First Structurally Characterized Linkage Isomers of Two Thiocyanatocopper(II) Complexes†

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Two linkage isomers of $[Cu(aat)_2(NCS)_2]$ (aat = 3-acetylamino-1,2,4-triazole), one with *S*- and one with *N*-bonded thiocyanate, have been prepared and characterized by spectroscopy and X-ray crystallography. These compounds are the first structurally characterized linkage isomers of a copper(II) thiocyanate complex. In both cases the copper atoms exhibit an elongated octahedral geometry with two axial thiocyanates and, in equatorial positions, two chelating aat ligands. The *N*-bonded isomer presents one of the smallest Cu–N–C angles [118.1(2)°] ever reported for thiocyanates and a quite long Cu–N(NCS) distance [2.521(3) Å]. In the *S*-bonded isomer the Cu–S(NCS) distance is 2.864(2) Å. As both compounds can be obtained from the same batch, packing differences must account for the isolation of the two different isomers. The different intermolecular hydrogen bonding between the ligands and anions exhibited by both crystal lattices is compared. *'Ab-initio'* molecular orbital calculations have also been performed to study the theoretical stabilities of the isomers.

Thiocyanate is a well known linear ambidentate ligand in co-ordination chemistry, capable of binding through the N or the S atoms, and of bridging metals by using the N,S bridging mode. As many as 10 bonding modes have been described.[1] The mode of binding depends on the nature of the metal centre (soft or hard Pearson acid character). This preference may be modified by the presence of other ligands, by the conditions of synthesis or by whether the complex is in the solid state or in solution.[2–11]

Copper(II) occupies a borderline position in Pearson's classification. In the equatorial plane, thiocyanate has always been found bonded *via* N; in the axial positions, co-ordination with both N and S has been observed.[4] Although in most of the Cu^{II}–NCS^- complexes described a preference for the *N*-bonding mode is exhibited, with equatorial ligands such as NH_3, ethane-1,2-diamine (en), propane-1,3-diamine (tn) and 1,3-diaminopropan-2-ol *S*-bonded complexes have also been reported.[4] In a few cases, even with the same equatorial ligands, different Cu^{II}–NCS^- isomers were obtained. An illustrative example is the group of compounds $[Cu(en)_2(NCS\text{-}S)_2]$,[8] $[Cu(en)_2(NCS\text{-}N)]ClO_4$,[9] $[Cu(en)_2(NCS\text{-}N)]Br$[10] and $[Cu(en)_2(NCS\text{-}N)]BF_4$,[11] which show changes from *N*- to *S*-bonding when the counter ion is switched from thiocyanate to another anion. In these cases, nevertheless, the complexes reported exhibit a different stoichiometry or crystallize with a different counter ion, as in the above example.

To the best of our knowledge, only three cases of genuine linkage isomers of thiocyanatocopper(II) complexes have been described: (*i*) $[Cu(tripyam)(NCS\text{-}S)_2]$, $[Cu(tripyam)(NCS\text{-}N)_2]$ and $[Cu(tripyam)(NCS\text{-}S)(NCS\text{-}N)]$ (tripyam = tri-2-pyridylamine);[12] (*ii*) $[Cu(dppa)(NCS\text{-}S)_2]$, $[Cu(dppa)(NCS\text{-}N)_2]$ and $[Cu(dppa)(NCS\text{-}S)(NCS\text{-}N)]$ (dppa = phenyldi-2-pyridylamine);[12] and (*iii*) $[Cu(dimeen)_2(NCS\text{-}N)_2]$ and $[Cu(dmen)_2(NCS\text{-}S)_2]\cdot 2H_2O$ where dmen = *N,N'*-dimethylethane-1,2-diamine.[13,14] Crystal structures could not prove the existence of these isomers in any of these cases [the structure of the *N*-bonded isomer of the example (*iii*) is known[13]] and the isomerism has been inferred only from spectroscopic data. For (*i*) and (*ii*) it is suggested[12] that there are three possible linkage isomers, but also that two or all three of the compounds could differ only in molecular complexity (thus, differences in the IR spectra could be due to a different hydrogen bonding/packing system).

We here report the first structurally characterized linkage isomers of a Cu^{II}–NCS^- complex with identical stoichiometry. In one isomer the anion is *S*- and in the other *N*-bonded. The latter is unusual in having one of the smallest Cu–N–C angles ever found for thiocyanates.[15] Inter- and intra-molecular hydrogen bonding between the ligands and the anions seems to be responsible for the unusual bond angle and the isomerism.

