

3.74 Å from H18A. This distance was only slightly less than that from three other H atoms in other molecules; furthermore, it was only 0.80 Å from an equivalent of itself.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Blessing, 1995; Sheldrick, 1996); program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL97*.

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μ -[1,1'-(1,2-Ethanediy)]bis(1H-1,2,4-triazole)-N⁴:N^{4'}-bis{bis[1,1,1-trifluoro-3-(2-thenoyl)acetonato-O,O']copper(II)}

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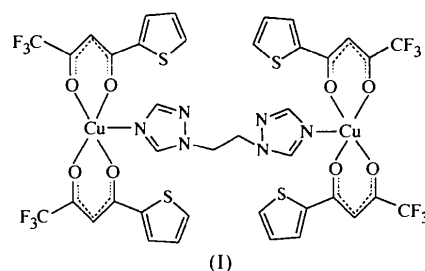
(Received 6 April 1998; accepted 15 September 1998)

Abstract

The crystal structure determination of the title complex, [Cu₂(C₈H₄F₃O₂S)₄(C₆H₈N₆)₂] or [Cu(TTA)₂]₂btrz, where TTA is 1,1,1-trifluoro-3-(2-thenoyl)acetone and btrz is μ -[1,1'-(1,2-ethanediy)]bis(1H-1,2,4-triazole)], shows that the btrz ligand links two Cu^{II} ions, forming a binuclear complex. Each Cu atom is in a distorted square-pyramidal coordination environment.

Comment

In the search for molecular-based materials with functions of catalysis, magnetism and clathration, polynuclear coordination complexes have recently been widely studied (Makoto *et al.*, 1994). Although many rigid bridging ligands, such as 4,4'-bipyridine (Fujita *et al.*, 1994), *trans*-1,2-bis(2-pyridyl)ethylene (Kitagawa *et al.*, 1991) and metalloporphyrins (Abrahams *et al.*, 1991), have been employed to build up these materials, relatively few flexible ligands have been exploited for this purpose. We report here the preparation and crystal structure of the binuclear copper(II) complex [Cu(TTA)₂]₂btrz, (I), where TTA is 1,1,1-trifluoro-3-(2-thenoyl)acetone and btrz is μ -[1,1'-(1,2-ethanediy)]bis(1H-1,2,4-triazole)]. In (I), the flexible btrz ligand (Torres *et al.*, 1988) links two Cu^{II} ions.



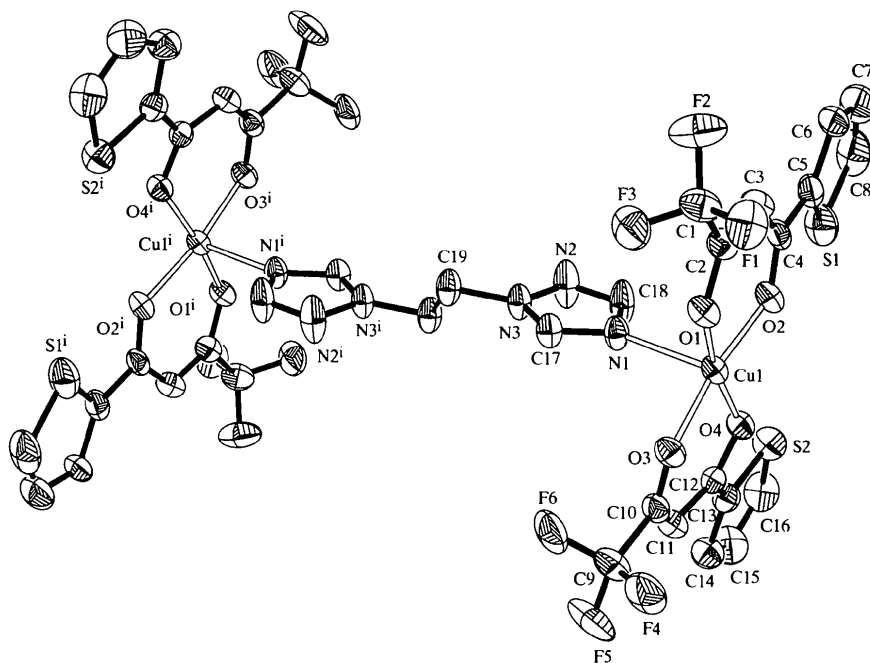


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i) $-1-x, 2-y, 1-z$]

The molecular structure of (I) is shown in Fig. 1. There are four potentially coordinating N atoms in the btrz ligand, but only two of them coordinate to the Cu atoms, forming a binuclear complex. The Cu atoms are in a distorted square-pyramidal environment: the basal plane is composed of four O atoms from two TTA ligands, with a mean deviation of 0.013 Å from the least-squares plane, and the apical site is occupied by an N atom of the btrz ligand. The intramolecular Cu1...Cu1ⁱ distance is 12.473(2) Å, precluding any interactions between the two Cu atoms in the molecule [symmetry code: (i) $-1-x, 2-y, 1-z$]. The shortest intermolecular Cu1...Cu1($-x, 1-y, 1-z$) distance is 4.995(2) Å. The Cu—O distances [1.936(2)–1.950(2) Å] are similar to those in Cu(TTA)₂ (1.945–1.970 Å; Li *et al.*, 1995). The Cu—N bond length is 2.290(3) Å, which is close to that in [Cu(TTA)₂(pyz)]_n (2.340 Å; Li *et al.*, 1995; pyz is pyrazine). The N3—C19—C19ⁱ bond angle is 110.7(3)°, which is near the expected value for Csp³ atoms (109.5°). Free intramolecular rotation around the single bond between the C19 and C19ⁱ atoms in btrz makes it quite flexible.

