C7	0.0898 (4)	0.6780 (3)	0.3188 (2)	0.0552 (14)
C8	0.0879 (4)	0.7366 (4)	0.3594 (2)	0.0583 (15)
C9	0.0872 (4)	0.8157 (3)	0.3439 (2)	0.0506 (13)
C10	0.3537 (4)	0.9821 (3)	0.2076 (2)	0.0527 (14)
C11	0.3132 (3)	0.8979 (3)	0.2152 (2)	0.0463 (13)
C12	0.3056 (4)	0.8222 (3)	0.1331 (2)	0.0462 (12)
C13	0.2712 (4)	0.7845 (3)	0.0832 (2)	0.0464 (13)
C14	0.1722 (4)	0.7901 (3)	0.0656 (2)	0.0477 (13)
C15	0.1460 (5)	0.7446 (4)	0.0171 (2)	0.065 (2)
C16	0.2150 (6)	0.7011 (4)	−0.0107 (2)	0.081 (2)
C17	0.3116 (6)	0.6988 (4)	0.0051 (2)	0.078 (2)
C18	0.3386 (5)	0.7389 (4)	0.0517 (2)	0.066 (2)
C19	0.2816 (4)	1.0730 (4)	0.1368 (2)	0.064 (2)
C20	0.2419 (4)	1.0126 (3)	0.0942 (2)	0.0542 (14)
C21	0.0729 (4)	1.0176 (3)	0.0794 (2)	0.0442 (12)
C22	−0.0298 (3)	1.0057 (3)	0.0846 (2)	0.0411 (12)
C23	−0.0708 (3)	0.9496 (3)	0.1223 (2)	0.0386 (11)
C24	−0.1739 (4)	0.9443 (3)	0.1247 (2)	0.0490 (13)
C25	−0.2323 (4)	0.9935 (3)	0.0920 (2)	0.0565 (15)
C26	−0.1916 (4)	1.0473 (3)	0.0549 (2)	0.0593 (15)
C27	−0.0920 (4)	1.0523 (3)	0.0514 (2)	0.0498 (13)
N5	0.0489 (6)	0.0834 (7)	0.3735 (4)	0.159 (4)
C28	0.0736 (8)	0.1542 (8)	0.3688 (4)	0.125 (4)
C29	0.1172 (8)	0.2254 (6)	0.3589 (5)	0.143 (4)
O4	0.4896 (14)	0.9588 (10)	0.0245 (7)	0.198 (7)

Table 2. *Selected geometric parameters* (Å, °)

Co1—O1	1.891 (3)	N1—C10	1.422 (6)
Co1—O2	1.891 (3)	N1—C19	1.436 (7)
Co1—O3	1.897 (3)	N1—C1	1.460 (7)
Co1—N2	1.940 (4)	N2—C3	1.289 (6)
Co1—N3	1.943 (4)	N2—C2	1.471 (6)
Co1—N4	1.959 (4)	N3—C12	1.283 (6)
O1—C5	1.312 (6)	N3—C11	1.482 (6)
O2—C14	1.291 (6)	N4—C21	1.286 (6)
O3—C23	1.302 (5)	N4—C20	1.470 (6)
O1—Co1—O2	84.71 (14)	C5—O1—Co1	127.5 (3)
O1—Co1—O3	86.28 (13)	C14—O2—Co1	126.4 (3)
O2—Co1—O3	86.33 (14)	C23—O3—Co1	127.1 (3)
O1—Co1—N2	94.03 (15)	C10—N1—C19	119.9 (5)
O2—Co1—N2	170.27 (15)	C10—N1—C1	120.7 (5)
O3—Co1—N2	83.96 (15)	C19—N1—C1	118.7 (4)
O1—Co1—N3	86.03 (15)	C3—N2—C2	114.3 (4)
O2—Co1—N3	95.16 (15)	C3—N2—Co1	123.9 (3)
O3—Co1—N3	172.00 (15)	C2—N2—Co1	121.6 (3)
N2—Co1—N3	94.4 (2)	C12—N3—C11	115.1 (4)
O1—Co1—N4	169.7 (2)	C12—N3—Co1	123.0 (3)
O2—Co1—N4	85.0 (2)	C11—N3—Co1	121.6 (3)
O3—Co1—N4	94.24 (15)	C21—N4—C20	115.5 (4)
N2—Co1—N4	96.3 (2)	C21—N4—Co1	122.0 (4)
N3—Co1—N4	93.7 (2)	C20—N4—Co1	122.0 (3)

H atoms were positioned geometrically except for three which were found from a difference synthesis. Water H atoms were excluded from all calculations.