The equatorial ligand, 3-acetylamino-1,2,4-triazole (aat), belongs to a group of compounds extensively studied because of their versatility as ligands and because of their ability to bridge metals through the N,N-diazinic ring atoms.[16–18] The compounds described were isolated as a part of a study of the synthesis of polynuclear ligand-bridged compounds.

Experimental

Materials.—The ligand aat was synthesised as indicated by van den Bos[19] and recrystallized from boiling water. The metal salts were reagent grade and used without further purification. Freshly prepared $Cu(NCS)_2$ was obtained from $CuSO_4$ and KNCS.

Synthesis of $[Cu(aat)_2(NCS\text{-}N)_2]$ **1**.—Copper(II) chloride (2 mmol) and NH_4NCS (4 mmol) were mixed in water (25 cm^3). To the resulting grey suspension, was added aat (4 mmol). A green product started to form immediately. Stirring was continued for about 1 h. Then, the green precipitate was filtered

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

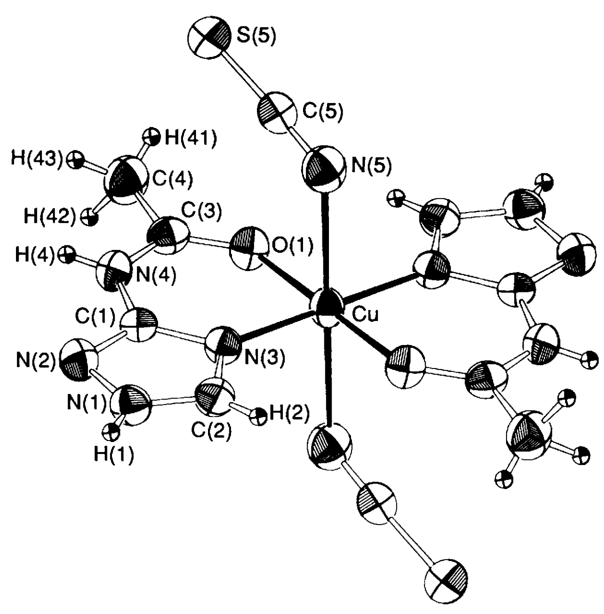

Fig. 1 An ORTEP representation of complex **1** showing the atom labelling scheme and the 90% probability ellipsoids (hydrogen atoms have been given an arbitrary overall isotropic thermal value for illustrative purposes)

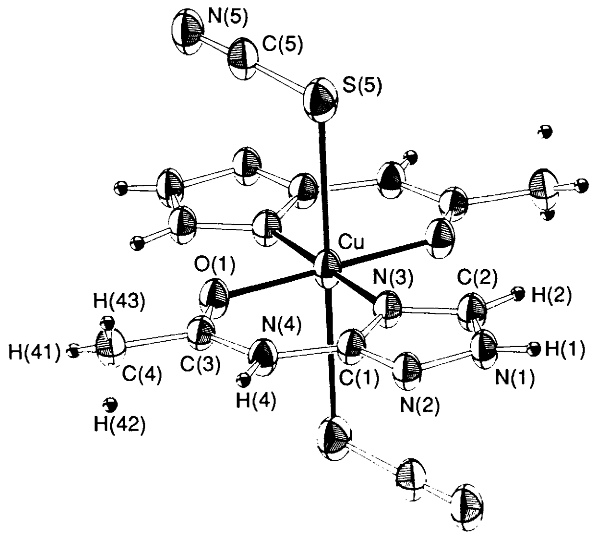

Fig. 2 An ORTEP representation of complex **2**. Details as in Fig. 1

off. The remaining grass-green solution was allowed to stand at 4 °C. Grass-green single crystals were observed after 1 d.

Synthesis of [Cu(aat)$_2$(NCS-*S*)$_2$] **2**.—A suspension of freshly prepared Cu(NCS)$_2$ (1.33 mmol) in water–methanol (1:1, 20 cm^3) and a suspension of aat (2.67 mmol) in water–ethanol (1:1, 20 cm^3) were mixed and stirred for 2–3 h. The green precipitate formed was filtered off and the remaining green solution kept at 4 °C in a Petri dish. After *ca.* 6 d a dark green product was formed. This precipitate was filtered off. Within *ca.* 12 d, from the resulting yellowish green solution, brownish green crystals appeared. Most of the time a few grass-green crystals, corresponding to compound **1**, could be observed together with the brownish green ones. The synthesis of **1** is reproducible, but that of **2** doesn't always give a high yield of the desired compound; in general, the more dilute the starting solution/suspension, the greater is the chance of getting compound **2**, instead of **1**; since at room temperature the crystals are redissolved, it is important to keep the solutions at low temperature (4 °C). (Found for **1**: C, 27.8; H, 2.8; Cu, 14.8; N, 32.7; S, 14.8. Found for **2**: C, 27.5; H, 2.8; N, 32.7; Cu, 15.0; S, 12.2. Calc. for $C_{10}H_{12}CuN_{10}O_2S_2$: C, 27.8; H, 2.8; Cu, 14.7; N, 32.4%).

