Crystal Structure, Spectroscopic and Magnetic Properties of the Complex [Cu(paphy)(NCS)(SCN)] (paphy = pyridine-2-carbaldehyde 2′-pyridylhydrazone). An Unusual Di-μ-thiocyanato-*N* Bridged Copper(II) Dimer†

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The crystal and molecular structure of [Cu(paphy)(NCS)(SCN)] (paphy = pyridine-2-carbaldehyde 2′-pyridylhydrazone) has been determined from three-dimensional *X*-ray data. It crystallizes in the monoclinic space group $P2_1/a$ with four formula units in a cell of dimensions a = 15.778(3), b = 9.937(2), c = 9.795(3) Å, and β = 91.31(2)°. Least-squares refinement of 1 163 reflections with $I \geqslant 2.5\sigma(I)$ gave a final R = 0.073 (R' = 0.073). The structure consists of isolated centrosymmetric $[Cu(paphy)(NCS)(SCN)]_2$ dimeric units where the two copper(II) ions are linked in an unusual way through the N end of two *N*-thiocyanate bridging groups. The resulting co-ordination geometry around each copper(II) ion is elongated tetragonal octahedral. The *N* bridging atoms occupy simultaneously an equatorial position in the co-ordination sphere of one of the copper atoms and an axial one in the other. The remaining axial positions are occupied by sulphur atoms of the *S*-bonded thiocyanate groups. Magnetic susceptibility measurements down to 2.8 K and e.s.r. spectra provide evidence of the existence of very weak exchange coupling. These results are discussed on the basis of the structural features. A comparison is made with previously published data on related copper(II) thiocyanate complexes.

With the aim of improving understanding of the chemical and structural factors that govern exchange coupling interactions, we have recently approached the design of synthetic pathways to low-dimensional magnetic systems.[1–3] In this context, we have reported the synthesis and magnetic characterization of dimers,[2,4–7] and linear[8,9] or ladder-like chains[3,9] containing $Cu(L_{III})X$ moieties bridged by the X groups {L_{III} = tridentate rigid quasi-planar ligands such as terpy (2,2′:6′,2″-terpyridine), paphy (pyridine-2-carbaldehyde 2′-pyridylhydrazone), tpt [2,4,6-tris(2′-pyridyl)-1,3,5-triazine], or *N*-2′-pyridylcarbonyl-2-pyridinecarboximidate; X = halide, pseudohalide, or one half of a 2− bridging anion such as oxalate or chloroanilate}. Five-co-ordinated monomeric $[Cu(L_{III})X_2]$ complexes can be considered as precursors of the condensed systems. Indeed, when an X ligand is extruded from the monomer, both the planarity of the tridentate ligands and the capability of the remaining X group to bridge metallic centres favour stacking of the resulting planar $Cu(L_{III})X$ entities.

In this work we report the crystal structure and the spectroscopic and magnetic properties of [Cu(paphy)(NCS)(SCN)]. Its dimeric arrangement, as well as the presence of both 'end-on' μ-NCS bridges and terminal –SCN co-ordinated groups, makes this complex of considerable interest.

Experimental

Preparation of the Complex.—The complex $[Cu(paphy)Cl_2]$ (0.200 g, 0.60 mmol), prepared from $CuCl_2 \cdot 2H_2O$ and pyridine-2-carbaldehyde 2′-pyridylhydrazone (ratio 1:1) in ethanolic solution as described in ref. 10, was dissolved in the minimum amount of water. The resulting solution was treated with a slight excess of KSCN (0.160 g, 1.65 mmol) to give a green precipitate. It was separated by filtration, washed with water and diethyl ether, and stored in a desiccator over P_2O_5 for 48 h. Green prismatic crystals suitable for *X*-ray analysis were obtained by recrystallization from methanol–water (3:1) (Found: C, 41.6; H, 2.5; Cu, 16.7; N, 22.5. $C_{13}H_{10}CuN_6S_2$ requires C, 41.3; H, 2.6; Cu, 16.8; N, 22.2%).

