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(meso-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane)-copper(II) bis(O,S-dibenzyl dithiophosphate)

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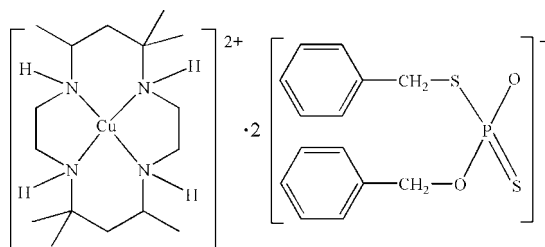
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Key indicators: single-crystal X-ray study; $T = 289$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.051; wR factor = 0.154; data-to-parameter ratio = 16.1.

In the crystal structure of the title compound, $[\text{Cu}(\text{C}_{16}\text{H}_{36}\text{N}_4)](\text{C}_{14}\text{H}_{14}\text{O}_2\text{PS}_2)_2$, the Cu^{II} atom is located on an inversion center and is chelated by four N atoms of the macrocyclic meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ligand in a square-planar geometry, with $\text{Cu}-\text{N}$ distances of 2.013 (3) and 2.014 (3) Å. In the crystal structure, one *O,S*-dibenzyl dithiophosphate counter-anion links with the Cu^{II} complex cation through $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonding. During the synthesis, the structure of the anion re-arranged from *O,O'*-dibenzyl dithiophosphate in the starting material to *O,S*-dibenzyl dithiophosphate in the title compound.

Related literature

For a related Ni^{II} complex, see: Xie *et al.* (2008). For bond-length data, see Allen *et al.* (1987).



Experimental

Crystal data

$[\text{Cu}(\text{C}_{16}\text{H}_{36}\text{N}_4)](\text{C}_{14}\text{H}_{14}\text{O}_2\text{PS}_2)_2$

$M_r = 966.71$

Monoclinic, $P2_1/c$
 $a = 11.476$ (4) Å
 $b = 17.592$ (4) Å
 $c = 11.945$ (4) Å
 $\beta = 99.78$ (2)°
 $V = 2376.4$ (13) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.75$ mm⁻¹
 $T = 289$ K
 $0.44 \times 0.40 \times 0.35$ mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.730$, $T_{\text{max}} = 0.770$
 4797 measured reflections

4420 independent reflections
 2900 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.006$
 3 standard reflections every 300 reflections
 intensity decay: 6.7%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.154$
 $S = 1.04$
 4420 reflections

275 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.45$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.69$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------------------|-------|-------------|-------------|---------------|
| $\text{N1}-\text{H1}\cdots\text{S1}$ | 0.91 | 2.61 | 3.359 (3) | 140 |
| $\text{N2}-\text{H2}\cdots\text{O2}^{\text{i}}$ | 0.91 | 1.85 | 2.762 (4) | 176 |

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2568).

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 Xie, B., Zou, L.-K., He, Y.-G., Feng, J.-S. & Zhang, X.-L. (2008). *Acta Cryst.* **E64**, m622.

supplementary materials

Acta Cryst. (2009). E65, m1022 [doi:10.1107/S1600536809030037]

(*meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) bis(*O,S*-dibenzyl dithiophosphate)

J.-S. Feng, L.-K. Zou, B. Xie and Y. Wu

Comment

As part of an investigation to the tetramine macrocyclic transition metal complexes and their potential applications as artificial enzyme models, we have reported the structures of $[\text{Ni}(\text{tet-a})][\text{S}_2\text{P}(\text{OCH}_2\text{Ph})_2]_2$, where tet-a is a macrocyclic tetramine, *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Xie *et al.*, 2008). Here we report the crystal structure of the corresponding title Cu^{II} compound, $[\text{Cu}(\text{tet-a})][\text{OSP}(\text{OCH}_2\text{Ph})(\text{SCH}_2\text{Ph})]_2$.

