5·467 (1) Å; (ii) $1-x, y, -z$, (iii) $-x, y, 1-z$] which are shorter than the Nd···Nd distance in the polymer of structure (I) [6·018 (2) Å]. The presence of two carboxylate bridges in (II) may explain this. The conformations of the two independent proline rings in (II) are defined as E, C_s [Q = 0·21 (2), 0·27 (3) and φ = 212 (6)°, 250 (4)°, respectively] (Cremer & Pople, 1975). The high temperature factors of atoms C(9) and C(10) and some anomalous interatomic distances [especially C(9)—C(10) = 1·23 (5) Å] suggests slight disorder of the proline rings.

It is interesting to note that, in both complexes, the coordination sphere involves both Cl and O atoms. This is not observed in other lanthanide complexes with carboxylic acids. The greater length of the Nd—Cl bonds compared with the Nd—O bonds causes rather large distortions of the coordination polyhedra around the Nd ions. The C—C, C—O and C—N bond lengths are within normal ranges. For both complexes the crystal structures are stabilized by hydrogen bonds of type O—H···Cl and N—H···Cl (Table 3).

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Structure of a Five-Coordinate Copper(II) Complex: (2,2′-Bipyridine)[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-*O*][4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-*O*,*O*′]copper(II)

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Abstract. $[Cu(C_8H_4F_3O_2S)_2(C_{10}H_8N_2)]$, M_r = 662·08, triclinic, $P\bar{1}$, a = 10·108 (2), b = 14·455 (3), c = 9·068 (2) Å, α = 96·11 (1), β = 90·92 (1), γ = 96·12 (1)°, V = 1309·4 Å^3, Z = 2, D_x = 1·68 g cm^{-3}, Mo $K\alpha$ radiation, λ = 0·71073 Å, μ = 11·06 cm^{-1}, T = 298 K, $F(000)$ = 666, R = 0·059, wR = 0·072 for 2900 unique observed [$I > 3\sigma(I)$] reflections. The title complex contains Cu^{II} in a square-pyramidal environment; the axial ligand is an O atom from the 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-*O* moiety.

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Introduction. Complexes of β-diketones and their derivatives with N bases have been extensively investigated in recent years, since they are extracting agents, chemiluminescent materials and chemical shift agents. It is important to determine the molecular structure and to explore the relationship between the structures and properties of these compounds. We have studied the structures of bis[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-*O*,*O*′]copper(II), and its adducts with pyridine, dimethyl sulfoxide and quinoline (Yu, Xu, You, Lu, Shi, Liu & Lin, 1988; Liu, Lin, Xu, Yu & You, 1986; Li You, Yao, Huang & Wang, 1987; Yu, Zhu, Xu, Gou, You, Liu & Lin,

Table 1. *Atomic parameters and equivalent isotropic thermal parameters* (Å²)

$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}]$.

