

# Crystal structures of nickel, copper and zinc naphthalocyanines

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The crystal and molecular structures of  $[M(nc)]$  ( $M = Ni, Cu$  or  $Zn$ ;  $H_2nc =$  naphthalocyanine) have been determined. The bond lengths Ni–N 1.929(7), Cu–N 1.951(4) and Zn–N 1.983(4) Å are nearly consistent with those in the phthalocyanines of the same metals. The patterns of the perpendicular displacements of atoms from the mean plane for the three molecules, although small, are identical with each other and also quite similar to those commonly observed in the  $\beta$  polymorphs of phthalocyanines. The three molecules pack in similar fashion. The molecules stack within the  $ab$  plane, forming a two-dimensional sheet, contrary to the one-dimensional stacking of the phthalocyanines of the same metals. The azamethine N atoms are not in close contact with the central metal atoms of adjacent molecules, although their deviations from the mean plane are appreciable.

Organic dye pigments, such as phthalocyanine ( $H_2pc$ ) and naphthalocyanine ( $H_2nc$ ), have recently attracted considerable attention from material chemists because of their potential use in semiconducting materials,<sup>1</sup> non-linear optics<sup>2</sup> and other optical devices.<sup>3</sup> Although phthalocyanines of divalent first-row transition metals are known to exist in at least two polymorphic modifications,  $\alpha$  and  $\beta$ ,<sup>4</sup> only one form ( $\beta$ ) has been examined by a single-crystal structure analysis.<sup>5</sup> In the stable  $\beta$  phase the molecules form one-dimensional stacking columns. The metastable  $\alpha$  phase has been thought to consist of a different type of one-dimensional stacking.<sup>6</sup> The optical properties of phthalocyanines are dependent upon the polymorphic forms,<sup>7</sup> that is the molecular stacking geometry. Naphthalocyanines show higher optical non-linearities<sup>8</sup> and electrical conductivities<sup>9</sup> compared to phthalocyanines because of their larger  $\pi$ -electron delocalization systems. No accurate crystal structure data for them have been reported to date, however, although the molecular stacking in vacuum-deposited thin films has been extensively studied.<sup>10</sup>

By their very nature, compounds such as phthalocyanines and naphthalocyanines are insoluble. Moreover, the latter are less volatile and also less resistant to thermal decomposition. This is perhaps the reason why no single-crystal structure analyses of them have been reported. Recently we obtained plate-like crystals of  $[M(nc)]$  ( $M = Ni, Cu$  or  $Zn$ ) suitable for single-crystal structure determination, by sublimation *in vacuo* after many trials. Here we report the crystal structures and discuss them in comparison with the molecular packing mode of the stable  $\beta$  form of the corresponding phthalocyanines.

## Experimental

The compounds  $[M(nc)]$  ( $M = Ni, Cu$  or  $Zn$ ) were prepared from 2,3-dicyanonaphthalene and the powdered metals, according to a known method.<sup>11</sup> The crude products were purified by exhaustive Soxhlet extraction with dimethylformamide and subsequent heating at 500 °C for 1 h *in vacuo*. Single crystals, suitable for diffraction analysis, were grown by vacuum sublimation in quartz tubes at 500–650 °C with subsequent evacuation.

## Crystallography

Plate-like crystals of the compounds were mounted on glass fibres. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Cu-K $\alpha$  radiation

( $\lambda = 1.5418$  Å). Cell constants and orientation matrices for data collection were obtained from a least-squares refinement using the setting angles of the following numbers of carefully centred reflections: 9 in the range  $8.50 < 2\theta < 26.43^\circ$  for Ni, 25 in the range  $22.66 < 2\theta < 54.32^\circ$  for Cu, and 25 in the range  $23.90 < 2\theta < 54.70^\circ$  for Zn. The crystal data and experimental conditions are listed in Table 1. The data were collected at a temperature of  $20 \pm 1$  °C using the  $\omega$ - $2\theta$  scan technique at a scan rate of  $16^\circ \text{ min}^{-1}$  to a maximum  $2\theta$  value of  $120^\circ$ . Three standard reflections were monitored every 150 for each sample and showed no systematic decrease in intensity. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz-polarization effects.

