

**Low-Temperature Structures of  
catena-(Bipyrimidine-*N,N'*)bis(thiocyanato)copper(II) and  
Poly-( $\mu$ -bipyrimidine-*N,N',N'',N'''*)tetrakis(thiocyanato)dicopper(II)**

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**Abstract.** Compound (1), *catena*-poly[(2,2'-bipyrimidine- $\kappa^2N,N'$ )copper(II)-bis- $\mu$ -(thiocyanato- $\kappa N:\kappa S$ )],  $[\text{Cu}(\text{NCS})_2(\text{C}_8\text{H}_6\text{N}_4)]_n$ ,  $M_r = 337.9$ , monoclinic,  $C2/c$ ,  $a = 11.403$  (2),  $b = 13.943$  (3),  $c = 7.722$  (2) Å,  $\beta = 93.93$  (2)°,  $V = 1224.9$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.832$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 21.1$  cm<sup>-1</sup>,  $F(000) = 676$ ,  $T = 153$  K, final  $R = 0.025$  and  $wR = 0.032$  for 1241 reflections with  $I > 3\sigma(I)$ . (2), poly[copper(II)- $\mu$ -(2,2'-bipyrimidine- $1\kappa^2N^1,N^{1'}$ : $2\kappa^2N^2,N^{2'}$ )-copper(II)-tetrakis- $\mu$ -(thiocyanato- $\kappa N:\kappa S$ )],  $[\text{Cu}_2(\text{NCS})_4(\text{C}_8\text{H}_6\text{N}_4)]_n$ ,  $M_r = 517.6$ , orthorhombic,  $Fddd$ ,  $a = 12.676$  (2),  $b = 22.171$  (3),  $c = 24.490$  (3) Å,  $V = 6883$  (2) Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 1.998$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 29.6$  cm<sup>-1</sup>,  $F(000) = 4096$ ,  $T = 153$  K, final  $R = 0.033$  and  $wR = 0.042$  for 1634 reflections with  $I > 3\sigma(I)$ . The structure of (1) consists of one-dimensional chains, in which the thiocyanate group bridges the  $[\text{Cu}(\text{bpm})]^{2+}$  (bpm = bipyrimidine) units in an end-to-end fashion. The structure of (2) consists of  $[\text{Cu}(\text{bpm})\text{Cu}]^{4+}$  units which are linked by thiocyanate groups acting in an end-to-end bridging fashion. In both complexes, the copper(II) ion displays a distorted octahedral coordination. There is a significant distortion towards tetrahedral coordination in (1) which is not observed in (2). The bipyrimidine group acts as a bidentate and bis-bidentate ligand in (1) and (2), respectively.

**Introduction.** Complexes containing paramagnetic centres bridged by multi-atom ligands are currently being investigated because of interest in the magnetic properties they exhibit (Gatteschi, Kahn & Willett, 1985; Delhaes & Drillon, 1987; Gatteschi, Kahn, Miller & Palacio, 1991). In this context, the synthesis and the structural and magnetic characterization of

metal complexes with the 2,2'-bipyrimidine ligand (bpm) has received particular attention in the last decade. It follows that bpm can act either as a bis-bidentate (De Munno & Bruno, 1984; Brewer & Sinn, 1985; Kaim & Kholmman, 1987; Brewer, Murphy & Petersen, 1987; Julve, De Munno, Bruno & Verdaguer, 1988; Julve, Verdaguer, De Munno, Real & Bruno, 1992) or as a bidentate ligand (Matsubayashi, Yamaguchi & Tanaka, 1988; De Munno, Bruno, Julve & Romeo, 1990; Castro, Julve, De Munno, Bruno, Real, Lloret & Faus, 1992; De Munno, Julve, Verdaguer & Bruno, 1992).

