**A new bidimensional compound containing
(μ -thiocyanate)(bpy) copper(II) molecules :
synthesis, crystal structure and magnetic properties of
[Cu(bpy)(NCS)₂]_n (bpy = 2, 2'-bipyridyl)**

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Abstract

The crystal structure of the first bidimensional copper(II) compound containing only thiocyanate as bridging ligands [Cu(bpy)(NCS)₂]_n, where bpy = 2, 2'-bipyridyl, has been determined by X-ray diffraction on single-crystals. Two different environments for both types of copper(II) ions in the unit cell are apparent: a distorted octahedron and a square pyramid. A bidimensional structure with a deformed honeycomb-layer motif is formed, the bipyridyl ligands filling the interlayer space. The magnetic susceptibility data of the compound have been investigated between 280 and 1.8 K. The compounds presents a very weak antiferromagnetic interaction, that has been fitted by using the Bleaney-Bowers expression for a dimeric unit, whereby a J value of -1.01 (1) cm⁻¹ () and a g value of 2.08 (1) has been obtained.

Keywords: Crystal structure; Magnetic interactions; Copper complexes; thiocyanate ligand;

1. Introduction

In the last few years, building new molecular species and addressing their architectures in order to control their physical properties, has been a topic for many research groups, dealing, for example, with supramolecular chemistry [1] and molecular magnetism [2]. Different ligands have been used to bridge the magnetic centers, like oxamato [3], cyanide [4] or oxalato [5], leading to compounds of various dimensionalities, ranging from isolated nanospecies to nD ($n = 1-3$) frameworks. Thereby, bridging ligands containing sulphur atoms which lead to extended networks, are not used very often. With respect to the thiocyanate ligand, very few crystal structures of extended networks containing copper(II) and the thiocyanate ligand are reported in the literature. The thiocyanate ligand presents a ambidentate ability with an "end-on" or an "end-to-end" coordination mode. Most of the extended networks are related to this latter coordination mode, leading either to one-dimensional compounds (see for example [6-7-8]) or three-dimensional compounds [6][9] ; no compounds with a bidimensional structure have been reported until now. Concerning the magnetic properties of this kind of systems, the thiocyanate ligand may act as an efficient mediator for the magnetic interaction between the paramagnetic copper(II) centers.

Here we report on the synthesis of the first, only thiocyanato-bridged, bidimensional copper(II) compound, with an end-to-end coordination mode. Its crystal structure exhibits a deformed honeycomb-layer motif. In addition, a short description of the magnetic properties is given.

2. Experimental

2.1. Materials

All chemicals were reagent grade and were used as commercially obtained. $[\text{Cu}(\text{bpy})_2]\text{Cl}_2 \cdot 6 \text{H}_2\text{O}$ was prepared following the literature method [10].

2.2. Preparation of $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$

Single-crystals were grown in a test tube with tetramethoxysilane gel [11] containing a 0.05 M solution of $[\text{Cu}(\text{bpy})_2]\text{Cl}_2 \cdot 6 \text{H}_2\text{O}$ and filled with a layer of a 0.05 M aqueous solution of CuCl_2 and a 0.05 M aqueous solution of KSCN. Within several days, air stable, green crystals were formed. An X-ray structural analysis was completed.

The microcrystalline compound was obtained by adding at room temperature 10 ml of an aqueous solution containing 5 mmol of $[\text{Cu}(\text{bpy})_2]\text{Cl}_2 \cdot 6 \text{H}_2\text{O}$ to 30 ml of an aqueous solution containing 10 mmol of KSCN and 5 mmol CuCl_2 , under continuous stirring. The resulting green precipitate was filtered off, washed with water and dried under vacuum. With thermal gravimetry, no water molecules of crystallisation were detected. The elemental analysis leads to the following formula : $[\text{Cu}(\text{bpy})(\text{NCS})_2]$. *Anal.* Calc. for $\text{C}_{12}\text{H}_8\text{N}_4\text{S}_2\text{Cu}$: C, 42.91; H, 2.40; N, 16.68; S, 19.09. Found : C, 42.20; H, 2.60; N, 16.50; S, 18.50. The powder X-ray diffraction pattern is consistent with the single-crystal structure determination.

2.3. Infrared spectrum

The infra-red spectrum was recorded on a Bio-Rad IR.FT spectrophotometer, in the 4000 - 250 cm^{-1} range, using pressed KBr pellets containing 1% in mass of the sample.

