C(3*B*)	0.3804 (1)	0.2859 (4)	−0.0789 (2)	4.8 (2)
C(4*B*)	0.4292 (1)	0.3478 (4)	−0.0859 (2)	5.0 (2)
C(5*B*)	0.4691 (1)	0.3153 (4)	−0.0326 (2)	4.8 (2)
C(6*B*)	0.4600 (1)	0.2223 (3)	0.0294 (2)	3.9 (2)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²) *for* (II)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$B_{\rm eq}$
W	0.35340 (1)	0.24254 (5)	0.20882 (2)	3.16 (2)
P	0.39599 (9)	0.0548 (3)	0.1220 (1)	2.8 (1)
O(1)	0.3087 (3)	−0.020 (1)	0.3121 (5)	8.1 (5)
O(2)	0.2560 (2)	0.244 (1)	0.0893 (4)	5.9 (4)
O(3)	0.2973 (3)	0.4959 (9)	0.3007 (4)	7.8 (5)
O(4)	0.4158 (3)	0.5134 (8)	0.1331 (5)	6.9 (5)
O(5)	0.4470 (3)	0.259 (1)	0.3305 (5)	11.0 (6)
C(1)	0.3241 (5)	0.073 (1)	0.2723 (6)	5.3 (7)
C(2)	0.2905 (3)	0.242 (1)	0.1311 (5)	4.0 (5)
C(3)	0.3177 (4)	0.402 (1)	0.2679 (6)	4.8 (5)
C(4)	0.3912 (4)	0.416 (1)	0.1565 (5)	4.2 (5)
C(5)	0.4143 (4)	0.249 (1)	0.2868 (6)	5.9 (6)
C(6)	0.4571 (3)	−0.0318 (9)	0.1600 (4)	3.0 (4)
C(7)	0.4512 (3)	−0.1364 (8)	0.2285 (4)	2.7 (4)
C(8)	1/2	−0.231 (1)	1/4	3.0 (5)
C(1*A*)	0.3603 (3)	−0.1135 (9)	0.0831 (5)	3.0 (4)
C(2*A*)	0.3182 (4)	−0.175 (1)	0.1178 (5)	4.1 (5)
C(3*A*)	0.2928 (4)	−0.306 (1)	0.0872 (7)	5.6 (6)
C(4*A*)	0.3090 (5)	−0.375 (1)	0.0224 (7)	6.0 (6)
C(5*A*)	0.3509 (5)	−0.316 (1)	−0.0124 (6)	5.4 (6)
C(6*A*)	0.3767 (4)	−0.186 (1)	0.0179 (5)	4.1 (5)
C(1*B*)	0.4119 (3)	0.1579 (9)	0.0376 (5)	2.9 (4)
C(2*B*)	0.3725 (3)	0.1891 (9)	−0.0167 (5)	3.8 (4)
C(3*B*)	0.3824 (4)	0.287 (1)	−0.0783 (5)	5.0 (5)
C(4*B*)	0.4306 (5)	0.350 (1)	−0.0855 (6)	5.1 (6)
C(5*B*)	0.4696 (4)	0.316 (1)	−0.0332 (6)	5.0 (6)
C(6*B*)	0.4609 (3)	0.217 (1)	0.0284 (5)	4.2 (5)

Table 3. *Selected geometric parameters* (Å, °) *for* (I)

