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Jahn–Teller distorted copper(II) in poly[bis(μ-4,4′-bipyridine)tetra-μ-cyanido-copper(II)disilver(I)]

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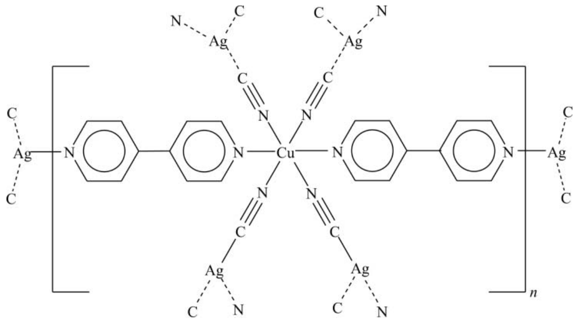
Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.005 Å; R factor = 0.024; wR factor = 0.065; data-to-parameter ratio = 14.1.

The title compound, $[Ag_2Cu(CN)_4(C_{10}H_8N_2)_2]_n$, contains a three-dimensional doubly penetrating framework structure composed of copper(II) bridged by 4,4′-bipyridine and dicyanoargentate groups. The Cu atom is located on an inversion center and is coordinated by six N atoms in a distorted tetragonal–bipyramidal geometry as a result of a significant Jahn–Teller distortion. The equatorial plane of Cu is coordinated by two bridging bipyridine ligands and two N-bound dicyanoargentate anions, while the axial positions are occupied by two N atoms from bridging dicyanoargentate anions. A three-coordinate Ag atom is present, due to two Ag—C bonds and one longer Ag—N interaction.

Related literature

For related literature, see: Dong *et al.* (2003); Lefebvre & Leznoff (2005); Niel *et al.* (2002); Potočňák *et al.* (2003); Shorrock *et al.* (2002); Soma *et al.* (1994); Triščíková *et al.* (2004); Černák *et al.* (1993, 2002).



Experimental

Crystal data

$[Ag_2Cu(CN)_4(C_{10}H_8N_2)_2]$
M_r = 695.73
Monoclinic, $P2_1/n$
a = 8.9056 (9) Å
b = 11.4712 (10) Å
c = 12.5918 (11) Å
β = 106.484 (8)°
V = 1233.5 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.46 mm^{-1}
T = 290 (2) K
1.00 × 0.51 × 0.42 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.255, $T_{\max}$ = 0.353
2418 measured reflections
2267 independent reflections
1969 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.065
S = 1.11
2267 reflections
161 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.45 e Å^{-3}
$\Delta\rho_{\min}$ = −0.38 e Å^{-3}

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2236).

References

Bruker (1998). *SHELXTL*. Version 5.1 for Windows. Bruker AXS Inc., Madison, Wisconsin, USA.
Černák, J., Gérard, F. & Chomič, J. (1993). *Acta Cryst.* C**49**, 1294–1296.
Černák, J., Orendáč, M., Potočňák, I., Chomič, J., Orendáčová, A., Skoršepa, J. & Feher, A. (2002). *Coord. Chem. Rev.* **224**, 51–66.
Dong, W., Wang, Q.-L., Si, S.-F., Liao, D.-Z., Jiang, Z.-H., Yan, S.-P. & Cheng, P. (2003). *Inorg. Chem. Commun.* **6**, 873–876.
Enraf–Nonius (1993). *CAD-4-PC Software*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1996). *XCAD4*. University of Marburg, Germany.
Lefebvre, J. & Leznoff, D. B. (2005). *Macromolecules Containing Metal and Metal-Like Elements*, Vol. 5, *Metal-Coordination Polymers*, edited by A. S. Abd-El-Aziz, C. E. Carraher Jr, C. U. Pittman Jr & M. Zeldin, pp. 155–208. London: John Wiley and Sons Ltd.
Niel, V., Muñoz, M. C., Gaspar, A. B., Galet, A., Levchenko, G. & Real, J. A. (2002). *Chem. Eur. J.* **8**, 2446–2453.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Potočňák, I., Triščíková, Ľ. & Wagner, C. (2003). *Acta Cryst.* C**59**, m249–m251.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Shorrock, C. J., Xue, B.-Y., Kim, P. B., Batchelor, R. J., Partick, B. O. & Leznoff, P. B. (2002). *Inorg. Chem.* **41**, 6743–6753.
Soma, T., Yuge, H. & Iwamoto, T. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1665–1666.
Triščíková, L., Chomič, J., Abboud, K. A., Park, J.-H., Meisel, M. W. & Černák, J. (2004). *Inorg. Chim. Acta*, **357**, 2763–2768.
Westrip, S. P. (2007). *publCIF*. In preparation.

