

***trans*-Bis[(*E*)-4-(4-methoxystyryl)-pyridine]dinitratocopper(II)**

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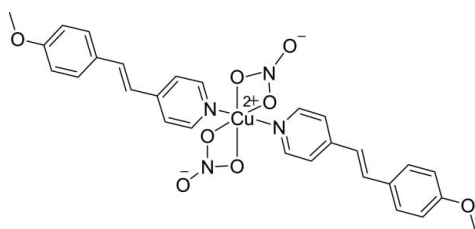
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.044; wR factor = 0.118; data-to-parameter ratio = 13.1.

The title compound, $[\text{Cu}(\text{NO}_3)_2(\text{C}_{14}\text{H}_{13}\text{NO})_2]$, has been synthesized by the reaction of (*E*)-4-(4-methoxystyryl)-pyridine with $\text{Cu}(\text{NO}_3)_2$ at room temperature in CH_3OH . The mononuclear complex sits across a crystallographic centre of inversion. The Cu^{II} ion is six-coordinated in a distorted octahedral fashion by the *trans*-disposed pyridine N atoms of two pyridine ligands and asymmetrically by two O atoms from each of the two nitrate ligands, where one of the Cu—O distances is quite long at 2.452 (3) Å.

Related literature

For related non-linear optical materials, see: Saltiel *et al.* (1995, 1996, 2005); Lubczyk *et al.* (2002); Taylor & Martin (1974); Vansant *et al.* (1980). For heteroarylethene molecules, see: Shi *et al.* (2004*a,b*, 2005, 2006). For the synthesis of the title compound, see: Zhang *et al.*, 2000.

**Experimental***Crystal data*

$[\text{Cu}(\text{NO}_3)_2(\text{C}_{14}\text{H}_{13}\text{NO})_2]$
 $M_r = 610.07$
 Monoclinic, $P2_1/c$

$a = 9.0605$ (19) Å
 $b = 12.714$ (3) Å
 $c = 12.450$ (3) Å

$\beta = 102.312$ (4)°
 $V = 1401.3$ (5) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.84$ mm⁻¹
 $T = 293$ (2) K
 $0.22 \times 0.14 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.838$, $T_{\text{max}} = 0.921$
 6918 measured reflections
 2469 independent reflections
 1401 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.118$
 $S = 1.03$
 2469 reflections
 188 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	1.980 (3)	Cu1—O3	2.452 (3)
Cu1—O2	2.034 (3)		
N1—Cu1—O2	89.81 (12)	O2—Cu1—O3	56.93 (11)
N1—Cu1—O3	91.55 (11)		

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker 1997); software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LN2006).

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supplementary materials

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***trans*-Bis[(*E*)-4-(4-methoxystyryl)pyridine]dinitratocopper(II)**

L. Yuan and X.-F. Shi

Comment

The heteroarylethene derivatives have attracted attention due to their optical properties and wide applications in nonlinear optical material (Saltiel *et al.*, 1995, 1996, 2005, Lubczyk *et al.*, 2002, Vansant *et al.*, 1980, Taylor & Martin 1974). A series of heteroarylethene molecules coordinated through donor nitrogen atoms has been reported (Shi *et al.*, 2004a,b, 2005, 2006). The investigation of the optical properties of heteroarylethene complexes in terms of structural correlation is still a challenging field. Herein we report the synthesis and crystal structure of a copper(II) complex with (*E*)-4-(4-methoxystyryl)pyridine (Mepy).

The neutral complex [Cu(Mepy)₂(NO₃)₂], (I), crystallizes with the unique molecule lying across a crystallographic centre of inversion. Each Cu^{II} ion is 6-coordinated in a distorted octahedral fashion by the *trans*-disposed pyridine N-atoms of two pyridine ligands and by two O-atoms from each of the two nitrate ligands, as shown in Fig. 1. Selected geometric parameters are given in Table 1. One of the N—O distances from each nitrate ligand is quite long at 2.452 (3) Å. In the Mepy ligands, the dihedral angle between the planes of the pyridinyl and phenyl rings is 14.5 (2)°.

Experimental

The (*E*)-4-(4-methoxystyryl)pyridine ligand (Mepy) was synthesized according to the literature methods (Zhang *et al.*, 2000, Shi *et al.*, 2004b). A solution of 4-Methoxybenzaldehyde (1.91 g, 14 mmol) in 2 ml DMF was added dropwise to a mixture of 4-methylpyridine (0.94 g, 10 mmol) and KOH (1.12 g, 20 mmol) in 15 ml DMF at 338 K over 2 h under nitrogen atmosphere. The mixture was then refluxed for another 2 h, cooled down and poured into 100 ml cold water. The resulting precipitate was filtered off and recrystallized from methanol/water (V_m:V_w=1:1) to give yellow crystals (yield 67%, m.p. 407 K).

