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# (2,2′-Bipyridine-$\kappa^2N,N'$)iodido(piperidine-1-carbodithioato-$\kappa^2S,S'$)copper(II)

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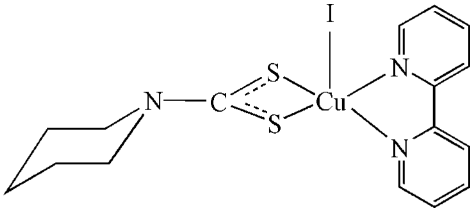
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.008 Å; $R$ factor = 0.047; $wR$ factor = 0.108; data-to-parameter ratio = 19.0.

In the title compound, [Cu($C_6H_{10}NS_2$)I($C_{10}H_8N_2$)], the $Cu^{II}$ ion is coordinated by one iodide ion, two N atoms of the bipyridine ligand and two S atoms from the piperidinecarbodithioate ligand in a distorted square-pyramidal environment. $\pi$–$\pi$ stacking interactions, with centroid–centroid distances of 3.643 (4) Å, between pyridyl rings of the bipyridyl ligands of neighbouring molecules lead to chains propagating parallel to the $a$ axis.

## Related literature

For background to transition metal complexes, see: Engelhardt *et al.* (1988); Fernández *et al.* (2000); Koh *et al.* (2003); Noro *et al.* (2000); Yaghi *et al.* (1998).



## Experimental

### *Crystal data*

[Cu($C_6H_{10}NS_2$)I($C_{10}H_8N_2$)]
$M_r$ = 506.89
Monoclinic, $P2_1/c$
$a$ = 6.532 (3) Å
$b$ = 16.859 (7) Å
$c$ = 17.578 (7) Å
$\beta$ = 108.047 (14)°
$V$ = 1840.5 (14) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 3.09 mm$^{-1}$
$T$ = 293 (2) K
0.45 × 0.08 × 0.05 mm

### *Data collection*

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000) $T_{\min}$ = 0.751, $T_{\max}$ = 1.000 (expected range = 0.643–0.857)
13746 measured reflections
3946 independent reflections
3389 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.036

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.108
$S$ = 1.08
3946 reflections
208 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.52 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.63 e Å$^{-3}$

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2153).

## References

Engelhardt, L. M., Healy, P. C., Shephard, R. M., Skelton, B. W. & White, A. H. (1988). *Inorg. Chem.* **27**, 2371–2373.
Fernández, E. J., López-de-Luzuriaga, J. M., Monge, M., Olmos, E., Laguna, A., Villacampa, M. D. & Jones, P. G. (2000). *J. Cluster Sci.* **11**, 153–167.
Koh, Y. W., Lai, C. S., Du, A. Y., Tiekink, E. R. T. & Loh, K. P. (2003). *Chem. Mater.* **15**, 4544–4554.
Noro, S., Kitagawa, S., Kondo, M. & Seki, K. (2000). *Angew. Chem. Int. Ed.* **39**, 2081–2084.
Rigaku (2000). *CrystalClear*. Rigaku Corporation, Akishima, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Yaghi, O. M., Li, H., Davis, C., Richardson, D. & Groy, T. L. (1998). *Acc. Chem. Res.* **31**, 474–484.

# supplementary materials

*Acta Cryst.* (2009). E**65**, m6 [ **doi:10.1107/S1600536808039901** ]

# (2,2'-Bipyridine-$\kappa^2N,N'$)iodido(piperidine-1-carbodithioato-$\kappa^2S,S'$)copper(II)

**L.-Q. Fan**

## Comment

Research into transition metal complexes has been rapidly expanding because of their fascinating structural diversity, as well as their potential applications as functional materials and enzymes (Noro *et al.*, 2000; Yaghi *et al.*, 1998). Dialkyldithiocarbamate anions, which are typical sulfur ligands, acting as monodentate, bidentate or bridging ligands, are often chosen for the preparation of complexes with a considerable structural variety (Engelhardt *et al.*, 1988; Fernández *et al.*, 2000; Koh *et al.*, 2003). I report here the crystal structure of the title copper(II) complex, (I), containing a piperidyldithiocarbamate ligand.