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supplementary materials

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Jahn-Teller distorted copper(II) in poly[bis(μ-4,4'-bipyridine)tetra-μ-cyanido-copper(II)disilver(I)]

J. Maher and **R. E. Sykora**

Comment

Numerous dicyanoargentates have been prepared in recent years due to their interesting structural and magnetic properties (Černák *et al.*, 2002; Lefebvre & Leznoff, 2005). By incorporating various amine ligands along with Cu^{2+} cations and dicyanoargentate anions, structure types containing molecular units, $Cu(pn)_2Ag_2(CN)_4$ (pn = 1,2-diaminopropane) (Triščíková *et al.*, 2004), one-dimensional chains, $Cu(bpy)_2Ag_2(CN)_4{\cdot}H_2O$ (bpy = 2,2'-bipyridine) (Černák *et al.*, 1993), two-dimensional sheets, $[Cu(en)_2][Ag_2(CN)_3][Ag(CN)_2]$ (en = ethylenediamine) (Shorrock *et al.*, 2002), and three-dimensional networks, $[Cu_2(C_4H_{12}N_2)_2\{Ag(CN)_2\}_4(NH_3)]{\cdot}2H_2O$ (Potočňák *et al.*, 2003) have all been prepared. Numerous other metal organic compounds containing various transition metal cations, amine ligands, and dicyanoargentate anions have also been prepared. One such structure-type type containing 4,4'-bipyridine (bpy), $M(bpy)_2[Ag(CN)_2]_2$, where *M* is Mn (Dong *et al.*, 2003), Fe (Niel *et al.*, 2002), or Cd (Soma *et al.*, 1994) has been prepared. This structure contains a distorted octahedral coordination polyhedron for the *M*(II) cations, bridging 4,4'-bipyridine ligands, and a three coordinate Ag atom. The title compound, bis(μ-4,4'-bipyridine)bis[μ-dicyanoargentate(I)]copper(II), was prepared in order to determine (1) if the same structure was possible with copper(II) and (2) to probe the effects on the structure.

There is one symmetrically unique copper atom in the structure of $Cu(bpy)_2[Ag(CN)_2]_2$ and it is located on an inversion center. The coordination geometry around the Cu atoms (Fig. 1) is composed of six nitrogen atoms in a tetragonal bipyramidal arrangement. Two bridging bipyridine ligands and two nitrogen-bound dicyanoargentate anions account for the nitrogen atoms located in the equatorial plane, while the apical positions are occupied by two nitrogen atoms from bridging dicyanoargentate anions. A significant Jahn-Teller distortion is evident in the lengthened Cu—N distance (2.563 (3) Å) of the apical nitrogen atoms as compared to the equatorial Cu—N distances (1.961 (3) and 2.056 (3) Å). In the previously reported Mn, Fe, and Cd structures, the coordination geometries of these metals can be described as distorted octahedral and the M—N bond distances showed much less variation. In $Cd(bpy)_2[Ag(CN)_2]_2$ the three unique Cd—N bond distances are 2.288, 2.369, and 2.377 Å, in $Fe(bpy)_2[Ag(CN)_2]_2$ the three Fe—N bond distances are 2.129, 2.188, and 2.248 Å, and in $Mn(bpy)_2[Ag(CN)_2]_2$ the three Mn—N bond distances are 2.193, 2.264, and 2.320 Å.