Experimental

The title complex was prepared from Cu(TTA)₂ and btrz. Ethanol solutions of btrz (1 mmol, 10 ml) and Cu(TTA)₂ (2 mmol, 20 ml) were stirred together, and the resulting

solution was allowed to stand for two weeks at room temperature. Green crystals were obtained in 40% yield.

Crystal data

[Cu₂(C₈H₄F₃O₂S)₄(C₆H₈N₆)]

M_r = 1175.95

Triclinic

P $\bar{1}$

a = 9.310(2) Å

b = 11.341(4) Å

c = 11.887(3) Å

α = 102.01(2)°

β = 97.05(2)°

γ = 104.81(2)°

V = 1166.2(5) Å³

Z = 1

D_x = 1.674 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 4.94–15.32°

μ = 1.195 mm⁻¹

T = 293(2) K

Block

0.43 × 0.38 × 0.36 mm

Green

Data collection

Siemens P4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan (North *et al.*, 1968)

T_{min} = 0.612, *T_{max}* = 0.650

4885 measured reflections

4065 independent reflections

3307 reflections with

I > 2σ(*I*)

R_{int} = 0.020

θ_{\max} = 25°

h = -1 → 11

k = -13 → 12

l = -14 → 14

3 standard reflections

every 97 reflections

intensity decay: 3.42%

RefinementRefinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.038$ $wR(F^2) = 0.123$ $S = 1.013$

4061 reflections

373 parameters

H atoms riding

 $w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 0.13P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.290 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.458 \text{ e } \text{\AA}^{-3}$

Extinction correction:

SHELXTL (Siemens, 1995)

Extinction coefficient:

0.0011 (11)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cu1—O4	1.936 (2)	Cu1—N1	2.290 (3)
Cu1—O2	1.941 (2)	N3—C19	1.454 (4)
Cu1—O1	1.943 (2)	C19—C19 ⁱ	1.486 (7)
Cu1—O3	1.950 (2)		
O4—Cu1—O2	84.24 (9)	O4—Cu1—N1	89.88 (10)
O4—Cu1—O1	170.40 (9)	O2—Cu1—N1	91.17 (10)
O2—Cu1—O1	92.39 (9)	O1—Cu1—N1	99.19 (10)
O4—Cu1—O3	92.29 (9)	O3—Cu1—N1	96.24 (10)
O2—Cu1—O3	171.81 (9)	N3—C19—C19 ⁱ	110.7 (3)
O1—Cu1—O3	89.84 (9)		

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

The F atoms of the two CF_3 groups are disordered. The site-occupancy factors were fixed at 0.5 for each of the F atoms. All C—F distances were constrained to be equal, with an s.u. of 0.01 \AA , and the F—F distances were also constrained. These constrained C—F and F—F distances were refined as free variables. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS (Siemens, 1994). The structure was solved by direct methods and refined on F^2 using full-matrix least-squares methods. All non-H atoms were refined anisotropically. H atoms were placed in calculated positions (C—H 0.96 \AA), assigned fixed isotropic displacement parameters at 1.2 times the equivalent U_{iso} of the atoms to which they are attached (1.5 times for methyl groups) and allowed to ride on their respective parent atoms. The contributions of these atoms were included in the structure-factor calculations.

Data collection: XSCANS. Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL (Siemens, 1995). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

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cis-Bis(2-amino-1,3-benzothiazole- N^3)bis(formato- O, O')copper(II)

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Abstract

The title complex, *cis*-bis(2-amino-1,3-benzothiazole- N^3)bis(formato- O, O')copper(II), $[\text{Cu}(\text{CHO}_2)_2(\text{C}_7\text{H}_6\text{N}_2\text{S})_2]$, displays C_2 symmetry with the Cu atom adopting a distorted octahedral (4 + 2) coordination. The four closest donor atoms are two N atoms of 2-aminobenzothiazole and two O atoms of the carboxylate groups. They form a distorted square-planar arrangement, with Cu—N and Cu—O distances of 1.991 (2) and 1.993 (2) \AA , respectively. Two longer out-of-plane Cu—O bonds [2.538 (2) \AA] from the remaining O atoms of the formate groups complete the strongly distorted square-bipyramidal coordination of the Cu atom. The H atoms of each amino group of the 2-aminobenzothiazole molecules form intra- and intermolecular hydrogen bonds with O atoms from the carboxylate groups. Intermolecular S...S secondary bonding of 3.502 (2) \AA is observed between neighbouring chains of molecules connected by hydrogen bonds.

Comment

Although expected to have important biological activity (Macíček *et al.*, 1987; Armstrong *et al.*, 1992), the structures of 2-aminobenzothiazole complexes have not been intensively investigated. A search of the Cambridge Structural Database (Allen *et al.*, 1979) did not reveal any information on 2-amino-