Data collection: Enraf–Nonius *SDP-Plus* (Frenz, 1985). Cell refinement: Enraf–Nonuis *SDP-Plus*. Data reduction: *REDU*4 (Stoe & Cie, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON*93 (Spek, 1993). Software used to prepare material for publication: *SHELXL*93.

One of the authors (YE) thanks the A. v. Humboldt-Stiftung (Bonn) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: MU1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Attia, W. M., Zangrando, E., Randaccio, L., Antolini, L. & Lopez, C. (1989). *Acta Cryst.* C**45**, 1500–1503.

Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Gatehouse, B. M., Martin, R. L., McLachlan, G., Platts, S. N. & Spiccia, L. (1992). *Acta Cryst.* C**48**, 271–274.

Koziol, A. E., Palenik, R. C. & Palenik, G. J. (1986). *Inorg. Chem.* **25**, 4461–4462.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Spek, A. L. (1993). *PLUTON93. Program for the Display and Analysis of Crystal and Molecular Structures*. Univ. of Utrecht, The Netherlands.

Stoe & Cie (1988). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1994). C**50**, 1696–1699

[2,3-Di(2-pyridyl)pyrazine-*N*^{1},*N*$^{2'}$]bis(triphenylphosphine)copper(I) Nitrate Ethanol Solvate

KREGG T. BROOKS, DANIEL C. FINNEN,
JON R. KIRCHHOFF* AND A. ALAN PINKERTON

Department of Chemistry, University of Toledo, Toledo, OH 43606, USA

(*Received* 24 *March* 1994; *accepted* 21 *June* 1994)

Abstract

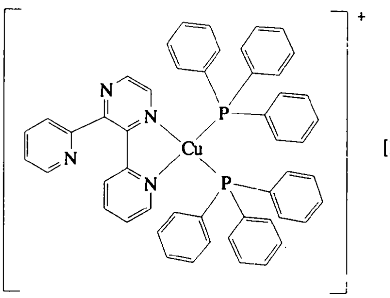
The copper(I) complex $[Cu(C_{14}H_{10}N_4)(C_{18}H_{15}P)_2]-(NO_3).C_2H_6O$, has been synthesized and its structure determined. The coordination geometry about the Cu atom is distorted tetrahedral with bidentate chelation to dpp, where dpp is 2,3-di(2-pyridyl)pyrazine, and monodentate coordination to two triphenylphosphine ligands.

Comment

The bridging ligand 2,3-di(2-pyridyl)pyrazine (dpp) has been used to prepare luminescent mono- and bimetallic complexes of ruthenium(II) and rhenium(I) (Berger, 1990; Braunstein, Baker, Strekas & Gafney, 1984; Ruminski & Cambron, 1990). However, until recently, structural information for complexes of these transition metals with dpp had not been reported (Lee, Kirschbaum, Berger & Kirchhoff, 1994). We have initiated research to synthesize and examine the luminescence properties of heterobimetallic complexes of

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

dpp with copper(I) as one metal center, and either ruthenium(II) or rhenium(I) as the second metal center. The structure of the title compound, (I), was undertaken to examine possible steric constraints with respect to coordination of a second metal center when $[Cu(dpp)(PPh_3)_2]^+$ is used as the bimetallic precursor.