The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final difference maps showed no peaks higher than  $0.9 \text{ e } \text{Å}^{-3}$  in each case. All calculations were performed using the TEXSAN package<sup>12</sup> with least-squares refinement based on  $F$ .

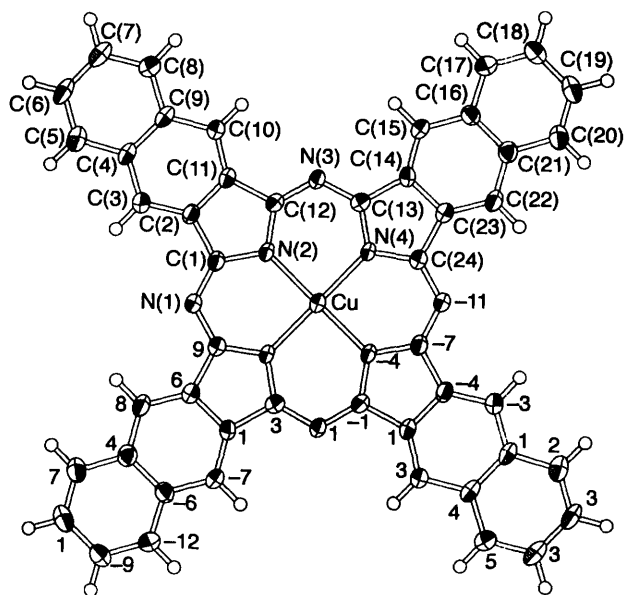
Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/231.

## Results and Discussion

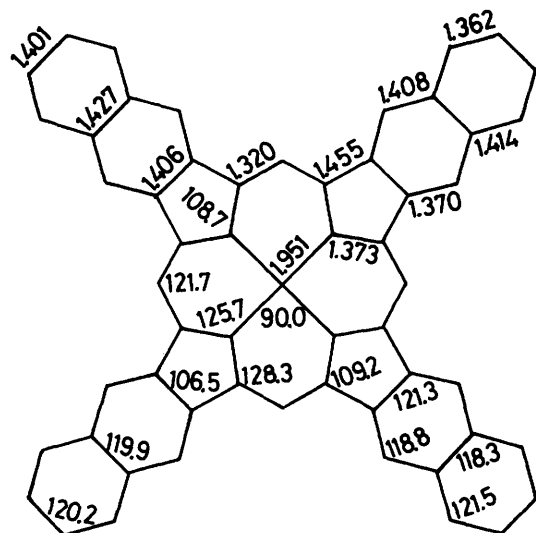
### Molecular stereochemistries

The molecular geometry and atom numbering of the centrosymmetric  $[Cu(nc)]$  molecule are shown in Fig. 1. Although the deviation of any atom from exact planarity is small, similar patterns of displacements from the mean plane were also observed for  $[Ni(nc)]$  and  $[Zn(nc)]$ . Average values for chemically equivalent bond distances and angles for  $[Cu(nc)]$  are displayed in Fig. 2.

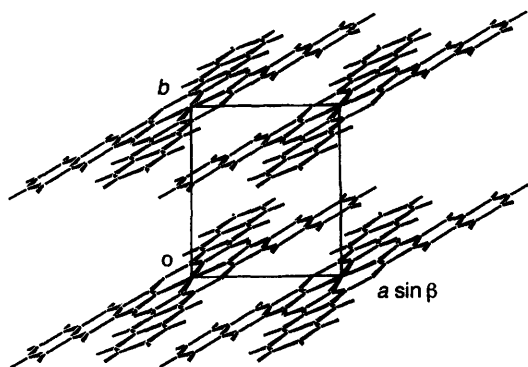
In the three compounds the metal atoms have essentially  $D_{4h}$  symmetry. The angles N(2)–M–N(4) are equal to  $90^\circ$  within the limit of the estimated standard deviations, while those of  $[M(pc)]$  have been reported to deviate by small but significant amounts from  $90^\circ$ .<sup>5</sup> The bond distances of Ni–N 1.929(7), Cu–N 1.951(4) and Zn–N 1.983(4) Å are nearly consistent with those  $[Ni-N \approx 1.83, Cu-N 1.934(6), Zn-N 1.980(2) \text{ Å}]$  determined for the corresponding  $[M(pc)s]$ .<sup>5</sup> Using  $C_s$  and  $C_2$



