C(7)	1.121 (2)	0.195 (1)	0.9071 (9)	0.05 (1)
C(8)	1.138 (1)	0.133 (1)	0.8675 (9)	0.05 (1)
C(9)	1.069 (1)	0.066 (1)	0.8663 (8)	0.04 (1)
C(10)	1.084 (1)	0.009 (1)	0.8228 (9)	0.05 (1)
C(11)	1.166 (2)	0.012 (1)	0.7846 (9)	0.06 (1)
C(12)	1.233 (2)	0.075 (1)	0.7859 (9)	0.06 (1)
C(13)	1.216 (2)	0.132 (1)	0.8269 (9)	0.05 (1)
C(14)	0.807 (2)	0.195 (1)	1.0450 (9)	0.06 (1)
C(15)	0.748 (2)	0.128 (1)	1.0475 (10)	0.06 (1)
C(16)	0.761 (2)	0.063 (1)	1.0097 (10)	0.05 (1)
C(17)	0.692 (2)	0.0055 (10)	1.0188 (9)	0.05 (1)
C(18)	0.621 (2)	0.010 (1)	1.063 (1)	0.07 (1)
C(19)	0.608 (2)	0.072 (2)	1.097 (1)	0.08 (1)
C(20)	0.672 (2)	0.134 (1)	1.0934 (10)	0.07 (1)
C(21)	1.146 (2)	0.118 (2)	1.110 (2)	0.14 (2)
C(22)	1.235 (2)	0.084 (1)	1.161 (1)	0.15 (2)
C(23)	0.814 (3)	0.158 (2)	0.781 (2)	0.11 (1)
C(24)	0.817 (3)	0.238 (1)	0.755 (3)	0.16 (2)
C(25)	0.832 (6)	0.213 (6)	0.806 (3)	0.08 (1)
C(26)	0.792 (5)	0.190 (5)	0.727 (3)	0.08 (1)
C(101)	0.0103 (10)	0.1821 (6)	0.4835 (4)	0.05 (2)
C(102)	0.0958 (8)	0.1416 (5)	0.5328 (6)	0.07 (2)
C(103)	0.1089 (8)	0.1490 (5)	0.6059 (6)	0.08 (2)
C(104)	0.0365 (10)	0.1968 (6)	0.6297 (4)	0.06 (2)
C(105)	−0.0490 (8)	0.2372 (5)	0.5804 (6)	0.06 (2)
C(106)	−0.0621 (8)	0.2299 (5)	0.5073 (5)	0.07 (2)
C(107)	0.0845 (9)	0.1079 (7)	0.3822 (5)	0.055 (5)
C(108)	0.192 (1)	0.1378 (5)	0.3822 (5)	0.074 (6)
C(109)	0.2772 (8)	0.0929 (7)	0.3678 (5)	0.069 (6)
C(110)	0.2551 (9)	0.0181 (7)	0.3534 (5)	0.081 (6)
C(111)	0.148 (1)	−0.0118 (5)	0.3534 (5)	0.098 (7)
C(112)	0.0624 (8)	0.0331 (7)	0.3677 (5)	0.077 (6)
C(113)	−0.1516 (7)	0.1308 (6)	0.3683 (6)	0.048 (5)
C(114)	−0.1737 (9)	0.0690 (6)	0.4049 (4)	0.066 (6)
C(115)	−0.284 (1)	0.0365 (5)	0.3851 (6)	0.074 (6)
C(116)	−0.3722 (8)	0.0660 (6)	0.3286 (6)	0.068 (6)
C(117)	−0.3501 (9)	0.1278 (6)	0.2920 (4)	0.070 (6)
C(118)	−0.240 (1)	0.1603 (5)	0.3118 (5)	0.064 (6)
C(119)	−0.0037 (8)	0.2432 (5)	0.3510 (6)	0.046 (5)
C(120)	0.0279 (8)	0.3114 (7)	0.3839 (4)	0.051 (5)
C(121)	0.0403 (8)	0.3725 (5)	0.3431 (6)	0.077 (6)
C(122)	0.0210 (9)	0.3653 (5)	0.2694 (6)	0.076 (6)
C(123)	−0.0106 (9)	0.2971 (7)	0.2365 (4)	0.080 (6)
C(124)	−0.0229 (8)	0.2360 (5)	0.2773 (6)	0.075 (6)
B(101)	−0.013 (2)	0.166 (1)	0.3945 (10)	0.042 (6)