(I)

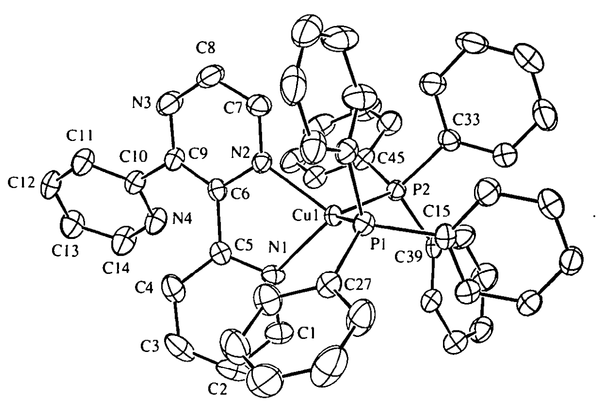


Fig. 1. View of the cation of (I) showing 50% probability ellipsoids. The H atoms are omitted for clarity. The phenyl C atoms are labelled systematically from the atom attached to the P atom.

The structure consists of discrete $[Cu(dpp)(PPh_3)_2]^+$ and NO_3^- ions with the coordination environment about the Cu cation best described as a distorted tetrahedron (Fig. 1). An ethanol molecule is found within hydrogen-bonding distance [O3···O4 2.735 (5) Å] of the NO_3^- ion and exhibits a twofold disorder of the methylene group over two sites, C52*A* and C52*B*. The Cu—P bond lengths are 2.249 (1) and 2.247 (1) Å, while the Cu—N bond lengths are 2.051 (3) Å for the pyridine N atom (N1), and 2.096 (3) Å for the pyrazine N atom (N2). These data are typical for tetrahedral bis(phosphine) copper complexes with α,α'-diimine ligands: $[Cu(2,2'\text{-bipyridine})(PPh_3)_2]^+$ Cu—P 2.246 (3) and 2.256 (3) Å, and Cu—N 2.056 (8) and 2.113 (9) Å (Engelhardt, Pakawatchai, White & Healy, 1985); $[Cu(1,10\text{-phenanthroline})(PPh_3)_2]^+$ Cu—P 2.271 (1) and 2.245 (1) Å, and Cu—N 2.070 (2) and 2.080 (2) Å, and $[Cu(2,9\text{-dimethyl-}1,10\text{-phenanthroline})(PPh_3)_2]^+$ Cu—P 2.305 (2) and 2.282 (2) Å, and Cu—N 2.105 (6) and 2.129 (4) Å (Kirchhoff, McMillin, Robinson, Powell, McKenzie & Chen, 1985). In addition, the Cu—N distances in the polymeric Cu^{II}(dpp) complex $[Cu(dpp)(H_2O)_2]_x(ClO_4)_{2x}.2xH_2O$ range from 2.005 (7) to 2.176 (8) Å (Morgan, Goodwin, Pennington & Petersen, 1992). This large range has been attributed to a pseudo Jahn–Teller distortion at the six-coordinate Cu^{II} metal center. The P1—Cu—P2 angle is 118.53 (4)° and is intermediate between those of the 1,10-phenanthroline [115.44 (4)°] and 2,2′-bipyridine [125.4 (1)°] complexes. The N1—Cu—N2 bite angle is 79.2 (1)°, which is also consistent with the analogous values for these complexes.

The dpp internal bond distances and angles are similar to those reported previously for dpp as the free ligand (Huang, Pennington & Petersen, 1991) and when coordinated in $[Re(CO)_3Cl]_2$dpp (Lee, Kirschbaum, Berger & Kirchhoff, 1994). The average deviation from planarity of the pyrazine moiety is 0.039 Å. This average deviation is intermediate between the observed deviation in the free ligand (0.007 Å) and in $[Re(CO)_3Cl]_2$dpp (0.062 Å). The dihedral angle between the pyrazine ring and the coordinated pyridyl group, N1–C5, is 26.8 (2)°, which is similar to the analogous dihedral angle in $[Re(CO)_3Cl]_2$dpp [29.7 (4)°]. The dihedral angle between the plane defined by the pyrazine and N1-pyridyl atoms, and the plane defined by the Cu and the two P atoms is 77.82 (3)°. By comparison, the analogous dihedral angles in the copper bis(phosphine) complexes with 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline are 73.35 and 82.2°, respectively (Kirchhoff, McMillin, Robinson, Powell, McKenzie & Chen, 1985). No significant inter-ligand steric interactions are observed in $[Cu(dpp)(PPh_3)_2]^+$.