The title compound was synthesized by the following method. Mepy ligand (0.42 g, 2.0 mmol) in CH₃OH (30 ml) was added dropwise to a solution of Cu(NO₃)₂·4H₂O (0.53 g, 1 mmol) in CH₃OH (30 ml) with stirring for 1 h at room temperature. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation after 2 days. Yield 55%. Decomp. point: 525 K.

Refinement

All H atoms were initially located in a difference Fourier map. The C—H atoms were then constrained to an ideal geometry, with C(methyl)—H distances of 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, and C(phenyl)—H distances of 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

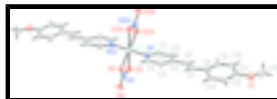


Fig. 1. The molecular structure of complex (I) with displacement ellipsoids at the 30% probability level. H atoms are shown as small spheres of arbitrary radii. Symmetry code: (A) $1 - x, 2 - y, 1 - z$.

Fig. 2. A section of the crystal structure of (I) viewed down the [010] direction, showing the ligands arranged in an antiparallel arrangement.

trans-Bis[(*E*)-4-(4-methoxystyryl)pyridine]dinitratocopper(II)

Crystal data

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$M_r = 610.07$

Monoclinic, $P2_1/c$

$a = 9.0605$ (19) Å

$b = 12.714$ (3) Å

$c = 12.450$ (3) Å

$\beta = 102.312$ (4)°

$V = 1401.3$ (5) Å³

$Z = 2$

$F_{000} = 630$

$D_x = 1.446$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1408 reflections

$\theta = 2.3$ – 21.3 °

$\mu = 0.84$ mm⁻¹

$T = 293$ (2) K

Black, green

$0.22 \times 0.14 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ (2) K

phi and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.838$, $T_{\max} = 0.921$

6918 measured reflections

2469 independent reflections

1401 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.061$

$\theta_{\text{max}} = 25.0$ °

$\theta_{\text{min}} = 2.3$ °

$h = -10 \rightarrow 9$

$k = -15 \rightarrow 10$

$l = -14 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.118$

$S = 1.04$

2469 reflections

188 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.266P]$$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\text{max}} = 0.39$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.38$ 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 $F^2 > 2\sigma(F^2)$ 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	1.0000	0.5000	0.0403 (2)
O1	1.3800 (4)	0.7888 (2)	-0.1442 (3)	0.0647 (9)
O2	0.3170 (3)	1.0079 (2)	0.3732 (2)	0.0483 (7)
O3	0.3939 (3)	1.1665 (2)	0.4188 (3)	0.0592 (9)
O4	0.1994 (4)	1.1421 (2)	0.2859 (3)	0.0694 (10)
N1	0.6334 (4)	0.9889 (3)	0.3935 (3)	0.0413 (8)
N2	0.3010 (4)	1.1078 (3)	0.3579 (3)	0.0462 (9)
C1	0.7574 (5)	1.0471 (4)	0.4018 (4)	0.0586 (14)
H1	0.7763	1.0992	0.4554	0.070*
C2	0.8589 (5)	1.0340 (3)	0.3350 (4)	0.0585 (14)
H2	0.9436	1.0771	0.3440	0.070*
C3	0.8358 (5)	0.9567 (3)	0.2539 (3)	0.0402 (10)
C4	0.7036 (5)	0.8984 (3)	0.2442 (3)	0.0453 (11)
H4A	0.6805	0.8468	0.1903	0.054*
C5	0.6073 (5)	0.9163 (3)	0.3131 (4)	0.0455 (11)
H5	0.5195	0.8764	0.3039	0.055*
C6	0.9475 (5)	0.9402 (3)	0.1863 (4)	0.0471 (11)
H6	1.0307	0.9848	0.1998	0.057*
C7	0.9436 (5)	0.8689 (3)	0.1078 (4)	0.0449 (11)
H7	0.8576	0.8271	0.0908	0.054*
C8	1.0605 (5)	0.8493 (3)	0.0455 (3)	0.0427 (11)
C9	1.2057 (5)	0.8901 (4)	0.0755 (4)	0.0566 (13)
H9	1.2305	0.9308	0.1389	0.068*
C10	1.3148 (5)	0.8729 (4)	0.0149 (4)	0.0575 (13)
H10	1.4105	0.9021	0.0372	0.069*
C11	1.2804 (5)	0.8117 (3)	-0.0788 (4)	0.0457 (11)
C12	1.1379 (5)	0.7688 (3)	-0.1100 (4)	0.0576 (13)
H12	1.1141	0.7274	-0.1728	0.069*
C13	1.0300 (5)	0.7871 (3)	-0.0481 (4)	0.0509 (12)
H13	0.9348	0.7570	-0.0700	0.061*
C14	1.5184 (6)	0.8457 (4)	-0.1266 (5)	0.0746 (16)