	x	y	z	B_{eq}
Cu	−0·11833 (8)	0·10326 (6)	−0·1450 (1)	2·60 (3)
S(1)	0·1845 (2)	0·2871 (2)	0·2020 (3)	3·1 (1)
S(2)	0·1933 (2)	0·3074 (1)	−0·1970 (2)	4·4 (1)
F(1)	−0·5073 (6)	0·2262 (5)	−0·0994 (7)	8·7 (4)
F(2)	−0·4623 (5)	0·3062 (5)	0·1035 (8)	10·8 (4)
F(3)	−0·5162 (6)	0·1629 (5)	0·0908 (8)	9·4 (4)
F(4)	−0·3557 (8)	0·4073 (6)	−0·529 (1)	11·7 (5)
F(5)	−0·4149 (9)	0·4205 (7)	−0·332 (1)	15·1 (7)
F(6)	−0·5104 (7)	0·3169 (6)	−0·451 (2)	20·1 (7)
O(1)	−0·0270 (4)	0·1787 (3)	0·0229 (5)	3·0 (2)
O(2)	−0·2876 (4)	0·1418 (3)	−0·0867 (5)	3·3 (2)
O(3)	−0·0586 (5)	0·2065 (3)	−0·3003 (5)	3·1 (2)
O(4)	−0·3229 (5)	0·2054 (4)	−0·4355 (6)	5·2 (3)
N(1)	−0·2028 (5)	0·0026 (4)	−0·2932 (6)	2·8 (2)
N(2)	0·0392 (5)	0·0342 (4)	−0·1884 (6)	2·5 (2)
C(1)	0·221 (1)	0·3630 (6)	0·353 (1)	5·3 (4)
C(2)	0·114 (1)	0·3926 (6)	0·4190 (9)	5·1 (4)
C(3)	−0·0093 (7)	0·3556 (4)	0·3500 (7)	2·7 (3)
C(4)	0·0194 (6)	0·2944 (5)	0·2190 (7)	2·9 (3)
C(5)	−0·0743 (7)	0·2408 (4)	0·1110 (7)	2·6 (3)
C(6)	−0·2082 (7)	0·2579 (5)	0·1081 (8)	3·0 (3)
C(7)	−0·3027 (7)	0·2082 (5)	0·0141 (8)	3·1 (3)
C(8)	−0·4444 (8)	0·2282 (7)	0·026 (1)	4·9 (4)
C(11)	0·2734 (8)	0·4126 (6)	−0·124 (1)	4·9 (4)
C(12)	0·191 (1)	0·4783 (6)	−0·107 (1)	5·8 (5)
C(13)	0·0611 (8)	0·4474 (5)	−0·158 (1)	4·3 (4)
C(14)	0·0461 (7)	0·3543 (5)	−0·2084 (7)	2·9 (3)
C(15)	−0·0703 (7)	0·2927 (5)	−0·2759 (7)	2·8 (3)
C(16)	−0·1832 (7)	0·3347 (5)	−0·3129 (8)	3·4 (3)
C(17)	−0·2961 (7)	0·2886 (6)	−0·3906 (9)	3·9 (3)
C(18)	−0·401 (1)	0·347 (1)	−0·453 (3)	14 (1)
C(21)	−0·3314 (6)	−0·0100 (5)	−0·3350 (8)	3·2 (3)
C(22)	−0·3822 (7)	−0·0786 (5)	−0·4428 (8)	3·7 (3)
C(23)	−0·2961 (8)	−0·1357 (5)	−0·5102 (8)	3·9 (3)
C(24)	−0·1622 (7)	−0·1229 (5)	−0·4710 (8)	3·2 (3)
C(25)	0·1225 (7)	−0·0836 (4)	−0·3552 (7)	2·8 (3)
C(26)	0·2456 (7)	−0·0633 (5)	−0·2882 (8)	3·3 (3)
C(27)	0·2656 (7)	0·0050 (5)	−0·1719 (9)	3·8 (3)
C(28)	0·1610 (7)	0·0543 (5)	−0·1266 (7)	3·1 (3)
C(29)	0·0196 (6)	−0·0352 (4)	−0·3020 (7)	2·5 (3)
C(30)	−0·1193 (6)	−0·0537 (4)	−0·3598 (7)	2·4 (3)

Table 2. *Bond lengths* (Å) *and angles* (°)

