the holes being located in the 5p orbitals within the plane.

It may be predicted, therefore, that the signs of the EFG, or QS, in the ditellurides and the Te$_4$Pd rings of the polytellurium complexes are opposite. At any rate, the study of ^{125}Te gamma ray resonance may reveal simple relationships *e.g.* between planar and linear bonding of tellurium in different compounds, adopting a scheme of partly filled 5s and 5p shells.

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Structure of Aqua(di-2-pyridylcarbonylaminato)isothiocyanatocopper(II)

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Abstract. [Cu(C$_{12}$H$_8$N$_3$O$_2$)(NCS)(H$_2$O)], $M_r =$ 365·78, triclinic, $P\bar{1}$, $a = 7·281$ (2), $b = 10·646$ (3), $c = 10·345$ (2) Å, $\alpha = 92·70$ (2), $\beta = 85·55$ (2), $\gamma = 116·26$ (2)°, $V = 717$ (1) Å^3, $Z = 2$, $D_x =$ 1·69 (1) g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu =$ 17·36 cm^{-1}, $F(000) = 370$, room temperature, $R =$ 0·033, $wR = 0·037$ for 2799 unique reflections with $I > 3\sigma(I)$. The structure consists of discrete neutral units linked through hydrogen bonds. The coordination geometry around copper ions can be described as tetragonal square pyramidal, the O atoms from the coordinated water molecule occupying the axial position and the N atoms from the pyridinecarboximidate and the thiocyanate groups the basal plane.

Introduction. In the course of our study on the interactions between Cu^{II} and easily stackable ligands we have recently reported the synthesis and characterization of a set of Cu^{II} pcpci [pcpci = *N*-(2'-pyridylcarbonyl)pyridine-2-carboximidate anion] complexes (Folgado, Escrivá, Beltrán-Porter & Beltrán-Porter, 1987; Folgado, Coronado, Beltrán-Porter, Burriel, Fuertes & Miravitlles, 1988). pcpci is a tridentate rigid quasi-planar *N*-donor ligand whose monoanionic character makes it different from other related ligands such as terpy (2,2':6',2''-terpyridine), paphy (pyridine-2-aldehyde-2'-pyridyl hydrazone), or tpt [2,4,6-tris(2-pyridyl)-1,3,5-triazine]. This renders possible the isolation of neutral Cu(pcpci)X entities (X = monoanion). When X is a potentially bridging ligand, condensed systems may result. Such an ability is well established for halide and pseudohalide

anions. In this sense, we have recently synthesized Cu(pcpci)$X.n$H$_2$O compounds (Folgado, Escrivá, Beltrán-Porter & Beltrán-Porter, 1987), with X = Cl or Br, n = 0, X = NCS, N$_3$, NCO or CN, n = 1, and have shown that the halides contain mono-μ-halo-bridged chains (Folgado, Coronado, Beltrán-Porter, Burriel, Fuertes & Miravitlles, 1988). In order to clarify the bonding in the pseudohalide derivatives the crystal structure of the title compound was undertaken.

Experimental. Powder samples of the title compound were prepared as described earlier (Folgado, Escrivá, Beltrán-Porter & Beltrán-Porter, 1987). Recrystallization from hot water/methanol solutions gave blue rhombohedral platelets suitable for X-ray analysis. A well formed crystal of dimensions 0·20 × 0·18 × 0·05 mm was selected and mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. Cell dimensions were obtained by least-squares refinement of 25 well centred reflections (4·3 < θ < 13·5°) using Mo $K\alpha$ radiation. Space group $P\bar{1}$ was assumed throughout the structure analysis and was confirmed by successful refinement of the structure. Examination of three standard reflections, monitored every 4 h, showed no substantial intensity decay. 4152 reflections were measured (3·97 < 2θ < 59·93°; 0 < h < 10, −14 < k ≤ 14, −14 < l < 14) with the variable-speed ω–2θ technique, of which 2799 were unique [with $I > 3\sigma(I)$ and R_{int} = 0·017] and used in the determination of the structure. Lorentz and polarization corrections were applied, but none for absorption. The structure was solved by direct methods with *MULTAN*11/84 (Main, Germain & Woolfson, 1984). The remaining non-H atoms were located from subsequent Fourier syntheses. The model obtained was refined with the *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) system by weighted anisotropic full-matrix least-squares methods. After refinement of positional and anisotropic thermal parameters for all non-H atoms, the H atoms belonging to the organic ligand were placed in their calculated positions and were included in the final refinement with common fixed isotropic thermal parameters (U = 0·08 Å^2). The final R values were R = 0·033 and wR = 0·037 (223 parameters refined); $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma^2(F_o)]$ with $\sigma^2(F_o)$ from counting statistics. The largest Δ/σ was 0·02. In the final difference map the residual maxima were less than 0·78 e Å^{-3}. Atomic scattering factors and corrections for anomalous dispersion for the Cu atom were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The geometrical calculations were performed with the *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) system and