Experimental

$[Cu(dpp)(PPh_3)_2]^+$ was synthesized by slow addition of a 95/5% ether/ethanol solution of 1 eq. of dpp to a suspension of $[Cu(PPh_3)_4]^+$ in ether (Kirchhoff, McMillin, Robinson, Powell, McKenzie & Chen, 1985). A crystal suitable for X-ray analysis was obtained by slow evaporation of a 5:1 ethanol/*n*-propanol solution. Elemental analysis is in excellent agreement with the crystallographically determined stoichiometry of $[Cu(dpp)(PPh_3)_2]NO_3.C_2H_6O$.

Crystal data

$[Cu(C_{14}H_{10}N_4)(C_{18}H_{15}P)_2]$-$(NO_3).C_2H_6O$
$M_r = 930.47$
Monoclinic
$P2_1/n$
$a = 12.377$ (1) Å
$b = 16.977$ (2) Å
$c = 21.583$ (2) Å
$\beta = 90.401$ (8)°
$V = 4535$ (1) Å^3
$Z = 4$
$D_x = 1.36$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–14°
$\mu = 0.601$ mm^{-1}
$T = 150$ K
Plate
0.42 × 0.22 × 0.16 mm
Yellow–orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$3\theta/4\theta$ scans
Absorption correction: refined empirical (Walker & Stuart, 1983)
$T_{min} = 0.915$, $T_{max} = 1.088$
7228 measured reflections
6571 independent reflections
5265 observed reflections [$I > 3.0\sigma(I)$]

$R_{int} = 0.036$
$\theta_{max} = 25.98°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 20$
$l = -26 \rightarrow 26$
3 standard reflections
frequency: 50 min
intensity variation: −0.53%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.053$
$S = 1.588$
5265 reflections
566 parameters
H atoms refined using a riding model