Cu—O(2)	1·920 (4)	C(2)—C(3)	1·41 (1)
Cu—O(1)	1·935 (4)	C(3)—C(4)	1·455 (9)
Cu—N(1)	1·983 (5)	C(4)—C(5)	1·452 (9)
Cu—N(2)	1·991 (5)	C(5)—C(6)	1·402 (9)
Cu—O(3)	2·204 (5)	C(6)—C(7)	1·36 (1)
S(1)—C(1)	1·673 (9)	C(7)—C(8)	1·49 (1)
S(1)—C(4)	1·692 (7)	C(11)—C(12)	1·33 (1)
S(2)—C(14)	1·706 (7)	C(12)—C(13)	1·40 (1)
S(2)—C(11)	1·707 (9)	C(13)—C(14)	1·37 (1)
F(1)—C(8)	1·29 (1)	C(14)—C(15)	1·480 (9)
F(2)—C(8)	1·295 (9)	C(15)—C(16)	1·40 (1)
F(3)—C(8)	1·32 (1)	C(16)—C(17)	1·40 (1)
F(4)—C(18)	1·23 (1)	C(17)—C(18)	1·56 (1)
F(5)—C(18)	1·46 (2)	C(21)—C(22)	1·37 (1)
F(6)—C(18)	1·15 (1)	C(22)—C(23)	1·37 (1)
O(1)—C(5)	1·274 (7)	C(23)—C(24)	1·38 (1)
O(2)—C(7)	1·276 (8)	C(24)—C(30)	1·373 (8)
O(3)—C(15)	1·260 (7)	C(25)—C(26)	1·36 (1)
O(4)—C(17)	1·228 (9)	C(26)—C(27)	1·36 (1)
N(1)—C(21)	1·336 (8)	C(27)—C(28)	1·38 (1)
N(1)—C(30)	1·341 (8)	C(29)—C(30)	1·478 (9)
N(2)—C(28)	1·335 (8)	C(25)—C(29)	1·380 (9)
N(2)—C(29)	1·356 (8)	C(1)—C(2)	1·33 (1)

O(2)—Cu—O(1)	92·2 (2)	C(1)—C(2)—C(3)	115·4 (7)
O(2)—Cu—N(1)	92·2 (2)	C(2)—C(3)—C(4)	107·2 (6)
O(2)—Cu—N(2)	166·1 (2)	C(3)—C(4)—C(5)	128·1 (6)
O(2)—Cu—O(3)	100·3 (2)	C(5)—C(4)—S(1)	119·8 (5)
O(1)—Cu—N(1)	167·3 (2)	C(3)—C(4)—S(1)	112·1 (5)
O(1)—Cu—N(2)	91·9 (2)	O(1)—C(5)—C(6)	123·6 (6)
O(1)—Cu—O(3)	93·3 (2)	O(1)—C(5)—C(4)	116·0 (6)
N(1)—Cu—N(2)	81·2 (2)	C(6)—C(5)—C(4)	120·4 (6)
N(1)—Cu—O(3)	97·6 (2)	C(7)—C(6)—C(5)	123·8 (6)
N(2)—Cu—O(3)	92·8 (2)	O(2)—C(7)—C(6)	127·9 (6)
C(1)—S(1)—C(4)	92·0 (4)	O(2)—C(7)—C(8)	112·4 (6)
C(14)—S(2)—C(11)	91·4 (4)	C(5)—O(1)—Cu	127·0 (4)
C(7)—O(2)—Cu	124·3 (4)	C(15)—O(3)—Cu	124·2 (4)
C(21)—N(1)—C(30)	119·0 (6)	C(6)—C(7)—C(8)	119·6 (6)
C(21)—N(1)—Cu	125·7 (5)	F(1)—C(8)—F(2)	107·3 (8)
C(30)—N(1)—Cu	115·2 (4)	F(1)—C(8)—F(3)	102·4 (8)
C(28)—N(2)—C(29)	118·4 (6)	F(1)—C(8)—C(7)	114·7 (7)
C(28)—N(2)—Cu	126·9 (5)	F(2)—C(8)—F(3)	104·9 (8)
C(29)—N(2)—Cu	114·4 (4)	F(2)—C(8)—C(7)	115·1 (7)
C(2)—C(1)—S(1)	113·3 (7)	F(3)—C(8)—C(7)	111·3 (8)
C(11)—C(12)—C(13)	113·6 (8)	C(12)—C(11)—S(2)	111·9 (6)
C(14)—C(13)—C(12)	112·1 (7)	C(21)—C(22)—C(23)	117·8 (7)
C(13)—C(14)—C(15)	131·2 (7)	C(22)—C(23)—C(24)	120·5 (6)
C(13)—C(14)—S(2)	111·0 (5)	C(15)—C(14)—S(2)	117·7 (5)
O(3)—C(15)—C(16)	124·9 (6)	C(30)—C(24)—C(23)	118·2 (6)
O(3)—C(15)—C(14)	117·3 (6)	C(16)—C(15)—C(14)	117·7 (6)
C(17)—C(16)—C(15)	125·2 (7)	C(26)—C(25)—C(29)	119·2 (6)
O(4)—C(17)—C(16)	129·9 (7)	C(27)—C(26)—C(25)	119·8 (6)
O(4)—C(17)—C(18)	110 (1)	C(16)—C(17)—C(18)	119 (1)
F(6)—C(18)—F(4)	126 (2)	C(26)—C(27)—C(28)	119·0 (6)
F(6)—C(18)—F(5)	93 (1)	F(6)—C(18)—C(17)	117 (1)
F(4)—C(18)—F(5)	89 (1)	N(2)—C(28)—C(27)	122·1 (6)
F(4)—C(18)—C(17)	115·2 (9)	N(2)—C(29)—C(25)	121·4 (6)
F(5)—C(18)—C(17)	104 (1)	N(2)—C(29)—C(30)	114·2 (5)
C(25)—C(29)—C(30)	124·4 (6)	N(1)—C(30)—C(24)	121·7 (6)
N(1)—C(21)—C(22)	122·7 (7)	N(1)—C(30)—C(29)	114·3 (6)
C(24)—C(30)—C(29)	123·9 (6)		