Crystallography.—*Crystal data.* Green prismatic crystals of $C_{13}H_{10}CuN_6S_2$, M = 377.8, monoclinic, space group $P2_1/a$, a = 15.778(3), b = 9.937(2), c = 9.795(3) Å, β = 91.31(2)°, U = 1 535(1) Å^3, D_m(flotation) = 1.59(1) g cm^{-3}, Z = 4, D_c = 1.63 g cm^{-3}, $F(000)$ = 764, μ(Mo-K_α) = 16.6 cm^{-1}, T = 293 K.

Data collection. Preliminary cell dimensions and the space group were obtained from Weissenberg and oscillation photographs. A well formed crystal of dimensions 0.07 × 0.10 × 0.13 mm was selected and mounted on a Phillips PW1100 diffractometer equipped with a graphite monochromator. The cell dimensions were obtained by least-squares refinement (LSUCRE[11]) of 35 well centred reflections ($3 < \theta < 20°$) using Mo-K_α radiation (λ = 0.7107 Å). Examination of three standard reflections, monitored after 2 h, showed no substantial intensity decay. A total of 3 051 reflections were measured ($2 < 2\theta < 50°$; $-18 < h < 18$, $0 < k < 11$, $0 < l < 11$) with the variable-speed ω—2θ technique, of which 1 163 were unique

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† Di-μ-isothiocyanato-bis[(pyridine-2-carbaldehyde 2′-pyridylhydrazone-$NN^{\alpha}N'$)thiocyanatocopper(II)].

Supplementary data available (No. SUP 56724): temperature dependence of magnetic susceptibility. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: G = 10^{-4} T.

with $I \geqslant 2.5\sigma(I)$ and used in the determination of the structure. Lorentz and polarization corrections were applied, but not absorption.

Structure solution and refinement. The position of the copper and sulphur atoms were obtained from a three-dimensional Patterson synthesis. The remaining non-hydrogen atoms were located from subsequent Fourier syntheses. The model obtained was refined with the SHELX 76 system[12] by weighted anisotropic full-matrix least-squares methods. After refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms, Fourier difference synthesis located the positions of all the hydrogen atoms, which were included in the final refinement with common fixed isotropic thermal parameters [$U = 0.05(1)$ Å^2]. The final R values were $R = 0.073$ and $R' = 0.073$ (239 parameters refined); $\Sigma w[|F_o| - |F_c|]^2$ was minimized, where $w = 5.4941/(\sigma^2|F_o| + 0.001\,950|F_o|^2)$ with $\sigma^2|F_o|$ from counting statistics. Maximum and minimum heights in the final Fourier difference synthesis were 0.618 and −0.574 e Å^{-3}, respectively. Atomic scattering factors were taken from ref. 13. The geometrical calculations were performed with BONDLA[14] and molecular illustrations were drawn with PLUTO.[15]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

Physical Measurements.—Infrared spectra in the 4 000—250 cm^{-1} region were obtained on KBr pellets using a Perkin-Elmer 1430 spectrophotometer. Diffuse reflectance electronic spectra were recorded on a Perkin-Elmer LAMBDA 9 UV/VIS/NIR spectrophotometer. E.s.r. spectra (polycrystalline samples) were recorded on a ER200 tt Bruker spectrometer (*X*-band) equipped with a standard low-temperature device, calibrated by an n.m.r. probe for magnetic field and a HP 5342A frequency counter for microwave frequency. Magnetic susceptibility measurements were made in the temperature range 2—30 K using a SQUID S.H.E. magnetometer. Experimental susceptibilities were corrected for the diamagnetic contributions and for the temperature-independent paramagnetism estimated to be 60 × 10^{-6} cm^3 mol^{-1} per copper(II) ion.

Results and Discussion

Molecular Structure.—Final atomic co-ordinates are given in Table 1. Figure 1 shows the molecule and the atomic numbering scheme; a stereoscopic view of the unit cell is given in Figure 2. Selected bond distances and angles are listed in Table 2. The structure consists of isolated centrosymmetric [Cu(paphy)(NCS)(SCN)]$_2$ dimeric units, where the two metallic centres are linked only through the N of the thiocyanate bridging groups.