There are no unusual features in the bond distances found in the dicyanoargentate anions in $Cu(bpy)_2[Ag(CN)_2]_2$, although there is a significant bond angle decrease from linearity, C1—Ag1—C2 angle of 157.40 (13)°, as also observed in the previous Mn, Fe, and Cd structures, which have angles of 153.9°, 154.2°, and 153.6°, respectively. The three-dimensional double penetrating framework (Fig 2.) (Soma *et al.*, 1994) built up by the bridging 4,4'-bipyridine and dicyanoargentate anions is preserved in the structure of $Cu(bpy)_2[Ag(CN)_2]_2$.

Experimental

A methanolic solution of 4,4'-bipyridine (0.25 ml, 1.0 *M*) and aqueous $KAg(CN)_2$ (2.5 ml, 0.2 *M*) were added to an aqueous solution of $CuSO_4$ (2.5 ml, 0.1 *M*). This resulted in the precipitation of a blue powder, which was then dissolved by the addition of 2.5 ml of a concentrated NH_3 (26%) solution. The solution was left for 5 days, resulting in dark blue crystals of the title compound suitable for single-crystal X-ray analysis.

Refinement

H atoms were placed in calculated positions and allowed to ride during subsequent refinement, with $U_{iso}(H) = 1.2U_{eq}(C)$ and C—H distances of 0.93 Å.

Figures

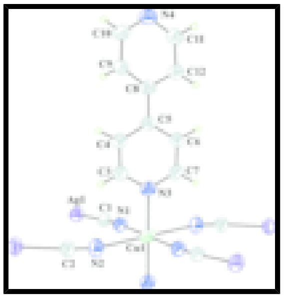

Fig. 1. Part of the structure of $Cu(bpy)_2[Ag(CN)_2]_2$, with atom labeling for the independent atoms. Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as spheres of arbitrary size.

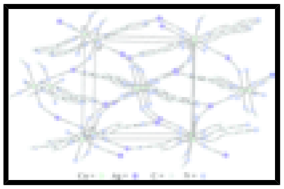

Fig. 2. The packing diagram of the three-dimensional network in $Cu(bpy)_2[Ag(CN)_2]_2$. The hydrogen atoms have been omitted for clarity.

poly[bis(μ-4,4'-bipyridine)tetra-μ-cyanido-copper(II)disilver(I)]

Crystal data

$[Ag_2Cu(CN)_4(C_{10}H_8N_2)_2]$	$F_{000} = 678$
$M_r = 695.73$	$D_x = 1.873$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 25 reflections
$a = 8.9056$ (9) Å	$\theta = 8.7$–12.0º
$b = 11.4712$ (10) Å	$\mu = 2.46$ mm^{-1}
$c = 12.5918$ (11) Å	$T = 290$ (2) K
$\beta = 106.484$ (8)º	Irregular prism, dark blue
$V = 1233.5$ (2) Å^3	1.00 × 0.51 × 0.42 mm
$Z = 2$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.022$
Radiation source: fine-focus sealed tube	$\theta_{max} = 25.4$º
Monochromator: graphite	$\theta_{min} = 2.5$º

T = 290(2) K	h = 0→10
θ/2θ scans	k = 0→13
Absorption correction: ψ scan (North *et al.*, 1968)	l = −15→14
$T_{\min}$ = 0.255, $T_{\max}$ = 0.353	3 standard reflections
2418 measured reflections	every 120 min
2267 independent reflections	intensity decay: none
1969 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.025$	$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 1.3204P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.065$	$(\Delta/\sigma)_{\max} = 0.001$
S = 1.11	$\Delta\rho_{\max}$ = 0.45 e Å^{-3}
2267 reflections	$\Delta\rho_{\min}$ = −0.38 e Å^{-3}
161 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0043 (4)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\sigma(F^2)$ 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	$U_{\rm iso}$*/$U_{\rm eq}$
Ag1	0.17340 (3)	0.82881 (2)	0.67239 (2)	0.04213 (12)
Cu1	0.0000	1.0000	1.0000	0.04178 (18)
N1	0.0760 (3)	0.9291 (3)	0.8833 (2)	0.0374 (6)
N2	0.1216 (4)	1.1913 (3)	0.9593 (3)	0.0479 (7)
N3	0.2061 (3)	0.9593 (3)	1.1172 (2)	0.0395 (6)
N4	0.9171 (3)	0.8550 (3)	1.5329 (2)	0.0475 (7)
C1	0.1135 (4)	0.8918 (3)	0.8110 (3)	0.0370 (7)
C2	0.1904 (4)	1.2467 (3)	0.9156 (3)	0.0408 (8)