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H14A	1.4975	0.9198	-0.1313	0.112*
H14B	1.5733	0.8264	-0.1816	0.112*
H14C	1.5777	0.8294	-0.0550	0.112*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0381 (4)	0.0492 (4)	0.0373 (4)	0.0021 (4)	0.0162 (3)	0.0008 (4)
O1	0.065 (2)	0.076 (2)	0.064 (2)	0.0086 (18)	0.0382 (19)	-0.0114 (17)
O2	0.0531 (18)	0.0437 (17)	0.0520 (18)	0.0019 (17)	0.0197 (14)	-0.0018 (16)
O3	0.059 (2)	0.058 (2)	0.057 (2)	-0.0076 (17)	0.0034 (18)	-0.0056 (16)
O4	0.052 (2)	0.073 (2)	0.073 (3)	0.0021 (17)	-0.0084 (19)	0.0208 (19)
N1	0.0384 (19)	0.048 (2)	0.041 (2)	0.0017 (18)	0.0155 (15)	-0.0013 (19)
N2	0.038 (2)	0.059 (3)	0.044 (2)	0.002 (2)	0.0137 (19)	0.002 (2)
C1	0.060 (3)	0.065 (3)	0.059 (3)	-0.019 (2)	0.030 (3)	-0.024 (2)
C2	0.051 (3)	0.063 (3)	0.068 (4)	-0.023 (2)	0.027 (3)	-0.018 (2)
C3	0.041 (3)	0.044 (2)	0.039 (3)	0.0035 (19)	0.016 (2)	0.0062 (19)
C4	0.050 (3)	0.042 (3)	0.048 (3)	-0.002 (2)	0.020 (2)	-0.006 (2)
C5	0.039 (3)	0.049 (3)	0.052 (3)	-0.006 (2)	0.020 (2)	0.000 (2)
C6	0.046 (3)	0.053 (3)	0.049 (3)	-0.003 (2)	0.025 (2)	-0.001 (2)
C7	0.041 (3)	0.054 (3)	0.042 (3)	-0.001 (2)	0.015 (2)	0.003 (2)
C8	0.041 (3)	0.050 (3)	0.038 (3)	0.009 (2)	0.012 (2)	0.001 (2)
C9	0.050 (3)	0.081 (3)	0.041 (3)	0.001 (3)	0.013 (2)	-0.029 (2)
C10	0.040 (3)	0.078 (3)	0.057 (3)	-0.004 (2)	0.015 (2)	-0.016 (3)
C11	0.049 (3)	0.050 (3)	0.043 (3)	0.014 (2)	0.021 (2)	0.000 (2)
C12	0.064 (3)	0.066 (3)	0.045 (3)	0.003 (3)	0.016 (3)	-0.018 (2)
C13	0.048 (3)	0.062 (3)	0.045 (3)	-0.004 (2)	0.012 (2)	-0.006 (2)
C14	0.085 (4)	0.068 (3)	0.087 (4)	0.011 (3)	0.056 (3)	0.012 (3)

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

Cu1—N1	1.980 (3)	C5—H5	0.9300
Cu1—O2	2.034 (3)	C6—C7	1.328 (5)
Cu1—O3	2.452 (3)	C6—H6	0.9300
O1—C11	1.369 (5)	C7—C8	1.462 (5)
O1—C14	1.424 (5)	C7—H7	0.9300
O2—N2	1.288 (4)	C8—C13	1.386 (6)
O3—N2	1.252 (4)	C8—C9	1.389 (6)
O4—N2	1.221 (4)	C9—C10	1.382 (6)
N1—C1	1.330 (5)	C9—H9	0.9300
N1—C5	1.345 (5)	C10—C11	1.381 (6)
C1—C2	1.376 (6)	C10—H10	0.9300
C1—H1	0.9300	C11—C12	1.379 (6)
C2—C3	1.392 (6)	C12—C13	1.387 (6)
C2—H2	0.9300	C12—H12	0.9300
C3—C4	1.392 (5)	C13—H13	0.9300
C3—C6	1.463 (5)	C14—H14A	0.9600
C4—C5	1.367 (5)	C14—H14B	0.9600
C4—H4A	0.9300	C14—H14C	0.9600