Physical Measurements.—Infrared spectra were obtained with a Perkin Elmer model 580B spectrophotometer in the region 4000–180 cm^{-1} as KBr pellets, ligand-field spectra in the region 28 000–4000 cm^{-1} on a Perkin Elmer 330 UV–VIS spectrophotometer by the use of the diffuse-reflectance technique with MgO as a reference and EPR spectra on polycrystalline samples at X-band frequencies on a JEOL JES-RE2X spectrometer.

Crystallography.—*Crystal data*. The conditions for crystallographic data collection and structure refinement are summarized in Table 1 for both compounds.

Data collection. Prismatic-shaped crystals, grass-green (compound **1**) and brownish green (compound **2**), were selected and sealed in a glass capillary. The density was determined by flotation in a mixture of hexane and 1,2-dibromoethane. Cell dimensions were obtained by a least-squares fit from the setting angles of 13 (**1**) and 30 (**2**) well centred reflections in the ranges $10 \leqslant \theta \leqslant 12$ (**1**) and $20 \leqslant \theta \leqslant 35°$ (**2**). Lorentz and polarization corrections were applied; an absorption correction was not applied for **1**, whereas for **2** the absorption effects were corrected by ABSORB.[20] The absorption coefficient T as a function of the two polar angles φ and μ of the incident and diffracted beam paths was in the range $0.72 \leqslant T \leqslant 1.26$. Atomic scattering factors and corrections for anomalous dispersion for the Cu atom were taken from ref. 21.

Solution and refinement. The crystal structures were solved by Patterson and Fourier methods (Table 1). Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were found in Fourier difference maps and their parameters included in the last cycles of refinement. For complex **1** the final difference map showed no residual density other than a peak of 0.80 e Å^{-3} located near the S- and C-atoms of NCS. For **2** the highest residual peak in the final Fourier difference map was at 0.74 e Å^{-3}. The refinements converged to the R values in Table 1. Illustrations were prepared with the aid of a modified version of the computer program ORTEP.[23] Geometrical calculations were performed with the program PLATON.[24]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthetic Aspects.—Single crystals of both linkage isomers have been isolated from the same mother-liquor, although a modification in the conditions of the synthesis allows one to obtain only the *N*-bonded isomer. The *S*-bonded isomer could not be obtained separately but it has been observed that, although crystals of the *N*-bonded isomer appear first, with time the yield of the *S*-bonded isomer increases. Indeed, after *ca.* 15 d, in the yellowish green solution the approximate ratio between the green and brownish green crystals is 1:25. This situation is different from that described by Kulasingam and McWhinnie[12] for the isomers of tripyam and dppa (see Introduction). In that case the three different linkage isomers were obtained independently by changing the conditions of synthesis (heating or cooling).

Description of the Structures.—The ORTEP diagrams of complexes **1** and **2** are shown in Figs. 1 and 2. Fractional coordinates and selected bond distances and angles are presented in Tables 2 and 3.

Both structures consist of discrete mononuclear copper(II) units linked by hydrogen bonds. The copper atoms exhibit a tetragonally elongated octahedral arrangement with two axial

Table 1 Physical properties and data relating to measurement and refinement of the structures of [Cu(aat)$_2$(NCS-*N*)$_2$] **1** and [Cu(aat)$_2$(NCS-*S*)$_2$] **2**[a]