As part of a systematic study dealing with 2,2'-bipyrimidine-containing copper(II) complexes, we have synthesized two new compounds of formula  $[\text{Cu}(\text{bpm})(\text{NCS})_2]_n$  (1) and  $[\text{Cu}_2(\text{bpm})(\text{NCS})_4]_n$  (2). Their crystal structures at room temperature and their magnetic properties as a function of temperature are the subject of a recent contribution (Julve *et al.*, 1992). In the present article we report the crystal structure analysis of (1) and (2) at 153 K. The change of colour observed in these compounds when the temperature is lowered to that of liquid nitrogen prompted us to investigate the low-temperature crystal structure in order to connect the changes in colour with the possible structural modifications.

**Experimental.** A blue-green prismatic crystal  $0.12 \times 0.10 \times 0.60$  mm for (1) and a brown needle crystal  $0.50 \times 0.20 \times 0.02$  mm for (2) were used for intensity data collection. Accurate unit-cell dimensions and crystal-orientation matrix were obtained from least-squares refinement of 25 strong reflections in the  $14 < 2\theta < 30^\circ$  range. Siemens four-circle diffractometer, Wyckoff-scan technique, graphite-monochromated Mo  $K\alpha$  radiation, scan range  $2\theta = 3.5\text{--}55^\circ$  [ $-14 \leq h$

$\leq 14$ ,  $0 \leq k \leq 18$ ,  $0 \leq l \leq 10$  for (1) and  $0 \leq h \leq 16$ ,  $0 \leq k \leq 28$ ,  $0 \leq l \leq 31$  for (2)]. No systematic loss of intensity of three standard reflections (550,  $\bar{5}53$ ,  $\bar{2}61$ ) for (1) and (800, 0,16,0, 0,0,20) for (2) was observed during data collection. 1579 and 2189 reflections were measured, 1418 ( $R_{\text{int}} = 0.0191$ ) and 1986 ( $R_{\text{int}} = 0.011$ ) were unique for (1) and (2), respectively. Lorentz and polarization corrections applied to the intensity data, face-indexed numerical absorption corrections performed, extinction corrections being ignored. The structures were solved by standard Patterson methods and subsequently completed by Fourier recycling, 1241 for (1) and 1634 reflections for (2) having  $I > 3\sigma(I)$  were used to refine 88 and 122 parameters by full-matrix least-squares procedure, the function minimized being  $\sum w(|F_o| - |F_c|)^2$ . Final  $R = 0.025$  [0.033],  $wR = 0.032$  [0.042],  $S = 1.465$  [1.134], max.  $\Delta/\sigma = 0.017$  [0.004], max.  $\Delta\rho$  excursions in  $\Delta F$  synthesis 0.42 [0.46] e  $\text{\AA}^{-3}$  were found for (1) [(2)]. The weighting scheme used in the last refinement cycles was  $w = 1.0000/[\sigma^2(F_o) + q(F_o)^2]$ , with  $q = 0.000633$  for (1) and 0.002000 for (2). All non-H atoms were refined anisotropically, while H atoms were placed in calculated positions and refined as riding atoms. A common thermal parameter was assigned to all H atoms. Anomalous-dispersion corrections and scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV) and scattering factors for H atoms from Stewart, Davidson & Simpson (1965). Solutions and refinements were performed with the *SHELXTL-Plus* system (Sheldrick, 1989). The final geometrical calculations were carried out with the *PARST* program (Nardelli, 1983). The graphical manipulations were performed using the *XP* utility of the *SHELXTL-Plus* system.\*

**Discussion.** Final atomic coordinates for non-H atoms of (1) and (2) are listed in Table 1. Bond distances and angles are given in Tables 2 and 3, for (1) and (2), respectively. *ORTEP* views of (1) and (2) are shown in Figs. 1 and 2, respectively.