In the title crystal structure, the complex cation $[\text{Cu}(\text{tet-a})]^{2+}$ possesses square-planar geometry about the Cu^{II} atom (Fig. 1), which lies across a centre of inversion and is four-coordinated by four N atoms of the tetramine macrocyclic ligand tet-a. All the bond lengths and angles in the adduct are generally within normal ranges (Allen *et al.*, 1987). The two *O,S*-dibenzyl dithiophosphate anions act as counter-ions to balance the charge of the Cu^{II} complex cation, they interact with the complex cation through N—H \cdots O and N—H \cdots S hydrogen bonds (Table 1).

Experimental

A solution of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane dihydrate (0.32 g, 1 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.17 g, 1 mmol) in 20 ml methanol was added to a solution of diethylammonium *O,O'*-dibenzyl dithiophosphate, $[\text{NH}_2(\text{C}_2\text{H}_5)_2]^+[(\text{PhCH}_2\text{O})_2\text{PS}_2]^-$ (Fig. 2), (0.77 g, 2 mmol) in 20 ml methanol. The mixture was refluxed for 24 h, then cooled to room temperature, the dark-violet precipitate was collected by filtration, washed with small amounts of methanol. A solution of the title compound in DMSO was kept at room temperature, and dark-violet block crystals suitable for X-ray diffraction studies were obtained in three months.

It should be noted that the title compound contains an unexpected re-arrangement product of the anion; in the starting reagent, $[\text{NH}_2(\text{C}_2\text{H}_5)_2]^+[(\text{PhCH}_2\text{O})_2\text{PS}_2]^-$, both of the two benzyl-groups bonded with O atoms, but in the title compound one of them migrated to the neighbouring S atom.

Refinement

All H atoms attached to C and N atom were fixed geometrically and treated as riding with C—H = 0.98 Å (methine), 0.97 Å (methylene), 0.96 Å (methyl) or 0.93 Å (aromatic) and N—H = 0.91 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl})$.

Figures

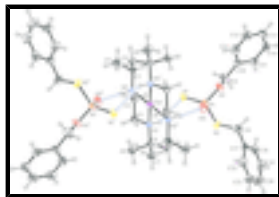


Fig. 1. A view of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen-bonds are shown as dashed lines. H atoms are represented as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1, -y, -z + 1$].

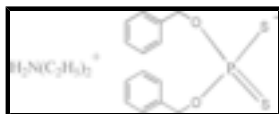


Fig. 2. The starting material $[\text{NH}_2(\text{C}_2\text{H}_5)_2]^+[(\text{PhCH}_2\text{O})_2\text{PS}_2]^-$.

(*meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) bis(*O,S*-dibenzyl dithiophosphate)

Crystal data

$[\text{Cu}(\text{C}_{16}\text{H}_{36}\text{N}_4)](\text{C}_{14}\text{H}_{14}\text{O}_2\text{PS}_2)_2$

$M_r = 966.71$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 11.476\ (4)\ \text{\AA}$

$b = 17.592\ (4)\ \text{\AA}$

$c = 11.945\ (4)\ \text{\AA}$

$\beta = 99.78\ (2)^\circ$

$V = 2376.4\ (13)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 1022$

$D_x = 1.351\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 29 reflections

$\theta = 4.4\text{--}11.5^\circ$

$\mu = 0.75\ \text{mm}^{-1}$

$T = 289\ \text{K}$

Block, dark-violet

$0.44 \times 0.40 \times 0.35\ \text{mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 289\ \text{K}$

$\omega/2\theta$ scans

Absorption correction: ψ scan (North *et al.*, 1968)