The crystal structure of (I) is built of discrete molecules of the $Cu^{II}$ complex (Fig. 1). The $Cu^{II}$ ion is five-coordinated in a distorted square-pyramidal environment by one I atom in the apical position, two N atoms from the bipyridine ligand and two S atoms from the piperidyldithiocarbamate ligand in the basal plane (Table 1).

There is a π-π stacking interaction between the pyridyl rings R1 [N(2)/C(7)–C(11)] and R2 [N3/C(12)–C(16)] with a centroid-to-centroid distance of 3.643 (4) Å. These face-to-face interactions result in the complexes assembling into chains.

## Experimental

A mixture of $Cu(Ac)_2.H_2O$ (0.08 g, 0.4 mmol), $NaS_2CNC_5H_{10}.2H_2O$ (0.09 g, 0.4 mmol), 2,2'-bipyridine (0.06 g 0.4 mmol) and $NaI.2H_2O$ (0.07 g, 0.4 mmol) was stirred in DMF (15 ml). 2-PrOH was diffused into the resulting solution, yielding single crystals of (I).

## Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 (aromatic) or 0.97 Å (piperidyl); $U_{iso}(H) = 1.2U_{eq}(C)$.

## Figures

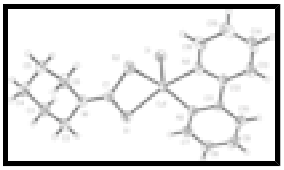


Fig. 1. The molecular structure of (I), showing the atom-labelling scheme, with 30% probability displacement ellipsoids.

## (2,2'-Bipyridine-κ$^2$*N*,*N'*)iodido(piperidine-1- carbodithioato-κ$^2$*S*,*S'*)copper(II)

### *Crystal data*

| | |
|---|---|
| $[Cu(C_6H_{10}NS_2)I(C_{10}H_8N_2)]$ | $F_{000}$ = 996 |
| $M_r$ = 506.89 | $D_x$ = 1.829 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo *K*α radiation<br>λ = 0.71073 Å |
| Hall symbol: -P 2ybc | Cell parameters from 3988 reflections |
| *a* = 6.532 (3) Å | θ = 3.3–27.5° |
| *b* = 16.859 (7) Å | μ = 3.09 mm$^{-1}$ |
| *c* = 17.578 (7) Å | *T* = 293 (2) K |
| β = 108.047 (14)° | Prism, black |
| *V* = 1840.5 (14) Å$^3$ | 0.45 × 0.08 × 0.05 mm |
| *Z* = 4 | |

### *Data collection*

| | |
|---|---|
| Rigaku Mercury CCD diffractometer | 3946 independent reflections |
| Radiation source: Sealed Tube | 3389 reflections with $I > 2\sigma(I)$ |
| Monochromator: Graphite Monochromator | $R_{int}$ = 0.036 |
| *T* = 293(2) K | $\theta_{max}$ = 27.5° |
| ω scans | $\theta_{min}$ = 2.4° |
| Absorption correction: Multi-scan (CrystalClear; Rigaku,2000) | *h* = −8→6 |
| $T_{min}$ = 0.751, $T_{max}$ = 1.000 | *k* = −21→21 |
| 13746 measured reflections | *l* = −22→22 |