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for non-H atoms with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
Cu	0·06041 (5)	0·26026 (3)	0·17466 (3)	0·03504 (9)
N(1)	0·1518 (3)	0·2043 (2)	−0·0016 (2)	0·0379 (7)
C(11)	0·0709 (4)	0·2336 (3)	−0·0997 (2)	0·0336 (7)
C(12)	0·1154 (5)	0·2043 (3)	−0·2274 (3)	0·046 (1)
C(13)	0·2482 (5)	0·1416 (4)	−0·2560 (3)	0·055 (1)
C(14)	0·3321 (5)	0·1147 (4)	−0·1568 (4)	0·060 (1)
C(15)	0·2817 (5)	0·1459 (3)	−0·0305 (3)	0·052 (1)
N(2)	−0·1047 (3)	0·3085 (2)	0·3209 (2)	0·0319 (6)
C(21)	−0·2210 (4)	0·3651 (3)	0·2813 (2)	0·0309 (7)
C(22)	−0·3327 (5)	0·4134 (3)	0·3674 (3)	0·0450 (9)
C(23)	−0·3295 (5)	0·4011 (4)	0·4997 (3)	0·051 (1)
C(24)	−0·2162 (5)	0·3410 (3)	0·5407 (3)	0·0450 (9)
C(25)	−0·1043 (4)	0·2960 (3)	0·4489 (3)	0·0400 (8)
N(3)	−0·1017 (3)	0·3113 (2)	0·0724 (2)	0·0335 (6)
C(31)	−0·2219 (4)	0·3683 (2)	0·1358 (2)	0·0304 (7)
O(31)	−0·3233 (3)	0·4164 (2)	0·0885 (2)	0·0453 (6)
C(32)	−0·0752 (4)	0·2985 (3)	−0·0604 (2)	0·0322 (7)
O(32)	−0·1515 (3)	0·3325 (2)	−0·1419 (2)	0·0519 (7)
N(4)	0·1791 (4)	0·1753 (3)	0·2769 (2)	0·0514 (8)
C(4)	0·2506 (4)	0·1131 (3)	0·3220 (2)	0·0368 (8)
S	0·3515 (1)	0·02571 (8)	0·38537 (8)	0·0584 (3)
O	0·3420 (3)	0·4831 (2)	0·1749 (2)	0·0390 (6)

molecular illustrations were drawn with *SCHAKAL*88 (Keller, 1988).

Discussion. The atomic parameters are given in Table 1,* and the interatomic distances and angles are listed in Table 2. Fig. 1 shows a perspective view of the molecule with the atomic numbering scheme, and Fig. 2 shows a view of the crystal packing in the solid.

The coordination sphere of Cu^{II} is best described as a tetragonal square pyramid. The basal positions are occupied by the three N atoms from the pcpci ligand and one N atom from the monodentate thiocyanate anion, while the apical position is occupied by the O atom from the water molecule. The Cu—N(pcpci) bond distances, ranging from 1·94 (2) to 2·01 (2) Å, are very similar to those in the Cu(pcpci)Br (Folgado, Coronado, Beltrán-Porter, Burriel, Fuertes & Miravitlles, 1988), [Cu(pcpci)-(OOCCH$_3$)(H$_2$O)].H$_2$O (Folgado, Martínez-Tamayo, Beltrán-Porter, Beltrán-Porter, Fuertes & Miravitlles, 1989), and other Cu^{II} complexes with related N-heterocyclic ligands (Folgado, Escrivá, Beltrán-Porter, Beltrán-Porter, Fuertes & Miravitlles, 1987; Folgado, Ibáñez, Coronado, Beltrán-Porter, Savariault & Galy,1988). The Cu—N(thiocyanate) bond distance agrees well with those

Table 2. *Bond and contact distances* (Å) *and angles* (°)
with e.s.d.'s in parentheses

Cu—N(1)	2·01 (2)	C(31)—N(3)	1·36 (1)	
Cu—N(2)	2·00 (2)	C(31)—O(31)	1·22 (1)	
Cu—N(3)	1·94 (2)	C(31)—C(21)	1·508 (4)	
Cu—N(4)	1·92 (2)	C(21)—N(2)	1·35 (1)	
Cu—O	2·35 (4)	C(21)—C(22)	1·36 (1)	
N(1)—C(15)	1·34 (1)	N(2)—C(25)	1·337 (4)	
N(1)—C(11)	1·35 (1)	C(22)—C(23)	1·386 (5)	
C(11)—C(12)	1·37 (1)	C(23)—C(24)	1·36 (1)	
C(12)—C(13)	1·39 (1)	C(24)—C(25)	1·38 (2)	
C(13)—C(14)	1·36 (1)	N(4)—C(4)	1·15 (1)	
C(14)—C(15)	1·38 (1)	C(4)—S	1·62 (1)	
C(11)—C(32)	1·51 (1)	O···O(31^i)	3·02 (2)	
C(32)—O(32)	1·22 (1)	O···O(32^i)	2·91 (2)	
C(32)—N(3)	1·371 (6)	O···O(31^{ii})	2·85 (2)	