Complex	**1**	**2**
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca* (no. 61)	$P\bar{1}$ (no. 2)
Z	4	1
a/Å	9.669(6)	9.057(3)
b/Å	12.192(3)	6.442(2)
c/Å	14.266(3)	7.602(3)
α/°	90	75.79(2)
β/°	90	73.16(2)
γ/°	90	77.82(2)
U/Å^3	1682(1)	406.8(3)
D_m, D_c/Mg m^{-3}	1.70, 1.71	1.75, 1.76
μ/cm^{-1}	15.7	45.20
F(000)	876	219
Crystal size/mm	0.60 × 0.50 × 0.15	0.60 × 0.30 × 0.20
Diffractometer	CAD-4 Enraf Nonius	A.E.D. Siemens
Radiation/filter	λ(Mo-Kα) = 0.710 73 Å/graphite	λ(Cu-Kα) = 1.541 78 Å/Ni
θ range/°	2–30	3–70
hkl ranges	0–13, 0–17, 0–20	−10 to 10, −7 to 7, 0–9
Decay (%)	3.47	4.00
No. of reflections measured	2799	1543
R_{int}	0.014	0.0
Transmission factor range	0.84–1.21	0.72–1.26
Programs[22] used	SHELXS 86	SHELX 86
for refinement	SHELX 76	SHELX 76
No. reflections used,[b] N_o	1556	1231
No. variables, N_v	139	139
Agreement factors[c]		
R	0.0357	0.0554
R′	0.0483	0.0743
S	1.6066	1.1750
$\Delta\rho_{max}$/e Å^{-3}	0.80	0.74

[a] Details in common: $C_{10}H_{12}CuN_{10}O_2S_2$, $M = 431.9$; $T = 293$ K; ω–2θ scans. [b] For **1**, $I > 2.5\sigma(I)$; for **2**, $I > 2.0\sigma(I)$. [c] Weighting schemes: for **1**, $1/[\sigma^2(F) + 0.0100F^2]$; for **2**, $1.0292/[\sigma^2(F) + 0.002\,529F^2]$.

Table 2 Atomic fractional coordinates with estimated standard deviations (e.s.d.s) in parentheses

	[Cu(aat)$_2$(NCS-*N*)$_2$] **1**			[Cu(aat)$_2$(NCS-*S*)$_2$] **2**		
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	0	1/2	0	0	0	0
S(5)	0.108 64(10)	0.447 08(10)	0.306 36(0)	0.155 2(2)	0.120 2(2)	0.230 6(2)
O(1)	−0.122 1(2)	0.402 73(10)	−0.074 69(10)	−0.054 6(4)	−0.263 9(5)	0.198 6(5)
N(1)	−0.295 8(2)	0.722 7(2)	0.069 09(10)	−0.393 9(4)	0.410 2(6)	0.183 0(6)
N(2)	−0.376 0(2)	0.657 2(2)	0.013 3(2)	−0.430 2(4)	0.227 1(6)	0.313 3(6)
N(3)	−0.156 8(2)	0.596 2(2)	0.022 07(10)	−0.193 7(4)	0.162 7(6)	0.115 8(5)
N(4)	−0.323 7(2)	0.499 0(2)	−0.073 9(2)	−0.295 5(4)	−0.128 7(6)	0.364 2(6)
N(5)	−0.046 8(3)	0.392 5(2)	0.147 6(2)	0.420 1(5)	−0.198 3(7)	0.194 8(7)
C(1)	−0.285 5(3)	0.582 7(2)	−0.013 21(10)	−0.306 6(5)	0.083 4(7)	0.265 3(6)
C(2)	−0.168 5(3)	0.686 2(2)	0.074 5(2)	−0.254 9(5)	0.371 4(7)	0.069 6(7)
C(3)	−0.242 9(3)	0.415 8(2)	−0.101 7(2)	−0.173 7(5)	−0.287 2(7)	0.329 1(6)
C(4)	−0.307 7(4)	0.334 6(3)	−0.166 5(3)	−0.188 1(6)	−0.499 1(7)	0.463 9(7)
C(5)	0.016 1(3)	0.414 7(2)	0.214 6(2)	0.312 0(6)	−0.064 1(7)	0.208 7(7)

thiocyanate molecules, and, in equatorial positions, two oxygen and two nitrogen (N^4) atoms from two *trans*-oriented chelating aat ligands. The difference between the compounds lies in the co-ordinating atom of the thiocyanate: N in the case of **1**, and S in the case of **2**. So these structures correspond to two genuine linkage NCS$^-$ isomers.

Comparison of distances and angles in the co-ordination polyhedra of complexes **1** and **2** with those usually found in NCS$^-$ compounds and with those observed in the previously reported [Cu(aat)$_2$(H$_2$O)$_2$]SO$_4$·5H$_2$O[25] shows that: (*a*) in both compounds the equatorial plane is comparable to that reported in ref. 25, and (*b*) in **1** the Cu–N(NCS) distance [2.521(3) Å] is rather long; in **2** the Cu–S(NCS) distance [2.864(2) Å] can be considered as normal, although much shorter than those reported for comparable CuN$_4$(NCS-*S*)$_2$ systems.[2] Nonetheless, a difference of *ca.* 0.3 Å makes the axial distances also closely comparable if the different sizes of the semi-co-ordinate ligand atoms are considered. As in [Cu(aat)$_2$(H$_2$O)$_2$]SO$_4$·5H$_2$O, the aat is in the non-deprotonated form.