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

Mn(1)—O(1)	1.85 (1)	O(1)—C(9)	1.31 (2)
Mn(1)—O(2)	1.85 (1)	O(2)—C(16)	1.32 (3)
Mn(1)—O(3)	2.27 (1)	N(1)—C(1)	1.44 (2)
Mn(1)—O(4)	2.28 (1)	N(1)—C(7)	1.27 (3)
Mn(1)—N(1)	1.97 (1)	N(2)—C(2)	1.40 (3)
Mn(1)—N(2)	1.99 (2)	N(2)—C(14)	1.32 (3)
O(1)—Mn(1)—O(2)	90.2 (5)	O(2)—Mn(1)—O(3)	89.5 (5)
O(1)—Mn(1)—O(3)	91.2 (5)	O(2)—Mn(1)—O(4)	90.8 (4)
O(1)—Mn(1)—O(4)	92.6 (4)	O(2)—Mn(1)—N(1)	176.0 (6)
O(1)—Mn(1)—N(1)	93.8 (6)	O(2)—Mn(1)—N(2)	91.9 (6)
O(1)—Mn(1)—N(2)	177.8 (6)		

The tetraphenylborate C atoms were constrained to be regular hexagons (C—C 1.40 Å) with isotropic vibrational parameters. Disorder in one of the capping ethanol molecules was represented by two semi-populated ethyl chains [C(23),C(24) and C(25),C(26)]. H atoms were placed in calculated positions except for those attached to O3 and O4, which were ignored.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson 1976). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *CSSR* (1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(η^6-Fluorene)(η^6-1-isopropyl-4-methylbenzene)ruthenium(II) Bis(tetrafluoroborate), $[Ru(C_{10}H_{14})(C_{13}H_{10})](BF_4)_2$

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Abstract

The Ru^{II} atom is located symmetrically between the two arene rings forming a sandwich-type complex. There are two BF_4^- counterions per molecule and the cations pack as canted stacks in the lattice. Many of the structural features of the coordinated fluorene ligand resemble those observed in the X-ray crystal structure of free fluorene. The arene ligands adopt an eclipsed conformation and are separated at a distance of 3.450 Å.

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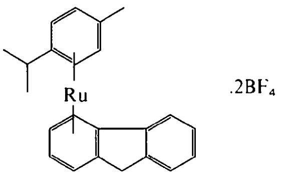
Comment

As part of a systematic investigation of arene complexes of the platinum group metals, we recently undertook an X-ray crystal structure determination of the 1:1 product obtained following reaction of the solvated (*p*-cymene)ruthenium(II) cation with fluorene (*p*-cymene is 1-isopropyl-4-methylbenzene). The structure of a related (fluorene)ruthenium(II) sandwich complex has recently been described (Suravajjala, Polam & Porter, 1993, 1994). However, it was discovered during the preparation of a new series of complexes containing two-coordinate transition metals that a second modification of this 1:1 complex existed. The number of ruthenium–arene complexes is potentially vast; however, few crystallographically characterized examples of bis(arene)ruthenium(II) complexes exist. Here we describe the structure of the title compound, (I).



(I)

The Ru atom coordinates to the two arene rings in an η^6 manner and is separated by 1.720 Å from the centroid defined by the atoms of the cymene ligand and by 1.730 Å from the C atoms comprising one of the six-atom arene rings of the fluorene ligand. The coordinated arenes are essentially parallel; the angle defined by the least-squares planes of each ring of six C atoms is 179°. The Ru$^{\rm II}$ center is not perfectly symmetrically disposed but lies shifted slightly toward C(3) of the fluorene ligand and the bond joining atoms C(21) and C(22) in the cymene molecule.

