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Key indicators

Single-crystal X-ray study

$T = 110\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.022

wR factor = 0.063

Data-to-parameter ratio = 18.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Diisothiocyanatotetrapyridinecopper(II)

The crystal structure of the title copper(II) complex, $[\text{Cu}(\text{NCS})_2(\text{C}_5\text{H}_5\text{N})_4]$, shows a tetragonally distorted octahedral coordination about the central copper(II) ion. The Cu ion lies at a site with $\bar{1}$ symmetry.

Comment

The quintessential ambidentate character of the thiocyanate ligand makes its chemistry with various transition or rare-earth metals unique. The bonding properties of the thiocyanate anion to copper centers have recently been reviewed (Kabešová *et al.*, 1995). When considering coordination to a Cu^{II} center, the NCS group is known to coordinate through either the N or the S end of the thiocyanate anion. In the title compound, (I), the Cu^{II} center of (I) is *N*-coordinated by two thiocyanate groups.

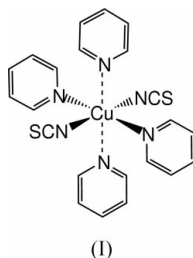


Fig. 1 shows the molecular structure of (I). Complex (I) crystallizes in space group $C2/c$ (No. 15), with four molecules in the unit cell. The six-coordinate copper(II) ion is located on an inversion center in Wyckoff position $4c$ ($\frac{3}{4}, \frac{1}{4}, \frac{1}{2}$) and exists in a tetragonally distorted octahedral coordination environment. The Cu metal center is equatorially coordinated by two isothiocyanate groups [$\text{Cu}-\text{N1} = 2.0096(11)\text{ \AA}$] and two pyridine ligands [$\text{Cu}-\text{N21} = 2.0684(10)\text{ \AA}$]; two additional pyridine moieties are bound to the Cu atom in axial positions [$\text{Cu}-\text{N11} = 2.4589(11)\text{ \AA}$].

The geometric parameters for (I) (Table 1) are reasonable when compared with similar Cu^{II} thiocyanate species (Youngme *et al.*, 2002; Kabešová *et al.*, 1995; Kabešová & Kožíšková, 1992; Soldánová *et al.*, 1983). The longer of the two unique $\text{Cu}-\text{N}_{\text{pyridine}}$ bonds corresponds to those groups in the axial position and is a result of the familiar pseudo-Jahn-Teller effect, commonly exhibited by six-coordinated Cu^{II} complexes incorporating non-equivalent ligands. The axial pyridine rings (N11/C12–C16) are essentially perpendicular [$89.06(4)^\circ$] to the equatorial plane (N1/N21/Cu), while the equatorial pyridine rings form an angle of $40.36(4)^\circ$ with this plane. The axial pyridine groups are rotated $22.05(7)^\circ$ from the plane Cu/N1/N11. The two unique pyridine ligands have a $78.05(4)^\circ$ dihedral angle between their planes.

In a recent study, Krautscheid *et al.* (1998) demonstrated that polymeric species of the general type $[\text{Cu}(\text{NCS})(\text{py})_x]$ are

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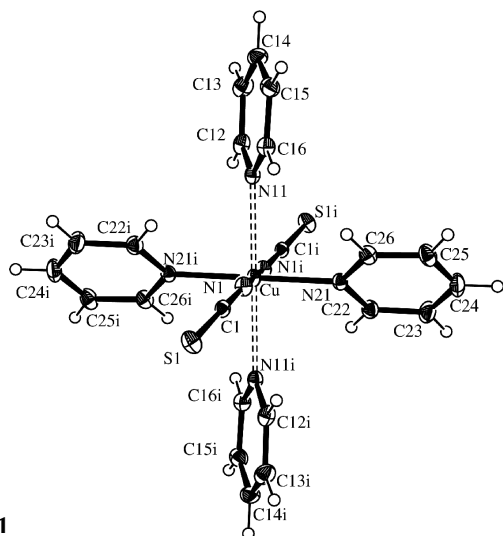