The spectrum presents two bands in the region near 2000 cm^{-1} , at 2107 and 2071 cm^{-1} , which correspond to the ν_{as} (NCS) stretching mode. This feature results results from a combination of four effects : (i) the presence of bridging thiocyanate ligands (Cu-NCS-Cu); (ii) the presence of non bridging thiocyanate ligands (Cu-NCS); (iii) the distortion around the Cu(1) octahedral environment caused by the non linearity of the Cu-NCS-Cu groups; (iv) the square pyramidal environment of Cu(2). Therefore, both bands cannot be clearly assigned, which, however, is in accordance with the discussion in the literature [12].

2.4. Physical measurements

Magnetic susceptibility data of the powdered sample were collected with a MPMS Quantum Design SQUID magnetometer in the temperature range of 280 - 1.8 K under magnetic fields of 1000 G and 50 G. The sample holder was a quartz tube. The data were corrected for the experimentally determined diamagnetism of the sample holder and the diamagnetism of the sample was calculated from Pascal's constants.

The thermal decomposition of the powdered sample was followed by a Perkin Elmer TAS7 thermobalance in a stream (30 ml/min) of synthetic air (80% N₂, 20% O₂).

2.5. X-ray crystallographic analysis

A crystal of the title compound with approximate dimensions 0.17x0.23x0.53 mm was selected for lattice parameter determination and collection of intensity data at room temperature, using an Enraf-Nonius CAD-4 diffractometer with graphite monochromated MoK α radiation ($\lambda=0.71073$ Å). Crystallographic details, data collection and refinement parameters are listed in Table 1. Lattice parameters were obtained by a least-squares fit of the θ angles of 25 reflections in the range $7.9^\circ < \theta < 17.8^\circ$. Intensities were collected by an ω -2 θ scan technique with zigzag mode and variable scan speeds between 2.06 and 16.48 $^\circ \text{ min}^{-1}$ and they were corrected for Lorentz-, polarization- and absorption-effects with the MolEN program package [13]. Systematic extinctions led to possible space groups Pbcm or the non centrosymmetric Pca2₁. It was not possible to achieve a correct structure in Pbcm but in Pca2₁, using 7608 unique reflections for the Patterson interpretation routine of SHELXS-97 [14], and subsequent difference Fourier calculations in further refinement cycles completed the structure. The correct choice of the absolute configuration was confirmed by refining Flack's x-parameter (see Table 1) in the program SHELXS-97 [14]. The Program MISSYM [15] in PLATON [16] was used to search for higher symmetry or additional symmetry elements between the structural units. However, no extra symmetry elements could be detected. Refinement was carried out by full-matrix least-squares techniques, with SHELXL-

97 [17] (see Table 1). Due to the relatively weak diffracting crystal, hydrogen atomic positions were calculated at distances of 0.93 Å and were fixed by using a riding model in the refinement. The maximum shift /s.u. was 0.001. Largest difference peak and hole were 0.76 and -0.66 e Å⁻³. The great value of R_w is probably due to the low quality of the crystal, as only 41% of the data are larger than 2σ(I). Selected bond distances and angles are shown in Table 2 and the atomic coordinates for the non-hydrogen atoms are available in the supplementary material.

3. Results and discussion

3.1. Crystal structure

The structure of the title compound consists of neutral [Cu(bpy)(NCS)₂] molecules, bridged by thiocyanate ligands. An ORTEP view of these molecules, together with the atomic labeling scheme is depicted in Figure 1. The compound presents a honeycomb-layer structure, with deformed hexagons and corrugated sheets as shown in Figure 2, where the bipyridine ligands are omitted for clarity. This structural feature can be easily understood when considering the three points of connectivity of each metal center : this has been already discussed in a more formal way [18].

Figures 1 and 2

The copper(II) ions exhibit two different coordination polyhedra. The Cu(1) atoms are in a deformed octahedral arrangement with four nitrogen atoms occupying the equatorial positions, two from the bipyridine ligand and two from the thiocyanate ligands, whereas two sulphur atoms, both from the bridging thiocyanate ligands of Cu(2), are occupying the axial positions completing the octahedral coordination. The Cu(2) atoms are in a square pyramidal arrangement, the equatorial plane being filled with nitrogen atoms, and a sulphur atom from one bridging ligand of Cu(1) occupies the apical position. Thus, the Cu(1) atoms bear one bridging thiocyanate ligand and one non bridging ligand. The octahedral [Cu(1)N₄S₂] and the

five coordinated $[\text{Cu(2)N}_4\text{S}]$ molecular units are presented in Figure 1, and also in Figure 3, where a tetrameric unit is represented.

