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THE PREPARATION AND CRYSTAL STRUCTURES OF Cu(Hdpa)(chp)₂ AND A NEW PHASE OF Cu(dpa)₂ [Hdpa = 2-(PYRIDYL-2-AMINO)-PYRIDINE, Hchp = 6-CHLORO-2-HYDROXYPYRIDINE]

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Abstract—The synthesis and crystal structure of Cu(Hdpa)(chp)₂ (**I**) are reported. The copper environment is six coordinate with Hdpa and one of the chp ligands bonding in a chelating fashion. The second pyridine is bound through N, the O atom takes up the sixth coordination site but is also hydrogen bonded to the Hdpa ligand of a second Cu(Hdpa)(chp)₂ unit, forming a centrosymmetric dimer. A new (orthorhombic) phase of Cu(dpa)₂ (**II**) has also been found, in which distorted tetrahedral copper(II) complexes are linked through a network of H bonds between the deprotonated dpa ligand and C—H bonds *meta*- to the pyridyl nitrogen donor.

We recently reported[1] the synthesis and characterization of several copper(II) pyridone complexes with 2,2′-bipyridyl (bipy). This work suggested that formation of monomeric or dimeric structures is finely balanced and subject to subtle influences. For example, Cu(chp)₂(bipy) is dimeric in the solid state, bridged through μ_2-O ligands, but appears monomeric in solution, whereas Cu(mhp)₂(bipy) is monomeric both as a solid and in solution [Hchp = 6-chloro-2-hydroxypyridine, Hmhp = 6-methyl-2-hydroxy pyridine]. As part of our continued exploration of such N-donor adducts, we have examined the reactivity of dipyridylamine [Hdpa] with Cu₂(chp)₄. We now report the synthesis and characterization of Cu(Hdpa)₂(chp)₂ (**I**) and a new phase of Cu(dpa)₂ (**II**).

EXPERIMENTAL

Cu(NO₃)₂·3H₂O, Hchp and Hdpa (Aldrich) were used without further purification. Na[dpa] was prepared by reaction of Hdpa with one equivalent

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of Na in MeOH, and dried *in vacuo*. Cu₂(chp)₄ was prepared according to the literature method.[2] Satisfactory i.r., elemental analyses and mass spectra were obtained for **I** and **II**.

Preparation of I

A solution of Hdpa in CH₂Cl₂ was added dropwise to a CH₂Cl₂ solution of Cu₂[chp]₄ (2:1 mole ratio). An immediate colour change from red to green occurred. Ether diffusion into the latter solution provided many well-formed crystals of Cu(Hdpa)(chp)₂. Yield 72%.

Preparation of II

Solid Na[dpa] and Cu(NO₃)₂·3H₂O were ground together in a 2:1 ratio to form a dark blue paste. Extraction with dichloromethane produced a royal blue solution. Diffusion of ether vapour into this solution yielded dark blue crystals of Cu(dpa)₂. Yield 48%.

Crystal structure determination

Crystals of **I** (0.27 × 0.14 × 0.06 mm) and **II** (0.35 × 0.19 × 0.12 mm) were mounted on glass fibres. Data collection was carried out at 150 K on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low temperature device,[3] using graphite-monochromated Mo-K_x radiation ($\lambda = 0.71073$ Å), ω–2θ scans and on-line profile-fitting.[4] For **I**, 2552 unique data were collected in the range $2.5 \leqslant \theta \leqslant 22.5°$ [$h = -10 \to 9$, $k = -10 \to 10$, $l = 0 \to 13$]; the data were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction based on ψ scans was applied (maximum and minimum transmission factors 0.864, 0.801). For **II**, 1771 data (1101 unique, $R_{int} = 0.0198$) were collected in the range $2.5 \leqslant \theta \leqslant 22.5°$ [$h = -1 \to 9$, $k_2 - 1 \to 13$, $l = -1 \to 16$]. An empirical absorption correction[5] was applied to **II**, with maximum and minimum correction factors of 1.086 and 0.898 respectively.