Cr—P	2.3998 (8)	Cr—C(3)	1.854 (3)
Cr—C(1)	1.888 (3)	Cr—C(4)	1.896 (3)
Cr—C(2)	1.913 (3)	Cr—C(5)	1.859 (3)
P—Cr—C(1)	94.56 (9)	C(1)—Cr—C(5)	87.2 (1)
P—Cr—C(2)	87.16 (8)	C(2)—Cr—C(3)	88.7 (1)
P—Cr—C(3)	174.41 (9)	C(2)—Cr—C(4)	94.4 (1)
P—Cr—C(4)	87.77 (9)	C(2)—Cr—C(5)	178.2 (1)
P—Cr—C(5)	94.44 (9)	C(3)—Cr—C(4)	88.8 (1)
C(1)—Cr—C(2)	93.4 (1)	C(3)—Cr—C(5)	89.6 (1)
C(1)—Cr—C(3)	89.5 (1)	C(4)—Cr—C(5)	84.9 (1)
C(1)—Cr—C(4)	171.9 (1)		
C(3)—Cr—P—C(1*A*)	−90.1 (10)	Cr—P—C(6)—C(7)	65.6 (1)
C(3)—Cr—P—C(1*B*)	27.6 (10)	P—C(6)—C(7)—C(8)	169.1 (2)
C(3)—Cr—P—C(6)	145.6 (10)	C(6)—C(7)—C(8)—C(7′)	59.0 (2)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

W—P	2.534 (2)	W—C(3)	1.99 (1)
W—C(1)	2.02 (1)	W—C(4)	2.04 (1)
W—C(2)	2.064 (9)	W—C(5)	2.03 (1)
P—W—C(1)	94.8 (3)	C(1)—W—C(5)	86.8 (5)
P—W—C(2)	87.1 (3)	C(2)—W—C(3)	88.8 (4)
P—W—C(3)	174.3 (3)	C(2)—W—C(4)	94.6 (4)
P—W—C(4)	86.4 (3)	C(2)—W—C(5)	178.1 (4)
P—W—C(5)	94.7 (3)	C(3)—W—C(4)	89.9 (4)
C(1)—W—C(2)	93.5 (4)	C(3)—W—C(5)	89.3 (4)
C(1)—W—C(3)	89.4 (4)	C(4)—W—C(5)	85.1 (4)
C(1)—W—C(4)	171.8 (4)		
C(3)—W—P—C(1*A*)	−91 (4)	W—P—C(6)—C(7)	64.2 (4)
C(3)—W—P—C(1*B*)	26 (4)	P—C(6)—C(7)—C(8)	169.5 (7)
C(3)—W—P—C(6)	144 (4)	C(6)—C(7)—C(8)—C(7′)	60.6 (5)

Data collection and cell refinement were performed using Enraf–Nonius CAD-4 diffractometer software. All other calulcations were performed using the *NRCVAX* package (Larson, Lee, Le Page, Webster, Charland & Gabe, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(*N*,*N*-dimethylformamide)(*μ*-sulfato)-dioxouranium(VI)

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Abstract

In the title compound, $[UO_2(SO_4)(C_3H_7NO)_2]$, the uranyl ion is in a pentagonal pseudo-planar equatorial environment, comprising two dimethylformamide and three sulfate O atoms. The uranyl ions are bridged by sulfate groups, giving rise to an infinite chain structure, *i.e. catena*-poly[(*NN*-dimethylformamide)dioxouranium-*μ*-sulfato-*O*,*O*′:*O*″]. Two of the sulfate O atoms are bonded to the same uranyl ion in a coordination mode previously not observed in uranyl sulfates.

Comment

Several structures of uranyl sulfates have been determined, in either their dehydrated forms (Ross & Evans,