The co-ordination geometry around copper(II) ion can be described as distorted elongated tetragonal octahedral [*i.e.* a copper(II) '4 + 1 + 1' co-ordination mode]. The equatorial positions are occupied by the three nitrogen atoms from the paphy ligand and the nitrogen atom from the *N*-thiocyanate group. The Cu–N(heterocyclic) distances are similar to those found in related copper(II) complexes,[3,5,7,10] whereas the Cu–N(thiocyanate) distance is slightly shorter than that of 2.020(7) Å reported for [Cu(terpy)(NCS)$_2$].[16] The four equatorial atoms are nearly coplanar within ±0.07 Å and the copper atom is displaced 0.18 Å from the least-squares plane. The sulphur atom of the *S*-thiocyanate ligand occupies an axial site. The observed Cu–S distance is similar to the values reported for related axially *S*-thiocyanate copper(II) complexes.[17,18] The co-ordination sphere is completed by the nitrogen atom of the other μ-*N*-thiocyanate group, which is 3.054(13) Å from the copper(II) ion. In line with previous observations,[19,20] steric hindrances arising from repulsions between the paphy and NCS π-electron clouds might lie behind this rather large Cu–N(axial) distance. The Cu–N(5)–Cu^I bridging angle is 94.4(5)° and the resulting intradimeric Cu–Cu^I distance is 3.730(3) Å.

Table 1. Final atomic co-ordinates in the [Cu(paphy)(NCS)(SCN)] complex

Atom	*X/a*	*Y/b*	*Z/c*
Cu	0.050 8(1)	0.331 7(2)	0.981 7(2)
N(1)	0.096 4(7)	0.341 4(13)	1.174 4(12)
N(2)	−0.016 9(8)	0.188 1(13)	1.066 1(15)
N(3)	−0.029 9(8)	0.279 7(15)	0.823 8(16)
N(4)	0.002 5(9)	0.163 6(15)	1.197 1(17)
C(1)	0.156 4(10)	0.424 4(18)	1.222 6(17)
C(2)	0.182 6(12)	0.419 5(19)	1.353 3(21)
C(3)	0.150 1(12)	0.321 2(23)	1.441 6(19)
C(4)	0.089 0(11)	0.235 0(19)	1.391 1(18)
C(5)	0.064 3(10)	0.246 5(16)	1.256 1(16)
C(6)	−0.074 9(10)	0.131 3(17)	0.993 8(22)
C(7)	−0.080 2(10)	0.179 9(20)	0.856 6(19)
C(8)	−0.135 4(11)	0.118 7(21)	0.758 5(27)
C(9)	−0.130 8(14)	0.175 6(32)	0.626 5(22)
C(10)	−0.077 7(15)	0.275 1(26)	0.593 8(25)
C(11)	−0.028 7(12)	0.327 1(22)	0.695 5(20)
N(5)	0.093 9(8)	0.497 3(13)	0.910 3(15)
C(12)	0.134 8(10)	0.561 5(16)	0.838 9(15)
S(1)	0.189 5(3)	0.653 8(6)	0.740 8(5)
S(2)	0.180 4(3)	0.175 9(6)	0.900 6(6)
C(13)	0.136 5(10)	0.103 6(18)	0.763 6(19)
N(6)	0.100 1(13)	0.047 3(20)	0.675 0(17)

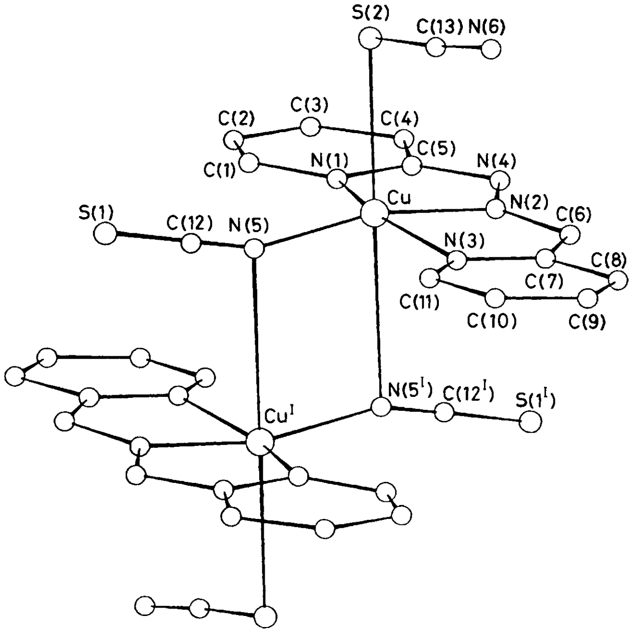

Figure 1. View of the [Cu(paphy)(NCS)(SCN)]$_2$ compound with the numbering scheme

Bond distances and angles in the paphy ligand are similar to those observed in related compounds.[3,10,21,22] The ligand may be considered as quasi-planar because the dihedral angle between the pyridine rings is 2.6°.

