

Tetrakis(μ -3-methoxybenzoato- $\kappa^2O^1:O^1$)bis[acetonitrilecopper(II)]

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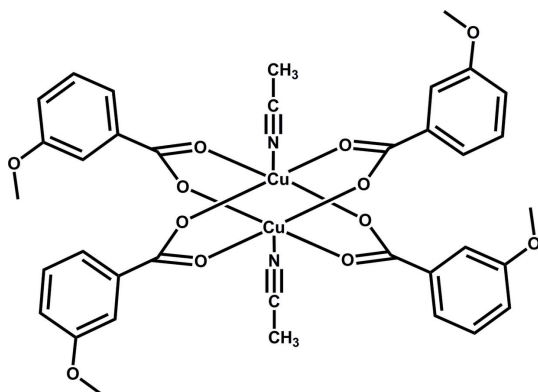
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.034; wR factor = 0.101; data-to-parameter ratio = 28.9.

The centrosymmetric binuclear Cu^{II} title complex, $[Cu_2(C_8H_7O_3)_4(CH_3CN)_2]$, has a paddle-wheel-type structure [$Cu-Cu$ distance = $2.6433(3)$ Å]. Each Cu^{II} ion is coordinated by four O atoms from two 3-methoxybenzoate ligands and one acetonitrile N atom in a square-pyramidal geometry.

Related literature

For applications of binuclear copper(II) complexes bridged by four benzoic acid groups in a paddle-wheel arrangement in inorganic synthesis, catalysis, magnetism and medicinal chemistry, see: Ozarowski (2008); Kirchner & Fernando (1980); Inoue *et al.* (1968); Bergant *et al.* (1994). For crystal structures of similar complexes, see: Lah *et al.* (2001). For the preparation of similar complexes, see: Bernard *et al.* (1989).



Experimental

Crystal data

$[Cu_2(C_8H_7O_3)_4(C_2H_3N)_2]$
 $M_r = 813.73$
Monoclinic, $P2_1/n$
 $a = 7.2117(7)$ Å
 $b = 19.6502(3)$ Å
 $c = 12.6186(9)$ Å
 $\beta = 90.016(9)^\circ$

$V = 1788.2(3)$ Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 1.26$ mm⁻¹
 $T = 293$ K
 $0.25 \times 0.22 \times 0.08$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2007)
 $T_{min} = 0.620$, $T_{max} = 0.746$
43230 measured reflections
6872 independent reflections
4883 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.101$
 $S = 1.01$
6872 reflections

238 parameters
H-atom parameters constrained
 $\Delta\rho_{max} = 0.40$ e Å⁻³
 $\Delta\rho_{min} = -0.34$ e Å⁻³

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SIR92 (Altomare, *et al.* 1993); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg, 1999); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2314).

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supplementary materials

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Tetrakis(μ -3-methoxybenzoato- $\kappa^2 O^1:O^1'$)bis[acetonitrilecopper(II)]

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Comment

Binuclear copper(II) complexes bridged by four benzoic acid groups in a paddle-wheel arrangement are very important from the perspectives of molecular magnetism (Inoue, *et al.*, 1968). These materials have potential applications in inorganic synthesis, catalysis, magnetism, and in medicinal chemistry (Ozarowski, 2008; Kirchner & Fernando, 1980; Inoue *et al.*, 1968; Bergant *et al.*, 1994). Herein we report the structure of the title compound (Fig.1). The structure is a centrosymmetric dinuclear Cu(II) complex having square pyramidal arrangement around each copper ion. There is a lot of research interest for studying the effect of apical ligand (here the apical ligand is acetonitrile) in tuning the intramolecular magnetic exchange interaction between two Cu(II) ions in various paddle-wheel type dinuclear copper(II) benzoate complexes.

Experimental

The title compound was obtained by addition of the solution of copper(II) acetate monohydrate (0.4 g, 2.0 mmol) in a 1:1 mixture of CH₃CN + CH₃OH (20 ml) to 3-methoxybenzoic acid (1.21 g, 8 mmol), and the mixture was stirred for 2 h. The green precipitate was filtered and washed thoroughly with diethyl ether (1.2 g, 80%). Recrystallization from acetonitrile gave green crystals suitable for X-ray diffraction.

Refinement

All H atoms were placed geometrically at idealized positions with C–H = 0.93 Å (C_{ar}H) and 0.96 Å (RCH₃), and were refined isotropically using a riding-model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ or $1.5U_{\text{eq}}$ (CH₃ only).