I: $C_{20}H_{15}Cl_2CuN_5O_2$, triclinic, space group $P\bar{1}$, $M_r = 491.82$ with cell dimensions $a = 9.676(8)$, $b = 9.714(8)$, $c = 12.822(10)$ Å, $\alpha = 91.52(9)$, $\beta = 109.53(5)$, $\gamma = 118.06(8)°$, $V = 977.6$ Å^3, $Z = 2$, $D_{calc} = 1.67$ gcm^{-3}, $F(000) = 498$, $\mu = 1.42$ mm^{-1}.

II: $C_{20}H_{16}CuN_6$, orthorhombic, space group *Pnaa*, $M_r = 403.92$ with cell dimensions $a = 9.247(3)$, $b = 12.201(6)$ and $c = 15.007(10)$ Å, $V = 1693$ Å^3, $Z = 4$, $D_{calc} = 1.59$ gcm^{-3}, $F(000) = 828$, $\mu = 1.31$ mm^{-1}.

For **I** and **II**, the positions of all non-hydrogen atoms were determined by heavy-atom methods,[6] and refined anisotropically using full-matrix least squares methods.[7] H atoms were located in the subsequent difference maps and refined with a common U_{iso} for **I** and refined freely for **II**. At convergence, for **I**, the final 'conventional' $R1$ value was 0.0382 [based on F and 2033 data with $F_0 > 4\sigma(F_0)$] with a goodness of fit of 1.073 for 317 parameters. $wR2$ [based on F^2 and all 2552 data] was 0.1088 [$w^{-1} = \sigma^2(F_0^2) + (0.0514P)^2 + 1.85P$, where $P = 1/3(\max(F_0^2, 0) + 2F_0^2)$]. In the final cycle of refinement, $(\Delta/\sigma)_{max} = 0.005$, and the highest peak and lowest trough were $+0.49$ and -0.69 eÅ^{-3} respectively. For **II**, the final 'conventional' $R1$ value was 0.0281 [based on F and 898 data with $F_0 > 4\sigma(F_0)$] with a goodness of fit of 1.063 for 155 parameters. $wR2$ [based on F^2 and all 1101 data] was 0.0852 [$w^{-1} = \sigma^{-2}(F_0^2) + (0.0537P)^2 + 1.36P$, where $P = 1/3(\max(F_0^20) + 2F_0^2)$]. In the final cycle of refinement, $(\Delta/\sigma)_{max} = 0.003$, and the difference synthesis maxima and minima were $+0.26$ and -0.41 eÅ^{-3} respectively.

Selected bond distances and angles for **I** and **II**

are summarized in Tables 1 and 2. Atomic coordinates, anisotropic thermal parameters and structure factor tables have been deposited with the Editor, from whom copies are available on request.

RESULTS AND DISCUSSION

We have previously shown[1] that reaction of $Cu_2(chp)_4$ (**III**) with bipy gives a compound which crystallizes as a dimeric species [$Cu_2(chp)_4(bipy)_2$] but that reaction of [$Cu_6Na(mhp)_{12}$][NO_3] with bipy gives a monomeric species [$Cu(mhp)_2bipy$]. In view of this difference we wished to investigate whether alteration of the chelating N-donor ligand might also influence the formation of a monomeric or dimeric species. Reaction of **III** with Hdpa in CH_2Cl_2 gave a green e.p.r. active solution [CH_2Cl_2, 298 K, $g = 2.116$], indicative of a monomeric species, $Cu(Hdpa)(chp)_2$. Recrystallization of this material by ether diffusion yielded many well-formed green crystals which were characterized by X-ray crystallography.