In the present two complexes the four equatorial atoms and the Cu^{II} are forced by symmetry reasons to be coplanar. As, on the other hand, the ligands are nearly planar [the maximum deviations from the plane defined by the non-hydrogen atoms of the aat are only 0.062(5) Å for O(1) in **1** and 0.55(5) Å for C(4) in **2**], the main equatorial portion of the complexes can be considered planar, even more than in the case of [Cu(aat)$_2$(H$_2$O)$_2$]SO$_4$·5H$_2$O [maximum deviation 0.112(3) Å]. One difference between structures **1** and **2** concerns the equatorial–axial angles: in **2** these can be considered as very regular, whereas in **1** they differ from the theoretical values of *ca.* 2° (see Table 3). Figs. 3 and 4 show the different orientations of the axial thiocyanates with respect to the aat molecules in each lattice, the torsion angles C(5)–N(5)–Cu–O(1) and C(5)–S(5)–Cu–O(1) being 6.7(3) and 73.0(2)° in **1** and **2**, respectively.

As mentioned above, in complex **1** the Cu–NCS group is non-linear; the observed Cu–N–C angle is as low as 118.1(2)°. In **2** the angle Cu–S–C is 99.5(2)°, as usual for the *S*-bonding mode. The N–C–S group is effectively linear in both cases with angles of 178.1(3) and 178.2(5)°, respectively. The N–C and C–S separations are also normal.

The most interesting feature of structure **1** is the small Cu–N(NCS) angle. Drew *et al.*[15] after searching in the Cambridge Data Centre files, concluded that in reported copper(II) thiocyanate structures the mean Cu–N–C angle is 161° and the mean Cu–N distance 2.055 Å. Then (1987) only five structures were known with angles lower than 150°. We have extended the search and only three more have been found, two being equivalent to another one previously described. Data for these structures are given in Table 4.

In the case of **3**, a dicopper(II) complex of a N_8 macrocycle, the authors provided evidence for proton transfer from the co-ordinated secondary amine to the thiocyanate, with the concomitant formation of an isothiocyanic acid complex. This proton transfer would explain the unusual geometry. We have considered this possibility in our structure but the ν(NCS) infrared band does not correspond to that of HCNS (see later); on the other hand, although the N atom of the thiocyanate forms a strong hydrogen bond [N(1)–H(N1)···N(NCS) 2.803(4) Å], the H atom involved, clearly visible in the Fourier map (as stated in the Experimental section), appears to belong to N(1) (compare the distances H···B and A···B in Table 5). So, in our case no apparent proton transfer has resulted.

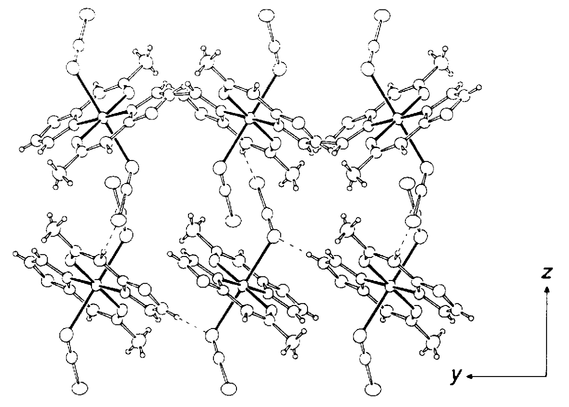

Fig. 3 An ORTEP drawing of several formula units of complex **1** showing the intermolecular hydrogen-bond interactions represented by dashed lines

Compound **7** is the most similar to ours. This structure was mentioned by Gažo *et al.*,[4] when considering the equatorial–axial influence between ligands, as the exception to the rule that ligands such as en and tn favour the *S*-bonding mode (and π acceptors such as pyridine the *N*-bonding mode). The *S*-bonded isomer has also been reported[14] but not its crystal structure.