### *Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.047 | H-atom parameters constrained |
| $wR(F^2)$ = 0.108 | $w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 2.8277P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| *S* = 1.09 | $(\Delta/\sigma)_{max}$ = 0.001 |
| 3946 reflections | $\Delta\rho_{max}$ = 0.52 e Å$^{-3}$ |
| 208 parameters | $\Delta\rho_{min}$ = −0.63 e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{\text{iso}}$*/$U_{\text{eq}}$ |
|---|---|---|---|---|
| Cu1 | 0.43714 (10) | 0.66212 (3) | 0.42086 (3) | 0.04099 (17) |
| I1 | 0.19321 (6) | 0.80141 (2) | 0.36188 (2) | 0.05420 (14) |
| S1 | 0.6396 (2) | 0.64039 (8) | 0.33518 (8) | 0.0502 (3) |
| S2 | 0.2619 (3) | 0.55763 (9) | 0.34096 (8) | 0.0586 (4) |
| N1 | 0.4731 (7) | 0.5184 (2) | 0.2378 (2) | 0.0423 (9) |
| N2 | 0.6611 (7) | 0.7232 (2) | 0.5076 (2) | 0.0401 (9) |
| N3 | 0.3271 (7) | 0.6421 (2) | 0.5154 (2) | 0.0420 (9) |
| C1 | 0.4607 (8) | 0.5651 (3) | 0.2965 (3) | 0.0386 (10) |
| C2 | 0.6306 (8) | 0.5319 (3) | 0.1943 (3) | 0.0496 (12) |
| H2A | 0.7044 | 0.4828 | 0.1907 | 0.059* |
| H2B | 0.7370 | 0.5706 | 0.2225 | 0.059* |
| C3 | 0.5104 (9) | 0.5620 (3) | 0.1113 (3) | 0.0556 (14) |
| H3A | 0.6106 | 0.5693 | 0.0811 | 0.067* |
| H3B | 0.4459 | 0.6130 | 0.1154 | 0.067* |
| C4 | 0.3347 (10) | 0.5035 (4) | 0.0674 (3) | 0.0620 (15) |
| H4A | 0.2530 | 0.5255 | 0.0160 | 0.074* |
| H4B | 0.4004 | 0.4544 | 0.0578 | 0.074* |
| C5 | 0.1852 (9) | 0.4865 (3) | 0.1159 (3) | 0.0533 (13) |
| H5A | 0.1057 | 0.5342 | 0.1194 | 0.064* |
| H5B | 0.0822 | 0.4461 | 0.0891 | 0.064* |
| C6 | 0.3075 (9) | 0.4585 (3) | 0.1993 (3) | 0.0499 (13) |
| H6A | 0.2094 | 0.4515 | 0.2304 | 0.060* |
| H6B | 0.3757 | 0.4079 | 0.1966 | 0.060* |
| C7 | 0.8254 (8) | 0.7641 (3) | 0.4972 (3) | 0.0464 (12) |
| H7A | 0.8406 | 0.7663 | 0.4464 | 0.056* |
| C8 | 0.9733 (9) | 0.8031 (3) | 0.5591 (3) | 0.0537 (13) |
| H8A | 1.0845 | 0.8323 | 0.5503 | 0.064* |
| C9 | 0.9520 (10) | 0.7979 (3) | 0.6347 (4) | 0.0615 (16) |
| H9A | 1.0515 | 0.8226 | 0.6777 | 0.074* |
| C10 | 0.7829 (9) | 0.7558 (3) | 0.6462 (3) | 0.0553 (14) |
| H10A | 0.7675 | 0.7519 | 0.6969 | 0.066* |
| C11 | 0.6367 (8) | 0.7197 (3) | 0.5814 (3) | 0.0430 (11) |
| C12 | 0.4453 (9) | 0.6746 (3) | 0.5851 (3) | 0.0417 (11) |

