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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 pre-

ferred 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)
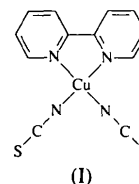
The structure of [Cu(bipy)(NCS)2] is analogous to the structures of [Cu(phen)(NCS)2] (phen = 1,10-phenanthroline) (Breneman & Parker, 1993) and [Cu(bpm)(NCS)2] (bpm = 2,2'-bipyrimidine) (Julve, Verdaguer, De Munno, Real & Bruno, 1993) from both a molecular structure and a crystal-packing perspective. 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)Br2] (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
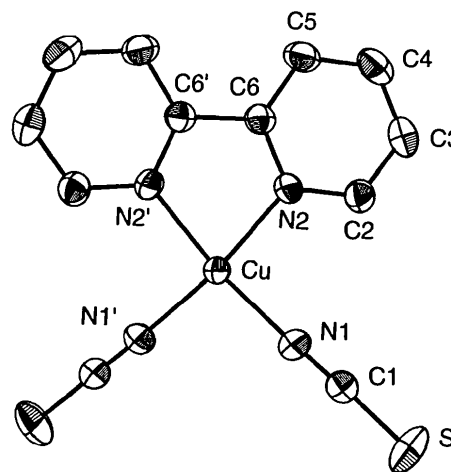

Fig. 1. *ORTEP* (Johnson, 1965) plot of [Cu(bipy)(NCS)2] showing the atom-numbering scheme. H atoms have been omitted. Displacement ellipsoids are plotted at the 50% probability level.

be compared with the torsion angle of 21.9 (4)° in [Cu(phen)(NCS)$_2$]. This distortion from square-planar geometry accommodates the bridging interactions of the S atoms of the thiocyanate ligands with neighboring Cu atoms, forming an infinite linear chain along the c axis. The Cu—S^i—C1^i angle is 103.6 (1)° and the S^i—Cu—S^{iii} angle is nearly linear with a value of 176.27 (4)° [symmetry codes: (i) x, $-y$, $\frac{1}{2}+z$; (iii) $2-x$, $-y$, $1-z$].
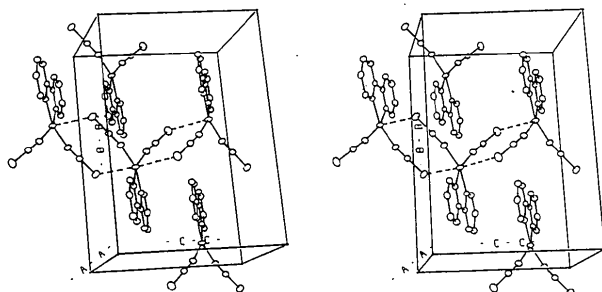

Fig. 2. Stereoscopic plot of the unit cell for [Cu(bipy)(NCS)$_2$] showing the tetragonal coordination of the Cu^{II} ion.

Experimental

[Cu(bipy)(NCS)$_2$] was prepared by the slow addition of 25 ml of a solution of 2,2'-bipyridine (1.56 g, 10.0 mmol) in ethanol to 20 ml of a solution of CuCl$_2$.2H$_2$O (1.71 g, 10.0 mmol) in water, resulting in a pale green precipitate. Solid NH$_4$SCN (1.52 g, 20.0 mmol) was slowly added to this mixture with continuous stirring. The product, a green solid, was washed with a small volume of ethanol and anhydrous ether and dissolved in dimethyl sulfoxide. A single crop of bright green crystals was produced by evaporation of the solvent.

Crystal data

[Cu(NCS)$_2$(C$_{10}$H$_8$N$_2$)]	Mo $K\alpha$ radiation
$M_r = 335.892$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 8.084$ (1) Å	$\theta = 15.33–21.39°$
$b = 15.557$ (1) Å	$\mu = 1.96$ mm^{-1}
$c = 10.518$ (2) Å	$T = 293$ K
$\beta = 95.10$ (1)°	Prism
$V = 1317.5$ (3) Å^3	$0.50 \times 0.30 \times 0.20$ mm
$Z = 4$	Dark green
$D_x = 1.69$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.025$
diffractometer	$\theta_{max} = 25.0°$
$\theta/2\theta$ scans	$h = -10 \rightarrow 10$
Absorption correction:	$k = 0 \rightarrow 20$
ψ scan	$l = 0 \rightarrow 13$
$T_{min} = 0.882$, $T_{max} = $	1 standard reflection
0.999	frequency: 167 min
1682 measured reflections	intensity variation: 1.98%
1599 independent reflections	
1177 observed reflections	
[$I > 3\sigma(I)$]	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.01$
$R = 0.041$	$\Delta\rho_{max} = 0.91$ e Å^{-3}
$wR = 0.050$	$\Delta\rho_{min} = -0.51$ e Å^{-3}
$S = 1.63$	Extinction correction: none
1177 reflections	Atomic scattering factors
103 parameters	from International Tables
All H-atom parameters	for X-ray Crystallography
refined	(1974, Vol. IV)
$w = 1/[\sigma^2(F) + 0.0004F^2]$	