Both NCS groups are practically linear and, as expected,[17,18] the C–S bond length is shorter [1.596(17) Å] in the *N*-bonded than in the *S*-bonded [1.660(21) Å] thiocyanate groups, while

Table 2. Selected bond distances (Å) and angles (°) in the $[Cu(paphy)(NCS)(SCN)]_2$ complex

Cu–N(1)	2.007(11)	S(2)–C(13)	1.660(21)	N(2)–N(4)	1.335(19)	N(1)–C(5)	1.344(18)
Cu–N(5)	1.919(13)	S(1)–C(12)	1.596(17)	N(3)–C(7)	1.315(21)	N(2)–C(6)	1.276(20)
Cu–Cu$^{\rm I}$	3.730(3)	Cu–N(2)	1.974(13)	N(6)–C(13)	1.172(21)	N(3)–C(11)	1.343(22)
C(5)–N(4)	1.392(20)	Cu–S(2)	2.699(5)	Cu–N(3)	2.047(14)	N(5)–C(12)	1.155(17)
C(6)–C(7)	1.428(25)	N(1)–C(1)	1.334(19)	Cu–N(5$^{\rm I}$)	3.054(13)		
N(1)–Cu–N(5$^{\rm I}$)	84.4(4)	Cu–N(5)–C(12)	154(1)	N(5)–Cu–N(5$^{\rm I}$)	85.6(5)	S(1)–C(12)–N(5)	178(1)
N(3)–Cu–N(5$^{\rm I}$)	86.8(4)	Cu–S(2)–C(13)	100.5(5)	S(2)–Cu–N(2)	97.4(4)	S(2)–C(13)–N(6)	174(2)
S(2)–Cu–N(1)	92.6(4)	C(1)–N(1)–C(5)	120(1)	S(2)–Cu–N(5)	96.2(4)	C(4)–C(5)–N(4)	122(2)
S(2)–Cu–N(3)	95.5(4)	N(1)–C(5)–N(4)	116(1)	N(2)–Cu–N(5)	166.4(6)	Cu–N(1)–C(5)	113(1)
S(2)–Cu–N(5$^{\rm I}$)	176.7(3)	N(2)–N(4)–C(5)	116(2)	N(1)–Cu–N(2)	80.0(5)	C(6)–N(2)–N(4)	127(1)
N(1)–Cu–N(3)	157.9(6)	C(6)–C(7)–C(8)	121(2)	N(2)–Cu–N(3)	78.5(6)	N(2)–C(6)–C(7)	113(1)
N(1)–Cu–N(5)	100.3(5)	Cu–N(3)–C(7)	112(1)	Cu–N(5)–Cu$^{\rm I}$	94.4(5)	C(7)–N(3)–C(11)	121(2)
N(3)–Cu–N(5)	99.3(6)	N(2)–Cu–N(5$^{\rm I}$)	80.9(4)				

Symmetry operation: I $-x, -y, -z$.

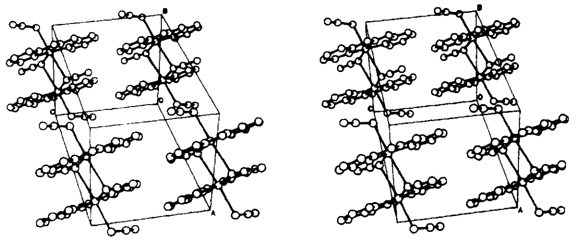

Figure 2. Stereoscopic view of the unit cell for $[Cu(paphy)(NCS)(SCN)]_2$

the C–N distance is similar in both cases [average value, 1.163(12) Å]. The Cu–N(5)–C(12) and the Cu–S(2)–C(13) bond angles [154(1) and 100.5(5)°, respectively] are in good accord with the literature values.[17,18]

The simultaneous presence of *N*- and *S*-bonded thiocyanate groups in the co-ordination polyhedron of the copper(II) ions, and the μ-N 'end-on' co-ordination mode of the thiocyanate bridging groups are two remarkable structural features. We will return to this below.