N(1)—Cu—N(2)	162·0 (1)	N(1)—Cu—N(3)	81·8 (1)
N(2)—Cu—N(3)	81·5 (1)	N(1)—Cu—N(4)	97·2 (1)
N(2)—Cu—N(4)	98·0 (1)	N(1)—Cu—O	96·0 (1)
N(2)—Cu—O	92·6 (1)	N(3)—Cu—O	97·0 (1)
N(4)—Cu—O	93·7 (1)	N(3)—Cu—N(4)	169·3 (1)
C(11)—N(1)—C(15)	118·7 (3)	N(1)—C(11)—C(12)	122·2 (3)
C(11)—C(12)—C(13)	118·6 (3)	C(12)—C(13)—C(14)	118·8 (3)
C(13)—C(14)—C(15)	120·1 (4)	C(14)—C(15)—N(1)	121·5 (4)
C(12)—C(11)—C(32)	121·9 (3)	N(1)—C(11)—C(32)	115·9 (2)
C(11)—C(32)—N(3)	110·8 (3)	O(32)—C(32)—C(11)	121·0 (2)
O(32)—C(32)—N(3)	128·3 (3)	C(32)—N(3)—C(31)	123·9 (3)
N(3)—C(31)—C(21)	110·9 (3)	N(3)—C(31)—O(31)	128·0 (2)
O(31)—C(31)—C(21)	121·1 (3)	C(31)—C(21)—C(22)	122·7 (3)
C(31)—C(21)—N(2)	115·3 (3)	C(22)—C(21)—N(2)	122·0 (3)
C(21)—N(2)—C(25)	118·6 (3)	C(21)—C(22)—C(23)	118·8 (4)
C(22)—C(23)—C(24)	119·5 (3)	C(23)—C(24)—C(25)	118·9 (3)
C(24)—C(25)—N(2)	122·1 (3)	Cu—N(4)—C(4)	170·0 (2)
N(4)—C(4)—S	180·0 (4)	C(11)—N(1)—Cu	113·3 (2)
C(15)—N(1)—Cu	128·9 (2)	C(21)—N(2)—Cu	113·8 (2)
C(25)—N(1)—Cu	127·6 (2)	C(32)—N(3)—Cu	118·0 (2)
C(31)—N(3)—Cu	117·9 (2)	O(31^i)···O···O(32^i)	57·2 (1)
O(31^i)···O···O(31^{ii})	95·0 (1)	O(32^i)···O···O(31^{ii})	146·0 (2)

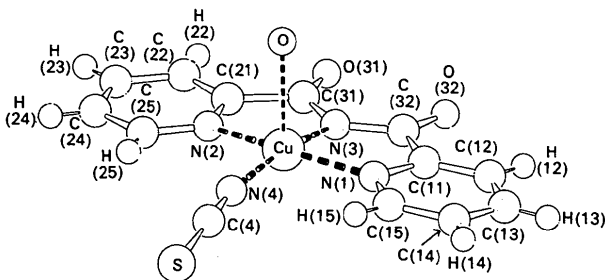Symmetry code: (i) $-x$, $1-y$, $-z$; (ii) $1+x$, y, z.

Fig. 1. View of the molecular unit of $Cu(pcpci)(NCS)(H_2O)$ with the atomic numbering scheme.
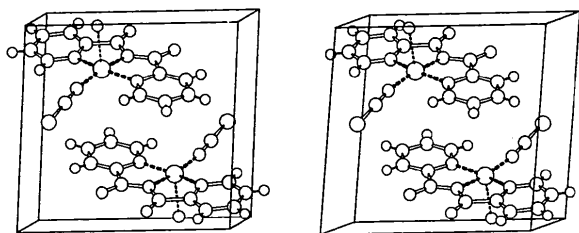

Fig. 2. Stereoscopic view of the crystal packing of $Cu(pcpci)(NCS)(H_2O)$. **b** is vertical, **c** is horizontal and **a** is into the plane of the paper.

found in [Cu(paphy)(NCS)(SCN)] (Mesa, Rojo, Arriortua, Villeneuve, Folgado, Beltrán-Porter & Beltrán-Porter, 1989). The apical Cu—O bond distance is 2·35 (4) Å, considerably larger than the basal ones. The four basal N atoms are coplanar within ±0·02 Å, and the Cu atom is displaced 0·16 Å above the mean plane.

The pcpci ligand is nearly planar within ±0·09 Å, although it is subject to some angular strain. This is clearly seen in the value of the angles around the C atoms involved in the carbonyl groups (see Table 1), which are far away from 120°. As previously noted (Lerner & Lippard, 1977), the coordination of the pcpci to the copper(II) ion, needing short metal–nitrogen bonds, introduces such a large angular strain. On the other hand, the thiocyanate ligand is fully linear [N(4)—C(4)—S = 180·0 (4)°], and the coordination to Cu^{II}, *via* the N atom, is achieved in a nearly linear mode [Cu—N(4)—C(4) = 170·0 (2)°], whereas the N—C and C—S bond distances have their typical values.

As the contact distances shown in Table 1 indicate, the crystal packing in the solid is achieved by inter-molecular hydrogen bonding. The coordinated water molecule is hydrogen bonded simultaneously to two [O(31^i) and O(32^i)] and one [O(31^{ii})] carbonyl O atoms from two different pcpci ligands (see Table 1).

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