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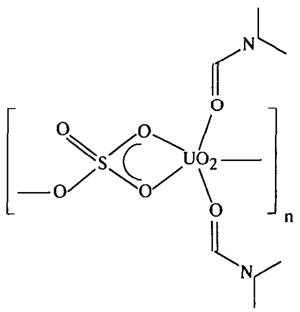
1960; Brandenburg & Loopstra, 1978), hydrated forms (Brandenburg & Loopstra, 1973; van der Putten & Loopstra, 1974; Baggio, de Benyacar, Perazzo & de Perazzo, 1977; Zalkin, Ruben & Templeton, 1978; Niinistö, Toivonen & Valkonen, 1978, 1979; Serezhkin & Serezhkina, 1982; Rogers, Bond, Hipple, Rollins & Henry, 1991), or in other forms involving organic molecules as ligands (Ruben, Spencer, Templeton & Zalkin, 1980; Soldatkina, Serezhkin & Serezhkina, 1981; Toivonen & Niinistö, 1983). A general feature of all these structures is the bridging of the uranyl ions by SO_4^{2-} moieties to form infinite chains, double chains (ribbons) or layers, with only one exception of a molecular species (Soldatkina, Serezhkin & Serezhkina, 1981). The sulfate ion has always been observed to bind by only one O atom to each uranyl unit. The geometry of the uranium environment is in all cases a more or less distorted pentagonal bipyramid, with uranyl O atoms at the apices. We report here the structure of $[UO_2(SO_4)(DMF)_2]$, (I), where DMF is *N*,*N*-dimethylformamide. An *ORTEP*II (Johnson, 1976) drawing is presented in Fig. 1.



(I)

The linear uranyl ion (with normal geometrical features) is surrounded in its equatorial plane by five donor O atoms: three from two SO_4^{2-} moieties, and two from the DMF molecules. SO_4^{2-} acts as a bridging ligand to form an infinite uranyl sulfate chain. The DMF molecules, with normal geometrical features, are located on each side of the chain axis. Two of the sulfate O atoms are bonded to the same uranyl unit, which is uncommon among uranyl sulfate structures. The five O-atom donors are in a plane with a maximum deviation of ±0.07 (1) Å, with the U atom 0.006 (1) Å from the mean plane. The U—O(S) distances, which are longer for the O atoms bonded to the same uranyl ion [2.44 (1) and 2.45 (1) Å] than for the 'bridging' O atom [2.35 (1) Å], are in agreement with previously published values (between 2.30 and 2.47 Å). T

The O(5)—U—O(6) angle [57.4 (4)°] is much smaller than the other O—U—O angles in the pentagonal environment [72.5 (4)–79.2 (5)°], but higher than the angle formed by the bidentate nitrate ion with uranyl [50.8 (2)°] which has longer U—O(N) distances [2.482 (6)–2.486 (6) Å] (Eller & Penneman, 1976). The U—O(DMF) distances are comparable to those found in $[UO_2(DMF)_5](BF_4)_2$ (Deshayes, Keller, Lance, Nierlich & Vigner, 1992), which range between 2.334 (5) and 2.383 (3) Å. The SO_4^{2-} moiety does not present any unusual feature [S—O distances 1.49 (1)–1.51 (1) Å for coordinated O atoms, 1.43 (2) Å for uncoordinated]. The packing consists of an assembly of single zigzag polymeric chains directed along the *a* axis. When viewed along the U–U axis, two successive UO_2 units along the chain are tilted, by 46.1 (2)°, with respect to each other.

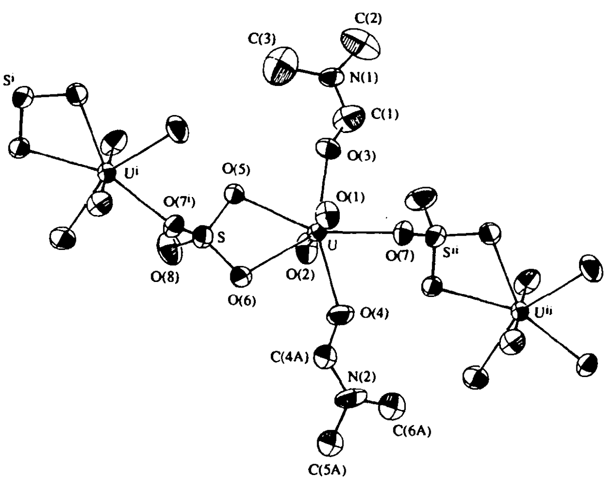


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of $[UO_2(SO_4)(DMF)_2]$ with atom labelling [symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, z$]. Only one of the two positions of C4, C5 and C6 is represented for clarity. Ellipsoids are drawn at the 45% probability level.