The structures of both compounds do not display any large difference with respect to those determined at room temperature (Julve *et al.*, 1992). In fact, as at room temperature, (1) consists of [Cu(bpm)(NCS)<sub>2</sub>] units held together by the S atoms of thiocyanate groups in such a way so as to form linear chains. Each Cu<sup>II</sup> atom is in a distorted octahedral environment in which the main distortion is the lengthening of the Cu—S axial distances followed by an out-of-

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for (1) and (2)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Compound	x	y	z	$U_{\text{eq}}$
<b>Compound (1)</b>				
Cu(1)	0	3685 (1)	2500	21 (1)
N(1)	546 (1)	2589 (1)	1082 (2)	18 (1)
C(1)	1050 (2)	2639 (1)	-430 (2)	21 (1)
C(2)	1319 (2)	1817 (1)	-1323 (2)	23 (1)
C(3)	1057 (2)	946 (2)	-571 (3)	23 (1)
N(2)	543 (1)	884 (1)	932 (2)	22 (1)
C(4)	304 (1)	1711 (1)	1680 (2)	17 (1)
N(3)	974 (1)	4628 (1)	1437 (2)	25 (1)
C(5)	1402 (1)	5339 (1)	1037 (2)	19 (1)
S(1)	2012 (1)	6337 (1)	451 (1)	23 (1)
<b>Compound (2)</b>				
Cu(1)	6250	1250	10131 (1)	18 (1)
N(1)	6243 (2)	651 (1)	10767 (1)	15 (1)
C(4)	6166 (2)	2186 (1)	9209 (1)	18 (1)
C(2)	6240 (2)	45 (1)	10764 (1)	17 (1)
C(3)	6250	-276 (2)	11250	19 (1)
C(1)	6250	921 (2)	11250	13 (1)
N(3)	6272 (2)	1888 (1)	9594 (1)	24 (1)
S(1)	3956 (1)	1181 (1)	10248 (1)	20 (1)
Cu(2)	3750	2510 (1)	8750	20 (1)
N(2)	3747 (2)	3216 (1)	8204 (1)	16 (1)
C(8)	3750	3750	8450 (1)	14 (1)
C(6)	3750	3216 (1)	7657 (1)	19 (1)
C(7)	3750	3750	7365 (2)	22 (1)
C(5)	3831 (2)	1615 (1)	9713 (1)	19 (1)
N(4)	3730 (2)	1922 (1)	9333 (1)	28 (1)
S(2)	6029 (1)	2631 (1)	8681 (1)	20 (1)

plane movement of the equatorial N atoms [the dihedral angle between the bpm rings is 10.2° and that between the N(3), Cu(1), N(3a) and N(1), N(1a), C(4), C(4a), N(2), N(2a), Cu mean planes is 23.5°].

Compound (2) is formed by [(NCS)<sub>2</sub>Cu(bpm)-(NCS)<sub>2</sub>] repeating units linked by Cu—S bonds. Two different [Cu(bpm)] units, mutually linked by NCS bridges, are observed in the structure; the Cu...Cu' axis of one is perpendicular to that of the other. Because of this particular geometry, (2) is a three-dimensional polymer in which the Cu(1)...Cu(1b) axis is parallel to the y axis and the Cu(2)—Cu(2f) axis is parallel to the z axis. The propagation along the x axis is ensured by the formation of the Cu—S bonds which are along this axis.

With respect to the NCS—Cu ribbon, the bpm moieties assume a zigzag disposition similar to that found in Cu<sub>2</sub>X<sub>4</sub>(bpm) (X = Br, Cl) (Julve *et al.*, 1988), apart from the fact that in (1) bpm acts as a bidentate outer ligand and not in a bis-bidentate fashion. On the other hand, in (2) bpm planar ligands adopt a helical arrangement with respect to the Cu—NCS—Cu bonds. As far as the chemical environment of Cu is concerned, important differences may be noticed between (1) and (2). Even though the chromophore is the same, in (1) a distortion of the atoms in the equatorial positions is noticed,

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55596 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and interbond angles (°) for (1)