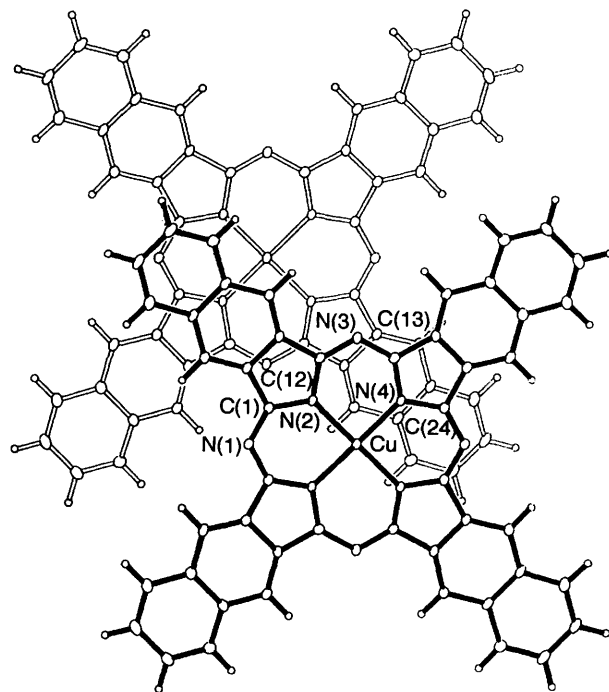
**Fig. 1** Structure of  $[\text{Cu}(\text{nc})]$  and the atom labelling scheme. Displacement ellipsoids are shown at the 50% probability level. In the lower half of the figure the symbol of each atom is replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the asymmetric unit of the molecule



**Fig. 2** Formal diagram of the naphthalocyanine skeleton. Values of the chemically distinct classes of bond lengths (Å) and angles ( $^{\circ}$ ) in  $[\text{Cu}(\text{nc})]$ , averaged in accord with  $D_{4h}$  geometry, are shown



**Fig. 3** View of the two-dimensional molecular stacking of the  $[\text{M}(\text{nc})]$  molecules within the  $ab$  plane, projected along  $c$



**Fig. 4** View of two molecules of  $[\text{Cu}(\text{nc})]$  viewed perpendicular to the mean plane. The atoms of the shaded molecule are at  $\pm x, \pm y, \pm z$ , and those of the other are at  $1 \pm x, \pm y, \pm z$ . Displacement ellipsoids are shown at the 20% probability level

to represent the  $\alpha$ - and  $\beta$ -carbon atoms of a pyrrole unit,  $N_p$  for a pyrrole nitrogen atom, and  $N_m$  for the azamethine atom, the following changes in bond parameters are observed. With increasing  $M-N$  bond distance, the  $C_a-N_p-C_a$  bond angle increases while  $M-N_p-C_a$  decreases. Concomitantly,  $C_a-N_m$  and  $C_b-C_b$  lengths. The other bond parameters remain almost unchanged. Such changes in skeletal parameters accompanying the expansion of the naphthalocyanine core are the same as those observed in accommodating radial expansion of the phthalocyanine core.<sup>5</sup> The naphthalo ring shows systematic deviations from that of naphthalene.<sup>13</sup> Individual units of the macrocycle, *i.e.* a pyrrole ring or naphthalo ring, are planar to within 0.02 Å. The dihedral angles between an individual pyrrole ring and its associated naphthalo ring are all less than  $2^{\circ}$ . The angles between planes of adjacent naphthalo rings are about  $5^{\circ}$  for all three molecules. The pattern of the perpendicular displacements, although small, is also quite similar to those observed for phthalocyaninates<sup>5</sup> of divalent first-row transition metals. The deviation of  $N(1)$  from the mean plane is appreciable. This has been thought to arise from the interactions between the azamethine  $N$  atom and the central metal of a neighbouring molecule in the case of the stable  $\beta$  form of phthalocyanines.<sup>5</sup>

