

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Berger, R. M. (1990). *Inorg. Chem.* **29**, 1920–1924.
 Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488–492.
 Braunstein, C. H., Baker, A. D., Strekas, T. C. & Gafney, H. D. (1984). *Inorg. Chem.* **23**, 857–864.
 Engelhardt, L. M., Pakawatchai, C., White, A. H. & Healy, P. C. (1985). *J. Chem. Soc. Dalton Trans.* pp. 125–133.
 Enraf–Nonius (1977). *CAD-4 Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
 Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
 Huang, N.-T., Pennington, W. T. & Petersen, J. D. (1991). *Acta Cryst.* **C47**, 2011–2012.
 Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Kirchhoff, J. R., McMillin, D. R., Robinson, W. R., Powell, D. R., McKenzie, A. T. & Chen, S. (1985). *Inorg. Chem.* **24**, 3928–3933.
 Lee, Y. F., Kirschbaum, K., Berger, R. M. & Kirchhoff, J. R. (1994). *Inorg. Chem.* Submitted.
 Morgan, L. W., Goodwin, K. V., Pennington, W. T. & Petersen, J. D. (1992). *Inorg. Chem.* **31**, 1103–1106.
 Ruminski, R. & Cambron, R. T. (1990). *Inorg. Chem.* **29**, 1575–1578.
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1994). **C50**, 1699–1701

A Binuclear Copper(II) Complex: μ -(4,4'-Bipyridine)-*N,N'*-bis[bis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato-*O,O'*)copper]

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(Received 10 August 1992; accepted 25 March 1994)

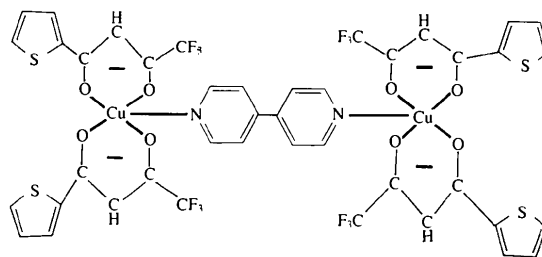
Abstract

The bisdiketonato-copper complex bis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato-*O,O'*]copper(II) and 4,4'-bipyridine give the binuclear title complex, $[\text{Cu}_2(\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S})_4(\text{C}_{10}\text{H}_8\text{N}_2)]$, when crystallized from

ethanol, which consists of two Cu-complex units bridged by a bipyridine molecule. Each copper(II) ion has a square-pyramidal environment with the axial position occupied by one N atom of 4,4'-bipyridine.

Comment

We are interested in binuclear transition metal compounds in which the metal ions are bridged by bidentate ligands (Kahn, 1985) and the phenomenon of magnetic interaction between paramagnetic metal ions. We have reported the chain structure *catena*-poly[bis{4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato-*O,O'*}copper- μ -(4,4'-bipyridine)-*N,N'*] (Gou, You, Xu, Zhou, Yu, Yu & Zhu, 1991). We now report the structure of a binuclear copper complex: 4,4'-bipyridine-bridged bis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato-*O,O'*]copper(II).



(I)

The title complex, (I), was prepared according to the literature method (Gou *et al.*, 1991). By dissolving the title complex in dmf solution, crystals of the above mentioned chain complex can be obtained, the crystal structure of which has been reported by Gou *et al.* (1991). In ethanol solution, crystals of the binuclear complex were grown. The structure proposed is consistent with elemental analysis: calculated for $\text{C}_{42}\text{H}_{24}\text{Cu}_2\text{F}_{12}\text{N}_2\text{O}_8\text{S}_4$, C 43.19, H 2.06, N 2.40%; found, C 42.96, H 2.11, N 2.27%.