For the sp^2-hybridized C atoms in the coordinated arenes, bond lengths range from a minimum of 1.362 (8) Å [C(5)—C(6)] to a maximum of 1.424 (7) Å [C(25)—C(26)]. C—C bonds within the coordinated arene ring of the fluorene ligand are longer on average by 0.015 Å compared with those in the free arene ring but show no regular alternation in length that would indicate any substantial degree of bond localization. A similar degree of C—C bond lengthening relative to the 1.39 Å value typically given for arenes is also seen in the cymene ligand (average C—C 1.409 Å), which displays many features similar to those of the coordinated arene ligands in the structure of $[\mathrm{Ru(C_{10}H_{14})_2}].(\mathrm{BF_4})_2$ (Suravajjala, Polam & Porter, 1993, 1994). All three independent arene rings are essentially planar, with no substantial out-of-plane deviations by any of the C atoms. Overall, however, the fluorene ligand is not planar, but is instead folded about the methylene bridge with a dihedral angle of 2.5°. Free fluorene has been the subject of two independent structure determinations and a similar conformation has been observed (Belsky, Zavodnik & Vozzhennikov, 1984; Gerkin, Lundstedt & Reppart, 1984).

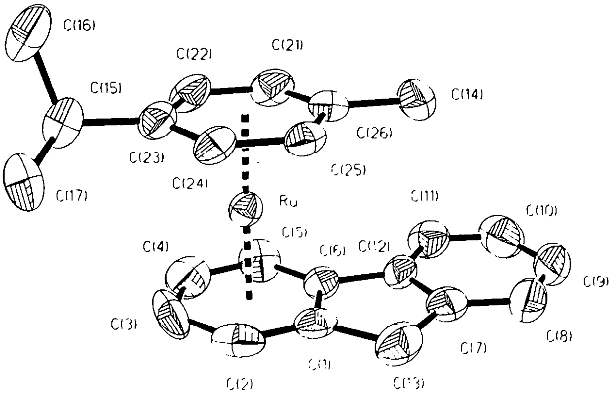


Fig. 1. A perspective view of the cation (with 50% probability ellipsoids) showing the atomic numbering scheme. H atoms have been omitted for clarity.

Principal differences between this crystal structure, (I), and that reported previously concern (*a*) the cation packing motif and (*b*) the orientation of the cymene ligand with respect to the coordinated fluorene molecule (Suravajjala, Polam & Porter, 1993, 1994). Instead of being arranged in a manner where the arene ligands form a network of parallel sheets, in this structure the individual cations are canted. We find, however, that in both instances the individual Ru atoms remain formally in the +2 oxidation state crystallizing with two $\mathrm{BF_4^-}$ anions per dication.

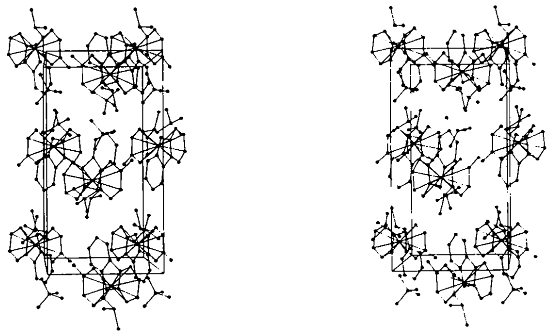


Fig. 2. A stereoview illustrating the canted packing motif of the cations.

Experimental

Cleavage of the chloro-bridged (cymene)ruthenium(II) dimer $[\mathrm{RuCl_2(C_{10}H_{14})}]_2$, using $\mathrm{AgBF_4}$ in acetone, leads to the formation of a monomeric complex containing three weakly coordinating molecules of solvent (Bennett & Matheson, 1979). Reaction of this dication with fluorene leads to the formation of a sandwich complex which can be obtained as amber colored crystals following crystallization from a diethyl ether/dimethyl sulfoxide solution.

Crystal data

$[Ru(C_{10}H_{14})(C_{13}H_{10})](BF_4)_2$
$M_r = 575.1$
Orthorhombic
$P2_12_12_1$
$a = 8.445$ (2) Å
$b = 16.345$ (5) Å
$c = 16.413$ (5) Å
$V = 2265.5$ (11) Å^3
$Z = 4$
$D_x = 1.686$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–$15.0°$
$\mu = 0.751$ mm^{-1}
$T = 295$ K
Regularly shaped fragment
$0.44 \times 0.36 \times 0.28$ mm
Amber

Data collection

Siemens *R3m/V* diffractometer
ω scans
Absorption correction: empirical (*SHELXTL-Plus*; Sheldrick, 1991)
$T_{min} = 0.4485$, $T_{max} = 0.4648$
2001 measured reflections
1948 independent reflections

1948 observed reflections $[I > \sigma(I)]$
$R_{int} = 0.1972$
$\theta_{max} = 22.50°$
$h = 0 \rightarrow 9$
$k = -17 \rightarrow 0$
$l = -17 \rightarrow 2$
3 standard reflections monitored every 97 reflections
intensity variation: <2%