The copper centre in **I** is six coordinate (Fig. 1) with longer contacts to N(11r) and O(12r) in the pseudo-axial positions. The Hdpa ligand chelates to the copper(II) centre with Cu—N distances being 2.003(4) and 2.013(4) Å. The hinge angle at N[134.6(4)°] and the associated N—C bond lengths [mean N—C 1.368(7) Å] are considerably larger than those found for the deprotonated complex **II** [126.8(3)° and 1.339(4) Å], consistent with the greater degree of delocalization (increased sp^2 character) on deprotonation. Although both pyridone ligands bridge across the axial-equatorial positions, one is strongly chelating whilst the second is more weakly coordinated; the first is N-bound in the axial position [Cu—N(11r) = 2.453(4) Å] and equatorially O-bound [Cu—O(11r) 1.963(4) Å]; the second is N-bound in the equatorial position [Cu—N(12r) = 2.020(4) Å] and very weakly axially bound through O [Cu—O(12r) = 2.722(4) Å]. Because of the small bite angle associated with the chelating 2-pyridone ligand, the coordination environment about copper is severely distorted from octahedral: the N—Cu—O angles made by the chelating pyridone ligands at the copper centre are 54.4(2)° and 60.4(2)°, and the mean deviation of the equatorial plane is 0.384 Å.

In some ways this structure is reminiscent of the mononuclear complex, $Cu(mhp)_2(bipy)$ **IV**,[1] which also features a chelating N-donor ligand and two deprotonated pyridone units. However, **I** differs in two ways. Firstly, in **IV** both mhp ligands are bound via N donors in the equatorial plane, with two equidistant long contacts to axial O ligands.

Table 1. Selected bond lengths [Å] and angles [°] for **I**

Cu—O(11R)	1.963(4)		Cu—O(12R)	2.722(4)
Cu—N(3A)	2.013(4)		Cu—N(1A)	2.003(4)
Cu—N(11R)	2.453(4)		Cu—N(12R)	2.020(4)
N(2A)—C(06A)	1.372(7)		C(05A)—N(2A)	1.363(7)
O(11R)—Cu—N(1A)	158.76(14)		O(11R)—Cu—N(3A)	91.6(2)
N(1A)—Cu—N(3A)	92.6(2)		O(11R)—Cu—N(12R)	92.6(2)
N(1A)—Cu—N(12R)	94.8(2)		N(3A)—Cu—N(12R)	147.9(2)
O(11R)—Cu—N(11R)	60.4(2)		N(1A)—Cu—N(11R)	98.4(2)
N(3A)—Cu—N(11R)	96.9(2)		N(12R)—Cu—N(11R)	112.7(2)
C(05A)—N(2A)—C(06A)	134.6(4)			

Table 2. Selected bond lengths [Å] and angles [°] for **II**

Cu—N(1R)	1.953(3)		Cu—N(2R)	1.967(3)
N(1)—C(11R)	1.338(4)		N(1)—C(12R)	1.339(4)
N(1R)—Cu—N(1R')	141.0(2)		N(1R)—Cu—N(2R)	93.59(10)
N(1R')—Cu—N(2R)	99.33(10)		N(1R)—Cu—N(2R')	99.33(10)
N(1R')—Cu—N(2R')	93.58(10)		N(2R)—Cu—N(2R')	140.7(2)
C(11R)—N(1)—C(12R)	126.8(3)			

Primed atoms are related to their unprimed equivalents by the symmetry operation $x, -y+1/2, -z+1/2$.

Secondly, **IV** forms discrete monomeric units in the crystal whereas there are strong H bonds between the pyridone oxygen and a Hdpa unit in a neighbouring complex (Fig. 2). The H atom involved was located and the N—H distance and O⋯H contact are 0.7 Å and 2.1 Å respectively. The resultant Cu⋯Cu distance within the dimeric unit is too large (6.697 Å) for any significant interaction.