C3	0.3430 (4)	0.9961 (4)	1.1058 (3)	0.0510 (10)
H3A	0.3437	1.0357	1.0415	0.061*
C4	0.4829 (4)	0.9777 (4)	1.1853 (3)	0.0492 (9)
H4A	0.5754	1.0053	1.1741	0.059*
C5	0.4869 (4)	0.9184 (3)	1.2819 (3)	0.0373 (7)
C6	0.3451 (4)	0.8779 (3)	1.2912 (3)	0.0427 (8)
H6A	0.3415	0.8355	1.3533	0.051*
C7	0.2092 (4)	0.9001 (3)	1.2089 (3)	0.0432 (8)
H7A	0.1152	0.8726	1.2176	0.052*
C8	0.6358 (4)	0.8986 (3)	1.3694 (3)	0.0349 (7)
C9	0.7772 (4)	0.8921 (3)	1.3440 (3)	0.0394 (8)
H9A	0.7809	0.9030	1.2716	0.047*
C10	0.9128 (4)	0.8692 (3)	1.4276 (3)	0.0459 (9)
H10A	1.0063	0.8634	1.4089	0.055*
C11	0.7813 (4)	0.8638 (4)	1.5570 (3)	0.0474 (9)
H11A	0.7821	0.8560	1.6307	0.057*
C12	0.6401 (4)	0.8835 (3)	1.4798 (3)	0.0423 (8)
H12A	0.5483	0.8867	1.5010	0.051*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.04338 (18)	0.04940 (19)	0.03717 (17)	0.00608 (12)	0.01719 (12)	−0.00403 (11)
Cu1	0.0309 (3)	0.0685 (4)	0.0239 (3)	0.0119 (3)	0.0044 (2)	−0.0064 (3)
N1	0.0332 (14)	0.0481 (17)	0.0309 (14)	0.0011 (12)	0.0091 (12)	−0.0005 (13)
N2	0.0454 (17)	0.0549 (19)	0.0482 (18)	−0.0031 (15)	0.0213 (15)	0.0052 (15)
N3	0.0309 (14)	0.0556 (18)	0.0306 (14)	0.0032 (13)	0.0064 (12)	−0.0008 (13)
N4	0.0367 (16)	0.063 (2)	0.0383 (16)	0.0033 (14)	0.0038 (13)	0.0012 (14)
C1	0.0333 (16)	0.0432 (19)	0.0343 (17)	0.0037 (14)	0.0094 (14)	0.0011 (14)
C2	0.0380 (17)	0.049 (2)	0.0346 (17)	−0.0039 (16)	0.0096 (15)	0.0002 (16)
C3	0.0386 (19)	0.073 (3)	0.0389 (19)	0.0012 (18)	0.0075 (15)	0.0181 (19)
C4	0.0309 (17)	0.067 (3)	0.046 (2)	−0.0084 (17)	0.0056 (15)	0.0126 (18)
C5	0.0349 (17)	0.0399 (18)	0.0344 (17)	−0.0007 (14)	0.0054 (14)	0.0018 (14)
C6	0.0362 (17)	0.056 (2)	0.0340 (17)	−0.0029 (16)	0.0070 (14)	0.0093 (16)
C7	0.0292 (16)	0.062 (2)	0.0390 (18)	−0.0035 (16)	0.0106 (14)	0.0030 (16)
C8	0.0321 (16)	0.0333 (17)	0.0358 (17)	−0.0029 (13)	0.0038 (14)	−0.0007 (13)
C9	0.0382 (17)	0.049 (2)	0.0296 (16)	−0.0027 (15)	0.0069 (14)	−0.0025 (14)
C10	0.0336 (18)	0.060 (2)	0.043 (2)	0.0023 (16)	0.0098 (15)	−0.0037 (17)
C11	0.0406 (19)	0.067 (2)	0.0318 (18)	0.0020 (17)	0.0055 (15)	0.0057 (17)
C12	0.0335 (17)	0.056 (2)	0.0363 (18)	0.0006 (15)	0.0078 (14)	0.0032 (16)