Infrared and Electronic Spectra.—The interest in the i.r. spectrum of the complex lies mainly in the bands due to the NCS groups. A first feature is the well defined splitting of the bands due to ν(CN) and ν(CS) vibrations to give doublets. The appearance of two strong bands at 2 090 (sharp) and 2 070br cm^{-1} [ν(CN)] and two weak ones at 795 and 675 cm^{-1} [ν(CS)] is clearly consistent with the presence of both *N*- and *S*-thiocynate groups.[17,18] The lack of ν(CN) bands above 2 100 cm^{-1} argues strongly in favour of the absence of normal 'end-to-end' SCN bridges.[18] Otherwise, whereas there is a relatively weak band centred at 470 cm^{-1} assignable to δ(NCS) of the *N*-thiocyanate group, the band due to the bending mode or the *S*-thiocyanate group is not observed because it may be obscured by paphy absorptions in the 420 cm^{-1} region. In the i.r. spectra of the related monomeric $[Cu(terpy)(NCS)_2]$ and $[Cu(tpt)(NCS)_2]$ complexes (where the thiocyanate groups are terminally *N*-bonded) the above absorptions are observed at 2 065, 790, and 480 cm^{-1} and 2 080, 805, and 475 cm^{-1} respectively.[2,16]

The reflectance electronic spectrum exhibits a very broad unresolved band in the visible region. The band intensity maximum in the absorption envelope is around 13 000 cm^{-1}. A charge-transfer band with a maximum above 19 500 cm^{-1} partially overlaps the copper(II) *d–d* transitions. This fact, besides the asymmetry of the CuN_4SN' chromophore, makes unreliable any tentative transition assignments.

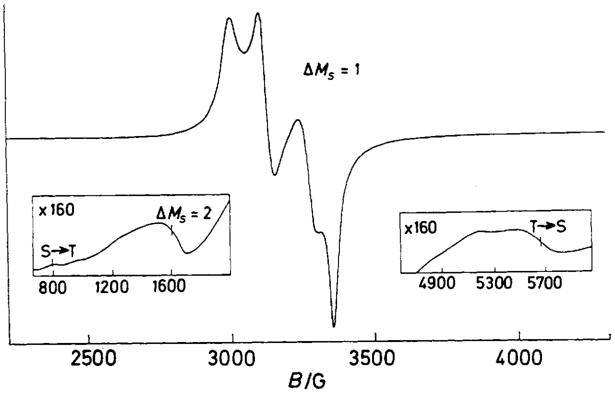

Figure 3. *X*-Band e.s.r. spectrum of a powdered sample of $[Cu(paphy)(NCS)(SCN)]_2$ at 4.2 K

Magnetic Behaviour and Electron Spin Resonance.—The present compound follows a Curie–Weiss behaviour from room temperature down to 2.8 K, corresponding to $C = 0.473$ cm^3 K mol^{-1} and $\theta \simeq 0$ K. The product χT is practically constant (0.473 cm^3 K mol^{-1}) between room temperature and 6 K. However, this product decreases smoothly from 0.470 to 0.456 cm^3 K mol^{-1} when cooling from 6 to 2.8 K. This *ca.* 3% variation is significant when compared with the dispersion of the experimental measurements, indicating a very weak ($|J| < 0.5$ cm^{-1}) antiferromagnetic coupling. Thus, using a normalized plot of χT *vs.* kT/J, drawn from the Bleaney–Bowers equation for isotropic exchange in a $S = \frac{1}{2}$ dimeric system,[23] a J value equal to -0.11 cm^{-1} can be estimated for the above decrease.

