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Key indicators

Single-crystal X-ray study
 T = 91 K
 Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
 R factor = 0.027
 wR factor = 0.064
 Data-to-parameter ratio = 24.4

For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

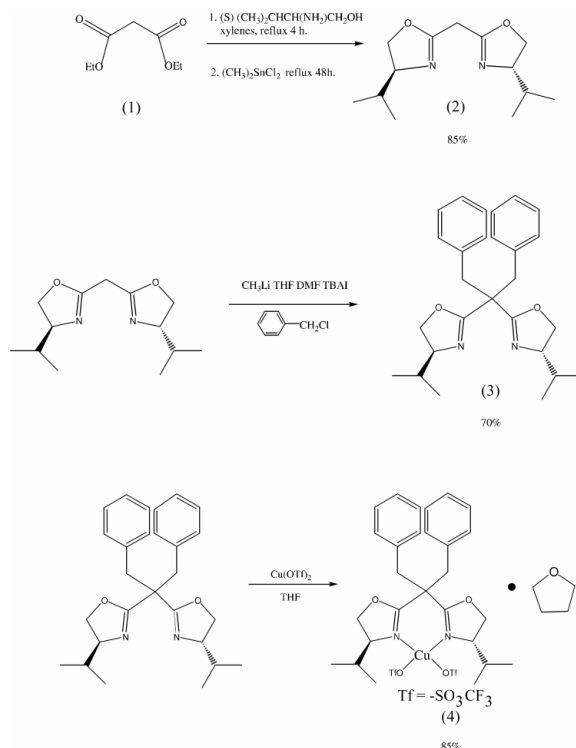
A solution phase catalyst for an enantioselective Diels–Alder reaction

A new chiral catalyst for the enantioselective Diels–Alder reaction has been synthesized, namely [(4*S*,4'*S*)-4,4',5,5'-tetrahydro-4,4'-diisopropyl-2,2'-(dibenzylmethylene)dioxazole- κ^2N,N']bis(trifluoromethanesulfonato- κO)copper(II) tetrahydrofuran solvate, $[\text{Cu}(\text{CF}_3\text{O}_3\text{S})_2(\text{C}_{27}\text{H}_{34}\text{N}_2\text{O}_2)] \cdot \text{C}_4\text{H}_8\text{O}$. It is used in a model study for comparing solid-phase and solution-phase catalyst activity.

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Comment

Diels–Alder reactions are among the most useful of all synthetic processes for the construction of complex molecules and, for this reason, they have been studied extensively and refined. Nonetheless, existing methodology is still not ideal, since there are drawbacks and limitations for all the known procedures. The utility of *C*₂-symmetric Cu^{II}-bis(oxazoline) complexes as chiral Lewis acids capable of catalyzing Diels–Alder reactions with high enantioselectivity is well documented (Annunziata *et al.*, 2001; Hallman & Moberg, 2001; Johnson & Evans, 2000; Orlandi *et al.*, 2001; Rechavi & Lemaire, 2001; Woerpel, 1998). We describe here the preparation and crystal structure of a solution-phase *C*₂-symmetric Cu^{II}-bis(oxazoline) catalyst, (4), which is used as a model for a practical solid-phase catalyst.



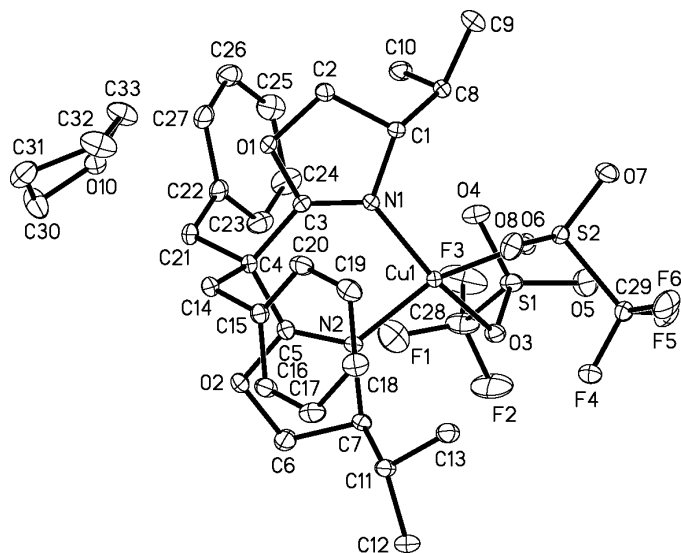


Figure 1

View of (4), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 35% probability level. H atoms have been omitted for clarity.