Cu(1)—N(1)	2.004 (2)	C(2)—C(3)	1.387 (3)
Cu(1)—N(3)	1.939 (2)	C(3)—N(2)	1.338 (3)
Cu(1)—S(1c)	3.121 (1)	N(2)—C(4)	1.327 (2)
N(1)—C(1)	1.339 (2)	C(4)—C(4a)	1.486 (3)
N(1)—C(4)	1.342 (2)	N(3)—C(5)	1.157 (2)
C(1)—C(2)	1.383 (3)	C(5)—S(1)	1.634 (2)
N(1)—Cu(1)—N(1a)	80.6 (1)	Cu(1)—N(1)—C(4)	115.4 (1)
N(1)—Cu(1)—N(3a)	163.1 (1)	C(4)—N(1)—C(1)	117.3 (2)
N(1)—Cu(1)—N(3)	94.4 (1)	N(1)—C(1)—C(2)	120.9 (2)
N(1)—Cu(1)—S(1b)	98.7 (1)	C(1)—C(2)—C(3)	117.1 (2)
N(1)—Cu(1)—S(1c)	80.5 (1)	C(2)—C(3)—N(2)	122.7 (2)
N(3a)—Cu(1)—N(3)	94.7 (1)	C(3)—N(2)—C(4)	115.9 (2)
N(3a)—Cu(1)—S(1b)	96.4 (1)	N(2)—C(4)—N(1)	126.1 (2)
N(3a)—Cu(1)—S(1c)	84.4 (1)	N(2)—C(4)—C(4a)	119.5 (1)
S(1b)—Cu(1)—S(1c)	178.9 (1)	N(1)—C(4)—C(4a)	114.3 (1)
C(5)—S(1)—Cu(1c)	83.6 (1)	Cu(1)—N(3)—C(5)	163.5 (2)
Cu(1)—N(1)—C(1)	127.2 (1)	N(3)—C(5)—S(1)	179.3 (2)

Symmetry code: (a)  $-x, y, 0.5 - z$ ; (b)  $x, 1 - y, 0.5 + z$ ; (c)  $-x, 1 - y, -z$ .

Table 3. Bond lengths (Å) and interbond angles (°) for compound (2)

Cu(1)—S(1)	2.926 (1)	Cu(2)—S(2)	2.906 (1)
Cu(1)—N(1)	2.047 (2)	Cu(2)—N(2)	2.058 (2)
Cu(1)—N(3)	1.933 (3)	Cu(2)—N(4)	1.933 (3)
N(1)—C(2)	1.344 (3)	N(2)—C(6)	1.340 (4)
N(1)—C(1)	1.325 (3)	N(2)—C(8)	1.329 (3)
C(1)—C(1a)	1.459 (7)	C(8)—C(8d)	1.468 (7)
C(2)—C(3)	1.396 (3)	C(6)—C(7)	1.382 (4)
N(3)—C(4)	1.159 (4)	N(4)—C(5)	1.161 (4)
C(4)—S(2)	1.635 (3)	C(5)—S(1)	1.633 (3)
N(1)—Cu(1)—N(1a)	80.9 (1)	N(2)—Cu(2)—N(2d)	81.0 (1)
N(1)—Cu(1)—N(3)	173.4 (1)	N(2)—Cu(2)—N(4)	172.9 (1)
N(1)—Cu(1)—N(3a)	92.5 (1)	N(2)—Cu(2)—N(4d)	91.9 (1)
N(1)—Cu(1)—S(1)	83.6 (1)	N(2)—Cu(2)—S(2)	83.9 (1)
N(1)—Cu(1)—S(1a)	88.0 (1)	N(2)—Cu(2)—S(2d)	88.0 (1)
N(1a)—Cu(1)—N(3)	92.5 (1)	N(2d)—Cu(2)—N(4)	91.9 (1)
N(3)—Cu(1)—N(3a)	94.1 (2)	N(4)—Cu(2)—N(4d)	95.1 (2)
N(3)—Cu(1)—S(1)	96.9 (1)	N(4)—Cu(2)—S(2)	96.8 (1)
S(1)—Cu(1)—S(1a)	168.8 (1)	S(2)—Cu(2)—S(2d)	169.4 (1)
Cu(1)—N(1)—C(1)	112.7 (2)	Cu(2)—N(2)—C(8)	112.5 (2)
Cu(1)—N(1)—C(2)	130.1 (2)	Cu(2)—N(2)—C(6)	130.5 (2)
C(2)—N(1)—C(1)	117.2 (3)	C(6)—N(2)—C(8)	117.0 (2)
N(1)—C(1)—C(1a)	116.9 (3)	N(2)—C(8)—C(8d)	117.0 (2)
N(1)—C(1)—N(1b)	126.3 (3)	N(2)—C(8)—N(2f)	126.0 (3)
N(1)—C(2)—C(3)	120.5 (3)	N(2)—C(6)—C(7)	121.1 (3)
C(2)—C(3)—C(2b)	118.4 (4)	C(6)—C(7)—C(6f)	117.8 (4)
Cu(1)—N(3)—C(4)	165.9 (2)	Cu(2)—N(4)—C(5)	170.5 (2)
N(3)—C(4)—S(2)	177.7 (3)	N(4)—C(5)—S(1)	179.2 (2)