Figures

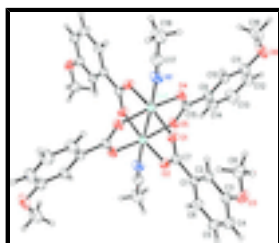


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as small arbitrary spheres. Unlabelled atoms are related to their labelled counterparts by inversion [(*x*,*y*,*z*) to (2-*x*,2-*y*,-*z*)].

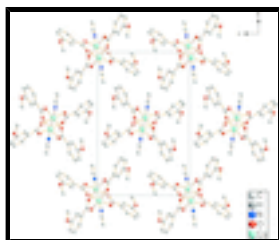


Fig. 2. A packing diagram viewed along the crystallographic *a* axis.

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Crystal data

$[\text{Cu}_2(\text{C}_8\text{H}_7\text{O}_3)_4(\text{C}_2\text{H}_3\text{N})_2]$	$F(000) = 836$
$M_r = 813.73$	$D_x = 1.512 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-P 2_1n$	Cell parameters from 9972 reflections
$a = 7.2117 (7) \text{ \AA}$	$\theta = 2.6\text{--}27.4^\circ$
$b = 19.6502 (3) \text{ \AA}$	$\mu = 1.26 \text{ mm}^{-1}$
$c = 12.6186 (9) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 90.016 (9)^\circ$	Block, green
$V = 1788.2 (3) \text{ \AA}^3$	$0.25 \times 0.22 \times 0.08 \text{ mm}$
$Z = 2$	

Data collection

Bruker SMART CCD area-detector diffractometer	6872 independent reflections
Radiation source: fine-focus sealed tube graphite	4883 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.036$
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2007)	$\theta_{\text{max}} = 33.5^\circ$, $\theta_{\text{min}} = 1.9^\circ$
$T_{\text{min}} = 0.620$, $T_{\text{max}} = 0.746$	$h = -11 \rightarrow 10$
43230 measured reflections	$k = -30 \rightarrow 29$
	$l = -18 \rightarrow 19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.034$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.101$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.2391P]$
6872 reflections	where $P = (F_o^2 + 2F_c^2)/3$
238 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

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	0.85578 (2)	0.959759 (8)	0.015468 (13)	0.03310 (6)
C1	0.7588 (2)	1.14438 (8)	0.17923 (12)	0.0428 (3)
C2	0.5838 (2)	1.13393 (8)	0.22195 (12)	0.0449 (3)
H2	0.5207	1.0935	0.2093	0.054*
C3	0.5037 (3)	1.18455 (9)	0.28383 (12)	0.0484 (4)
C4	0.5971 (3)	1.24540 (9)	0.30041 (16)	0.0588 (5)
H4	0.5442	1.2790	0.3426	0.071*
C5	0.7672 (3)	1.25604 (9)	0.25470 (16)	0.0626 (5)
H5	0.8271	1.2975	0.2642	0.075*
C6	0.8508 (3)	1.20571 (9)	0.19449 (15)	0.0547 (4)
H6	0.9671	1.2129	0.1646	0.066*
C7	0.8464 (2)	1.08987 (8)	0.11286 (11)	0.0401 (3)
C8	0.2380 (3)	1.11606 (12)	0.32315 (18)	0.0671 (5)
H8A	0.2120	1.1065	0.2500	0.101*
H8B	0.1237	1.1189	0.3619	0.101*
H8C	0.3131	1.0803	0.3521	0.101*
C9	0.7489 (2)	1.07841 (8)	-0.26044 (12)	0.0428 (3)
C10	0.5683 (2)	1.05961 (9)	-0.28718 (12)	0.0461 (4)
H10	0.5042	1.0283	-0.2458	0.055*
C11	0.4845 (3)	1.08807 (10)	-0.37628 (14)	0.0555 (4)
C12	0.5780 (3)	1.13632 (12)	-0.43556 (16)	0.0695 (6)
H12	0.5201	1.1568	-0.4931	0.083*
C13	0.7561 (4)	1.15386 (13)	-0.40930 (17)	0.0787 (7)
H13	0.8192	1.1856	-0.4503	0.094*
C14	0.8439 (3)	1.12486 (10)	-0.32223 (15)	0.0614 (5)
H14	0.9655	1.1366	-0.3057	0.074*
C15	0.8413 (2)	1.04876 (7)	-0.16352 (11)	0.0389 (3)
C16	0.2271 (3)	1.01287 (14)	-0.3747 (2)	0.0789 (7)
H16A	0.3109	0.9755	-0.3852	0.118*
H16B	0.1147	1.0047	-0.4135	0.118*
H16C	0.1991	1.0172	-0.3007	0.118*
C17	0.5228 (3)	0.84701 (10)	0.04591 (16)	0.0570 (4)
C18	0.3797 (3)	0.79457 (13)	0.0586 (2)	0.0804 (7)
H18A	0.3836	0.7770	0.1295	0.121*
H18B	0.4019	0.7583	0.0092	0.121*
H18C	0.2599	0.8141	0.0452	0.121*
N1	0.6281 (2)	0.88878 (8)	0.03641 (12)	0.0559 (4)
O1	0.75919 (17)	1.03482 (5)	0.10169 (10)	0.0476 (3)