Geometric parameters (Å, °)

Ag1—C2^{i}	2.086 (4)	C3—H3A	0.9300
Ag1—C1	2.093 (3)	C4—C5	1.385 (5)
Ag1—N4^{ii}	2.472 (3)	C4—H4A	0.9300
Cu1—N1^{iii}	1.961 (3)	C5—C6	1.381 (5)
Cu1—N1	1.961 (3)	C5—C8	1.481 (4)

Cu1—N3$^{\text{iii}}$	2.056 (3)	C6—C7	1.376 (5)
Cu1—N3	2.056 (3)	C6—H6A	0.9300
Cu1—N2	2.563 (3)	C7—H7A	0.9300
N1—C1	1.138 (4)	C8—C9	1.386 (5)
N2—C2	1.128 (4)	C8—C12	1.391 (5)
N3—C7	1.333 (5)	C9—C10	1.384 (5)
N3—C3	1.336 (5)	C9—H9A	0.9300
N4—C10	1.325 (5)	C10—H10A	0.9300
N4—C11	1.332 (5)	C11—C12	1.372 (5)
N4—Ag1$^{\text{iv}}$	2.472 (3)	C11—H11A	0.9300
C2—Ag1$^{\text{v}}$	2.086 (4)	C12—H12A	0.9300
C3—C4	1.375 (5)		

C2$^{\text{i}}$—Ag1—C1	157.40 (13)	C4—C3—H3A	118.7
C2$^{\text{i}}$—Ag1—N4$^{\text{ii}}$	103.67 (12)	C3—C4—C5	120.5 (3)
C1—Ag1—N4$^{\text{ii}}$	98.52 (12)	C3—C4—H4A	119.8
N1—Cu1—N1$^{\text{iii}}$	180	C5—C4—H4A	119.8
N1—Cu1—N3$^{\text{iii}}$	89.09 (11)	C6—C5—C4	116.3 (3)
N1$^{\text{iii}}$—Cu1—N3$^{\text{iii}}$	90.91 (11)	C6—C5—C8	122.2 (3)
N1—Cu1—N3	90.91 (11)	C4—C5—C8	121.5 (3)
N1$^{\text{iii}}$—Cu1—N3	89.09 (11)	C7—C6—C5	120.3 (3)
N3$^{\text{iii}}$—Cu1—N3	180	C7—C6—H6A	119.9
N1—Cu1—N2$^{\text{iii}}$	92.88 (11)	C5—C6—H6A	119.9
N1$^{\text{iii}}$—Cu1—N2$^{\text{iii}}$	87.12 (11)	N3—C7—C6	123.0 (3)
N3$^{\text{iii}}$—Cu1—N2$^{\text{iii}}$	89.78 (11)	N3—C7—H7A	118.5
N3—Cu1—N2$^{\text{iii}}$	90.22 (11)	C6—C7—H7A	118.5
N1—Cu1—N2	87.12 (11)	C9—C8—C12	117.1 (3)
N1$^{\text{iii}}$—Cu1—N2	92.88 (11)	C9—C8—C5	121.1 (3)
N3$^{\text{iii}}$—Cu1—N2	90.22 (11)	C12—C8—C5	121.8 (3)
N3—Cu1—N2	89.78 (11)	C10—C9—C8	119.3 (3)
N2$^{\text{iii}}$—Cu1—N2	180	C10—C9—H9A	120.4
C1—N1—Cu1	175.9 (3)	C8—C9—H9A	120.4
C7—N3—C3	117.3 (3)	N4—C10—C9	123.8 (3)
C7—N3—Cu1	122.2 (2)	N4—C10—H10A	118.1
C3—N3—Cu1	120.5 (2)	C9—C10—H10A	118.1
C10—N4—C11	116.6 (3)	N4—C11—C12	124.0 (3)
C10—N4—Ag1$^{\text{iv}}$	119.0 (2)	N4—C11—H11A	118.0
C11—N4—Ag1$^{\text{iv}}$	124.2 (2)	C12—C11—H11A	118.0
N1—C1—Ag1	176.9 (3)	C11—C12—C8	119.2 (3)
N2—C2—Ag1$^{\text{v}}$	172.6 (3)	C11—C12—H12A	120.4
N3—C3—C4	122.7 (3)	C8—C12—H12A	120.4
N3—C3—H3A	118.7		