Refinement

Refinement on F
$R = 0.0275$
$wR = 0.0231$
$S = 2.18$
1948 reflections
307 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ru	−0.9100 (1)	−0.0833 (1)	−0.8362 (1)	0.035 (1)
F(1)	−1.1070 (6)	0.1438 (2)	−0.6449 (2)	0.098 (2)
F(2)	−0.9623 (4)	0.0674 (2)	−0.5586 (2)	0.072 (1)
F(3)	−0.9285 (4)	0.2046 (2)	−0.5672 (2)	0.079 (1)
F(4)	−1.1458 (5)	0.1546 (2)	−0.5109 (3)	0.112 (2)
F(5)	−1.5107 (6)	−0.3590 (3)	−0.7033 (4)	0.152 (3)
F(6)	−1.3068 (7)	−0.2971 (3)	−0.6537 (3)	0.134 (2)
F(7)	−1.4169 (6)	−0.2507 (2)	−0.7660 (3)	0.112 (2)
F(8)	−1.2849 (7)	−0.3682 (3)	−0.7630 (3)	0.126 (2)
B(1)	−1.0336 (8)	0.1411 (4)	−0.5711 (4)	0.046 (2)
B(2)	−1.3878 (11)	−0.3176 (4)	−0.7227 (4)	0.063 (3)
C(1)	−0.8300 (6)	−0.1086 (3)	−0.9640 (3)	0.042 (2)
C(2)	−0.7628 (7)	−0.1660 (3)	−0.9122 (4)	0.052 (2)
C(3)	−0.6724 (7)	−0.1382 (4)	−0.8453 (6)	0.059 (3)
C(4)	−0.6557 (7)	−0.0549 (4)	−0.8309 (7)	0.063 (2)
C(5)	−0.7275 (7)	0.0018 (4)	−0.8831 (4)	0.056 (2)
C(6)	−0.8117 (6)	−0.0244 (3)	−0.9489 (3)	0.040 (2)
C(7)	−0.9699 (7)	−0.0341 (4)	−1.0630 (4)	0.049 (2)
C(8)	−1.0644 (7)	−0.0059 (4)	−1.1279 (4)	0.067 (3)
C(9)	−1.0832 (8)	0.0774 (5)	−1.1360 (3)	0.074 (3)
C(10)	−1.0122 (8)	0.1309 (4)	−1.0829 (4)	0.077 (3)
C(11)	−0.9214 (9)	0.1044 (3)	−1.0194 (4)	0.061 (2)
C(12)	−0.9006 (7)	0.0223 (3)	−1.0109 (3)	0.044 (2)
C(13)	−0.9284 (8)	−0.1203 (3)	−1.0403 (4)	0.061 (2)
C(14)	−1.2491 (7)	0.0091 (3)	−0.9032 (3)	0.055 (2)
C(15)	−0.9131 (9)	−0.1694 (3)	−0.6459 (3)	0.056 (2)
C(16)	−1.0094 (8)	−0.1601 (4)	−0.5681 (3)	0.076 (3)
C(17)	−0.8739 (8)	−0.2593 (3)	−0.6609 (4)	0.074 (3)
C(21)	−1.0760 (8)	0.0021 (3)	−0.7773 (3)	0.048 (2)
C(22)	−0.9952 (7)	−0.0403 (3)	−0.7163 (3)	0.049 (2)
C(23)	−0.9957 (7)	−0.1270 (3)	−0.7144 (3)	0.042 (2)
C(24)	−1.0784 (8)	−0.1684 (3)	−0.7768 (3)	0.041 (2)
C(25)	−1.1593 (6)	−0.1254 (3)	−0.8377 (6)	0.040 (2)
C(26)	−1.1623 (6)	−0.0383 (3)	−0.8385 (6)	0.042 (2)