Figure 1
The molecular structure of (I). Symmetry code (i) as in Table 1.

obtained upon dissolution of CuSCN in pyridine, followed by the precipitation of the product with diethyl ether or slow evaporation. In these compounds, each Cu^{I} center is four-coordinated, with the $[\text{SCN}]^-$ ligand present in several different bridging modes. In stark contrast, complex (I) is entirely molecular in nature, with six-coordinate Cu^{II} centers and two monodentate N-bound $[\text{NCS}]^-$ groups, a likely consequence of the 'hard' acidic Cu^{II} center preferentially binding to the 'harder' base N over the 'softer' S end of the $[\text{NCS}]^-$ anion, in accordance with Pearson's principle of hard and soft Lewis acids and bases (Pearson, 1963). The Cu^{I} centers discussed by Krautscheid and co-workers are expected to be softer Lewis acids than the Cu^{II} ion present in complex (I) and thus have an affinity for both the S and N ends of adjacent $[\text{NCS}]^-$ ligands, resulting in the formation of polymeric chains. It is also interesting to note that, in the synthesis of complex (I), CuCl_2 was used as the source of Cu^{II} and was reacted with a carefully controlled stoichiometric amount of NaSCN .

Experimental

Compound (I) was prepared as a fine green powder in ~70% yield by the reaction of copper(II) chloride dihydrate (1 mmol) and sodium thiocyanate (2 mmol) in pyridine, followed by precipitation in water. X-ray quality crystals were grown from a pyridine solution of the crude product layered with ethanol. IR (KBr disc, Nicolet FT-IR): $\nu(\text{CN})$ 2092 (*vs*) cm^{-1} . UV-Vis (Shimadzu UV-2101PC): λ_{max} 716, 395 nm.

Crystal data

$[\text{Cu}(\text{NCS})_2(\text{C}_5\text{H}_5\text{N})_4]$
 $M_r = 496.10$
 Monoclinic, $C2/c$
 $a = 12.1203$ (19) Å
 $b = 12.868$ (2) Å
 $c = 15.502$ (2) Å
 $\beta = 107.481$ (6)°
 $V = 2306.0$ (6) Å³
 $Z = 4$
 $D_x = 1.429$ Mg m⁻³
 $D_m = 1.42$ (1) Mg m⁻³

D_m measured by flotation in aqueous ZnCl_2
 Mo $K\alpha$ radiation
 Cell parameters from 8843 reflections
 $\theta = 2.5$ – 34.8°
 $\mu = 1.15$ mm⁻¹
 $T = 110$ (2) K
 Block, green
 $0.25 \times 0.24 \times 0.18$ mm

Data collection

Bruker X8 APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\text{min}} = 0.765$, $T_{\text{max}} = 0.822$
 15 123 measured reflections

2637 independent reflections
 2457 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -15 \rightarrow 15$
 $k = -16 \rightarrow 14$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.063$
 $S = 1.06$
 2637 reflections
 142 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 1.4528P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu—N1	2.0096 (11)	S1—C1	1.6356 (12)
Cu—N21	2.0684 (10)	N1—C1	1.1657 (16)
Cu—N11	2.4589 (11)		
N1—Cu—N1 ⁱ	180.0	N1—Cu—N11	90.95 (4)
N1—Cu—N21 ⁱ	89.44 (4)	N21—Cu—N11	92.89 (4)
N1—Cu—N21	90.56 (4)	N1 ⁱ —Cu—N11	180.0
N1 ⁱ —Cu—N21	89.44 (4)	C1—N1—Cu	152.75 (10)
N21 ⁱ —Cu—N21	180.0	N1—C1—S1	179.22 (11)

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$.

H atoms were included in calculated positions ($\text{C—H} = 0.950$ Å) and refined as riding; isotropic displacement parameters were fixed [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$].

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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