$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.933$ e Å^{-3}
$\Delta\rho_{min} = -0.094$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for C51, C52*A*/*B*; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	U_{iso}/U_{eq}
Cu1	0.25699 (3)	0.22998 (3)	0.10809 (2)	0.0214 (1)
P1	0.41529 (7)	0.25636 (6)	0.15549 (4)	0.0235 (2)
P2	0.16704 (7)	0.32943 (6)	0.06239 (4)	0.0229 (2)
O1	0.5591 (3)	0.1947 (2)	0.9755 (2)	0.073 (1)
O2	0.5632 (3)	0.2640 (2)	0.8912 (2)	0.086 (1)
O3	0.4751 (4)	0.1554 (2)	0.8946 (2)	0.087 (1)
O4	0.4780 (3)	0.1533 (2)	0.7679 (2)	0.0573 (9)
N1	0.2569 (2)	0.1203 (2)	0.0683 (1)	0.0240 (7)
N2	0.1524 (2)	0.1695 (2)	0.1674 (1)	0.0235 (7)
N3	−0.0124 (3)	0.0858 (2)	0.2230 (1)	0.0380 (9)
N4	−0.0238 (3)	−0.0069 (2)	0.0795 (1)	0.0340 (9)
N5	0.5340 (3)	0.2053 (2)	0.9202 (2)	0.056 (1)
C1	0.3288 (3)	0.0957 (2)	0.0259 (2)	0.033 (1)
C2	0.3465 (3)	0.0169 (3)	0.0133 (2)	0.044 (1)
C3	0.2895 (3)	−0.0383 (3)	0.0460 (2)	0.045 (1)
C4	0.2150 (3)	−0.0141 (2)	0.0888 (2)	0.036 (1)
C5	0.1985 (3)	0.0657 (2)	0.0988 (2)	0.0234 (9)
C6	0.1249 (3)	0.0973 (2)	0.1465 (2)	0.0219 (9)
C7	0.1006 (3)	0.1977 (2)	0.2164 (2)	0.031 (1)
C8	0.0232 (3)	0.1533 (3)	0.2463 (2)	0.043 (1)
C9	0.0351 (3)	0.0592 (2)	0.1711 (2)	0.0262 (9)
C10	−0.0219 (3)	−0.0084 (2)	0.1414 (2)	0.028 (1)
C11	−0.0732 (3)	−0.0657 (2)	0.1760 (2)	0.036 (1)
C12	−0.1244 (3)	−0.1267 (2)	0.1455 (2)	0.038 (1)
C13	−0.1249 (3)	−0.1273 (3)	0.0822 (2)	0.040 (1)
C14	−0.0748 (3)	−0.0662 (3)	0.0510 (2)	0.042 (1)
C15	0.4795 (3)	0.3452 (2)	0.1273 (2)	0.0241 (9)
C16	0.5155 (3)	0.3452 (2)	0.0661 (2)	0.0272 (9)
C17	0.5603 (3)	0.4125 (2)	0.0407 (2)	0.030 (1)
C18	0.5702 (3)	0.4796 (2)	0.0749 (2)	0.034 (1)
C19	0.5329 (3)	0.4810 (2)	0.1352 (2)	0.039 (1)
C20	0.4872 (3)	0.4140 (2)	0.1609 (2)	0.035 (1)
C21	0.3939 (3)	0.2709 (2)	0.2382 (2)	0.0290 (9)
C22	0.3064 (3)	0.3167 (3)	0.2558 (2)	0.040 (1)
C23	0.2768 (4)	0.3213 (3)	0.3179 (2)	0.053 (1)
C24	0.3331 (4)	0.2825 (3)	0.3622 (2)	0.055 (1)
C25	0.4208 (4)	0.2381 (3)	0.3460 (2)	0.054 (1)
C26	0.4520 (4)	0.2312 (2)	0.2838 (2)	0.041 (1)
C27	0.5207 (3)	0.1820 (2)	0.1534 (2)	0.0279 (9)
C28	0.6298 (3)	0.1997 (3)	0.1535 (2)	0.049 (1)
C29	0.7071 (4)	0.1400 (3)	0.1547 (2)	0.067 (2)
C30	0.6739 (4)	0.0622 (3)	0.1541 (2)	0.061 (1)
C31	0.5659 (4)	0.0434 (3)	0.1532 (2)	0.051 (1)
C32	0.4900 (3)	0.1032 (2)	0.1535 (2)	0.038 (1)
C33	0.1787 (3)	0.4239 (2)	0.1023 (2)	0.0274 (9)
C34	0.2459 (3)	0.4835 (2)	0.0817 (2)	0.036 (1)
C35	0.2606 (4)	0.5513 (3)	0.1167 (2)	0.047 (1)
C36	0.2099 (4)	0.5595 (3)	0.1727 (2)	0.047 (1)
C37	0.1432 (4)	0.5009 (3)	0.1936 (2)	0.047 (1)
C38	0.1276 (3)	0.4327 (2)	0.1590 (2)	0.037 (1)
C39	0.1992 (3)	0.3503 (2)	−0.0187 (2)	0.0256 (9)
C40	0.1343 (3)	0.3994 (3)	−0.0548 (2)	0.041 (1)
C41	0.1542 (4)	0.4099 (3)	−0.1169 (2)	0.047 (1)
C42	0.2402 (3)	0.3712 (3)	−0.1441 (2)	0.041 (1)
C43	0.3048 (3)	0.3231 (2)	−0.1094 (2)	0.040 (1)
C44	0.2844 (3)	0.3132 (2)	−0.0467 (2)	0.031 (1)
C45	0.0212 (3)	0.3119 (2)	0.0574 (2)	0.0258 (9)
C46	−0.0121 (3)	0.2355 (2)	0.0478 (2)	0.031 (1)
C47	−0.1209 (3)	0.2182 (3)	0.0367 (2)	0.042 (1)
C48	−0.1951 (3)	0.2781 (3)	0.0361 (2)	0.049 (1)
C49	−0.1631 (3)	0.3548 (3)	0.0467 (2)	0.047 (1)
C50	−0.0547 (3)	0.3721 (3)	0.0575 (2)	0.037 (1)
C51	0.3186 (6)	0.1044 (5)	0.7185 (4)	0.115 (3)
C52*A*†	0.3550 (9)	0.1826 (7)	0.7292 (5)	0.072 (3)
C52*B*†	0.371 (1)	0.1451 (8)	0.7608 (6)	0.089 (4)

† Site occupation factor 0.5.