Symmetry code: (a)  $1.25 - x, 0.25 - y, z$ ; (b)  $1.25 - x, y, 2.25 - z$ ; (d)  $0.75 - x, y, 1.75 - z$ ; (f)  $0.75 - x, 0.75 - y, z$ .

which is not found in (2) where the Cu—S distances are somewhat shorter.

Both compounds become blue when the temperature is lowered to about 153 K. Compound (1) turned blue and compound (2) blue-green, instead of blue-green and brown, respectively, which are seen at room temperature. If this change in colour depended on relevant structural variations, these would result in large differences between the present structure at 153 K and those determined at room temperature. Quite surprisingly this is not the case.

As normally found, in (1) all three cell parameters diminish in almost equal, in (1) all three cell parameters diminish in almost equal amounts at low tempera-

ture, whereas in (2) only the  $a$  and  $b$  axes decrease, while, quite surprisingly,  $c$  increases from 24.259 (1) to 24.490 (3) Å, in such away that the cell volume remains almost unchanged. This may be attributed to the fact that the structure of (2) is a three-dimensional polymer.

Apart from this, no significant variations in the geometrical parameters of the structures from room to low temperature is observed. The only small geometrical difference which could be responsible for the change in colour of (1) is the shortening of the Cu—S distances [Cu(1)—S(1c) = 3.121 (1) instead of

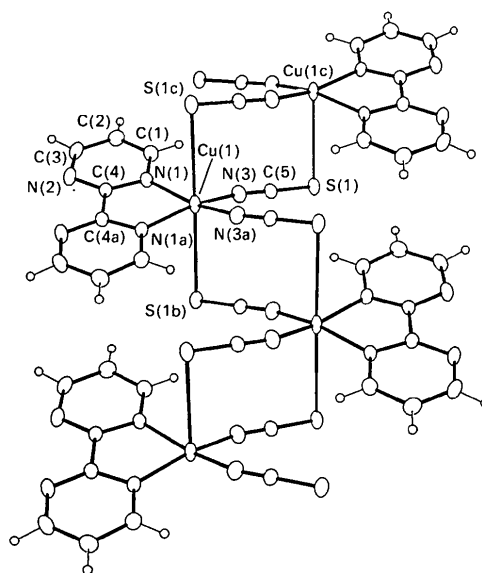


Fig. 1. ORTEP view of compound (1).