$T_{\min} = 0.730, T_{\max} = 0.770$

4797 measured reflections

4420 independent reflections

2900 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.006$

$\theta_{\max} = 25.6^\circ$

$\theta_{\min} = 1.8^\circ$

$h = -13 \rightarrow 13$

$k = 0 \rightarrow 21$

$l = -4 \rightarrow 14$

3 standard reflections

every 300 reflections

intensity decay: 6.7%

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.051$$

$$wR(F^2) = 0.154$$

$$S = 1.04$$

4420 reflections

275 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0968P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.69 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|-------------|----------------------------------|
| Cu1 | 0.5000 | 0.0000 | 0.5000 | 0.0373 (2) |
| S1 | 0.45680 (10) | 0.16085 (8) | 0.65146 (9) | 0.0633 (3) |
| S2 | 0.60091 (9) | 0.16270 (6) | 0.90486 (8) | 0.0523 (3) |
| P1 | 0.46223 (8) | 0.11046 (6) | 0.79879 (8) | 0.0426 (3) |
| O1 | 0.3474 (2) | 0.12698 (17) | 0.8538 (2) | 0.0550 (7) |
| O2 | 0.4729 (3) | 0.02701 (17) | 0.8069 (3) | 0.0610 (8) |
| N1 | 0.6456 (2) | 0.06574 (17) | 0.5164 (2) | 0.0376 (7) |
| H1 | 0.6323 | 0.1022 | 0.5669 | 0.045* |
| N2 | 0.4441 (2) | 0.05885 (17) | 0.3564 (2) | 0.0369 (7) |
| H2 | 0.4682 | 0.0312 | 0.3002 | 0.044* |
| C1 | 0.6406 (3) | 0.1077 (2) | 0.4085 (3) | 0.0475 (9) |
| H1A | 0.6712 | 0.0762 | 0.3535 | 0.057* |
| H1B | 0.6886 | 0.1533 | 0.4211 | 0.057* |
| C2 | 0.5149 (3) | 0.1285 (2) | 0.3647 (3) | 0.0431 (9) |
| H2A | 0.4867 | 0.1642 | 0.4159 | 0.052* |
| H2B | 0.5086 | 0.1522 | 0.2906 | 0.052* |
| C3 | 0.3165 (3) | 0.0731 (2) | 0.3165 (3) | 0.0444 (9) |
| H3 | 0.2894 | 0.1101 | 0.3679 | 0.053* |
| C4 | 0.2455 (3) | 0.0014 (2) | 0.3192 (3) | 0.0480 (9) |
| H4A | 0.2786 | -0.0366 | 0.2747 | 0.058* |
| H4B | 0.1658 | 0.0117 | 0.2804 | 0.058* |
| C5 | 0.2935 (4) | 0.1062 (3) | 0.1966 (4) | 0.0708 (14) |