| | | | | |
|---|---|---|---|---|
| C13 | 0.3853 (10) | 0.6676 (3) | 0.6542 (3) | 0.0528 (13) |
| H13A | 0.4662 | 0.6917 | 0.7016 | 0.063* |
| C14 | 0.2037 (10) | 0.6243 (3) | 0.6510 (3) | 0.0587 (15) |
| H14A | 0.1636 | 0.6173 | 0.6970 | 0.070* |
| C15 | 0.0828 (10) | 0.5918 (3) | 0.5800 (4) | 0.0614 (16) |
| H15A | −0.0417 | 0.5634 | 0.5769 | 0.074* |
| C16 | 0.1483 (9) | 0.6016 (3) | 0.5129 (3) | 0.0515 (13) |
| H16A | 0.0661 | 0.5794 | 0.4646 | 0.062* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0480 (4) | 0.0472 (3) | 0.0298 (3) | −0.0078 (3) | 0.0150 (3) | −0.0058 (2) |
| I1 | 0.0605 (3) | 0.0538 (2) | 0.0489 (2) | 0.00754 (16) | 0.01783 (18) | 0.01277 (15) |
| S1 | 0.0491 (8) | 0.0629 (8) | 0.0430 (6) | −0.0169 (6) | 0.0207 (6) | −0.0195 (6) |
| S2 | 0.0670 (10) | 0.0688 (8) | 0.0495 (7) | −0.0287 (7) | 0.0322 (7) | −0.0201 (6) |
| N1 | 0.043 (3) | 0.048 (2) | 0.0346 (19) | −0.0025 (18) | 0.0103 (18) | −0.0079 (16) |
| N2 | 0.043 (3) | 0.0428 (19) | 0.0308 (18) | 0.0023 (17) | 0.0068 (17) | −0.0013 (15) |
| N3 | 0.057 (3) | 0.0387 (19) | 0.0343 (19) | 0.0032 (18) | 0.0195 (18) | 0.0019 (15) |
| C1 | 0.044 (3) | 0.040 (2) | 0.031 (2) | −0.002 (2) | 0.011 (2) | −0.0012 (17) |
| C2 | 0.043 (3) | 0.062 (3) | 0.042 (3) | −0.001 (2) | 0.011 (2) | −0.017 (2) |
| C3 | 0.060 (4) | 0.066 (3) | 0.042 (3) | −0.010 (3) | 0.019 (3) | −0.003 (2) |
| C4 | 0.069 (4) | 0.070 (4) | 0.038 (3) | −0.011 (3) | 0.003 (3) | −0.004 (3) |
| C5 | 0.056 (4) | 0.045 (3) | 0.047 (3) | −0.010 (2) | −0.001 (3) | −0.001 (2) |
| C6 | 0.065 (4) | 0.040 (2) | 0.042 (3) | −0.012 (2) | 0.013 (2) | −0.007 (2) |
| C7 | 0.047 (3) | 0.048 (3) | 0.044 (3) | −0.005 (2) | 0.013 (2) | −0.002 (2) |
| C8 | 0.048 (3) | 0.048 (3) | 0.058 (3) | −0.002 (2) | 0.005 (3) | −0.008 (2) |
| C9 | 0.060 (4) | 0.053 (3) | 0.054 (3) | 0.001 (3) | −0.008 (3) | −0.019 (3) |
| C10 | 0.067 (4) | 0.052 (3) | 0.037 (3) | 0.012 (3) | 0.003 (3) | −0.007 (2) |
| C11 | 0.050 (3) | 0.044 (2) | 0.030 (2) | 0.014 (2) | 0.006 (2) | −0.0001 (18) |
| C12 | 0.058 (3) | 0.042 (2) | 0.027 (2) | 0.012 (2) | 0.016 (2) | 0.0019 (17) |
| C13 | 0.071 (4) | 0.054 (3) | 0.037 (3) | 0.017 (3) | 0.022 (3) | 0.010 (2) |
| C14 | 0.085 (5) | 0.058 (3) | 0.046 (3) | 0.021 (3) | 0.038 (3) | 0.013 (2) |
| C15 | 0.082 (4) | 0.046 (3) | 0.073 (4) | 0.007 (3) | 0.048 (3) | 0.006 (3) |
| C16 | 0.067 (4) | 0.045 (3) | 0.052 (3) | −0.004 (2) | 0.033 (3) | −0.004 (2) |