#### Intermolecular arrangements

The three compounds pack in similar fashion, the arrangement viewed parallel to the  $c$  axis being shown in Fig. 3. The molecules stack within the  $ab$  plane, forming a two-dimensional stacking sheet, contrary to the one-dimensional stacking of phthalocyanines.<sup>5</sup> All the  $\text{nc}$  molecules in each  $ab$  plane are parallel and the orientation of the molecules alternates along the  $c$  axis. Alternatively, the stacking arrangement can be regarded as built up of successive rows of close-packed molecules. The angles between the stacking  $a$  axes and the normals to the mean planes of the  $[\text{Ni}(\text{nc})]$ ,  $[\text{Cu}(\text{nc})]$  and  $[\text{Zn}(\text{nc})]$  molecules are  $61.0$ ,  $61.2$  and  $61.3^{\circ}$ , respectively, significantly larger than those reported for the stable  $\beta$  phases of the corresponding phthalocyaninates.<sup>5</sup> The perpendicular distances between successive planes of molecules along the

**Table 1** Crystal data and experimental conditions \*

	[Ni(nc)]	[Cu(nc)]	[Zn(nc)]
Formula	C <sub>48</sub> H <sub>24</sub> N <sub>8</sub> Ni	C <sub>48</sub> H <sub>24</sub> CuN <sub>8</sub>	C <sub>48</sub> H <sub>24</sub> N <sub>8</sub> Zn
<i>M</i>	771.47	776.32	778.15
<i>a</i> /Å	6.8800(9)	6.873(2)	6.850(2)
<i>b</i> /Å	7.8730(8)	7.906(1)	7.997(4)
<i>c</i> /Å	30.48(2)	30.385(9)	30.273(4)
$\beta$ /°	90.50(9)	91.02(2)	91.88(2)
<i>U</i> /Å <sup>3</sup>	1650.8(2)	1650.9(6)	1657.5(8)
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.552	1.562	1.559
<i>F</i> (000)	792	794	796
$\mu$ (Cu-K $\alpha$ )/cm <sup>-1</sup>	12.69	13.55	14.48
Crystal dimensions/mm	0.10 × 0.10 × 0.02	0.20 × 0.09 × 0.02	0.20 × 0.07 × 0.01
No. observed reflections [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]	1245	1508	1654
No. unique reflections	2676	2665	2671
<i>R</i>	0.070	0.045	0.052
<i>R'</i>	0.071	0.042	0.060
$\Delta/\sigma$ in final cycle	0.13	0.23	0.15
$\rho_{\max}/e \text{ \AA}^{-3}$	0.86	0.35	0.56

\* Details in common: green; monoclinic, space group *P2<sub>1</sub>/c*; *Z* = 2; 272 variables;  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ;  $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ .

stacking axes are 3.33, 3.31 and 3.29 Å, respectively, being nearly equal to those found in the phthalocyaninates.<sup>5</sup> A view of two molecules perpendicular to the mean plane of [Cu(nc)] (Fig. 4) shows that the azamethine nitrogen atom N(1) is not in close contact with the copper atom of an adjacent molecule. This suggests that the deviation of the azamethine N atom from the mean plane of the molecules commonly observed in the stable phases of the naphthalocyaninates and phthalocyaninates of divalent first-row transition metals is inherent to the free molecules rather than the result of the intermolecular interactions.

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