Shown in Figure 3 is the *X*-band e.s.r. spectrum at 4.2 K of a polycrystalline powdered sample. The spectrum remains unchanged over the range 4.2—300 K, and exhibits the characteristic features of a triplet state with non-negligible zero field splitting (D). Thus, besides the signal corresponding to the triplet $\Delta M_s = \pm 1$ allowed transitions ($\approx$3 200 G), a weak feature is observed near 1 600 G, corresponding to the $\Delta M_s = 2$ forbidden transition. Likewise, two very weak signals, symmetrically located at lower (810 G) and higher (5 600 G) field values of the normal $\Delta M_s = \pm 1$ transitions, are seen. These can be assigned as forbidden transitions between the singlet electronic state of a very weakly exchange-coupled copper(II) dimer and the $M_s = +1$ components of the triplet state.[5,24] When it is taken into account that each of these transitions are separated from the allowed transitions by a field value of $2|J|(g\beta)^{-1}$, $|J| = 0.12$ cm^{-1} can be calculated assuming a mean g

value equal to 2.12. This $|J|$ value is in very good agreement with that estimated from the magnetic susceptibility measurements.

Otherwise, the complexity of the main signal can be understood on the basis of the resemblance among the $|J|$, D, and Δg values. According to a simple dipolar model,[25] and using the crystallographic intradimeric Cu–Cu$^{\text{I}}$ distance [3.730(3) Å], $D = 0.055\ \text{cm}^{-1}$ results. This D value is of the same order of magnitude as $|J|$. Nevertheless, the splitting between the low-field maximum and the high-field minimum of the signal leads to an effective D value of *ca.* 0.02 cm^{-1}, significantly lower than that estimated from the point-dipole model. Hence, an accurate analysis is difficult without spectral simulation.

A final notable result is based on Eaton's perturbation calculation of the e.s.r. spectra of spin-labelled copper(II) complexes.[26,27] In accordance with Eaton *et al.*, for two $S = \frac{1}{2}$ centres with g values near 2, the integrated intensity of the half-field signal is determined only by the interspin distance (r). This interspin distance (in Å) can be calculated from the expression: relative intensity = intensity of $\Delta M_s = 2$/total intensity of $\Delta M_s = \pm 1 = Ar^{-6}(9.1/\nu)^2$, where ν is the spectrometer operating frequency in GHz and $A = 21 \pm 2$ is a calculated parameter. From the spectrum in Figure 3, we obtain $r = 3.8$ Å. This value is in good accord with the crystallographically determined value of 3.730(3) Å.

Conclusions

As far as we know, only one copper compound, $[\text{Cu(en)}_2(\text{NCS})]\text{ClO}_4$ (en = ethylenediamine), containing 'end-on' μ-NCS groups has been characterized by *X*-ray diffraction prior to this work.[28] Notwithstanding, in that case, the nitrogen atoms are equidistant to two copper(II) atoms (Cu–N 2.73 Å) belonging to square-planar $[\text{Cu(en)}_2]^{2+}$ moieties, and a polymeric array (having Cu–N–Cu angles near 180°) results. Moreover, the thiocyanate groups remain practically ionic.[28] Thus, the presence of asymmetric μ-NCS bridging groups can be considered as a remarkable structural feature of the compound reported here. Antisymbiotic arguments might be invoked to explain the inversion of the co-ordination of the SCN group,[29,30] although, from another view, this compound also might be thought of as an example of bond inversion due to structural factors. Axial Cu–SCN bonds (implying Cu–S–C angles near 90°) should allow a packing in the crystal closer than that resulting from axial Cu–NCS bonds (with Cu–N–C angles near 180°). Probably, a synergic combination of both kind of factors (*i.e.* electronic plus steric) determines the actual structure. In any case, if it is considered that the formally analogous $[\text{Cu(terpy)(NCS)}_2]$ complex is monomeric and only contains *N*-bonded terminal equivalent thiocyanate groups,[16] the delicate balance among the factors determining the final array becomes evident. At present the knowledge of these effects is only partial, and it should not be surprising that, as in the case of dithiocyanato(tri-2-pyridylamine)copper complexes,[31] new isomers of the reported complex may be isolated.

Finally, the weakness of the antiferromagnetic coupling interaction found in the complex can be understood on the basis of the poor effective overlap between the magnetic orbitals involved in the dimeric entity, as observed for related compounds.[4–7]

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