*Geometric parameters (Å, °)*

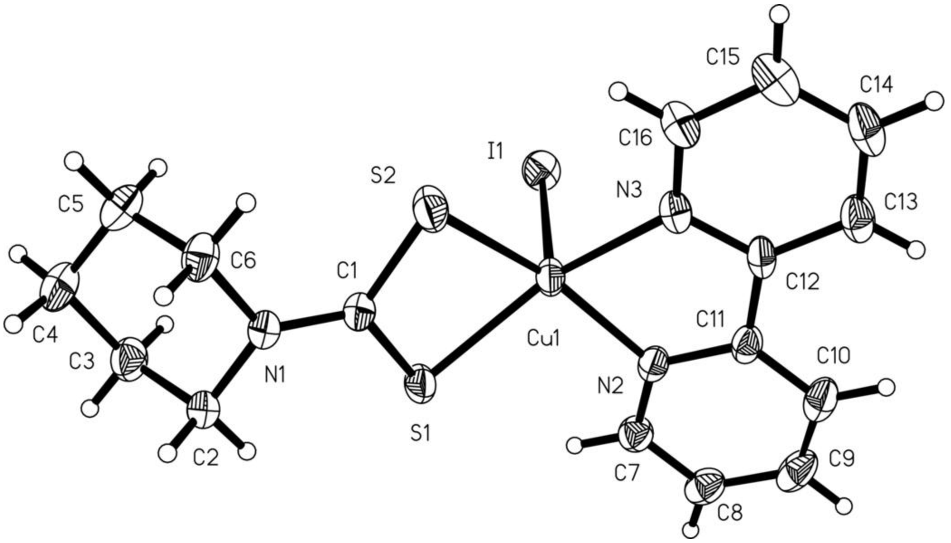
| | | | |
|---|---|---|---|
| Cu1—N3 | 2.033 (4) | C5—C6 | 1.510 (7) |
| Cu1—N2 | 2.035 (4) | C5—H5A | 0.9700 |
| Cu1—S1 | 2.3205 (15) | C5—H5B | 0.9700 |
| Cu1—S2 | 2.3218 (15) | C6—H6A | 0.9700 |
| Cu1—I1 | 2.8470 (11) | C6—H6B | 0.9700 |
| S1—C1 | 1.717 (5) | C7—C8 | 1.379 (7) |
| S2—C1 | 1.716 (5) | C7—H7A | 0.9300 |
| N1—C1 | 1.320 (6) | C8—C9 | 1.380 (8) |
| N1—C2 | 1.476 (6) | C8—H8A | 0.9300 |
| N1—C6 | 1.482 (6) | C9—C10 | 1.379 (9) |
| N2—C7 | 1.335 (6) | C9—H9A | 0.9300 |

| | | | |
|---|---|---|---|
| N2—C11 | 1.357 (6) | C10—C11 | 1.380 (7) |
| N3—C16 | 1.342 (6) | C10—H10A | 0.9300 |
| N3—C12 | 1.345 (6) | C11—C12 | 1.481 (7) |
| C2—C3 | 1.514 (7) | C12—C13 | 1.392 (6) |
| C2—H2A | 0.9700 | C13—C14 | 1.380 (8) |
| C2—H2B | 0.9700 | C13—H13A | 0.9300 |
| C3—C4 | 1.529 (7) | C14—C15 | 1.369 (8) |
| C3—H3A | 0.9700 | C14—H14A | 0.9300 |
| C3—H3B | 0.9700 | C15—C16 | 1.384 (7) |
| C4—C5 | 1.511 (8) | C15—H15A | 0.9300 |
| C4—H4A | 0.9700 | C16—H16A | 0.9300 |
| C4—H4B | 0.9700 | | |