supplementary materials

| | | | | |
|------|-------------|-------------|------------|-------------|
| H5A | 0.3397 | 0.1514 | 0.1943 | 0.106* |
| H5B | 0.2111 | 0.1183 | 0.1757 | 0.106* |
| H5C | 0.3152 | 0.0695 | 0.1442 | 0.106* |
| C6 | 0.7638 (3) | 0.0344 (2) | 0.5661 (3) | 0.0415 (8) |
| C7 | 0.8558 (4) | 0.0984 (3) | 0.5855 (4) | 0.0667 (13) |
| H7A | 0.8587 | 0.1237 | 0.5149 | 0.100* |
| H7B | 0.9321 | 0.0773 | 0.6147 | 0.100* |
| H7C | 0.8343 | 0.1342 | 0.6392 | 0.100* |
| C8 | 0.8018 (4) | -0.0231 (2) | 0.4853 (4) | 0.0546 (10) |
| H8A | 0.7366 | -0.0559 | 0.4572 | 0.082* |
| H8B | 0.8662 | -0.0528 | 0.5246 | 0.082* |
| H8C | 0.8268 | 0.0029 | 0.4228 | 0.082* |
| C9 | 0.3028 (5) | 0.2003 (3) | 0.8600 (5) | 0.0731 (14) |
| H9A | 0.2887 | 0.2232 | 0.7851 | 0.088* |
| H9B | 0.3597 | 0.2314 | 0.9092 | 0.088* |
| C10 | 0.1885 (3) | 0.1965 (2) | 0.9066 (3) | 0.0476 (9) |
| C11 | 0.1010 (5) | 0.1453 (3) | 0.8683 (4) | 0.0669 (12) |
| H11 | 0.1119 | 0.1113 | 0.8114 | 0.080* |
| C12 | -0.0002 (4) | 0.1428 (3) | 0.9107 (5) | 0.0750 (14) |
| H12 | -0.0577 | 0.1070 | 0.8832 | 0.090* |
| C13 | -0.0188 (4) | 0.1915 (3) | 0.9925 (4) | 0.0703 (14) |
| H13 | -0.0894 | 0.1895 | 1.0208 | 0.084* |
| C14 | 0.0652 (5) | 0.2437 (3) | 1.0342 (4) | 0.0700 (14) |
| H14 | 0.0530 | 0.2772 | 1.0914 | 0.084* |
| C15 | 0.1705 (4) | 0.2460 (2) | 0.9893 (4) | 0.0579 (11) |
| H15 | 0.2284 | 0.2817 | 1.0163 | 0.070* |
| C16 | 0.5930 (4) | 0.1139 (3) | 1.0376 (3) | 0.0676 (14) |
| H16A | 0.5285 | 0.1346 | 1.0710 | 0.081* |
| H16B | 0.5778 | 0.0603 | 1.0230 | 0.081* |
| C17 | 0.7064 (3) | 0.1235 (3) | 1.1178 (3) | 0.0492 (10) |
| C18 | 0.7318 (4) | 0.1904 (3) | 1.1759 (4) | 0.0618 (12) |
| H18 | 0.6778 | 0.2303 | 1.1655 | 0.074* |
| C19 | 0.8376 (6) | 0.1983 (3) | 1.2498 (4) | 0.0812 (17) |
| H19 | 0.8536 | 0.2437 | 1.2893 | 0.097* |
| C20 | 0.9167 (5) | 0.1428 (4) | 1.2658 (4) | 0.0847 (18) |
| H20 | 0.9882 | 0.1496 | 1.3145 | 0.102* |
| C21 | 0.8919 (5) | 0.0752 (3) | 1.2098 (5) | 0.0809 (16) |
| H21 | 0.9456 | 0.0352 | 1.2222 | 0.097* |
| C22 | 0.7873 (4) | 0.0666 (3) | 1.1349 (4) | 0.0663 (12) |
| H22 | 0.7718 | 0.0211 | 1.0955 | 0.080* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|-------------|------------|-------------|
| Cu1 | 0.0326 (3) | 0.0406 (4) | 0.0394 (3) | 0.0051 (3) | 0.0081 (2) | 0.0141 (3) |
| S1 | 0.0623 (7) | 0.0895 (9) | 0.0385 (5) | 0.0165 (6) | 0.0100 (5) | 0.0071 (5) |
| S2 | 0.0512 (6) | 0.0614 (7) | 0.0420 (5) | -0.0119 (5) | 0.0015 (4) | 0.0061 (5) |
| P1 | 0.0407 (5) | 0.0505 (6) | 0.0381 (5) | 0.0035 (4) | 0.0110 (4) | -0.0066 (4) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.0499 (16) | 0.0567 (18) | 0.0628 (17) | 0.0093 (14) | 0.0223 (13) | -0.0028 (14) |
| O2 | 0.083 (2) | 0.0394 (16) | 0.0649 (18) | 0.0009 (15) | 0.0241 (16) | -0.0094 (14) |
| N1 | 0.0390 (15) | 0.0383 (17) | 0.0360 (15) | 0.0010 (13) | 0.0080 (12) | 0.0041 (13) |
| N2 | 0.0401 (15) | 0.0398 (17) | 0.0317 (14) | 0.0087 (13) | 0.0085 (12) | 0.0053 (13) |
| C1 | 0.051 (2) | 0.049 (2) | 0.044 (2) | -0.0070 (18) | 0.0104 (17) | 0.0137 (17) |
| C2 | 0.054 (2) | 0.034 (2) | 0.0422 (19) | 0.0028 (17) | 0.0115 (16) | 0.0112 (16) |
| C3 | 0.040 (2) | 0.045 (2) | 0.047 (2) | 0.0107 (17) | 0.0050 (16) | 0.0115 (17) |
| C4 | 0.041 (2) | 0.056 (2) | 0.045 (2) | 0.0057 (18) | -0.0001 (16) | 0.0022 (18) |
| C5 | 0.060 (3) | 0.088 (4) | 0.059 (3) | 0.010 (3) | -0.003 (2) | 0.036 (3) |
| C6 | 0.0346 (18) | 0.043 (2) | 0.046 (2) | -0.0012 (16) | 0.0029 (15) | 0.0039 (17) |
| C7 | 0.052 (3) | 0.067 (3) | 0.075 (3) | -0.019 (2) | -0.004 (2) | 0.010 (2) |
| C8 | 0.053 (2) | 0.058 (3) | 0.055 (2) | 0.011 (2) | 0.0157 (19) | 0.006 (2) |
| C9 | 0.077 (3) | 0.051 (3) | 0.100 (4) | 0.000 (2) | 0.041 (3) | 0.006 (3) |
| C10 | 0.040 (2) | 0.050 (2) | 0.056 (2) | 0.0059 (18) | 0.0167 (17) | 0.0112 (19) |
| C11 | 0.084 (3) | 0.055 (3) | 0.064 (3) | 0.006 (3) | 0.015 (2) | -0.004 (2) |
| C12 | 0.056 (3) | 0.080 (4) | 0.087 (4) | -0.015 (3) | 0.007 (3) | 0.006 (3) |
| C13 | 0.051 (3) | 0.096 (4) | 0.068 (3) | 0.015 (3) | 0.019 (2) | 0.028 (3) |
| C14 | 0.081 (3) | 0.082 (4) | 0.049 (2) | 0.035 (3) | 0.015 (2) | 0.003 (2) |
| C15 | 0.057 (3) | 0.050 (3) | 0.062 (3) | 0.002 (2) | -0.003 (2) | 0.001 (2) |
| C16 | 0.055 (3) | 0.102 (4) | 0.045 (2) | -0.023 (3) | 0.0031 (19) | 0.018 (2) |
| C17 | 0.046 (2) | 0.063 (3) | 0.039 (2) | -0.013 (2) | 0.0062 (16) | 0.0060 (19) |
| C18 | 0.074 (3) | 0.066 (3) | 0.048 (2) | -0.006 (2) | 0.018 (2) | 0.005 (2) |
| C19 | 0.114 (5) | 0.084 (4) | 0.044 (3) | -0.044 (4) | 0.008 (3) | -0.004 (3) |
| C20 | 0.070 (3) | 0.113 (5) | 0.061 (3) | -0.036 (3) | -0.016 (3) | 0.023 (3) |
| C21 | 0.059 (3) | 0.093 (4) | 0.085 (4) | 0.012 (3) | -0.004 (3) | 0.029 (3) |
| C22 | 0.072 (3) | 0.055 (3) | 0.070 (3) | -0.010 (2) | 0.008 (2) | 0.004 (2) |