Figure 3

The Cu(1) and Cu(2) atoms are bound to the nitrogen atoms of the planar bipyridine, with bond lengths in accordance with those found in other copper(II)-bipyridyl compounds [19][20]. The interatomic distances within the bipyridyl ligand of the title compound are also comparable with those of these copper(II)-bipyridyl compounds. The Cu(1)-N and Cu(2)-N distances, N from the thiocyanate ligands, vary from 1.931(8) Å to 1.956(7) Å (see Table 2), in accordance with the ones found in the literature, with N in equatorial positions [21] [22].

The Cu(1)-S(3) and the Cu(1)-S(4) distances are 3.038(3) Å and 3.021(3) Å respectively. These distances are close to the ones found in the similar $[\text{Cu(bpm)(NCS)}_2]$ complex [6] and in others copper(II) octahedral complexes with the sulphur atoms in axial position [22]. On the contrary, the coordination of Cu(2), with a Cu(2)-S(1) distance of 2.728 (3) Å and a Cu(2)-S(2) distance of 4.629(2) Å, is close to square pyramidal.

The thiocyanato groups are almost linear, $178.6(8)^\circ$, $178.4(8)^\circ$, $178.3(8)^\circ$ and $176.8(8)^\circ$ for N(1)-C(1)-S(1), N(2)-C(2)-S(2), N(3)-C(3)-S(3) and N(4)-C(4)-S(4), respectively. The Cu-N-C linkages are bent ($169.0(7)^\circ$, $168.3(8)^\circ$ and $164.8(8)^\circ$ for C(1)-N(1)-Cu(1), C(3)-N(3)-Cu(2) and C(4)-N(4)-Cu(2) respectively), that value is decreasing when the thiocyanate ligand is non bridging : $163.6(8)^\circ$ for C(2)-N(2)-Cu(1). These structural features have been already observed in other thiocyanato-containing metal complexes [19][23]. The S-C average distance of 1.615(13) Å and C-N average distance of 1.161 (9) Å, are in accordance with the values given in the literature [24].

The Cu(1) $\cdots$ Cu(2) distance within the layer is equal to 5.93(4) Å, and the Cu(1) $\cdots$ Cu(1) separation distance between the layers is 12.120(2) Å. This large separation results from the presence of the bipyridine ligands lying alternately on both sides of the layers.

3.2. Magnetic properties

The temperature dependence of the magnetic susceptibility was measured in the temperature

range 280 to 4.2 K. Upon cooling from room temperature, the value of the product of the molar susceptibility and the temperature, $\chi_M T$, decreases slowly until 50 K and sharply below 15 K. This behaviour indicates a weak antiferromagnetic interaction. In a first approximation, the susceptibility data, obtained with two different fields, $H = 1000$ G and $H = 50$ G, were analysed by a Bleaney-Bowers expression for dinuclear units [25], while neglecting uncoupled species and using the Heisenberg exchange Hamiltonian :

$$\text{[Empty Box]} \quad (1)$$

where N_A is the Avogadro constant, g is the g factor, β is the Bohr magneton, k is the Boltzmann constant, and J is the exchange coupling constant. The best fit gave a g value of 2.08 (1) and a J value of -1.01 (1) cm^{-1} (coefficient of determination $r^2 = 0.999562$). We tried to use the Bonner-Fischer equation, valid for 1D systems, and containing an intrachain interaction θ , but this leads to insignificant values for J .

This very weak character of the antiferromagnetic interaction is due to intrinsic structural reasons : the basal planes formed by $[\text{Cu}(1)\text{N}_4]$ or $[\text{Cu}(2)\text{N}_4]$ are perpendicular to the planes containing the bridging NCS ligands and both copper(II) centers, which leads to a very weak overlap between the involved magnetic orbitals. The J value has a similar value than the one found for the one-dimensional compound $[\text{Cu}(\text{bpm})(\text{NCS})_2]$ (-0.6 cm^{-1}) [6b], where the thiocyanate ligand has the analogous coordination mode. In order to have a rather large value with the end-to-end bridging mode of the ligand, both metal centers must be confined to the same equatorial plane : this has been recently shown with the compound $[\text{Cu}(\text{NCS})(\mu\text{-NCS})(\text{Hmtpo})(\text{H}_2\text{O})]_{2n}$ [7], where $J = -74 \text{ cm}^{-1}$.

