Crystals of (isothiocyanato)(2-pyridinecarboxaldehydebenzoylhydrasonato)copper(I), Cu(C13H10N3O)(NCS)

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Received March 19, 2007, accepted and available on-line September 25, 2007; CCDC no. 12672026

Abstract

C14H10CuN4O3 or Cu(NCS)2Cl, monoclinic, P121/n1 (no. 14),  
a = 9.4827(1) Å, b = 17.0160(2) Å, c = 10.366(1) Å,  
β = 103.36(1)°, V = 1392.6 Å³, Z = 4, R_{cal} = 0.029,  
wR_cal(F^2) = 0.076, T = 150 K.

Source of material

Single crystals of copper complex were prepared by placing a 0.5 M solution of copper(II) chloride and 1 M ammonium thiocyanate in one arm of a narrow U-tube and an ethanolic 0.5 M solution of picolinaldehyde benzoylhydrasone and 0.5 M tetrabutylammonium hydroxide in the other arm. Suitable crystals with well-formed faces appeared after a few days in the middle zone of one arm of the U-tube.

Discussion

In recent years, the research on supramolecular complexes has been rapidly expanding [1]. One aspect is their fascinating structural diversity. Another aspect is their potential application as functional materials in catalysis and magnetism. As part of our work on hydrazine complexes, we report here the crystal structure of a new copper-hydrazine supramolecular derivative.

The main structural feature is the presence of an NCS–Cu bridge that connects the crystallographic asymmetric unit to its adjacent forming continuous chains. This is caused by the bidentate ligand NCS which is N-bonded to the metal ion. The copper ion is five-coordinated in a distorted tetragonal pyramidal arrangement. The Cu environment involves three nitrogen atoms and an oxygen atom at the base and a sulfur atom in apical position. Four of the atoms of the base of the pyramid namely the O, Cu, N2, and N3 form a least-squares plane from which the N4 deviates by 0.599(3) Å and the S atom is in the apex at a distance of 2.847(1) Å. If we consider the plane formed by the four atoms N2, N3, N4 and O then the Cu atom deviates from their plane by 0.2075(8) Å towards the apex. The two five-membered rings involving Cu (Cu, O, C7, N1, N2 and Cu, N3, C9, C8, N2) form a dihedral angle of 2.44° and the latter of these form a dihedral angle of 1.1° with the pyridine ring to which it is attached. The six-membered ring formed by the atoms C1, C2, C3, C4, C5 and C6 forms a dihedral angle of 3.31° with the best plane through the other three rings. The whole hydrazine molecule forms a least-squares plane with an r.m.s. deviation of the fitted atoms of 0.0398 Å, from which the N4 atom deviates by 0.697(2) Å and the S atom is 2.800(1) Å away. All the bond lengths of the five-membered rings lie in the middle of the range observed in a number of pentacoordinated copper(II) complexes [2-6] while the apical distance (Cu–S) of 2.84 Å is quite longer than previous values as usually found for bonds in apical positions. The complex is in the enolic form (–C=N–N=), which is also confirmed by the bond lengths of C7–O of 1.28 Å and C7–N1 of 1.33 Å [7].

Table 1. Data collection and handling.

| Crystal: | black block,  
| Wavelength: | size 0.30 × 0.50 × 1.20 mm  
| μ: | Mo Kα radiation (0.70930 Å)  
| Diffraclor, scan mode: | 17.21 cm⁻¹  
| 2θmax: | 0.0°  
| N(hkl)measured, N(hkl)unique: | 56.46°  
| Criterion for I(obs), N(hkl)gt: | 90 > 2σ(I(obs), 2392  
| N(param)refined: | 230  
| Programs: | SHELXS-97 [8], SHELXL-97 [9],  
| | PLATON [10] |
### Table 2. Atomic coordinates and displacement parameters (in Å²).

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<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<th>U₂₂</th>
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### Table 2. Continued.

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### References