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O2	1.00189 (17)	1.10313 (6)	0.07340 (10)	0.0503 (3)
O3	0.33498 (19)	1.17917 (7)	0.33120 (11)	0.0611 (3)
O4	0.75562 (16)	1.00329 (6)	-0.11367 (9)	0.0458 (3)
O5	0.99825 (17)	1.07201 (6)	-0.13874 (9)	0.0492 (3)
O6	0.3093 (2)	1.07285 (10)	-0.41088 (13)	0.0801 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.03442 (10)	0.03078 (9)	0.03410 (10)	-0.00225 (6)	-0.00097 (6)	0.00015 (6)
C1	0.0519 (9)	0.0379 (7)	0.0386 (7)	0.0095 (6)	-0.0042 (6)	-0.0037 (6)
C2	0.0551 (10)	0.0401 (7)	0.0394 (7)	0.0106 (7)	-0.0036 (7)	-0.0036 (6)
C3	0.0580 (10)	0.0463 (8)	0.0410 (8)	0.0182 (7)	-0.0024 (7)	-0.0031 (6)
C4	0.0748 (13)	0.0453 (9)	0.0561 (10)	0.0156 (9)	-0.0011 (9)	-0.0123 (7)
C5	0.0797 (14)	0.0404 (9)	0.0677 (12)	0.0021 (9)	-0.0052 (10)	-0.0142 (8)
C6	0.0595 (11)	0.0454 (9)	0.0593 (10)	0.0022 (8)	-0.0016 (8)	-0.0082 (7)
C7	0.0459 (8)	0.0380 (7)	0.0365 (7)	0.0056 (6)	-0.0040 (6)	-0.0017 (5)
C8	0.0561 (12)	0.0765 (14)	0.0687 (12)	0.0080 (10)	0.0022 (9)	-0.0186 (10)
C9	0.0523 (9)	0.0392 (7)	0.0367 (7)	0.0038 (6)	-0.0064 (6)	0.0014 (6)
C10	0.0530 (10)	0.0461 (8)	0.0390 (7)	0.0048 (7)	-0.0053 (7)	0.0040 (6)
C11	0.0599 (11)	0.0621 (11)	0.0444 (8)	0.0071 (8)	-0.0117 (8)	0.0039 (7)
C12	0.0854 (16)	0.0740 (13)	0.0492 (10)	-0.0003 (11)	-0.0182 (10)	0.0206 (9)
C13	0.0931 (17)	0.0831 (15)	0.0598 (12)	-0.0198 (13)	-0.0127 (11)	0.0347 (11)
C14	0.0682 (13)	0.0629 (11)	0.0531 (10)	-0.0130 (9)	-0.0114 (9)	0.0144 (8)
C15	0.0466 (9)	0.0356 (7)	0.0347 (7)	0.0044 (6)	-0.0036 (6)	-0.0012 (5)
C16	0.0613 (14)	0.1005 (19)	0.0749 (15)	-0.0078 (13)	-0.0137 (11)	0.0090 (13)
C17	0.0519 (10)	0.0576 (10)	0.0615 (11)	-0.0063 (8)	-0.0024 (8)	0.0131 (8)
C18	0.0665 (14)	0.0763 (15)	0.0984 (17)	-0.0306 (11)	-0.0125 (12)	0.0349 (13)
N1	0.0525 (9)	0.0597 (9)	0.0553 (9)	-0.0205 (7)	-0.0018 (7)	0.0092 (7)
O1	0.0501 (7)	0.0416 (6)	0.0511 (6)	0.0006 (5)	0.0081 (5)	-0.0104 (5)
O2	0.0510 (7)	0.0418 (6)	0.0581 (7)	-0.0008 (5)	0.0076 (5)	-0.0112 (5)
O3	0.0631 (8)	0.0580 (8)	0.0623 (8)	0.0173 (6)	0.0086 (6)	-0.0118 (6)
O4	0.0477 (6)	0.0489 (6)	0.0408 (5)	-0.0043 (5)	-0.0083 (5)	0.0093 (5)
O5	0.0511 (7)	0.0499 (6)	0.0465 (6)	-0.0077 (5)	-0.0123 (5)	0.0122 (5)
O6	0.0659 (10)	0.1017 (12)	0.0726 (10)	-0.0032 (9)	-0.0282 (8)	0.0271 (9)