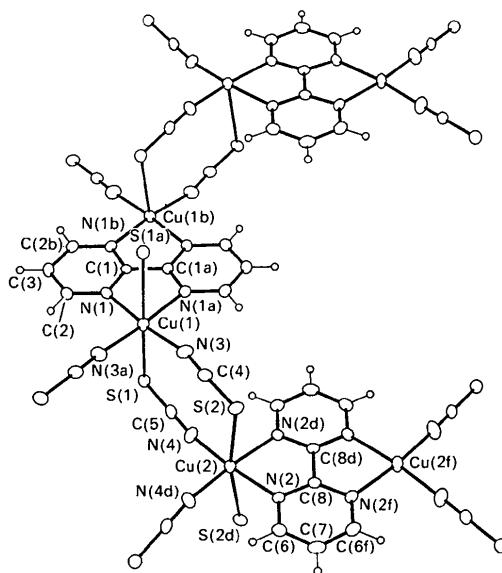


Fig. 2. ORTEP view of compound (2).

3.174 (1) Å for (1) and Cu(1)—S(1) = 2.926 (1), Cu(2)—S(2) = 2.906 (1) instead of 2.947 (1) and 2.933 (1) Å for (2)]. In this case, one should assume that very small geometrical variations are capable of modifying the electronic state of the Cu<sup>II</sup> atom to the point of causing a change of colour. Further investigation by electronic spectroscopy will be carried out in order to check this hypothesis.

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## Structure of the Dinuclear Platinum Monohydrido Bridged Complex [(PEt<sub>3</sub>)<sub>2</sub>HPt(μ-H)PtH(PEt<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>]

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**Abstract.** (μ-Hydrido)-dihydridotetrakis(triethylphosphine)diplatinum(II) tetraphenylborate, [Pt<sub>2</sub>H<sub>3</sub>(C<sub>6</sub>H<sub>15</sub>P)<sub>4</sub>][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>], *M<sub>r</sub>* = 1185.1, monoclinic, *C*2/*n*, *a* = 23.284 (10), *b* = 20.923 (7), *c* = 21.822 (8) Å, β = 93.10 (3)°, *V* = 10 615 (6) Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.483 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71073 Å, μ = 54.7 cm<sup>-1</sup>, *F*(000) = 4736, *T* = 293 K, *R* = 0.074 for 4646 observed reflections. The structure of the cationic complex consists of two Pt-containing units, which lie on reciprocally perpendicular planes. In each unit, the Pt atom is coordinated in a square-planar arrangement, with one terminal hydride ligand and another hydride ligand, bound to both Pt atoms, in a bridging position.

**Introduction.** Dinuclear platinum complexes containing one or two bridging H atoms have been widely investigated. Often the hydrido bridges are accompanied by other bridging atoms or groups such as phosphides and carbon monoxide. Among this

type of dinuclear compound, a few trihydridodiplatinum systems have been studied: those containing bridging phosphines [Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (Brown, Puddephatt, Rashidi & Seddon, 1977)], chelating phosphines [(*t*-Bu)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(*t*-Bu)<sub>2</sub> (Tulip, Yamagata, Yoshida, Wilson, Ibers & Otsuka, 1979) and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (Minghetti, Bandini, Banditelli & Bonati, 1977; Chiang, Bau, Minghetti, Bandini, Banditelli & Koetzle, 1984)] and monodentate phosphines [PEt<sub>3</sub>, PPh<sub>3</sub> and PCy<sub>3</sub> (Bracher, Grove, Pregosin & Venanzi, 1979; Bachechi, Bracher, Grove, Kellenberger, Pregosin, Venanzi & Zambonelli, 1983)].

The X-ray structure of the trihydrido cation [(PEt<sub>3</sub>)<sub>2</sub>Pt(μ-H)<sub>2</sub>PtH(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (1*a*) with two hydrido bridges has already been reported (Bachechi *et al.*, 1983). Its structural isomer, [(PEt<sub>3</sub>)<sub>2</sub>HPt(μ-H)-PtH(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (1) with a single hydrido bridge could also be prepared and crystallized as the [BPh<sub>4</sub>]<sup>-</sup> salt (Kellenberger, 1982). It readily rearranges in solution