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

Ru—C(1)	2.243 (5)	Ru—C(2)	2.220 (6)
Ru—C(3)	2.203 (6)	Ru—C(4)	2.199 (6)
Ru—C(5)	2.214 (6)	Ru—C(6)	2.245 (6)
Ru—C(21)	2.202 (6)	Ru—C(22)	2.210 (6)
Ru—C(23)	2.242 (5)	Ru—C(24)	2.215 (6)
Ru—C(25)	2.215 (5)	Ru—C(26)	2.254 (5)
F(1)—B(1)	1.361 (8)	F(2)—B(1)	1.362 (7)
F(3)—B(1)	1.367 (7)	F(4)—B(1)	1.387 (8)
F(5)—B(2)	1.279 (10)	F(6)—B(2)	1.365 (10)
F(7)—B(2)	1.327 (8)	F(8)—B(2)	1.370 (10)
C(1)—C(2)	1.388 (8)	C(1)—C(6)	1.408 (7)
C(1)—C(13)	1.515 (8)	C(2)—C(3)	1.412 (10)
C(3)—C(4)	1.389 (9)	C(4)—C(5)	1.399 (10)
C(5)—C(6)	1.362 (8)	C(6)—C(12)	1.478 (8)
C(7)—C(8)	1.408 (9)	C(7)—C(12)	1.386 (8)
C(7)—C(13)	1.499 (8)	C(8)—C(9)	1.378 (10)
C(9)—C(10)	1.372 (10)	C(10)—C(11)	1.364 (10)
C(11)—C(12)	1.360 (7)	C(14)—C(26)	1.506 (9)
C(15)—C(16)	1.521 (8)	C(15)—C(17)	1.525 (8)
C(15)—C(23)	1.494 (8)	C(21)—C(22)	1.395 (8)
C(21)—C(26)	1.405 (9)	C(22)—C(23)	1.417 (8)
C(23)—C(24)	1.413 (8)	C(24)—C(25)	1.401 (9)
C(25)—C(26)	1.424 (7)		
F(1)—B(1)—F(2)	111.4 (5)	F(1)—B(1)—F(3)	108.2 (5)
F(2)—B(1)—F(3)	112.2 (5)	F(1)—B(1)—F(4)	108.5 (5)
F(2)—B(1)—F(4)	109.6 (5)	F(3)—B(1)—F(4)	106.9 (5)
F(5)—B(2)—F(6)	109.2 (6)	F(5)—B(2)—F(7)	114.8 (8)
F(6)—B(2)—F(7)	109.6 (6)	F(5)—B(2)—F(8)	108.4 (6)
F(6)—B(2)—F(8)	103.3 (7)	F(7)—B(2)—F(8)	110.9 (6)
C(2)—C(1)—C(6)	120.5 (5)	C(2)—C(1)—C(13)	130.3 (5)
C(6)—C(1)—C(13)	109.2 (5)	C(1)—C(2)—C(3)	118.7 (5)
C(2)—C(3)—C(4)	120.2 (7)	C(3)—C(4)—C(5)	120.1 (8)
C(4)—C(5)—C(6)	120.2 (6)	C(1)—C(6)—C(5)	120.3 (5)
C(1)—C(6)—C(12)	109.1 (5)	C(5)—C(6)—C(12)	130.5 (5)
C(8)—C(7)—C(12)	119.2 (5)	C(8)—C(7)—C(13)	128.9 (6)
C(12)—C(7)—C(13)	112.0 (5)	C(7)—C(8)—C(9)	117.5 (6)
C(8)—C(9)—C(10)	121.1 (6)	C(9)—C(10)—C(11)	121.9 (6)
C(10)—C(11)—C(12)	117.6 (6)	C(6)—C(12)—C(7)	107.2 (5)
C(6)—C(12)—C(11)	130.2 (5)	C(7)—C(12)—C(11)	122.6 (5)
C(1)—C(13)—C(7)	102.4 (5)	C(16)—C(15)—C(17)	110.4 (5)
C(16)—C(15)—C(23)	109.6 (5)	C(17)—C(15)—C(23)	115.2 (5)
C(22)—C(21)—C(26)	122.2 (5)	C(21)—C(22)—C(23)	120.7 (5)
C(15)—C(23)—C(22)	118.7 (5)	C(15)—C(23)—C(24)	123.6 (5)
C(22)—C(23)—C(24)	117.7 (5)	C(23)—C(24)—C(25)	121.2 (5)
C(24)—C(25)—C(26)	121.1 (7)	C(14)—C(26)—C(21)	121.1 (5)
C(14)—C(26)—C(25)	121.9 (7)	C(21)—C(26)—C(25)	117.0 (6)

