5)—H(3) C(11)—C(12)—H(6)	119·2 (3) 119·9 (3)
C(5)—C(4)—H(2) C(12)—C(13)—H(7)	118·3 (4) 119·6 (4)	C(4)—C(5)—H(3) C(13)—C(12)—H(6)	119·8 (3) 119·1 (3)

while smaller than the quartic ones, are still significant. Almost half the anharmonic improvement can be attributed to terms of the form $|s|^2k^2$ for each atom. These observations indicate that the intermolecular potential is more anharmonic for motion along **b** than in other directions. The harmonic thermal motion in the **b** direction is larger than in the *ac* plane. On introducing the anharmonic parameters U_{22} increases by up to 50%, but the other parameters hardly change. This softer intermolecular potential for motion along **b** might be expected to imply larger anharmonicity. The anharmonic parameters imply that the various motions along **b** are better described by potentials with flatter bottoms and steeper sides than harmonic. The anharmonic parameters are not well enough defined for a more quantitative analysis.

The net apparent anharmonicity above, after correction for TDS, is significant – increasing the highest angle, k, intensities by a factor of about 1·7. Calculated total TDS corrections at these highest angles add a further factor of 1·6. Comparison of refinements (2), (10) and (11) indicates that the anharmonic terms introduced *via* the combination of TDS and scan widths is not insignificant – perhaps slightly less than half the observed anharmonicity in the data. Scan truncation would depress higher angle intensities. Since we see the opposite effect, the apparent anharmonicity may be a real anharmonic effect of comparable size to the TDS correction, rather than a further neglected experimental correction.

Concluding remarks

This data set extends further in reciprocal space and has better counting statistics than most neutron diffraction experiments on relatively complex molecules. Because of this we are able to show that even at 115 K, TDS and anharmonicity are both still significant, and not interpretable with simple models. This has two more general implications. Firstly, in a more common, lower resolution, neutron diffraction experiment interpreted neglecting TDS and anharmonicity [as refinement (1)] the resulting errors in both positional and thermal parameters may be between 50 and 70% of the errors resulting from a more complete experiment and analysis [refinement (11)]. Thus the normal neglect of these systematic errors results in unrealistically good positional and thermal parameter errors. Secondly, if we are to use neutron results to produce charge information from X-ray experiments *via* the *X–N* procedure, then we must correct both types of data for TDS *and* also use anharmonic refinements. Otherwise the systematic (here *ca* 10%) differences in thermal parameters may severely bias the information obtained about the charge density.

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