In summary, the structure determination of the herein reported thiocyanate bridged system reveals a bidimensional structure. A consequence of this distinct feature is that neither of the magnetic orbitals of the copper(II) ions is overlapping with the orbitals of the bridging ligand, which leads to a very low value of the exchange parameter between the magnetic centers. The

magnetic susceptibility data and their analysis confirm this interpretation.

4. Supplementary material

- Thermal dependence of the molar susceptibility χ_M versus the temperature for $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$ in an applied field of 1000 Oe. The solid line shows the best fit using Eq. (1).

- Thermal dependence of the product of the molar susceptibility χ_M and the temperature for $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$ in an applied field of 1000 Oe.

- H-atom coordinates, displacement parameters and a full list of bond lengths and angles can be obtained on request from author H.W.S (or Cambridge Crystal Database).

5. Acknowledgements

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6. References

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7. Figure Captions

- Figure 1** ORTEP drawing of the two $[\text{Cu}(\text{bpy})(\text{NCS})_2]$ molecules. Thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary size.
- Figure 2** A perspective view of a layer of $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$ enhancing the distorted honeycomb-layer type structure. The bipyridyl ligands have been omitted for clarity. Black ions indicate Cu(1) and gray ions indicate Cu(2).
- Figure 3** A tetrameric section of $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$ illustrating the connectivity and the environment of the copper(II) atoms. Black ions indicate Cu(1) and gray ions indicate Cu(2).

Tables

Table 1 : Summary of crystal data, data collection and structure refinement for the complex $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$.

Formula	$\text{C}_{24}\text{H}_{16}\text{N}_8\text{S}_4\text{Cu}_2$
M	335.56
Crystal system	orthorhombic
Space group	$Pca2_1$ (No. 29)
a (Å)	19.717 (4)
b (Å)	9.799 (4)
c (Å)	13.570 (6)
V (Å ³)	2621.8 (1.7)
Z	4
D_c (g cm ⁻³)	1.702
Absorption coefficient (mm ⁻¹)	1.97
Transmission factor ^a range	0.78190- 0.8850
$F(000)$	1352
2θ range (°)	4.14 - 60.06
Index ranges	$0 \leq h \leq 27, 0 \leq k \leq 13, 0 \leq l \leq 19$
Reflections collected	7689 (including 81 standards)
Independent reflections	7608
Reflections used in refinement	7608
Data / restraints / parameters	7608 / 0 / 343
Goodness-of-fit on F^2 0.956 0.956 Flack, s x-parameter 0.06 (3) Final R_1 ^b , wR_2 ^c indices ($I > 2\sigma(I) = 3122$ observed) 0.059, 0.1422 0.059, 0.1422 R_1 , wR_2 indices (all data) 0.2058, 0.1964	
^a Absorption corrections based on seven indexed and measured crystal faces.	
^b R_1 factor definition: $R_1 = \sum(F_O - F_C) / \sum F_O $	
^c wR_2 factor definition : $wR_2 = [\sum w(F_O^2 - F_C^2)^2 / \sum (F_O^2)^2]^{1/2}$	

Table 2 : Selected bond Lengths [Å] and Angles [deg] for the complex [Cu(bpy)(NCS)₂]_n.

Distances

Cu (1)-N(2)	1.931 (8)
Cu(1)-N(1)	1.956 (7)
Cu(1)-N(11)	2.003 (6)
Cu(1)-N(12)	2.010 (7)
Cu(1)-S(3)	3.038 (3)
Cu(1)-S(4)	3.021 (3)
Cu(2)-N(3)	1.943 (7)
Cu(2)-N(4)	1.957 (7)
Cu (2)-N(13)	2.008 (7)
Cu(2)-N(14)	2.003 (7)
Cu (2)-S(1)	2.728 (3)
Cu(2)-S(2)	4.629 (2)
S(1)-C(1)	1.645 (10)
N(1)-C(1)	1.155 (11)
S(2)-C(2)	1.604 (9)
N(2)-C(2)	1.155 (10)
S(3)-C(3)	1.610 (10)
N(3)-C(3)	1.150 (11)
S(4)-C(4)	1.602 (9)
N(4)-C(4)	1.185 (10)