Geometric parameters (\AA , $^\circ$)

Cu1—O2 ⁱ	1.9591 (11)	C9—C10	1.395 (2)
Cu1—O1	1.9606 (11)	C9—C15	1.510 (2)
Cu1—O4	1.9769 (11)	C10—C11	1.394 (2)
Cu1—O5 ⁱ	1.9791 (11)	C10—H10	0.9300
Cu1—N1	2.1703 (14)	C11—O6	1.369 (2)
Cu1—Cu1 ⁱ	2.6416 (3)	C11—C12	1.383 (3)
C1—C2	1.388 (2)	C12—C13	1.370 (3)
C1—C6	1.389 (2)	C12—H12	0.9300
C1—C7	1.499 (2)	C13—C14	1.390 (3)
C2—C3	1.390 (2)	C13—H13	0.9300

C2—H2	0.9300	C14—H14	0.9300
C3—O3	1.360 (2)	C15—O4	1.2554 (19)
C3—C4	1.388 (3)	C15—O5	1.2594 (19)
C4—C5	1.371 (3)	C16—O6	1.396 (3)
C4—H4	0.9300	C16—H16A	0.9600
C5—C6	1.385 (3)	C16—H16B	0.9600
C5—H5	0.9300	C16—H16C	0.9600
C6—H6	0.9300	C17—N1	1.124 (2)
C7—O2	1.254 (2)	C17—C18	1.467 (3)
C7—O1	1.2588 (19)	C18—H18A	0.9600
C8—O3	1.427 (3)	C18—H18B	0.9600
C8—H8A	0.9600	C18—H18C	0.9600
C8—H8B	0.9600	O2—Cu1 ⁱ	1.9591 (11)
C8—H8C	0.9600	O5—Cu1 ⁱ	1.9791 (11)
C9—C14	1.382 (3)		
O2 ⁱ —Cu1—O1	168.03 (5)	C14—C9—C10	120.08 (15)
O2 ⁱ —Cu1—O4	89.55 (5)	C14—C9—C15	119.54 (15)
O1—Cu1—O4	90.13 (5)	C10—C9—C15	120.38 (14)
O2 ⁱ —Cu1—O5 ⁱ	88.43 (6)	C11—C10—C9	119.58 (17)
O1—Cu1—O5 ⁱ	89.42 (5)	C11—C10—H10	120.2
O4—Cu1—O5 ⁱ	168.11 (5)	C9—C10—H10	120.2
O2 ⁱ —Cu1—N1	93.49 (6)	O6—C11—C12	115.27 (16)
O1—Cu1—N1	98.44 (6)	O6—C11—C10	124.71 (18)
O4—Cu1—N1	95.86 (5)	C12—C11—C10	120.00 (18)
O5 ⁱ —Cu1—N1	95.96 (5)	C13—C12—C11	119.90 (17)
O2 ⁱ —Cu1—Cu1 ⁱ	83.13 (4)	C13—C12—H12	120.0
O1—Cu1—Cu1 ⁱ	84.93 (4)	C11—C12—H12	120.0
O4—Cu1—Cu1 ⁱ	84.64 (3)	C12—C13—C14	120.98 (19)
O5 ⁱ —Cu1—Cu1 ⁱ	83.48 (4)	C12—C13—H13	119.5
N1—Cu1—Cu1 ⁱ	176.58 (5)	C14—C13—H13	119.5
C2—C1—C6	120.59 (15)	C9—C14—C13	119.39 (19)
C2—C1—C7	119.64 (14)	C9—C14—H14	120.3
C6—C1—C7	119.74 (16)	C13—C14—H14	120.3
C1—C2—C3	119.36 (16)	O4—C15—O5	125.17 (14)
C1—C2—H2	120.3	O4—C15—C9	117.60 (14)
C3—C2—H2	120.3	O5—C15—C9	117.23 (13)
O3—C3—C4	115.76 (15)	O6—C16—H16A	109.5
O3—C3—C2	124.28 (17)	O6—C16—H16B	109.5
C4—C3—C2	119.96 (18)	H16A—C16—H16B	109.5
C5—C4—C3	120.11 (16)	O6—C16—H16C	109.5
C5—C4—H4	119.9	H16A—C16—H16C	109.5
C3—C4—H4	119.9	H16B—C16—H16C	109.5
C4—C5—C6	120.75 (18)	N1—C17—C18	177.7 (2)
C4—C5—H5	119.6	C17—C18—H18A	109.5
C6—C5—H5	119.6	C17—C18—H18B	109.5
C5—C6—C1	119.18 (19)	H18A—C18—H18B	109.5