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}
Cu	1	0.09919 (3)	3/4	0.0386 (1)
S	0.7282 (1)	-0.09246 (7)	0.4558 (1)	0.0602 (2)
N1	0.8721 (4)	0.0161 (2)	0.6436 (3)	0.0393 (6)
N2	0.8490 (3)	0.1970 (2)	0.6971 (2)	0.0301 (6)
C1	0.8110 (4)	-0.0284 (2)	0.5654 (3)	0.0351 (7)
C2	0.6915 (4)	0.1901 (2)	0.6449 (3)	0.0350 (7)
C3	0.5945 (4)	0.2614 (2)	0.6145 (3)	0.0410 (9)
C4	0.6610 (4)	0.3420 (2)	0.6373 (3)	0.0438 (9)
C5	0.8227 (4)	0.3495 (2)	0.6911 (3)	0.0404 (9)
C6	0.9125 (4)	0.2759 (2)	0.7201 (3)	0.0296 (6)

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

Cu···S^i	3.220 (1)	N2—C6	1.345 (4)
Cu—N1	1.946 (3)	C2—C3	1.379 (5)
Cu—N2	1.998 (2)	C3—C4	1.378 (5)
S—C1	1.622 (3)	C4—C5	1.382 (5)
N1—C1	1.153 (4)	C5—C6	1.376 (4)
N2—C2	1.345 (4)	C6—C6^{ii}	1.496 (6)
S^i···Cu···S^{iii}	176.27 (4)	Cu—N2—C2	125.8 (2)
N1—Cu—N1^{ii}	96.7 (2)	Cu—N2—C6	115.5 (2)
N1—Cu—N2	93.8 (1)	C2—N2—C6	118.6 (3)
N1—Cu—N2^{ii}	161.1 (1)	S—C1—N1	178.7 (3)
N2—Cu—N2^{ii}	80.9 (1)	N2—C2—C3	121.9 (3)
S^i···Cu—N1^{ii}	87.2 (1)	C2—C3—C4	119.1 (3)
S^i···Cu—N2^{ii}	105.9 (1)	C3—C4—C5	119.2 (3)
S^i···Cu—N1	90.3 (1)	C4—C5—C6	118.8 (3)
S^i···Cu—N2	77.0 (1)	N2—C6—C5	122.3 (3)
Cu···S^i—C1^i	103.6 (1)	N2—C6—C6^{ii}	114.0 (2)
Cu—N1—C1	169.1 (3)	C5—C6—C6^{ii}	123.6 (2)

Symmetry codes: (i) x, $-y$, $\frac{1}{2}+z$; (ii) $2-x$, y, $\frac{3}{2}-z$; (iii) $2-x$, $-y$, $1-z$.

Data collection and cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction, structure solution, structure refinement, molecular graphics and preparation of material for publication: *MolEN* (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: HR1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(9-methylhypoxanthinium) Oxonium Hexachlororuthenate(III) Trihydrate

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Abstract

The unit cell of the title compound, $2(C_6H_7N_4O)(H_3O)[RuCl_6].3H_2O$, contains the octahedral $[RuCl_6]^{3-}$ ion lying on an inversion centre. Its charge is balanced by one H_3O^+ and two N7-protonated 9-methyl-hypoxanthinium cations (9-methyl-6-oxo-1,9-dihydro-$7H^+$-purinium). The H_3O^+ ion and three water molecules form a disordered hydrogen-bonded chain parallel to the a axis.