Whilst examining the chemistry of the copper (II)/Hdpa/Hchp system, we also found a new phase of Cu(dpa)₂. The structure of Cu(dpa)₂ (Fig. 3) has previously been reported by Rodig *et al.*,[8] and was found to be monoclinic (space group *C2/c*). Here we have crystallized an orthorhombic phase. Bond distances and angles are formally equivalent (within error) in both phases, with copper centres in both phases lying on crystallographic 2-fold axes. However, the dihedral angle, Φ, which defines the distortion between tetrahedral and square planar geometries[8] [$\Phi = 0°$ for square planar and $90°$ for tetrahedral] is $58.8(4)°$ in the monoclinic (α) phase

and $54.8(4)°$ in the orthorhombic (β) phase. The molecular packing is also significantly different; the α-phase is characterized by hydrogen bonding between C—H bonds *ortho* to the N-donor and the deprotonated hinge N (Fig. 4a), whereas the β-phase exhibits H bonding between C—H bonds *meta* to the pyridyl N-atom (Fig. 4b). Although both form polymeric H-bonded networks, we can usefully describe the structures in terms of the smallest number of monomers which need to be considered before the network returns to the first unit. Thus, the α-phase can be described as dimeric and the β-phase at tetrameric. The calculated densities are significantly different (1.51 g cm⁻³ and 1.59 g cm⁻³ for the α- and β-phases respectively), and this appears to be due to more efficient packing in the β-phase.
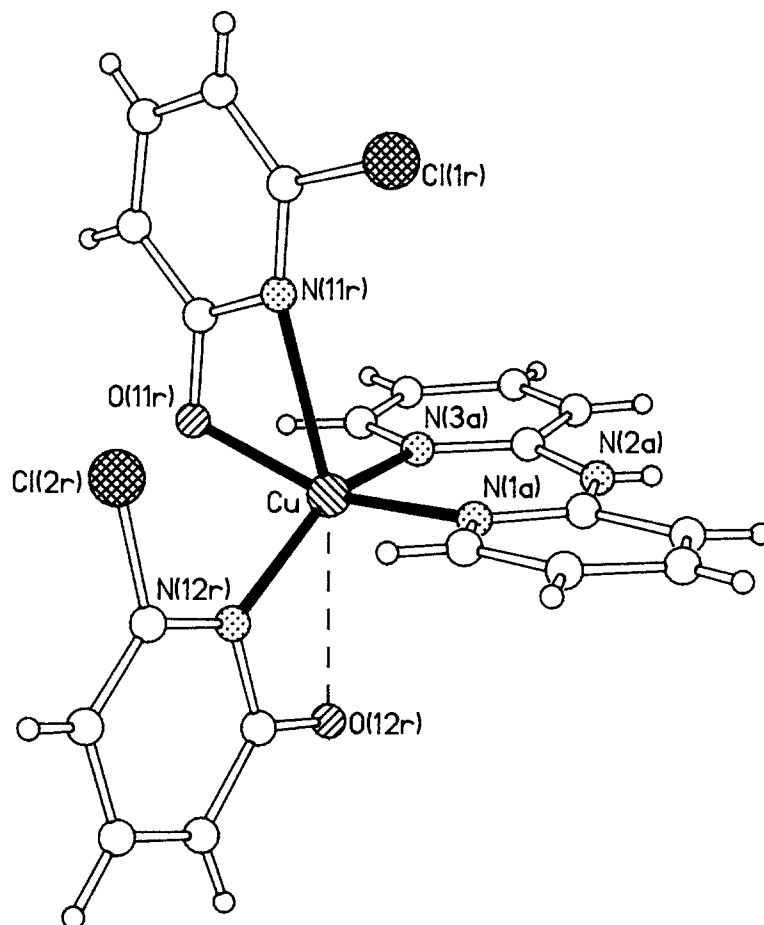
Fig. 1. Crystal structure of Cu(Hdpa)(chp)$_2$ (I) showing atom numbering scheme
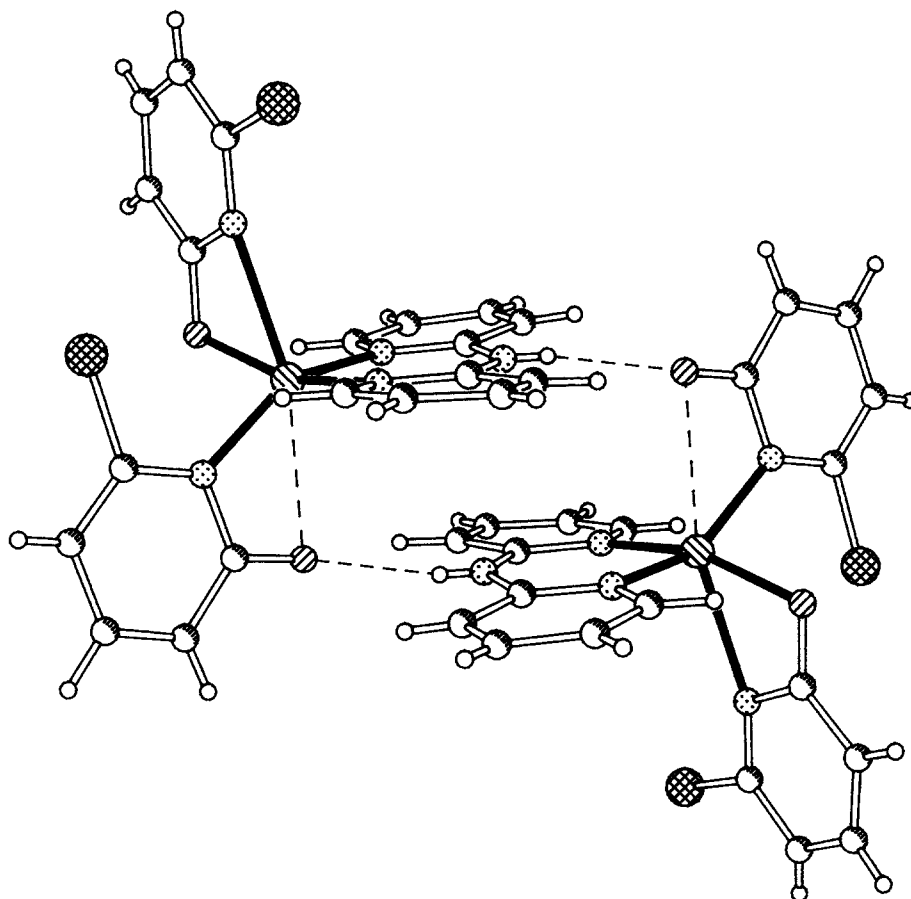
Fig. 2. The dimeric nature of **I**, showing the N—H $\cdots$ O hydrogen bonding.
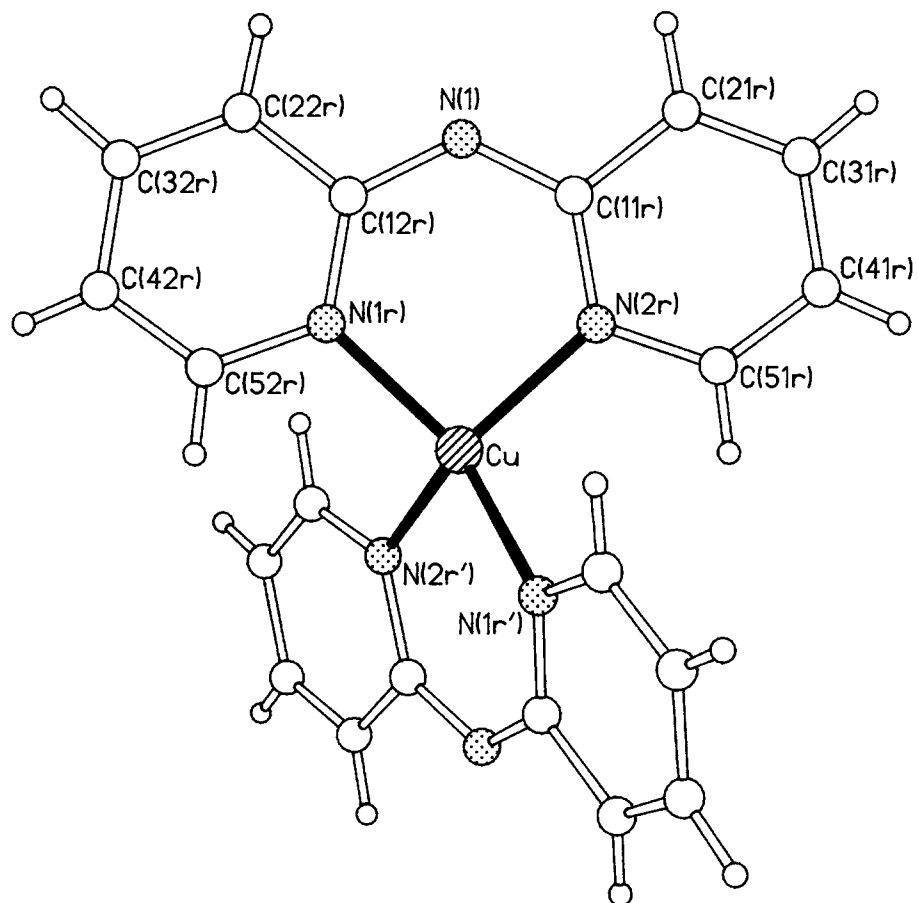
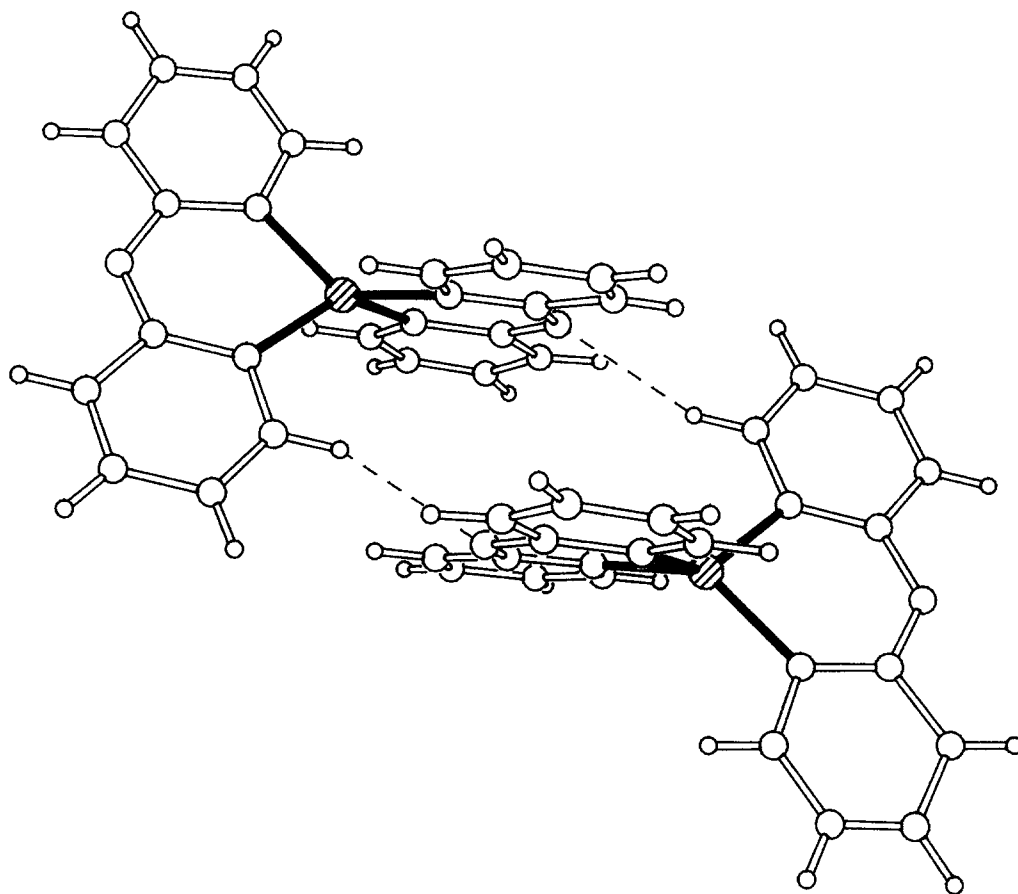Fig. 3. Crystal structure of Cu(dpa)$_2$ (**II**) showing atom numbering scheme.