N1 ⁱ —Cu1—N1	180	C7—C6—H6	116.3
N1—Cu1—O2	89.81 (12)	C3—C6—H6	116.3
N1—Cu1—O3	91.55 (11)	C6—C7—C8	126.8 (4)
O2 ⁱ —Cu1—O2	180	C6—C7—H7	116.6
O2—Cu1—O3	56.93 (11)	C8—C7—H7	116.6
C11—O1—C14	118.1 (4)	C13—C8—C9	116.5 (4)
N2—O2—Cu1	102.1 (2)	C13—C8—C7	120.4 (4)
C1—N1—C5	116.7 (3)	C9—C8—C7	123.0 (4)
C1—N1—Cu1	122.3 (3)	C10—C9—C8	122.7 (4)
C5—N1—Cu1	120.8 (3)	C10—C9—H9	118.7
O4—N2—O3	122.4 (4)	C8—C9—H9	118.7
O4—N2—O2	120.3 (4)	C11—C10—C9	119.5 (4)
O3—N2—O2	117.3 (4)	C11—C10—H10	120.3
N1—C1—C2	123.3 (4)	C9—C10—H10	120.3
N1—C1—H1	118.3	O1—C11—C12	116.4 (4)
C2—C1—H1	118.3	O1—C11—C10	124.3 (4)
C1—C2—C3	120.4 (4)	C12—C11—C10	119.3 (4)
C1—C2—H2	119.8	C11—C12—C13	120.4 (4)
C3—C2—H2	119.8	C11—C12—H12	119.8
C4—C3—C2	115.7 (4)	C13—C12—H12	119.8
C4—C3—C6	124.2 (4)	C8—C13—C12	121.6 (4)
C2—C3—C6	120.2 (4)	C8—C13—H13	119.2
C5—C4—C3	120.6 (4)	C12—C13—H13	119.2
C5—C4—H4A	119.7	O1—C14—H14A	109.5
C3—C4—H4A	119.7	O1—C14—H14B	109.5
N1—C5—C4	123.2 (4)	H14A—C14—H14B	109.5
N1—C5—H5	118.4	O1—C14—H14C	109.5
C4—C5—H5	118.4	H14A—C14—H14C	109.5
C7—C6—C3	127.5 (4)	H14B—C14—H14C	109.5
N1—Cu1—O2—N2	-92.2 (2)	C4—C3—C6—C7	-0.8 (7)
O2 ⁱ —Cu1—N1—C1	-47.6 (4)	C2—C3—C6—C7	178.5 (4)
O2—Cu1—N1—C1	132.4 (4)	C3—C6—C7—C8	-176.1 (4)
O2 ⁱ —Cu1—N1—C5	127.9 (3)	C6—C7—C8—C13	-167.3 (4)
O2—Cu1—N1—C5	-52.1 (3)	C6—C7—C8—C9	13.0 (7)
Cu1—O2—N2—O4	179.9 (3)	C13—C8—C9—C10	1.5 (7)
Cu1—O2—N2—O3	0.4 (4)	C7—C8—C9—C10	-178.8 (4)
C5—N1—C1—C2	-1.8 (7)	C8—C9—C10—C11	-0.7 (7)
Cu1—N1—C1—C2	173.8 (4)	C14—O1—C11—C12	169.2 (4)
N1—C1—C2—C3	-0.3 (8)	C14—O1—C11—C10	-11.6 (6)
C1—C2—C3—C4	2.0 (7)	C9—C10—C11—O1	-179.4 (4)
C1—C2—C3—C6	-177.4 (4)	C9—C10—C11—C12	-0.2 (7)
C2—C3—C4—C5	-1.6 (6)	O1—C11—C12—C13	179.5 (4)
C6—C3—C4—C5	177.7 (4)	C10—C11—C12—C13	0.3 (7)
C1—N1—C5—C4	2.3 (6)	C9—C8—C13—C12	-1.5 (7)
Cu1—N1—C5—C4	-173.5 (3)	C7—C8—C13—C12	178.8 (4)
C3—C4—C5—N1	-0.5 (7)	C11—C12—C13—C8	0.6 (7)

Symmetry codes: (i) $-x+1, -y+2, -z+1$.

Fig. 1