1990). Continuing this research, the crystal structure of the title complex was determined.

Experimental. 1 mmol of bis[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-*O*,*O*′]copper(II) was dropped into a solution of 10 ml of absolute ethanol containing 1 mmol of 2,2′-bipyridine, and the resulting mixture was left to evaporate slowly in air at room temperature. After a few days, dark-green column-shaped crystals of the title complex were obtained. The molecular structure proposed is consistent with elemental analysis. $C_{26}H_{16}CuF_6N_2O_4S_2$: calc: C 47·13, H 2·42, N 4·23%; found: C 46·96, H 2·48, N 4·14%.

Cell dimensions and crystal orientation matrix determined on an AFC5R diffractometer by a least-squares treatment of the setting angles of 20 reflections in the range $10 < \theta < 15°$. Crystal dimensions 0·16 × 0·28 × 0·50 mm; intensities of reflections with indices h 0 to 12, k −17 to 17, l −11 to 11 with $2\theta < 52°$ measured; ω–2θ scans; ω-scan width $(1·732 + 0·400\tan\theta)°$, graphite-monochromated Mo $K\alpha$ radiation. Intensities of three reflections measured every two hours showed no evidence of crystal decay. 5483 reflections measured, 5166 unique. 2900 with $I > 3\sigma(I)$ were used in structure solution and refinement; $R_{int} = 0·033$. Data corrected for Lorentz, polarization and absorption effects (max. and min. transmission factors 1·071 and 0·896). Gaussian integration grid 6 × 6 × 6. Space group $P\bar{1}$.

The crystal structure was solved by the heavy-atom method, and refined by full-matrix least-squares calculations, initially with isotropic and later with anisotropic thermal parameters. At an intermediate stage in the refinement, difference maps showed maxima in positions consistent with the expected locations of the H atoms; in the final round

of calculations, the H atoms were positioned on geometrical grounds (C—H 0·95 Å) and included (as riding atoms) in the structure-factor calculations. Final refinement was on F by least-squares methods, refining 370 parameters. $R = 0{\cdot}059$, $wR = 0{\cdot}072$, goodness-of-fit = 1·73, $w = 1/\sigma^2(F_o)$. Max. shift/e.s.d. = 0·05. Largest positive and negative peaks on a difference Fourier synthesis were 0·90 and $-0{\cdot}88$ e Å^{-3}; no chemically significant features. Scattering factors and anomalous-dispersion corrections of non-H atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a MicroVAX II computer using the *TEXSAN* software package (Molecular Structure Corporation, 1985). Atomic coordinates and details of molecular geometry are given in Tables 1 and 2.*