The structure was determined using direct methods (*SHELXTL-Plus*; Sheldrick, 1991). All non-H atoms were refined anisotropically. H atoms were included in idealized positions with fixed isotropic $U = 0.08$ Å^2. Absorption corrections were applied empirically on the basis of azimuthal scans of several strong reflections spanning a range of 2θ values. Correct assignment of the enantiomorph was made by comparing the final R value of the structure with that of its mirror image, obtained by inverting all of the fractional atomic coordinates.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CD1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(2,2′-Bipyridine)bis(thiocyanato-*N*)-copper(II), [Cu(bipy)(NCS)$_2$]

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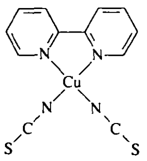
Abstract

The crystal structure of green [Cu(bipy)(NCS)$_2$] (bipy = 2,2′-bipyridine, $C_{10}H_8N_2$) containing six-coordinate copper(II) with a tetragonal [$Cu^{II}N_4S_2$] core is reported. The Cu to N(NCS) distance is 1.946 (3) Å with Cu bonded to the N-atom end of two thiocyanate ligands occupying two of the four equatorial positions. The two remaining short bonds in the tetragonal core are Cu—N(bipy) bonds to the 2,2′-bipyridine ligand [1.998 (2) Å]. The long axial bonds to the Cu center involve S atoms from neighboring [Cu(bipy)(NCS)$_2$] units with a Cu—S(SCN) distance of 3.220 (1) Å.

Comment

Several tetracoordinate molecular complexes of Cu^{II} containing the bidentate ligand 1,10-phenanthroline and two monodentate ligands or another bidentate ligand have been synthesized. The present work was undertaken in order to determine the type of structure preferred by copper(II)–bipyridine compounds. The crystal structure of the title complex, (I), contains neutral [Cu(bipy)(NCS)$_2$] units (Fig. 1) linked by the S-atom ends of the thiocyanate ligands to produce a one-dimensional chain as shown in Fig. 2. The Cu atom lies on a twofold axis parallel to the *b* axis.



(I)

The structure of [Cu(bipy)(NCS)$_2$] is analogous to the structures of [Cu(phen)(NCS)$_2$] (phen = 1,10-phenanthroline) (Breneman & Parker, 1993) and [Cu(bpm)(NCS)$_2$] (bpm = 2,2′-bipyrimidine) (Julve, Verdaguer, De Munno, Real & Bruno, 1993) from both a molecular structure and a crystal-packing perspective. The Cu—N(NCS) and Cu—S(SCN) distances in [Cu(phen)(NCS)$_2$] are 1.945 (4) and 3.163 (2) Å, respectively, and are 1.941 (6) and 3.174 (2) Å, respectively, in [Cu(bpm)(NCS)$_2$], compared with 1.946 (3) and 3.220 (1) Å, respectively, in the title complex. The molecular structure of [Cu(phen)Br$_2$] (Garland, Grandjean, Spodine, Atria & Manzur, 1988) is analogous to that of the title complex but the crystal packing is very different.

The equatorial tetracoordinate geometry is not square planar, as can be seen in Fig. 2. The thiocyanate ions are clearly twisted at a significant angle relative to the plane of the 2,2′-bipyridine ring. The twisting of the thiocyanate ligands is accompanied by a similar twisting of the two S atoms that occupy the two long axial positions in the tetragonal stereochemistry. The N1—Cu—N2—C2 torsion angle is 19.7 (3)°, which may

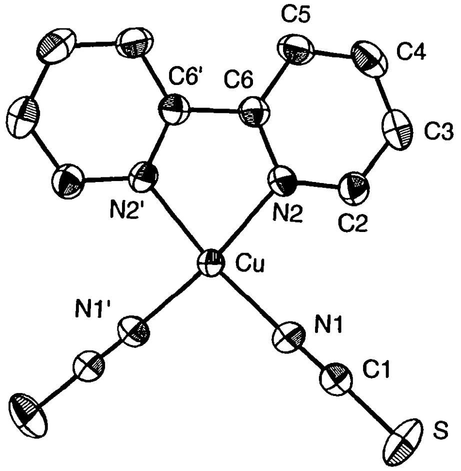


Fig. 1. *ORTEP* (Johnson, 1965) plot of [Cu(bipy)(NCS)$_2$] showing the atom-numbering scheme. H atoms have been omitted. Displacement ellipsoids are plotted at the 50% probability level.

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