The fact that both compounds, **1** and **2**, can be obtained from the same batch, together with the fact that in the *N*-bonded isomer the Cu–N–C angle is unusually small, indicates that packing differences could account for the isolation of two different isomers. Scheidt *et al.*,[28] in an article on isothio-

Table 3 Selected bond distances (Å) and angles (°) for [Cu(aat)$_2$(NCS-*N*)$_2$] **1** and [Cu(aat)$_2$(NCS-*S*)$_2$] **2**, with e.s.d.s in parentheses

	1	2
Cu–N(5)	2.521(3)	
Cu–S(5)		2.864(2)
Cu–O(1)	1.984(2)	2.019(3)
Cu–N(3)	1.943(2)	1.932(3)
S(5)–C(5)	1.634(3)	1.643(5)
N(5)–C(5)	1.165(4)	1.160(6)
O(1)–C(3)	1.240(4)	1.243(5)
O(1)–Cu–N(3)	89.06(8)	89.1(1)
O(1)–Cu–N(5)	91.78(7)	
O(1)–Cu–S(5)		90.3(1)
N(3)–Cu–N(5)	92.20(8)	
N(3)–Cu–S(5)		90.0(1)
Cu–N(5)–C(5)	118.1(2)	
Cu–S(5)–C(5)		99.5(2)
N(5)–C(5)–S(5)	178.1(3)	178.2(5)
Cu–O(1)–C(3)	130.6(2)	129.8(3)
N(1)–N(2)–C(1)	101.1(2)	102.3(4)
N(2)–N(1)–C(2)	111.6(2)	110.6(4)
Cu–N(3)–C(1)	125.8(2)	126.4(3)
Cu–N(3)–C(2)	130.9(2)	130.6(3)
O(1)–C(3)–N(4)	123.7(2)	124.2(2)
O(1)–C(3)–C(4)	120.2(2)	120.6(4)
N(4)–C(3)–C(4)	116.1(3)	115.1(4)

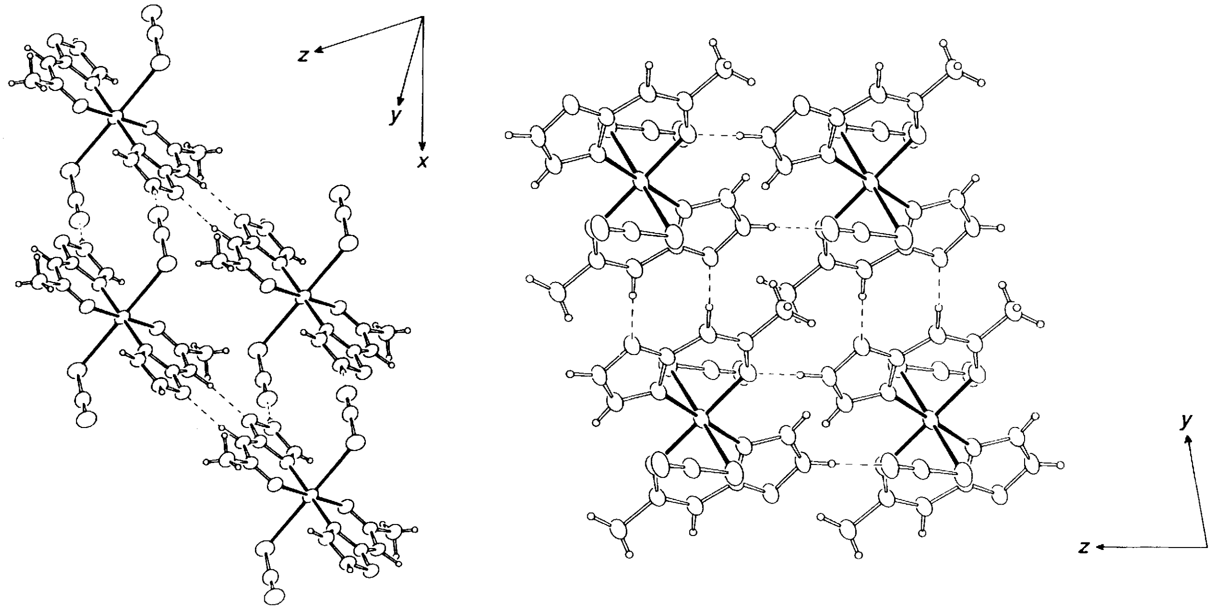

Fig. 4 An ORTEP drawing of several formula units of complex **2** showing the intermolecular hydrogen-bond interactions (two projections)

Table 4 Structures containing the Cu–N(thiocyanate) group with the smallest Cu–N–C angles (Table adapted from ref. 15)

Structure	Cu–N–C/°	Cu–N/Å	Ref.
1 $[Cu(aat)_2(NCS)_2]$	118.1	2.521	This work
3 $[Cu_2L(HNCS)_2][BPh_4]_2 \cdot 1.5MeCN$	100, 109	2.31, 2.33	15
4 $[Cu(en)_2(NCS)]X$			
$X = ClO_4$	97.2	2.73	9
Br	102.5	2.674	10
BF_4	96.0	2.72	11
5 $[Cu](\mu\text{-dapo})_2(Hdapo)_{23}[NCS]_4$	120.6	2.696	26
6 $[CuL'(NCS)]PF_6$	122.6	2.383	27
7 $[Cu(dmen)_2(NCS)_2]$	128.6	2.517	13
8 $[\{CuL''_2(NCS)\}_2(\mu\text{-NCS})_2]$	142.8	2.205	16

H_2L = 28-Membered N_8 macrocycle; Hdapo = 1,3-diaminopropan-2-ol; L′ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; L″ = 2*H*-5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine.