Angles

N(1)-Cu(1)-N(2)	91.8 (3)
N(3)-Cu(2)-N(4)	91.9 (3)
N(3)-Cu(2)-S(1) ⁱ	97.7 (3)
N(4)-Cu(2)-S(1) ⁱ	101.7 (3)
C(1)-S(1)-Cu(2) ⁱⁱ	97.9 (3)
S(1)-Cu(2)-S(2)	142.4 (2)
C(1)-N(1)-Cu(1)	169.0 (7)
N(1)-C(1)-S(1)	178.6 (8)
C(2)-N(2)-Cu(1)	163.6 (8)
N(2)-C(2)-S(2)	178.4 (8)
C(3)-N(3)-Cu(2)	168.3 (8)
N(3)-C(3)-S(3)	178.3 (9)
C(4)-N(4)-Cu(2)	164.8 (8)
N(4)-C(4)-S(4)	176.8 (8)

Symmetry transformations used to generate equivalent atoms:

(i): $-x+3/2, y-1, z+1/2$; (ii): $-x+3/2, y+1, z-1/2$

Figures

Figure 1

Figure 2

Figure 3

Supplementary material

Figure S1 Thermal dependence of the molar susceptibility χ_M versus the temperature for $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$ in an applied field of 1000 Oe (Insert : 50 Oe). The solid line shows the best fit using Eq. (1) .

Figure S2 Thermal dependence of the product of the molar susceptibility χ_M and the temperature for $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$ in an applied field of 1000 Oe. The solid line shows the best fit using Eq. (1) .

Table S1 : Fractional coordinates ($\times 10^4$) and equivalent isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for the complex $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$.

	x / a	y / b	z / c	U_{eq}
Cu(1)	9485(1)	8587(1)	10000(1)	42(1)
Cu(2)	6513(1)	3568(1)	13020(1)	38(1)
S(1)	8378(1)	12875(2)	9961(2)	41(1)
N(1)	9114(4)	10433(7)	9900(6)	50(2)
C(1)	8805(4)	11434(10)	9916(6)	39(2)
S(2)	7463(1)	6309(3)	10613(2)	59(1)
N(2)	8589(4)	7798(8)	10067(7)	54(2)
C(2)	8117(4)	7185(8)	10307(7)	38(2)
S(3)	4530(1)	1175(3)	12231(2)	56(1)
N(3)	5628(4)	2768(8)	12777(6)	52(2)
C(3)	5162(5)	2115(10)	12554(7)	43(2)
S(4)	5402(1)	7817(2)	12851(2)	50(1)
N(4)	6130(4)	5406(7)	13105(7)	53(2)
C(4)	5806(4)	6412(9)	12984(8)	40(2)
N(11)	10449(3)	9227(7)	9938(6)	36(2)
C(21)	10917(4)	8226(8)	10045(6)	38(2)
C(31)	11590(4)	8513(10)	10012(7)	49(2)
C(41)	11823(5)	9840(10)	9869(7)	55(3)
C(51)	11341(5)	10844(10)	9770(7)	52(3)
C(61)	10666(5)	10484(10)	9824(7)	49(3)
N(12)	9952(3)	6786(7)	10204(5)	36(2)
C(22)	10635(4)	6856(9)	10213(7)	39(2)
C(32)	11038(5)	5729(10)	10381(7)	51(3)

C(42)	10714(5)	4477(10)	10584(7)	55(3)
C(52)	10043(5)	4413(10)	10571(7)	51(3)
C(62)	9654(5)	5563(10)	10380(8)	50(3)
N(13)	6993(3)	1831(7)	12658(6)	40(2)
C(23)	7674(4)	1939(9)	12540(7)	39(2)
C(33)	8056(5)	805(11)	12270(7)	49(3)
C(43)	7765(6)	-431(11)	12202(8)	58(3)
C(53)	7080(5)	-558(10)	12341(7)	52(3)
C(63)	6697(5)	595(10)	12584(7)	50(3)
N(14)	7467(4)	4263(6)	12939(6)	39(2)
C(24)	7950(4)	3324(9)	12684(6)	38(2)
C(34)	8629(4)	3670(11)	12631(6)	44(2)
C(44)	8825(5)	4961(12)	12805(7)	59(3)
C(54)	8333(5)	5946(10)	13031(9)	60(3)
C(64)	7660(5)	5553(9)	13107(8)	47(2)

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

Table S2 : Bond Lengths [Å] and Angles [deg] for the complex [Cu(bpy)(NCS)₂]_n.