Unlike the chain complex, the Cu atom of the binuclear complex has a square-pyramidal coordination geometry. Four O atoms of two 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato ligands lie around each Cu atom, forming a square plane. The Cu atom and the N atom of 4,4'-bipyridine are located 0.178 (1) and 2.430 (6) Å, respectively, above the plane. This results in the square-pyramidal configuration of the pentacoordinate copper(II) ion. The two pyridyl units of the 4,4'-bipyridine moiety have a coplanar arrangement [dihedral angle 0.68 (2)°]. The four Cu—O bond lengths are shorter, whereas Cu—N is longer than the relevant values of the chain complex described by Gou *et al.* (1991). The bond angles N—Cu—O(*n*) (*n* = 1–4) are 91.1(2), 100.4 (2), 99.3 (2) and 90.1 (2)°, respectively. The two thiophene rings around each Cu atom are in a *cis* orientation; unlike those of the chain complex, which are *trans* to each other.

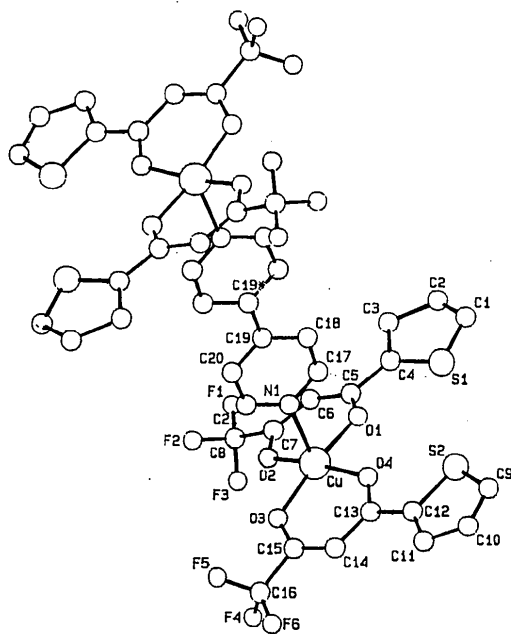


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of the title molecule.

Experimental

Crystal data

[Cu₂(C₈H₄F₃O₂S)₄·
(C₁₀H₈N₂)]

M_r = 1167.99

Triclinic

P $\bar{1}$

a = 8.547 (2) Å

b = 10.187 (4) Å

c = 13.895 (6) Å

α = 72.45 (3)°

β = 85.20 (3)°

γ = 86.06 (3)°

V = 1148.2 (6) Å³

Z = 1

D_x = 1.689 Mg m⁻³

Data collection

Enraf-Nonius CAD-4
diffractometer

θ - 2θ scans [width (0.70 +
0.35tan θ)°; speed 1-5°
min⁻¹]

Absorption correction:
empirical

T_{min} = 0.773, *T_{max}* =
0.998

4695 measured reflections

4301 independent reflections

Mo *K* α radiation

λ = 0.7107 Å

Cell parameters from 25
reflections

θ = 10-15°

μ = 1.20 mm⁻¹

T = 295 K

Prism

0.40 × 0.30 × 0.20 mm

Green

Crystal source: ethanol

solution at room
temperature for one month

2881 observed reflections

[*F_o* ≥ 3σ(*F_o*)]

R_{int} = 0.018

θ_{max} = 26°

h = -10 → 10

k = -12 → 12

l = 0 → 17

3 standard reflections

frequency: 60 min

intensity variation: <0.6%

Refinement

Refinement on *F*

R = 0.056

wR = 0.063

(Δ/σ)_{max} = 0.09

$\Delta\rho_{max}$ = 0.79 e Å⁻³

$\Delta\rho_{min}$ = -0.09 e Å⁻³

S = 1.52

2881 reflections

317 parameters

H-atom parameters not
refined

w = 1/σ²(*F_o*)