Table 5 Hydrogen bonds in complexes **1** and **2**

A–H ··· B[a]	H ··· B/Å	A ··· B/Å	A–H ··· B/°
(*a*) Complex **1**			
N(1)–H(N1) ··· N(5^{I})	2.05(3)	2.803(4)	165(3)
N(4)–H(N4) ··· S(5^{II})	2.54(3)	3.308(3)	175(3)
(*b*) Complex **2**			
N(1)–H(N1) ··· N(5^{I})	1.87(6)	2.727(5)	171(7)
N(4)–H(N4) ··· N(2^{II})	2.02(5)	2.993(5)	173(6)

[a] The second atom (B) is related to the atom listed in Table 2 by the following symmetry operations: I $-\frac{1}{2} - x, \frac{1}{2} + y, z$; II $-\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$. [b] The second atom (B) is related to the atom listed in Table 2 by the following symmetry operations: I $-1 + x, 1 + y, z$; II $-1 - x, -y, 1 - z$.

Table 6 Total energies* and energies of the highest occupied and lowest unoccupied orbitals

Compound	E	ε_{HOMO}	ε_{LUMO}
1	−3471.5960	−0.033 98	0.067 81
2	−3472.3039	−0.104 02	0.087 41

* Energies in atomic units ($E_h \approx 4.359\ 75 \times 10^{-18}$ J)

cyanato(porphyrinato)(pyridine)iron(II) complexes, described a similar situation. After doing some theoretical molecular calculations, they concluded that significantly shorter intermolecular contacts between NCS^- atoms and other atoms would result if Fe–NCS were linear. To study this aspect in more detail the 'surroundings' of the NCS anions in both structures have been checked. No short intra- or inter-molecular contacts have been observed (the minimum distance between any of the NCS^- atoms and the rest of the non-H atoms of the molecule is 3.2 Å). Whether or not linear bending of the NCS in **1** would have produced a greater steric crowding is not clear. In any case, the bending of the thiocyanate seems to favour the formation of strong hydrogen bonds in both structures (see Table 5). The observed crystal packing, however, is different in the two compounds (Figs. 3 and 4). In **1** the NCS^- 'determines' that packing with its two donor atoms taking part in the hydrogen-bond network. The N atom of the thiocyanate co-ordinates to the Cu^{II} and, at the same time, forms a hydrogen bond with N(1) (with a A–H ··· B angle of 165°). In **2** only the non-co-ordinating thiocyanate atom, N, is involved in the hydrogen bond network, as expected. In this case, a 'pairing' of the aat ligands, *via* the pairs of hydrogen bonds N(4)–H ··· N(2′)/N(4′)–H ··· N(2) and N(1^a)–H ··· N($NCS^{a''}$)/N($1^{b''}$)–H ··· N(NCS^b) (where a and b are the two parts of the formula unit), is produced. As a result the crystal lattice is built up by strict layers of ligands.

'Ab-initio' *Calculations*.—To obtain a deeper insight into the structure of the two isomers we have investigated the electronic structure of the two isolated molecules by carrying out '*ab-initio*' unrestricted Hartree–Fock self-consistent field molecular orbital (UHF-SCF-MO) calculations at the experimental geometry, the distances and angles between the atoms being those found in these structure determinations. A STO-3G basis set was employed, which is standard in quantum chemistry; this minimal basis set allows calculations which consume relatively little time, yet give sufficient agreement with experiment to be used predictively at ordinary chemical accuracy.

The total energy and the energy of the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals of the two isomers are summarized in Table 6; in both cases the HOMO and the LUMO orbital symmetries of the wavefunction result in A_u and A_g, respectively. The results in Table 6 suggest that the *S*-bonded isomer is the most stable, having the lowest total energy and the highest ionization energy (as calculated from Koopman's theorem). This apparently contrasts with the experimental evidence in that the *N*-bonded isomer is preferably obtained from the starting solution/suspension. It is important to emphasize, however, that, as the dilution of the starting solution increases, the percentage of *S*-bonded isomer isolated increases.