Experimental

Crystals were obtained as a by-product during the preparation of uranyl complexes, by slow evaporation of a DMF/water solution of uranyl nitrate hexahydrate containing sulfate ions as an impurity.

Crystal data

$[UO_2(SO_4)(C_3H_7NO)_2]$
$M_r = 512.3$
Monoclinic
$P2_1/a$
$a = 12.328$ (4) Å
$b = 8.596$ (4) Å
$c = 13.294$ (5) Å
$\beta = 97.21$ (3)°
$V = 1398$ (1) Å^3
$Z = 4$
$D_x = 2.43$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–12°
$\mu = 11.2$ mm^{-1}
$T = 295$ K
Platelet
0.50 × 0.40 × 0.20 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 23°$

$\omega/2\theta$ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968).
$T_{\min} = 0.28$, $T_{\max} = 1.00$
2216 measured reflections
1945 independent reflections
1345 observed reflections
[$I > 3\sigma(I)$]

$h = 0 \rightarrow 13$
$k = 0 \rightarrow 9$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: 7.7% in 30 h

Refinement

Refinement on F
$R = 0.035$
$wR = 0.043$
$S = 1.2$
1345 reflections
160 parameters
H atoms not included
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 1.40$ e Å^{-3}
$\Delta\rho_{\min} = -1.00$ 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 equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
U	0.34102 (4)	0.23333 (7)	0.22577 (5)	3.15 (1)
S	0.1219 (3)	0.3690 (6)	0.2683 (4)	4.2 (1)
O(1)	0.2880 (9)	0.155 (2)	0.108 (1)	5.3 (3)
O(2)	0.3953 (9)	0.309 (2)	0.345 (1)	6.1 (4)
O(3)	0.335 (1)	−0.017 (2)	0.290 (1)	5.9 (3)
O(4)	0.416 (1)	0.446 (2)	0.145 (1)	6.4 (4)
O(5)	0.1657 (9)	0.210 (1)	0.2910 (9)	4.4 (3)
O(6)	0.2032 (9)	0.440 (1)	0.207 (1)	5.3 (3)
O(7)	0.5150 (9)	0.141 (1)	0.1998 (9)	4.6 (3)
O(8)	0.110 (1)	0.451 (2)	0.360 (1)	7.1 (4)
N(1)	0.342 (1)	−0.212 (2)	0.401 (1)	4.4 (3)
N(2)	0.480 (1)	0.671 (2)	0.100 (1)	6.4 (4)
C(1)	0.386 (2)	−0.119 (3)	0.343 (2)	7.7 (7)
C(2)	0.408 (3)	−0.341 (2)	0.456 (2)	10.0 (9)
C(3)	0.228 (2)	−0.196 (4)	0.423 (2)	10 (1)
C(4*A*)*	0.395 (2)	0.576 (4)	0.110 (2)	5.2 (7)
C(4*B*)	0.503 (5)	0.521 (7)	0.139 (4)	5 (1)
C(5*A*)	0.445 (3)	0.823 (5)	0.043 (3)	7.7 (9)
C(5*B*)	0.411 (6)	0.784 (9)	0.053 (5)	7 (2)
C(6*A*)	0.588 (3)	0.651 (4)	0.125 (3)	7.0 (9)
C(6*B*)	0.618 (6)	0.729 (9)	0.110 (5)	7 (2)

* *A* denotes a site-occupancy factor of 0.66, *B* denotes a site-occupancy factor of 0.33.