Extinction correction: none

Atomic scattering factors

from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Cu	0.0239 (1)	0.36942 (8)	0.24668 (6)	3.66 (2)
S1	-0.2598 (3)	0.0578 (3)	0.1491 (2)	8.00 (7)
S2	-0.3143 (3)	0.5698 (2)	-0.0163 (2)	5.79 (5)
F1	0.2828 (8)	-0.0739 (6)	0.4810 (6)	13.5 (2)
F2	0.3169 (8)	0.1132 (7)	0.5017 (4)	11.3 (2)
F3	0.4303 (7)	0.0711 (9)	0.3801 (5)	11.9 (2)
F4	0.4140 (6)	0.6712 (6)	0.1741 (6)	10.6 (2)
F5	0.2722 (8)	0.7408 (6)	0.2754 (4)	10.8 (2)
F6	0.2704 (7)	0.8486 (5)	0.1238 (5)	12.3 (2)
O1	-0.0779 (5)	0.2147 (4)	0.2299 (4)	4.2 (1)
O2	0.1634 (6)	0.2511 (5)	0.3416 (4)	4.7 (1)
O3	0.1527 (5)	0.5195 (5)	0.2438 (4)	4.6 (1)
O4	-0.0888 (5)	0.4817 (4)	0.1321 (3)	4.1 (1)
N1	-0.1772 (7)	0.4058 (6)	0.3540 (4)	4.2 (1)
C1	-0.330 (1)	-0.0963 (8)	0.1638 (7)	6.6 (2)
C2	-0.270 (1)	-0.1945 (9)	0.2385 (8)	7.5 (3)
C3	-0.1535 (7)	-0.1616 (6)	0.2975 (5)	3.7 (1)
C4	-0.1444 (8)	-0.0078 (7)	0.2460 (5)	4.3 (2)
C5	-0.0494 (8)	0.0886 (6)	0.2742 (5)	3.9 (2)
C6	0.0662 (9)	0.0385 (7)	0.3426 (6)	5.0 (2)
C7	0.1628 (9)	0.1208 (7)	0.3687 (5)	4.5 (2)
C8	0.297 (1)	0.0540 (9)	0.4322 (7)	6.7 (2)
C9	-0.391 (1)	0.7047 (9)	-0.1047 (6)	6.1 (2)
C10	-0.320 (1)	0.8216 (8)	-0.1173 (6)	5.5 (2)
C11	-0.1936 (8)	0.8094 (7)	-0.0548 (5)	4.0 (2)
C12	-0.1773 (7)	0.6695 (6)	0.0062 (5)	3.6 (1)
C13	-0.0682 (7)	0.6067 (6)	0.0829 (5)	3.5 (1)
C14	0.0494 (8)	0.6845 (7)	0.1016 (5)	4.4 (2)
C15	0.1482 (8)	0.6345 (7)	0.1766 (5)	4.1 (1)
C16	0.275 (1)	0.7258 (8)	0.1852 (7)	6.3 (2)
C17	-0.3220 (9)	0.3905 (8)	0.3391 (6)	5.5 (2)
C18	-0.4515 (8)	0.4238 (8)	0.3927 (6)	5.4 (2)
C19	-0.4318 (8)	0.4798 (7)	0.4702 (5)	3.9 (2)
C20	-0.280 (1)	0.497 (1)	0.4854 (6)	6.8 (2)
C21	-0.1582 (9)	0.459 (1)	0.4277 (6)	6.9 (2)

Table 2. Selected geometric parameters (Å, °)

Cu—O1	1.933 (4)	Cu—O2	1.929 (4)
Cu—O3	1.933 (4)	Cu—O4	1.944 (4)
Cu—N1	2.266 (5)	O1—C5	1.262 (6)
C5—C6	1.391 (8)	C6—C7	1.359 (8)
O2—C7	1.266 (7)	C4—C5	1.474 (7)
N1—C17	1.299 (7)	C17—C18	1.362 (9)
C18—C19	1.389 (8)	C19—C20	1.359 (8)
C20—C21	1.368 (9)	N1—C21	1.320 (8)
N1—Cu—O1	91.1 (2)	N1—Cu—O2	100.4 (2)
N1—Cu—O3	99.3 (2)	N1—Cu—O4	90.1 (2)
O1—Cu—O2	92.5 (2)	O2—Cu—O3	87.0 (2)
O3—Cu—O4	92.3 (2)	O1—Cu—O4	86.1 (2)
O1—C5—C6	124.4 (5)	C5—C6—C7	123.4 (5)
O2—C7—C6	128.9 (6)	O1—C5—C4	115.4 (5)
C17—N1—C21	115.5 (5)		