Geometric parameters (Å, °)

| | | | |
|---------------------|-------------|---------|-----------|
| Cu1—N2 ⁱ | 2.013 (3) | C7—H7B | 0.9600 |
| Cu1—N2 | 2.013 (3) | C7—H7C | 0.9600 |
| Cu1—N1 ⁱ | 2.014 (3) | C8—H8A | 0.9600 |
| Cu1—N1 | 2.014 (3) | C8—H8B | 0.9600 |
| S1—P1 | 1.9619 (15) | C8—H8C | 0.9600 |
| S2—C16 | 1.818 (4) | C9—C10 | 1.510 (6) |
| S2—P1 | 2.0729 (15) | C9—H9A | 0.9700 |
| P1—O2 | 1.475 (3) | C9—H9B | 0.9700 |
| P1—O1 | 1.596 (3) | C10—C15 | 1.359 (6) |
| O1—C9 | 1.394 (5) | C10—C11 | 1.368 (6) |
| N1—C1 | 1.478 (4) | C11—C12 | 1.344 (7) |
| N1—C6 | 1.491 (4) | C11—H11 | 0.9300 |
| N1—H1 | 0.9100 | C12—C13 | 1.343 (7) |
| N2—C2 | 1.465 (5) | C12—H12 | 0.9300 |
| N2—C3 | 1.482 (4) | C13—C14 | 1.364 (7) |
| N2—H2 | 0.9100 | C13—H13 | 0.9300 |
| C1—C2 | 1.493 (5) | C14—C15 | 1.404 (7) |
| C1—H1A | 0.9700 | C14—H14 | 0.9300 |
| C1—H1B | 0.9700 | C15—H15 | 0.9300 |
| C2—H2A | 0.9700 | C16—C17 | 1.489 (5) |