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

U—O(1)	1.76 (1)	U—O(2)	1.76 (1)
U—O(3)	2.32 (1)	U—O(4)	2.37 (1)
U—O(5)	2.44 (1)	U—O(6)	2.45 (1)
U—O(7)	2.35 (1)		
S—O(5)	1.49 (1)	S—O(6)	1.50 (1)
S—O(7^{i})	1.51 (1)	S—O(8)	1.43 (2)
O(3)—C(1)	1.24 (3)	C(1)—N(1)	1.27 (3)
N(1)—C(2)	1.51 (3)	N(1)—C(3)	1.48 (3)
O(4)—C(4*A*)	1.22 (3)	O(4)—C(4*B*)	1.26 (6)
C(4*A*)—N(2)	1.34 (3)	C(4*B*)—N(2)	1.41 (6)
N(2)—C(5*A*)	1.54 (6)	N(2)—C(5*B*)	1.4 (1)
N(2)—C(6*A*)	1.35 (4)	N(2)—C(6*B*)	1.76 (8)
O(1)—U—O(2)	179.0 (7)	O(1)—U—O(3)	87.2 (6)
O(1)—U—O(4)	90.7 (6)	O(1)—U—O(5)	92.3 (5)
O(1)—U—O(6)	90.7 (5)	O(1)—U—O(7)	89.0 (5)
O(2)—U—O(3)	91.9 (7)	O(2)—U—O(4)	89.9 (7)
O(2)—U—O(5)	88.0 (5)	O(2)—U—O(6)	90.3 (6)
O(2)—U—O(7)	90.3 (5)	O(3)—U—O(7)	79.2 (5)
O(7)—U—O(4)	77.2 (5)	O(4)—U—O(6)	72.5 (4)
O(6)—U—O(5)	57.4 (4)	O(5)—U—O(3)	73.8 (4)
O(5)—S—O(6)	103.7 (7)	O(5)—S—O(7^{i})	109.8 (7)
O(5)—S—O(8)	110.6 (9)	O(6)—S—O(7^{i})	106.8 (8)
O(6)—S—O(8)	114.3 (9)	O(7^{i})—S—O(8)	111.3 (8)
O(3)—C(1)—N(1)	124 (2)	C(1)—N(1)—C(2)	121 (2)
C(1)—N(1)—C(3)	123 (2)	C(2)—N(1)—C(3)	116 (2)
O(4)—C(4*A*)—N(2)	118 (3)	O(4)—C(4*B*)—N(2)	111 (5)
C(4*A*)—N(2)—C(5*A*)	113 (3)	C(4*B*)—N(2)—C(5*B*)	153 (5)
C(4*A*)—N(2)—C(6*A*)	131 (3)	C(4*B*)—N(2)—C(6*B*)	94 (4)
C(5*A*)—N(2)—C(6*A*)	116 (3)	C(5*B*)—N(2)—C(6*B*)	112 (5)

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

U atoms were located from a Patterson map interpretation using *SHELXS*86 (Sheldrick, 1985). Other atom positions were determined from subsequent difference Fourier syntheses. H atoms were not included. Refinement was by full-matrix least squares on F. Anisotropic displacement parameters were used for all atoms except the disordered ones. Analytical scattering factors for neutral atoms were corrected for f' and f''. All calculations were performed on a VAX 4200 computer.

Data collection: Enraf–Nonius CAD-4 diffractometer software. Cell refinement: Enraf–Nonius CAD-4 diffractometer software. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: AB1210). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1529–1531

cis-Chloro(isothiocyanato)bis(1,10-phenanthroline)copper(II), *cis*-[CuCl(NCS)(phen)$_2$]

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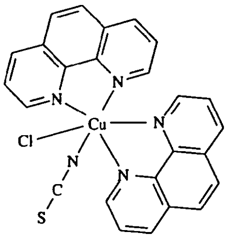
Abstract

The crystal structure of green [CuCl(NCS)($C_{12}H_8N_2$)$_2$], containing six-coordinate copper(II) with a tetragonal [$Cu^{II}N_5Cl$] core, is reported. The copper to isothiocyanate distance is 1.960 (6) Å, with Cu bonded to the N-atom end of the thiocyanate moiety. The three remaining short distances for the tetragonal core are Cu—N distances to the 1,10-phenanthrolines which are 2.043 (5), 2.060 (4) and 2.064 (4) Å. One of the long distances to the Cu-atom center is occupied by an N atom of a 1,10-phenanthroline with a Cu—N distance of 2.370 (5) Å, and the other long interaction has a Cu—Cl distance of 2.679 (2) Å.