These facts seem to confirm the crucial role played by the intermolecular packing forces in stabilizing the growth of the *N*-bonded isomer, even though it possesses the highest total energy and the lowest ionization energy.

All calculations were performed on the CRAY Y-MP8/432 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (CINECA, Casalecchio, Bologna), employing the program Gaussian 90.[29]

Spectroscopic Characterization.—Table 7 summarizes the most relevant spectroscopic data for complexes **1** and **2**.

Infrared. Infrared spectroscopy has been used as a diagnostic tool to determine the co-ordination mode of the thiocyanate. The regions corresponding to the ν(CN), δ(NCS) and ν(CS) vibrations have been studied (see Table 7) and compared with those reported in the literature[2,30] for mononuclear O_h copper(II) complexes. The δ(NCS) bands, often used to characterize the bond type, indicate *N*-bonding for compound **1** and *S*-bonding for **2** (lower wavenumber for **2** than for **1**), in agreement with the crystal structures. It has to be pointed out, nevertheless, that the ligand aat exhibits a medium-intensity band at 440 cm^{-1}; so the former assignment is not completely unambiguous. The ν(CN) frequencies (higher wavenumber for **2** than for **1**) are also consistent with the described bonding modes. In the case of compound **1**, with the unusual bent Cu–N–C moiety, this band excludes the presence of terminally *N*-co-ordinated HNCS (or a single-atom thiocyanate bridge) as, in that case, the ν(CN) vibration should have been observed at values lower than 2000 cm^{-1} (IR spectrum of structure **3**

Table 7 Spectroscopic data

		IR thiocyanate bands/cm^{-1}			Diffuse reflectance, $\nu_{max}/10^3$ cm^{-1}		ESR	
Complex	Colour	ν(CN)	δ(NCS)	ν(CS)	c.t. (L→M)	d–d	$g_{\parallel}$	$g_{\perp}$
1	Grass green	2050–2065(sp)(sha)	485–470(sp), w–m, 440w	770w	23.3s	14.8s, 12.1(sh)	2.32	2.09
2	Brownish green	2090s, 2020(sh)	445m, 415w	760m	28.3(sh), 23.3vs	14.4s, 10.2w, 8.7w	2.30	2.10

s = Strong, v = very, m = medium, w = weak, sp = split, sha = sharp, s = shoulder.

displays two peaks at 1992 and 2080 cm^{-1}, respectively). The ν(CS) mode of **1** appears at frequencies somewhat low for a *N*-co-ordination, and, of **2** at frequencies in the upper limit for a *S*-co-ordination. The position of this band could be related with the strong hydrogen bonds which the non-co-ordinating donor atoms of the thiocyanate form in both compounds. Indeed, these ν(CS) frequencies fit well with the values described in the literature for compounds of type M–NCS–M.[2]

Other remarkable features of the IR spectra are the presence for both complexes of numerous and quite intense (especially for **2**) bands between 2500 and 2900 cm^{-1}, of uncertain assignment, as the existence of the above-mentioned hydrogen bonds cannot explain these *low* frequencies. Furthermore, there is a strong sharp band at 3145 cm^{-1} for **1** and at 3185 cm^{-1} for **2**, characteristic of the C–H stretching mode of aromatic protons. The group of sharp peaks observed at 3210 and 3245 cm^{-1} for **1** and at 3320, 3275 and 3225 cm^{-1} for **2** are likely to be overtones.

Diffuse reflectance. The observation of bands at 14 000–15 000 cm^{-1} is in agreement with the tetragonal geometry around the Cu^{II}. In addition, the two spectra are consistent with the well established fact that co-ordination through sulfur causes less perturbation than co-ordination through the N of the thiocyanate ion (or –SCN occurs lower in the spectrochemical series than –NCS).[2] For both complexes important charge-transfer bands are also observed; that of the *S*-bonded isomer, very intense, must be responsible for the brownish colour of the compound.

EPR. Compound **1** exhibits a poorly defined axial spectrum; the spectrum of **2** is clearly axial. The corresponding $g_{\parallel}$ and $g_{\perp}$ values (Table 7) lie in the range expected for tetragonal geometries, thus confirming the electronic spectra and being in accord with the structures.[31]

Acknowledgements

S. Ferrer thanks the Spanish Ministerio de Educacion y Ciencia for a postdoctoral research fellowship. We also thank the Consiglio Nazionale delle Ricerche for financial support.

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Received 5*th March* 1992; *Paper* 2/01206E