Distances

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Cu(2)-N(14)	2.003 (7)
Cu (2)-S(1) ⁱ	2.728 (3)
S(1)-C(1)	1.645 (10)
N(1)-C(1)	1.155 (11)
S(2)-C(2)	1.604 (9)
N(2)-C(2)	1.155 (10)
S(3)-C(3)	1.610 (10)
N(3)-C(3)	1.150 (11)
S(4)-C(4)	1.602 (9)
N(4)-C(4)	1.185 (10)
N(11)-C(61)	1.312 (11)
N(11)-C(21)	1.354 (10)
C(21)-C(31)	1.358 (11)
C(21)-C(22)	1.470 (11)
C(31)-C(41)	1.391 (13)
C(31)-H(31)	0.9300
C(41)-C(51)	1.376 (14)
C(41)-H(41)	0.9300
C(51)-C(61)	1.379 (12)
C(51)-H(51)	0.9300
C(61)-H(61)	0.9300
N(12)-C(22)	1.349 (10)
N(12)-C(62)	1.356 (11)
C(22)-C(32)	1.378 (12)

C(32)-C(42)	1.410 (14)
C(32)-H(32)	0.9300
C(42)-C(52)	1.324 (13)
C(42)-H(42)	0.9300
C(52)-C(62)	1.388 (13)
C(52)-H(52)	0.9300
C(62)-H(62)	0.9300
N(13)-C(63)	1.348 (12)
N(13)-C(23)	1.356 (11)
C(23)-C(33)	1.392 (13)
C(23)-C(24)	1.475 (12)
C(33)-C(43)	1.34 (2)
C(33)-H(33)	0.9300
C(43)-C(53)	1.368 (14)
C(43)-H(43)	0.9300
C(53)-C(63)	1.399 (13)
C(53)-H(53)	0.9300
C(63)-H(63)	0.9300
N(14)-C(64)	1.340 (10)
N(14)-C(24)	1.367 (11)
C(24)-C(34)	1.384 (11)
C(34)-C(44)	1.343 (14)
C(34)-H(34)	0.9300
C(44)-C(54)	1.40 (2)
C(44)-H(44)	0.9300
C(54)-C(64)	1.386 (13)
C(54)-H(64)	0.9300
C(64)-H(64)	0.9300

Angles

N(1)-Cu(1)-N(2)	91.8 (3)
N(2)-Cu(1)-N(11)	174.6 (3)
N(1)-Cu(1)-N(11)	93.6 (3)
N(2)-Cu(1)-N(12)	93.5 (3)
N(1)-Cu(1)-N(12)	173.3 (3)
N(12)-Cu(1)-N(11)	81.2 (3)
N(3)-Cu(2)-N(4)	91.9 (3)
N(3)-Cu(2)-N(14)	166.4 (3)
N(4)-Cu(2)-N(14)	93.0 (3)
N(3)-Cu(2)-N(13)	92.3 (3)
N(4)-Cu(2)-N(13)	167.5 (3)
N(13)-Cu(2)-N(14)	80.3 (3)
N(3)-Cu(2)-S(1) ⁱ	97.7 (3)
N(4)-Cu(2)-S(1) ⁱ	101.7 (3)
N(14)-Cu(2)-S(1) ⁱ	93.7 (2)
N(13)-Cu(2)-S(1) ⁱ	89.3 (2)
C(1)-S(1)-Cu(2) ⁱⁱ	97.9 (3)
C(1)-N(1)-Cu(1)	169.0 (7)
N(1)-C(1)-S(1)	178.6 (8)
C(2)-N(2)-Cu(1)	163.6 (8)
N(2)-C(2)-S(2)	178.4 (8)
C(3)-N(3)-Cu(2)	168.3 (8)
N(3)-C(3)-S(3)	178.3 (9)
C(4)-N(4)-Cu(2)	164.8 (8)
N(4)-C(4)-S(4)	176.8 (8)
C(21)-N(11)-C(61)	118.1 (7)
Cu(1)-N(11)-C(61)	127.4 (6)
Cu(1)-N(11)-C(21)	114.5 (5)
N(11)-C(21)-C(31)	120.8 (8)
N(11)-C(21)-C(22)	115.0 (7)
C(31)-C(21)-C(22)	124.3 (8)
C(21)-C(31)-C(41)	121.4 (9)
C(21)-C(31)-H(31)	119.3
C(41)-C(31)-H(31)	119.3