supplementary materials

| | | | |
|--------------------------------------|-------------|------------------------|-----------|
| C2—H2B | 0.9700 | C16—H16A | 0.9700 |
| C3—C4 | 1.506 (5) | C16—H16B | 0.9700 |
| C3—C5 | 1.527 (5) | C17—C22 | 1.356 (6) |
| C3—H3 | 0.9800 | C17—C18 | 1.372 (6) |
| C4—C6 ⁱ | 1.528 (5) | C18—C19 | 1.382 (7) |
| C4—H4A | 0.9700 | C18—H18 | 0.9300 |
| C4—H4B | 0.9700 | C19—C20 | 1.325 (8) |
| C5—H5A | 0.9600 | C19—H19 | 0.9300 |
| C5—H5B | 0.9600 | C20—C21 | 1.370 (8) |
| C5—H5C | 0.9600 | C20—H20 | 0.9300 |
| C6—C8 | 1.513 (5) | C21—C22 | 1.379 (7) |
| C6—C4 ⁱ | 1.528 (5) | C21—H21 | 0.9300 |
| C6—C7 | 1.533 (5) | C22—H22 | 0.9300 |
| C7—H7A | 0.9600 | | |
| N2 ⁱ —Cu1—N2 | 180.0 | C4 ⁱ —C6—C7 | 108.6 (3) |
| N2 ⁱ —Cu1—N1 ⁱ | 85.80 (11) | C6—C7—H7A | 109.5 |
| N2—Cu1—N1 ⁱ | 94.20 (12) | C6—C7—H7B | 109.5 |
| N2 ⁱ —Cu1—N1 | 94.20 (12) | H7A—C7—H7B | 109.5 |
| N2—Cu1—N1 | 85.80 (11) | C6—C7—H7C | 109.5 |
| N1 ⁱ —Cu1—N1 | 180.0 | H7A—C7—H7C | 109.5 |
| C16—S2—P1 | 100.18 (15) | H7B—C7—H7C | 109.5 |
| O2—P1—O1 | 102.66 (17) | C6—C8—H8A | 109.5 |
| O2—P1—S1 | 119.89 (13) | C6—C8—H8B | 109.5 |
| O1—P1—S1 | 112.60 (12) | H8A—C8—H8B | 109.5 |
| O2—P1—S2 | 110.77 (14) | C6—C8—H8C | 109.5 |
| O1—P1—S2 | 105.65 (12) | H8A—C8—H8C | 109.5 |
| S1—P1—S2 | 104.60 (7) | H8B—C8—H8C | 109.5 |
| C9—O1—P1 | 121.8 (3) | O1—C9—C10 | 109.2 (4) |
| C1—N1—C6 | 115.4 (3) | O1—C9—H9A | 109.8 |
| C1—N1—Cu1 | 107.0 (2) | C10—C9—H9A | 109.8 |
| C6—N1—Cu1 | 120.7 (2) | O1—C9—H9B | 109.8 |
| C1—N1—H1 | 103.9 | C10—C9—H9B | 109.8 |
| C6—N1—H1 | 103.9 | H9A—C9—H9B | 108.3 |
| Cu1—N1—H1 | 103.9 | C15—C10—C11 | 118.1 (4) |
| C2—N2—C3 | 112.7 (3) | C15—C10—C9 | 119.2 (4) |
| C2—N2—Cu1 | 106.3 (2) | C11—C10—C9 | 122.6 (4) |
| C3—N2—Cu1 | 121.0 (2) | C12—C11—C10 | 121.9 (5) |
| C2—N2—H2 | 105.2 | C12—C11—H11 | 119.1 |
| C3—N2—H2 | 105.2 | C10—C11—H11 | 119.1 |
| Cu1—N2—H2 | 105.2 | C13—C12—C11 | 120.5 (5) |
| N1—C1—C2 | 108.7 (3) | C13—C12—H12 | 119.8 |
| N1—C1—H1A | 110.0 | C11—C12—H12 | 119.8 |
| C2—C1—H1A | 110.0 | C12—C13—C14 | 120.4 (4) |
| N1—C1—H1B | 110.0 | C12—C13—H13 | 119.8 |
| C2—C1—H1B | 110.0 | C14—C13—H13 | 119.8 |
| H1A—C1—H1B | 108.3 | C13—C14—C15 | 118.7 (4) |
| N2—C2—C1 | 108.1 (3) | C13—C14—H14 | 120.7 |