Comment

Several five-coordinate complexes of Cu^{II} have been synthesized with one of the two potentially single-charged negative ions residing in the coordination sphere of copper and the other singly charged anion occupying a position outside the copper coordination sphere. In most cases the anion occupying the position external to the coordination sphere is a ligand such as perchlorate which has a low tendency to coordinate. The isothiocyanato complex [Cu(NCS)(phen)$_2$]ClO_4, where phen = 1,10-phenanthroline, has been synthesized and its structure determined (Parker, Manson & Breneman, 1994). The five-coordinate copper(II) complex [Cu(bipy)$_2$I]I (bipy = 2,2′-bipyridine) (Barclay & Kennard, 1961), has a potential ligand, I^-, as an anion external to the coordination sphere of the Cu atom. A structural determination of [Cu(bipy)$_2$Cl]Cl.6H_2O (Stephens & Tucker, 1973) revealed five-coordinate copper(II) with an external Cl^- ion. This work indicates that other five-coordinate copper(II) complexes might be synthesized with a free Cl^- anion. This paper reports the results of an attempt to use thiocyanate as the coordinating ligand and Cl^- as a counterion. The synthesis and structural determination of [CuCl(NCS)(phen)$_2$], (I), showed it to be a six-coordinate copper(II) complex. Preliminary work with the analogous bromide complex [CuBr(NCS)(phen)$_2$] (Parker & Breneman, 1994) shows that it is also six-coordinate.



(I)

The stereochemistry of the five-coordinate complex [Cu(NCS)(phen)$_2$]ClO_4 (Parker, Manson, & Breneman, 1994) has an N-atom-bonded thiocyanate as the stem of an inverted umbrella formed by the two 1,10-phenanthroline ligands. On the reverse side of the thiocyanate ligand, the perchlorate anion snuggles in the void formed by the two 1,10-phenanthroline ligands. The perchlorate anion is slightly displaced in [Cu(NCS)(phen)$_2$]ClO_4 unlike the perchorate anion in [CuBr(phen)$_2$]ClO_4 (Greiner, Breneman, Parker & Willett, 1994), which occupies a similar position on the twofold axis parallel to the *b* axis on which the atoms Cl, Cu and Br reside. In contrast to the two previous compounds, the chloride ion in the six-coordinate complex [CuCl(NCS)(phen)$_2$] resides in the coordination sphere of the Cu atom and is *cis* to the thiocyanate ligand. The Cl^- ion occupies one of the two long-bonding positions. An *ORTEP* (Johnson, 1965) plot of the complex is shown in Fig. 1 with the atom-numbering system. The packing of the complex in a unit cell is shown as a stereoscopic plot in Fig. 2.

The long distance of one of the 1,10-phenanthroline N atoms from the metal center is in contrast to the Cu—N distances in the two previously mentioned five-coordinate complexes, all of which are almost equal. The short Cu—N(phen) distances of 2.043 (5)–2.064 (4) Å for the equatorial and 2.370 (5) Å for the axial position are comparable to those reported for [Cu(phen)$_3$](ClO_4)$_2$ [2.00 (1)–2.06 (1) Å for the equatorial and 2.32 (1)–2.34 (1) Å for the axial (Anderson, 1973)], [Cu(PF_6)(Him)(phen)$_2$] (Him = imidazole) [2.008 (6)–2.042(5) for the equatorial and 2.219 (7) Å for the axial (Mikuriya, Kushida, Okawa & Oshio, 1989)], and [Cu(bipy)$_3$](ClO_4)$_2$ [2.026 (5)–2.036 (5) Å for the equatorial and 2.226 (7)–2.450 (7) Å for the axial (Anderson, 1972)]. The Cu—N(NCS) distance is 1.960 (6) Å with