Comment

The title compound was obtained as a by-product of a reaction between $RuCl_3$ and 9-methylhypoxanthine. An activated solution was first made by refluxing commercial hydrated $RuCl_3$ (0.4 mmol) in a mixture of ethanol (5 ml) and $1M$ aqueous HCl (5 ml) for 2 h. The solution was cooled to room temperature and three equivalents of 9-methylhypoxanthine dissolved in $1M$ HCl (5 ml) were added. After stirring vigorously for 15 min, two thirds of the solution was evaporated and an orange powder, subsequently identified as $RuCl_3(H_2O)_2(9\text{-methylhypoxan-thine})$, was removed by filtration. Red crystals, first believed to be the latter complex, appeared after several days at room temperature. The unit cell was found to contain the $[RuCl_6]^{3-}$ anion with two protonated 9-methylhypoxanthinium and one H_3O^+ counter-ions. The UV-VIS spectrum of the crystals in $12\,M$ HCl is in agreement with that reported by James & McMillan (1975) for $K_3[RuCl_6]$, thereby confirming the Ru^{III} oxidation state.
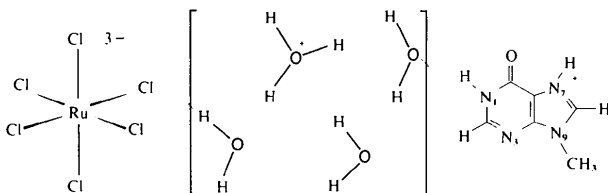
The $[RuCl_6]^{3-}$ anion (Fig. 1*a*) lies on a crystallographic inversion centre and its angles correspond to the ideal octahedral values to within $\pm 2.6°$ (Table 2). The mean Ru—Cl distance (2.376 Å) is close to those of the $[Al(H_2O)_6]^{3+}$ salt (Hopkins, Zalkin, Templeton & Adamson, 1969). A small tetragonal distortion makes the Ru—Cl(2) bonds [2.364 (1) Å] slightly shorter than Ru—Cl(1) and Ru—Cl(3) [2.382 (1) Å].

The geometry of the 9-methylhypoxanthinium unit (Fig. 1*b* and Table 2) confirms its protonation state. The C(5)—N(7)—C(8) angle of 108.2 (2)°, definitely greater than in the neutral molecule (~104°), is clear evi-
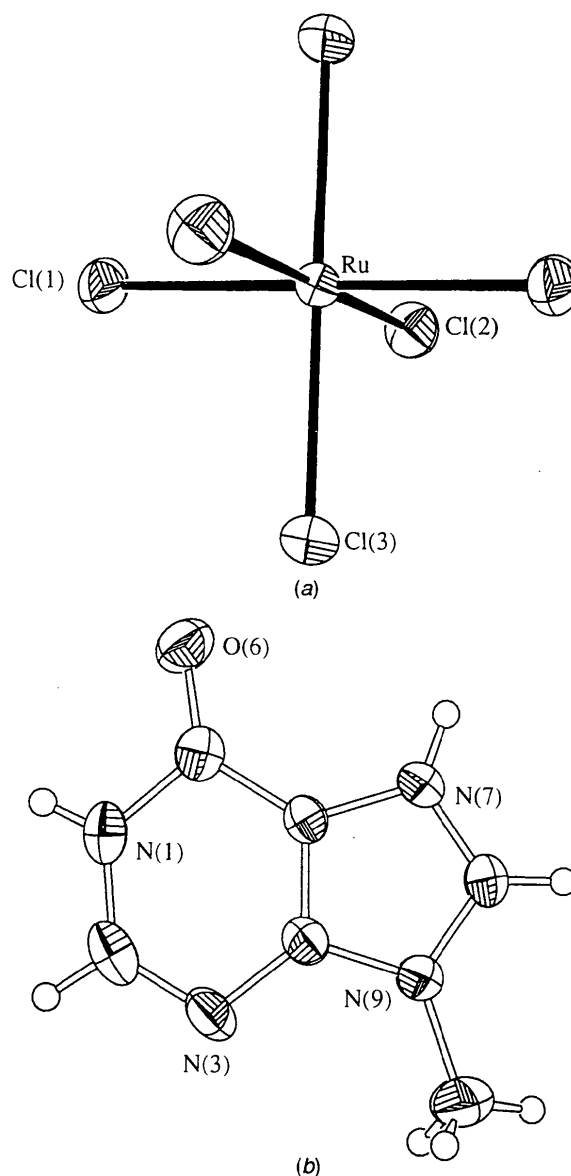
(*a*)

(*b*)

Fig. 1. *ORTEP* (Johnson, 1965) drawings of (*a*) the $[RuCl_6]^{3-}$ anion and (*b*) the 9-methylhypoxanthinium cation. Ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary size.