Data collection: Enraf-Nonius CAD-4 software. All calculations were performed on a MicroVAX II computer using the *SDP* programs (Enraf-Nonius, 1985). The structure was solved by Patterson methods and difference Fourier syntheses, refinement was by the full-matrix least-squares techniques, and H atoms were placed in calculated positions.

This work was supported by a grant for key research projects from the State Science and Technology Commission and National Nature Science Foundation of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Enraf-Nonius (1985). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
 Gou, S.-H., You, X.-Z., Xu, Z., Zhou, Z.-Y., Yu, K.-B., Yu, Y.-P. & Zhu, D.-L. (1991). *Acta Cryst.* C47, 1303–1305.
 Kahn, O. (1985). *Angew. Chem. Int. Ed. Engl.* 24, 834–850.
 Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

Acta Cryst. (1994). C50, 1701–1703

Bis(3,3'-dimethylene-2,2'-biquinolinium) Tetrabromoaurate(III) Dibromoaurate(I)

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(Received 6 July 1993; accepted 4 January 1994)

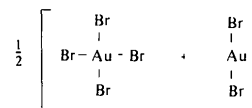
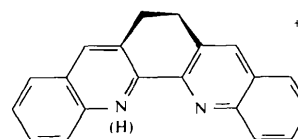
Abstract

The structure of the title compound, $(C_{20}H_{15}N_2)[AuBr_3]$, has been determined. It consists of two anions, $[AuBr_4]^-$ and $[AuBr_2]^-$, attached to two 3,3'-dimethylene-2,2'-

biquinolinium (or 6,7-dihydro-benzo[2,1-*b*:3,4-*b'*]diquinolinium) cations by hydrogen bonds.

Comment

For some time, gold chemistry has received great attention, mainly because of the specific properties and structure of its compounds (Schmidbaur, 1990). It is known that the reaction of Au^{III} with bidentate nitrogen-containing ligands produced either tetra- or pentacoordinated auriferous complexes of Au^{III} having distorted square-planar, tetrahedral, square-pyramidal or bipyramidal coordination (O'Connor & Sinn, 1978; Robinson & Sinn, 1975; Chalton, Harris, Petit & Stephenson, 1966). However, reactions carried out under special conditions using similar bidentate nitrogen ligands can generate gold compounds having an ionic structure different from the classic complex one. In the title ionic structure, (I), the protonated nitrogen-containing ligand plays the role of the cation while the two associated anions are tetrabromoaurate(III) and dibromoaurate(I). Though the mechanism of the reaction is not yet clear, the origin of the Au^I species should be found in the oxidation of the solvent by the starting Au^{III} compound. In this work we report the structure of $(C_{20}H_{15}N_2)[AuBr_3]$ obtained from the reaction of potassium tetrabromoaurate(III) and 3,3'-dimethylene-2,2'-biquinoline under refluxing methanol conditions.



(I)

The structure of the title compound consists of discrete $[AuBr_4]^-$ and $[AuBr_2]^-$ units, with the gold ions located at inversion centers, and substituted biquinolinium cations as counterions (Fig. 1). The $[AuBr_4]^-$ unit has regular square-planar geometry with *trans* angles of 90.0° and Au—Br distances of 2.420 (1) and 2.416 (1) Å. The $[AuBr_2]^-$ unit is strictly linear with an Au—Br distance of 2.386 (1) Å. The two 'wings' of the organic cation are effectively planar and are twisted around the C(19)—C(20) bond by equal amounts, which is seen in the two identical torsion angles C(12)—C(11)—C(10)—C(9) = C(7)—C(8)—C(9)—C(10) = -153.8° .