Discussion. An *ORTEP* drawing of the title complex, prepared using *TEXSAN* (Molecular Structure Corporation 1985), is shown in Fig. 1. Unlike the other adducts of β-diketone complexes with N bases, the Cu atom has a square-pyramidal geometry. Two O atoms [O(1) and O(2)] of 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-O,O' and two N atoms [N(1) and N(2)] of 2,2′-bipyridine lie around the Cu atom, forming a square plane of CuN_2O_2. The Cu atom is 0·2058 Å above the plane, while one O atom [O(3)] of 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-O is located 2·4035 Å above that plane. This results in the square-pyramidal configuration of the pentacoordinate copper(II) ion. In the square plane of CuN_2O_2, the bond lengths Cu—O are 1·935 and 1·920 Å and Cu—N are 1·983 and 1·991 Å, respectively. However, Cu—O(3) is 2·204 Å. Complexes of bis[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-O,O']copper(II) and its adducts which we have studied so far indicate however that four O atoms of two 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione moieties coordinate the copper(II) ion. However, for the compound discussed in this paper, the coordination between the copper(II) ion and two N atoms of 2,2′-bipyridine is so strong that it not only affects the original plane of CuO_4, but also makes one β-diketone coordinate the copper(II) ion with only one O atom.

The bond angle O(1)—Cu—O(2) is 92·2°. The chelate ring between O(1) and O(2) with the Cu atom is basically a plane, where the deviations of the six ring atoms from the least-squares plane are all less than 0·0768 Å. Both thiophene rings are coplanar (atoms deviate from their respective mean planes by less than 0·014 Å). The dihedral angle between the thiophene ring of C(1)C(2)C(3)C(4)S(1) and the chelate ring of O(1)O(2)C(5)C(6)C(7) is small (9·2°), and the conjugation effect between the two rings leads to C(4)—C(5) (1·452 Å) being shorter than a normal C—C single bond. S(1) and O(1) lie in the *cis* position, and there is an interaction between them, with S(1)···O(1) = 2·88 Å.

O(3), O(4), C(15), C(16) and C(17) lie in a plane, and the Cu atom is 1·854 Å from this plane, unlike the situation in 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-O,O'.

The distance S(2)···O(3) is 2·89 Å, which shows that an interaction exists between these atoms.

Ten C and two N atoms of 2,2′-bipyridine are coplanar such that the deviations of the atoms from the least-squares plane are in the range 0·004–0·067 Å. Also, the pyridine ring and chelate ring are almost coplanar with a very small dihedral angle of 4°.

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* Lists of structure factors, thermal parameters, calculated hydrogen coordinates, mean-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53241 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

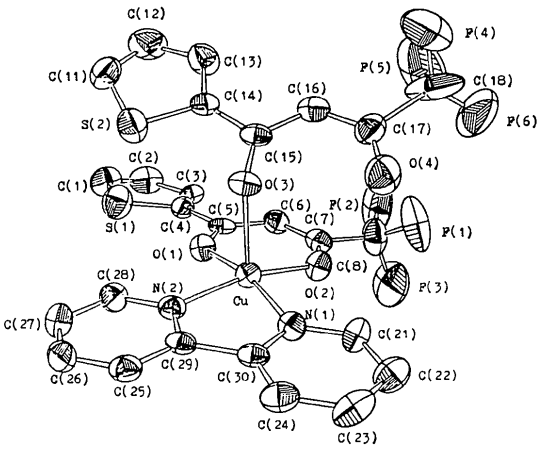

Fig. 1. *ORTEP* drawing of the title compound.

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