Table 2. *Selected geometric parameters* (Å, °)

Cu1—P1	2.249 (1)	P1—C21	1.823 (4)
Cu1—P2	2.247 (1)	P1—C27	1.817 (4)
Cu1—N1	2.051 (3)	P2—C33	1.826 (4)
Cu1—N2	2.096 (3)	P2—C39	1.833 (4)
P1—C15	1.812 (4)	P2—C45	1.832 (4)
P1—Cu1—P2	118.53 (4)	C33—P2—C45	104.2 (2)
P1—Cu1—N1	111.66 (9)	C39—P2—C45	101.2 (2)
P1—Cu1—N2	111.05 (8)	Cu1—N1—C1	124.5 (3)
P2—Cu1—N1	119.98 (8)	Cu1—N1—C5	114.7 (2)
P2—Cu1—N2	109.28 (8)	C1—N1—C5	118.5 (3)
N1—Cu1—N2	79.2 (1)	Cu1—N2—C6	113.3 (2)
Cu1—P1—C15	113.3 (1)	Cu1—N2—C7	127.8 (3)
Cu1—P1—C21	109.9 (1)	C6—N2—C7	118.1 (3)
Cu1—P1—C27	118.3 (1)	C10—N4—C14	116.8 (3)
C15—P1—C21	106.5 (2)	N2—C6—C5	114.0 (3)
C15—P1—C27	104.7 (2)	N2—C6—C9	119.5 (3)
C21—P1—C27	103.1 (2)	N2—C7—C8	121.0 (4)
Cu1—P2—C33	114.6 (1)	N4—C10—C9	114.9 (3)
Cu1—P2—C39	117.0 (1)	N4—C10—C11	123.2 (3)
Cu1—P2—C45	112.9 (1)	N4—C14—C13	123.5 (4)
C33—P2—C39	105.3 (2)		

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). The ethanol molecule was refined isotropically and the disordered methylene modelled with two sites each of population 0.5. CAD-4 software (Enraf–Nonius, 1977) was used for data collection and cell refinement. Data reduction was performed using *MolEN PROCESS* (Fair, 1990). The structure was solved by the Patterson method and Fourier synthesis. *MolEN LSFM* was used to refine the structure. Molecular graphics were produced using *ORTEP*II (Johnson, 1976) and the material for publication was prepared with *MolEN CIF IN*.

We thank the College of Arts and Sciences of the University of Toledo for generous financial support of the X-ray diffraction facility. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is also gratefully acknowledged (grant No. 23968-G3).

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.* C**47**, 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.* A**39**, 158–166.

Acta Cryst. (1994). C**50**, 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}

MING-XING LI, ZHENG XU* AND XIAO-ZENG YOU

Coordination Chemistry Institute, Coordination Chemistry State Key Laboratory, Nanjing University, Nanjing 210093, People's Republic of China

CHENG-GANG CHEN

Central Laboratory, Hangzhou University, Hangzhou 310028, People's Republic of China

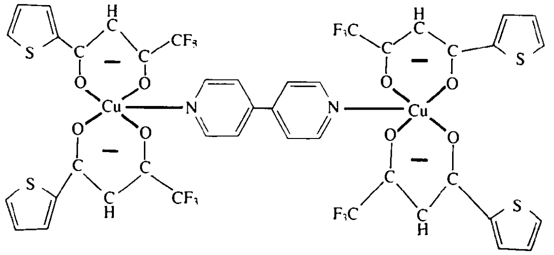
(*Received* 10 *August* 1992; *accepted* 25 *March* 1994)

Abstract

The bisdiketonato–copper complex bis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato-*O*,*O*′]copper(II) and 4,4′-bipyeridine give the binuclear title complex, $[Cu_2(C_8H_4F_3O_2S)_4(C_{10}H_8N_2)]$, 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 $C_{42}H_{24}Cu_2F_{12}N_2O_8S_4$, 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.