The crystal structure of (4) shows unusual four-coordinate geometry for Cu^{II} . The bis(oxazoline) ligand provides two N-donors, while the two trifluoromethanesulfonate anions coordinate through O atoms. The resulting geometry at Cu is square planar, with a tetrahedral distortion. For the CuN_2O_2 plane, displacements are Cu1 0.0247 (5), N1 -0.3739 (6), N2 0.3822 (6), O3 -0.4059 (6), and O6 0.3728 (6) Å. As depicted in Fig. 1, the Cu^{II} center is highly congested. There are long axial contacts from Cu to the H atom of an isopropyl group ($\text{Cu1}\cdots\text{H13}$ 2.68 Å) and to an O atom of one of the trifluoromethanesulfonates [$\text{Cu1}\cdots\text{O4}$ 2.6751 (12) Å]. The ligated oxygen S—O bond lengths are longer than the average of the other two, by 0.053 Å for S1 and 0.041 Å for S2.

Experimental

The method of preparation of the enantiomerically pure product is based on the synthesis which begins with *S*-(CH_3)₂-CHCH(NH_2)CH₂OH (see Scheme). The complex is formed as follows: to an oven-dried round-bottomed flask containing a magnetic stirrer bar were added in an inert atmosphere *S,S*-bis(isopropyl-oxazoline) (418.58 mg, 1 mmol) and Cu(trifluoromethanesulfonate)₂ (361.68 mg, 1 mmol). The flask was capped and charged with solvent (tetrahydrofuran, 50 ml). The resulting suspension was stirred rapidly for 1 h to give a dark-green solution. The reaction mixture was concentrated in vacuum to incipient crystallization. Overnight storage in a *ca* 253 K refrigerator yielded the title compound as large green crystals.

Crystal data

$[\text{Cu}(\text{CF}_3\text{O}_3\text{S})_2(\text{C}_{27}\text{H}_{34}\text{N}_2\text{O}_2)] \cdot \text{C}_4\text{H}_8\text{O}$
 $M_r = 852.35$
 Orthorhombic, $P2_12_12_1$
 $a = 10.5996$ (14) Å
 $b = 17.933$ (2) Å
 $c = 19.575$ (3) Å
 $V = 3720.7$ (8) Å³
 $Z = 4$

$D_x = 1.522$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 973 reflections
 $\theta = 2.2\text{--}30.0^\circ$
 $\mu = 0.78$ mm⁻¹
 $T = 91$ (2) K
 Plate, green
 $0.43 \times 0.17 \times 0.09$ mm

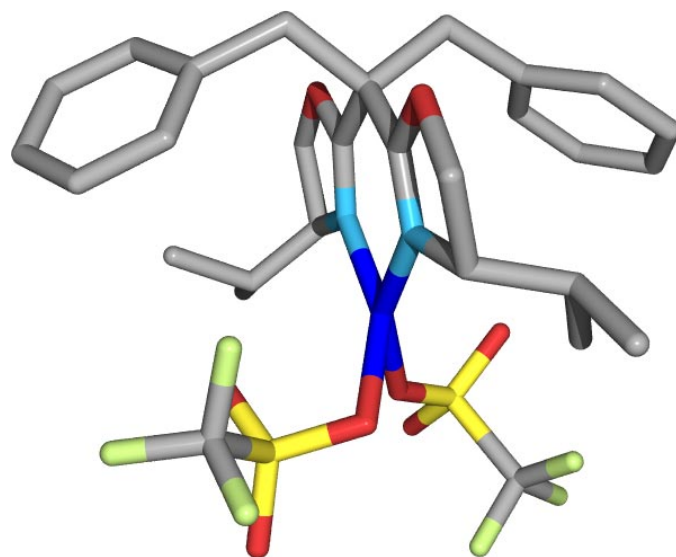


Figure 2

A drawing of (4) generated using *PovChem* (Thiessen, 2000) and *POV-Ray* (The POV-Ray Team, 1999).

Data collection

Bruker SMART 1000
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 2001)
 $T_{\text{min}} = 0.729$, $T_{\text{max}} = 0.932$
 50497 measured reflections

11771 independent reflections
 10510 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 31.5^\circ$
 $h = -15 \rightarrow 15$
 $k = -25 \rightarrow 25$
 $l = -28 \rightarrow 27$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.064$
 $S = 1.02$
 11771 reflections
 482 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.032P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³
 Absolute structure: Flack (1983);
 5111 Friedel reflections
 Flack parameter = 0.000 (5)

Table 1

Selected geometric parameters (Å, °).

Cu1—N2	1.9344 (12)	Cu1—O6	1.9598 (10)
Cu1—N1	1.9471 (12)	Cu1—O3	2.0183 (11)
N2—Cu1—N1	92.07 (5)	N2—Cu1—O3	91.46 (5)
N2—Cu1—O6	157.99 (5)	N1—Cu1—O3	155.85 (5)
N1—Cu1—O6	98.95 (5)	O6—Cu1—O3	86.25 (5)

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

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