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C5—C6—H6	120.4	C17—C18—H18C	109.5
C1—C6—H6	120.4	H18A—C18—H18C	109.5
O2—C7—O1	125.48 (14)	H18B—C18—H18C	109.5
O2—C7—C1	116.75 (14)	C17—N1—Cu1	173.08 (18)
O1—C7—C1	117.77 (15)	C7—O1—Cu1	122.06 (11)
O3—C8—H8A	109.5	C7—O2—Cu1 ⁱ	124.38 (10)
O3—C8—H8B	109.5	C3—O3—C8	118.32 (14)
H8A—C8—H8B	109.5	C15—O4—Cu1	122.76 (10)
O3—C8—H8C	109.5	C15—O5—Cu1 ⁱ	123.93 (10)
H8A—C8—H8C	109.5	C11—O6—C16	118.17 (16)
H8B—C8—H8C	109.5		

Symmetry codes: (i) $-x+2, -y+2, -z$.

Fig. 1

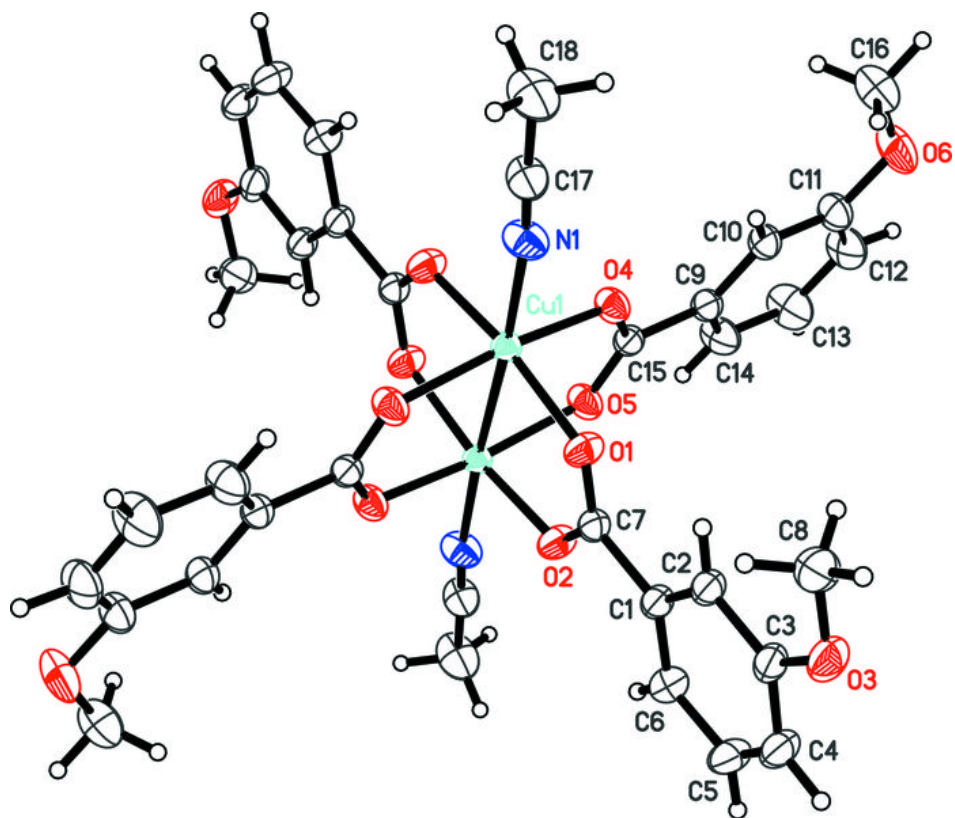


Fig. 2