C(31)-C(41)-C(51)	117.0 (9)
C(51)-C(41)-H(41)	121.5
C(31)-C(41)-H(41)	121.5
C(41)-C(51)-C(61)	118.6 (9)
C(41)-C(51)-H(51)	120.7
C(61)-C(51)-H(51)	120.7
N(11)-C(61)-C(51)	124.1 (9)
N(11)-C(61)-H(61)	118.0
C(51)-C(61)-H(61)	118.0
C(22)-N(12)-C(62)	118.5 (7)
Cu(1)-N(12)-C(22)	114.5 (5)
Cu(1)-N(12)-C(62)	127.0 (6)
N(12)-C(22)-C(32)	122.4 (8)
N(12)-C(22)-C(21)	114.9 (7)
C(32)-C(22)-C(21)	122.7 (7)
C(22)-C(32)-C(42)	117.9 (9)
C(22)-C(32)-H(32)	121.0
C(42)-C(32)-H(32)	121.0
C(32)-C(42)-C(52)	119.4 (9)
C(52)-C(42)-H(42)	120.3
C(32)-C(42)-H(42)	120.3
C(42)-C(52)-C(62)	121.1 (10)
C(42)-C(52)-H(52)	119.4
C(62)-C(52)-H(52)	119.4
N(12)-C(62)-C(52)	120.7 (9)
N(12)-C(62)-H(62)	119.7
C(52)-C(62)-H(62)	119.7
C(23)-N(13)-C(63)	119.3 (8)
Cu(2)-N(13)-C(63)	125.1 (6)
Cu(2)-N(13)-C(23)	115.4 (6)
N(13)-C(23)-C(33)	120.3 (9)
N(13)-C(23)-C(24)	114.9 (8)
C(33)-C(23)-C(24)	124.8 (8)
C(43)-C(33)-C(23)	120.4 (10)
C(43)-C(33)-H(33)	119.8
C(23)-C(33)-H(33)	119.8
C(33)-C(43)-C(53)	119.6 (10)

C(33)-C(43)-H(43)	120.2
C(53)-C(43)-H(43)	120.2
C(43)-C(53)-C(63)	119.5 (10)
C(43)-C(53)-H(53)	120.3
C(63)-C(53)-H(53)	120.3
N(13)-C(63)-C(53)	120.6 (9)
N(13)-C(63)-H(63)	119.7
C(53)-C(63)-H(63)	119.7
C(24)-N(14)-C(64)	118.8 (8)
Cu(2)-N(14)-C(64)	125.2 (6)
Cu(2)-N(14)-C(24)	116.0 (5)
N(14)-C(24)-C(34)	121.4 (8)
N(14)-C(24)-C(23)	113.4 (7)
C(34)-C(24)-C(23)	125.1 (8)
C(44)-C(34)-C(24)	120.0 (9)
C(44)-C(34)-H(34)	120.0
C(24)-C(34)-H(34)	120.0
C(34)-C(44)-C(54)	119.2 (9)
C(34)-C(44)-H(44)	120.4
C(54)-C(44)-H(44)	120.4
C(64)-C(54)-C(44)	119.2 (9)
C(64)-C(54)-H(54)	120.4
C(44)-C(54)-H(54)	120.4
N(14)-C(64)-C(54)	121.4 (9)
N(14)-C(64)-H(64)	119.3
C(54)-C(64)-H(64)	119.3

Symmetry transformations used to generate equivalent atoms:

(i): $-x+3/2, y-1, z+1/2$; (ii): $-x+3/2, y+1, z-1/2$

Table S3 : Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the complex $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$.