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+3/2; (ii) *x*−1, *y*, *z*−1; (iii) −*x*, −*y*+2, −*z*+2; (iv) *x*+1, *y*, *z*+1; (v) −*x*+1/2, *y*+1/2, −*z*+3/2.

Fig. 1

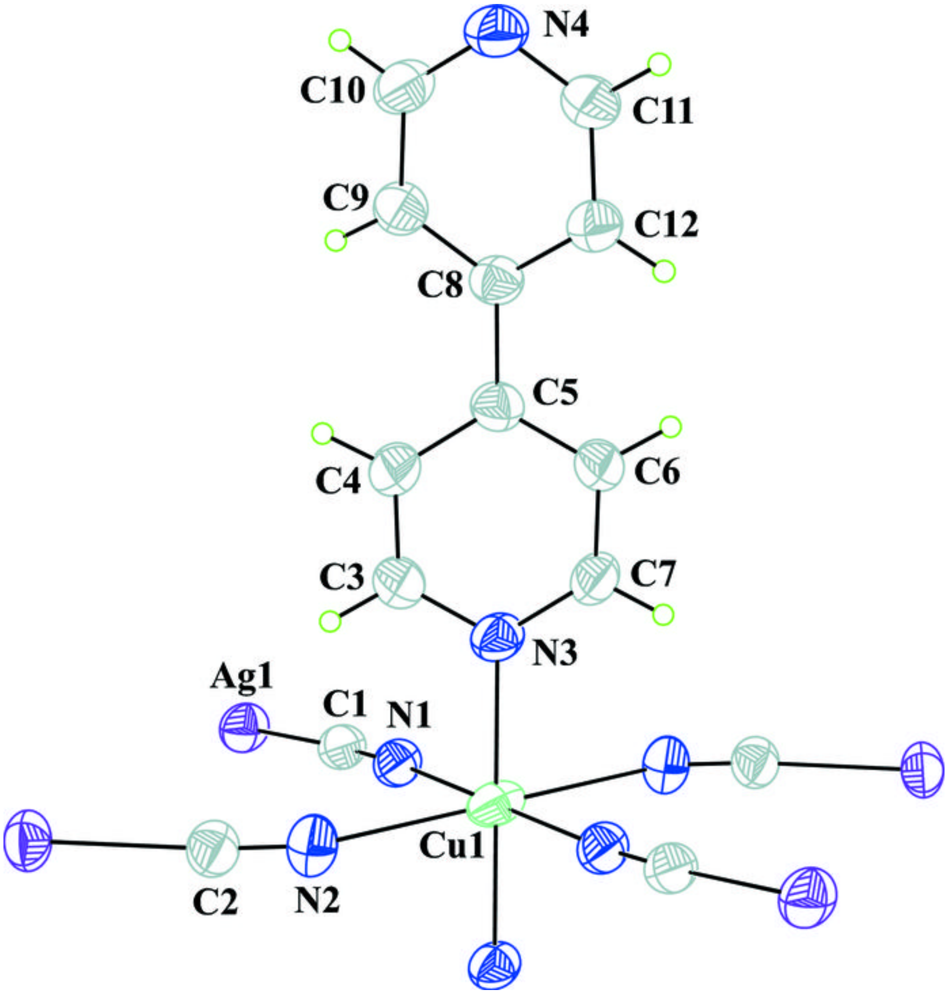

Fig. 2