Fig. 4. Molecular packing in the two forms of Cu(dpa)$_2$: (a) monoclinic $C2/c$ [taken from ref. 8].
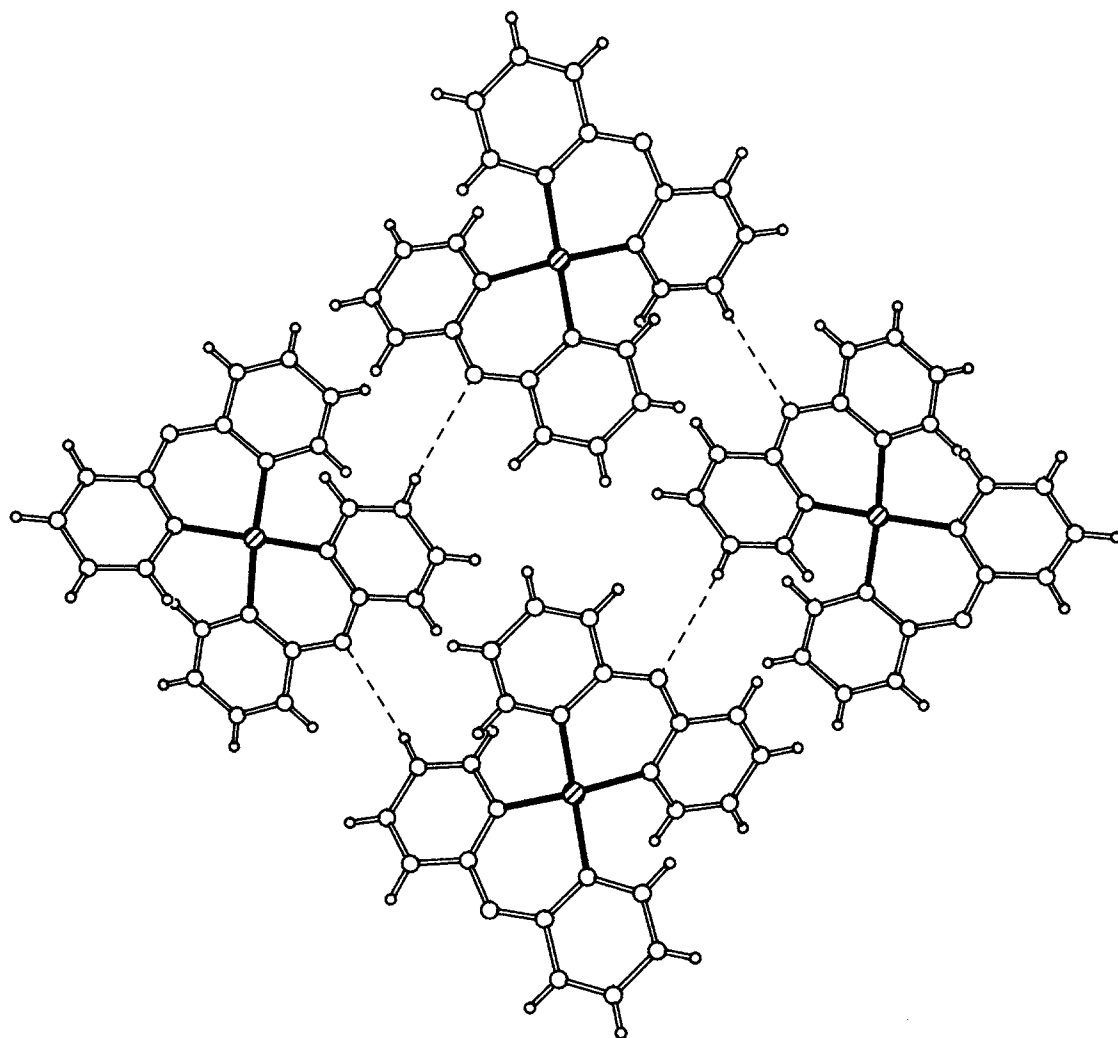
Fig. 4(b). Orthorhombic *Pnaa* [this work].

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