| | | | |
|---|---|---|---|
| N3—Cu1—N2 | 79.95 (16) | C6—C5—C4 | 111.5 (5) |
| N3—Cu1—S1 | 157.11 (12) | C6—C5—H5A | 109.3 |
| N2—Cu1—S1 | 98.30 (12) | C4—C5—H5A | 109.3 |
| N3—Cu1—S2 | 97.80 (12) | C6—C5—H5B | 109.3 |
| N2—Cu1—S2 | 160.43 (12) | C4—C5—H5B | 109.3 |
| S1—Cu1—S2 | 76.17 (5) | H5A—C5—H5B | 108.0 |
| N3—Cu1—I1 | 97.76 (11) | N1—C6—C5 | 108.8 (4) |
| N2—Cu1—I1 | 92.69 (11) | N1—C6—H6A | 109.9 |
| S1—Cu1—I1 | 105.13 (5) | C5—C6—H6A | 109.9 |
| S2—Cu1—I1 | 106.86 (6) | N1—C6—H6B | 109.9 |
| C1—S1—Cu1 | 85.37 (16) | C5—C6—H6B | 109.9 |
| C1—S2—Cu1 | 85.37 (16) | H6A—C6—H6B | 108.3 |
| C1—N1—C2 | 122.3 (4) | N2—C7—C8 | 122.3 (5) |
| C1—N1—C6 | 123.4 (4) | N2—C7—H7A | 118.8 |
| C2—N1—C6 | 113.3 (4) | C8—C7—H7A | 118.8 |
| C7—N2—C11 | 119.4 (4) | C7—C8—C9 | 118.3 (6) |
| C7—N2—Cu1 | 125.5 (3) | C7—C8—H8A | 120.8 |
| C11—N2—Cu1 | 115.1 (3) | C9—C8—H8A | 120.8 |
| C16—N3—C12 | 119.0 (4) | C10—C9—C8 | 119.9 (5) |
| C16—N3—Cu1 | 125.6 (3) | C10—C9—H9A | 120.1 |
| C12—N3—Cu1 | 115.4 (3) | C8—C9—H9A | 120.1 |
| N1—C1—S2 | 123.5 (4) | C9—C10—C11 | 119.2 (5) |
| N1—C1—S1 | 123.5 (4) | C9—C10—H10A | 120.4 |
| S2—C1—S1 | 113.1 (2) | C11—C10—H10A | 120.4 |
| N1—C2—C3 | 108.3 (4) | N2—C11—C10 | 120.9 (5) |
| N1—C2—H2A | 110.0 | N2—C11—C12 | 114.5 (4) |
| C3—C2—H2A | 110.0 | C10—C11—C12 | 124.7 (5) |
| N1—C2—H2B | 110.0 | N3—C12—C13 | 121.5 (5) |
| C3—C2—H2B | 110.0 | N3—C12—C11 | 115.1 (4) |
| H2A—C2—H2B | 108.4 | C13—C12—C11 | 123.4 (5) |
| C2—C3—C4 | 110.8 (4) | C14—C13—C12 | 118.7 (5) |
| C2—C3—H3A | 109.5 | C14—C13—H13A | 120.6 |
| C4—C3—H3A | 109.5 | C12—C13—H13A | 120.6 |
| C2—C3—H3B | 109.5 | C15—C14—C13 | 119.6 (5) |
| C4—C3—H3B | 109.5 | C15—C14—H14A | 120.2 |
| H3A—C3—H3B | 108.1 | C13—C14—H14A | 120.2 |
| C5—C4—C3 | 110.6 (4) | C14—C15—C16 | 119.1 (6) |

| | | | |
|---|---|---|---|
| C5—C4—H4A | 109.5 | C14—C15—H15A | 120.4 |
| C3—C4—H4A | 109.5 | C16—C15—H15A | 120.4 |
| C5—C4—H4B | 109.5 | N3—C16—C15 | 121.9 (5) |
| C3—C4—H4B | 109.5 | N3—C16—H16A | 119.1 |
| H4A—C4—H4B | 108.1 | C15—C16—H16A | 119.1 |

**Fig. 1**


C15
C14
C16
I1
S2
N3
C13
C5
C6
C1
C12
Cu1
C11
C10
C4
C3
N1
N2
S1
C9
C2
C7
C8