| | | | |
|-------------------------|-----------|---------------|-----------|
| N2—C2—H2A | 110.1 | C15—C14—H14 | 120.7 |
| C1—C2—H2A | 110.1 | C10—C15—C14 | 120.4 (4) |
| N2—C2—H2B | 110.1 | C10—C15—H15 | 119.8 |
| C1—C2—H2B | 110.1 | C14—C15—H15 | 119.8 |
| H2A—C2—H2B | 108.4 | C17—C16—S2 | 109.9 (3) |
| N2—C3—C4 | 111.1 (3) | C17—C16—H16A | 109.7 |
| N2—C3—C5 | 111.7 (3) | S2—C16—H16A | 109.7 |
| C4—C3—C5 | 109.3 (3) | C17—C16—H16B | 109.7 |
| N2—C3—H3 | 108.2 | S2—C16—H16B | 109.7 |
| C4—C3—H3 | 108.2 | H16A—C16—H16B | 108.2 |
| C5—C3—H3 | 108.2 | C22—C17—C18 | 118.4 (4) |
| C3—C4—C6 ⁱ | 119.0 (3) | C22—C17—C16 | 120.9 (4) |
| C3—C4—H4A | 107.6 | C18—C17—C16 | 120.6 (4) |
| C6 ⁱ —C4—H4A | 107.6 | C17—C18—C19 | 119.8 (5) |
| C3—C4—H4B | 107.6 | C17—C18—H18 | 120.1 |
| C6 ⁱ —C4—H4B | 107.6 | C19—C18—H18 | 120.1 |
| H4A—C4—H4B | 107.0 | C20—C19—C18 | 121.6 (5) |
| C3—C5—H5A | 109.5 | C20—C19—H19 | 119.2 |
| C3—C5—H5B | 109.5 | C18—C19—H19 | 119.2 |
| H5A—C5—H5B | 109.5 | C19—C20—C21 | 119.3 (5) |
| C3—C5—H5C | 109.5 | C19—C20—H20 | 120.3 |
| H5A—C5—H5C | 109.5 | C21—C20—H20 | 120.3 |
| H5B—C5—H5C | 109.5 | C20—C21—C22 | 119.8 (5) |
| N1—C6—C8 | 109.6 (3) | C20—C21—H21 | 120.1 |
| N1—C6—C4 ⁱ | 108.1 (3) | C22—C21—H21 | 120.1 |
| C8—C6—C4 ⁱ | 111.6 (3) | C17—C22—C21 | 121.0 (5) |
| N1—C6—C7 | 110.2 (3) | C17—C22—H22 | 119.5 |
| C8—C6—C7 | 108.8 (3) | C21—C22—H22 | 119.5 |

Symmetry codes: (i) $-x+1, -y, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------|-------|-------------|-------------|---------------|
| N1—H1 \cdots S1 | 0.91 | 2.61 | 3.359 (3) | 140 |
| N2—H2 \cdots O2 ⁱ | 0.91 | 1.85 | 2.762 (4) | 176 |

Symmetry codes: (i) $-x+1, -y, -z+1$.

Fig. 2