The anisotropic displacement factor exponent takes the form :

$$-2\pi^2[h^2a^2U_{11}+...+2hkabU_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{14}
Cu(1)	32(1)	31(1)	63(1)	6(1)	1(1)	3(1)
Cu(2)	39(1)	33(1)	43(1)	-2(1)	-1(1)	2(1)
S(1)	42(1)	39(1)	43(1)	2(1)	0(1)	6(1)
N(1)	62(5)	34(4)	52(5)	11(4)	10(4)	19(3)
C(1)	48(4)	48(4)	22(4)	2(4)	-3(4)	-11(4)
S(2)	43(1)	62(1)	71(2)	2(2)	-1(1)	-12(2)
N(2)	52(4)	45(4)	64(5)	-5(4)	3(5)	7(4)
C(2)	29(4)	35(4)	51(5)	-14(4)	-8(4)	7(4)
S(3)	44(1)	67(2)	56(1)	6(1)	-4(1)	-14(1)
N(3)	39(4)	47(4)	69(6)	-1(4)	-3(4)	-2(4)
C(3)	50(5)	39(5)	40(5)	6(4)	4(4)	5(4)
S(4)	48(1)	37(1)	65(2)	1(1)	-3(1)	10(1)
N(4)	60(5)	48(4)	51(5)	-5(4)	0(5)	10(4)
C(4)	28(3)	35(4)	57(5)	-16(5)	2(4)	2(4)
N(11)	34(3)	37(3)	36(3)	1(4)	4(4)	-7(3)
C(21)	40(4)	51(5)	24(4)	-8(4)	-6(4)	4(3)
C(31)	40(4)	70(6)	39(4)	-4(5)	-9(5)	2(5)
C(41)	51(5)	68(6)	46(6)	5(5)	-3(5)	-24(5)
C(51)	60(6)	47(5)	50(6)	-7(4)	6(5)	-26(5)
C(61)	42(5)	49(5)	56(7)	2(5)	0(5)	0(4)
N(12)	35(3)	40(4)	31(4)	-5(3)	0(3)	-1(3)
C(22)	32(4)	43(4)	43(5)	-3(4)	-3(4)	7(3)
C(32)	52(5)	46(5)	55(6)	-4(5)	5(5)	12(5)
C(42)	64(6)	41(5)	59(6)	6(5)	5(5)	25(5)
C(52)	53(6)	35(5)	63(7)	3(5)	-13(5)	-5(5)
C(62)	50(5)	40(5)	61(6)	12(5)	3(5)	-1(5)
N(13)	40(4)	37(4)	43(4)	-4(3)	2(3)	2(3)
C(23)	52(6)	39(4)	28(4)	4(4)	6(4)	-1(4)
C(33)	53(6)	52(6)	42(5)	1(5)	1(5)	14(5)

C(43)	69(7)	41(5)	64(7)	-13(5)	6(6)	20(5)
C(53)	56(6)	43(5)	58(7)	-5(5)	3(5)	1(5)
C(63)	54(6)	39(5)	57(6)	-9(5)	-4(5)	14(5)
N(14)	51(4)	29(3)	37(4)	4(4)	1(4)	0(3)
C(24)	43(4)	49(5)	24(4)	2(4)	04)	-8(4)
C(34)	28(4)	69(6)	36(4)	-5(5)	5(3)	-3(5)
C(44)	45(5)	83(7)	49(7)	-4(6)	-4(4)	-27(5)
C(54)	68(6)	52(5)	60(6)	2(7)	-7(7)	-25(5)
C(64)	55(5)	34(4)	52(6)	2(5)	-4(5)	-12(4)

Table S4 : Hydrogen coordinates ($\times 10^4$) and isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for the complex $[\text{Cu}(\text{bpy})(\text{NCS})_2]_n$.

	x / a	y / b	z / c	U_{iso}
H(31)	11902	7809	10086	59
H(41)	12284	10036	9841	66
H(51)	113467	11747	9669	63
H(61)	10344	11174	9777	59
H(32)	11508	5793	10362	61
H(42)	10969	3703	10726	66
H(52)	9829	3583	10691	61
H(62)	9183	5494	10373	61
H(33)	8516	903	12137	59
H(43)	8027	-1196	12061	70
H(53)	6872	-1404	12275	63
H(63)	6234	509	12695	60
H(34)	8950	3009	12475	53
H(44)	9281	5198	12775	71
H(54)	8457	6852	13130	72
H(64)	7335	6199	13279	56