Inorganica Chimica Acta, *129* (1987) 217–222

Preparation, Spectroscopic and Magnetic Characterization of Two Pseudo Layered Copper(II) Systems. The X-ray Structures of Bis(thiocyanato-*N*)bis([1,2,4]triazolo[1,5-*a*]pyrimidine-N^3)copper(II) and Dichlorobis([1,2,4]triazolo[1,5-*a*]pyrimidine-N^3)copper(II)

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(Received October 30, 1986)

Abstract

The structures of α-$Cu(NCS)_2(tp)_2$ (**1**) and $CuCl_2(tp)_2$ (**2**), with tp = [1,2,4]triazolo[1,5-*a*]pyrimidine, $C_5H_4N_4$, have been determined by single crystal X-ray diffraction methods. **1** is monoclinic, space group $P2_1/c$, with $a = 11.669(2)$, $b = 8.808(2)$, $c = 7.951(2)$ Å, $\beta = 102.52(2)°$ and $Z = 2$. **2** is also monoclinic, space group $P2_1/c$, with $a = 9.546(1)$, $b = 8.958(1)$, $c = 8.082(1)$ Å, $\beta = 107.32(1)°$ and $Z = 2$. Both compounds show essentially layered structures with the copper atoms square planarly coordinated by two nitrogen atoms (*trans*) from N_3-coordinating tp ligands and by two donor atoms (*trans*) from anions [N atoms from thiocyanate ligands in **1** and Cl atoms from chloride ligands in **2**; in **1** Cu–N (tp ligand) = 2.035(5) and Cu–N(thiocyanate group) = 1.935(6) Å, in **2** Cu–N(tp ligand) = 2.021(4) and Cu–Cl = 2.297(1) Å]; the coordination is completed to octahedral by two nitrogen atoms from adjacent tp molecules which N_1-coordinate axially to the metals at relatively long distances (Cu–N = 2.633(6) in **1** and 2.692(4) Å in **2**) so that in both compounds two-dimensional systems parallel to each other are formed. The structural properties of the two compounds are correlated to their IR, UV and ESR spectra and magnetic susceptibilities.

Introduction

Polynuclear metal compounds with imidazole bridges between the metal centers have frequently been investigated as model systems for certain metalloproteins, like superoxide dismutase [1]. The particular geometry of the imidazolate bridge seems to be of great importance to the biological role of such metalloproteins [2]. The result of this understanding is growing research in this area which emphasized the preparation of simple model compounds. The 1,2,4-triazole ring has a geometry and an electronic structure that are rather similar to those of imidazole [3]. Therefore, it is especially suited for mimicking imidazole or, more precisely, imidazolate in model compounds.

In a previous study [4] the structure of the two-dimensional compound $Fe(NCS)_2(tp)_2$, with tp = [1,2,4]triazolo[1,5-*a*]pyrimidine, was reported. Isostructural two-dimensional systems could be obtained with other metal ions like Mn^{2+}, Co^{2+} and Ni^{2+}. Although Cu^{2+} gave compounds of identical composition, their magnetic properties were not in accordance with an identical two-dimensional arrangement of copper ions [5].

Earlier results with $Cu(NCS)_2$ and the dimethyl-substituted ligand (5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine, dmtp) have shown that the ambidentate thiocyanate ion, whose versatile bonding mode was already pointed out [6], may give several other isomers of the same molecular formula with bridging thiocyanate rather than bridging dmtp ligand [7, 8].

With the unsubstituted ligand tp and $Cu(NCS)_2$ two different compounds were prepared, both with molecular formula $Cu(NCS)_2(tp)_2$. One of these, α-form, could be obtained in crystals suitable for X-ray analysis. Its structure determination is described here. A chloride complex with spectral and magnetic properties analogous to the thiocyanate compound could be crystallized as well. The structure determination of this complex is also described below.

The following scheme shows the structure formula and IUPAC numbering of the ligand compared with the biochemical numbering of purine.

Experimental

Materials

The metal salts used in the preparations were reagent grade and used without further purification.

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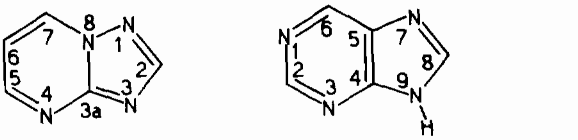

Scheme 1. IUPAC numbering scheme of tp and biochemical numbering of purine.

tp was prepared from 3-amino-1,2,4-triazole and 1,1,3,3-tetramethoxypropane according to a described method [9].

Preparation of Metal Compounds

α-$Cu(NCS)_2(tp)_2$ (**1**) was prepared by adding a solution of 4 mmol of NH_4NCS and 4 mmol of tp in 10 ml water to an aqueous solution of $Cu(NO_3)_2$ (2 mmol in 20 ml water). A dark brown product precipitated immediately. Upon leaving it in the mother liquor for 1 or 2 days, the substance dissolved slowly and dark green crystals were deposited. These crystals are easily separated from any brown powder left by decantation. This compound was called α-$Cu(NCS)_2(tp)_2$.

However, when freshly prepared $Cu(NCS)_2$, dissolved in methanol (2 mmol in 30 ml), was treated with 4 mmol of tp dissolved in 30 ml of methanol, olive green flat crystals formed fairly rapidly; they were separated by filtration. This compound was called β-$Cu(NCS)_2(tp)_2$. Crystals suitable for X-ray diffraction analysis could not yet be obtained. *Anal.* Found for α-$Cu(NCS)_2(tp)_2$: C, 33.79; H, 1.74, N, 32.82; Cu, 14.94. Found for β-$Cu(NCS)_2(tp)_2$: C, 34.09; H, 1.83; N, 33.27; Cu, 14.85. Calc. for $Cu(NCS)_2(C_5H_4N_4)_2$: C, 34.32; H, 1.91; N, 33.37; Cu, 15.15%.

$CuCl_2(tp)_2$ (**2**) was prepared by addition of an aqueous solution of tp (4 mmol in 10 ml) to a solution of 2 mmol $CuCl_2$ in 20 ml of ethanol. After standing for about 1 day, clear blue crystals separated. The compound was recovered by filtration. *Anal.* Found: C, 31.80; H, 2.10; N, 29.91; Cu, 16.70. Calc. for $CuCl_2(C_5H_4N_4)_2$: C, 32.05; H, 2.14; N, 29.91; Cu, 16.97%.

Physical Measurements

Ligand field spectra were taken in the UV–Vis region on a Perkin-Elmer 330 spectrophotometer with MgO as a reference using the diffuse reflectance technique. Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer as Nujol mulls between KRS-5 as polyethene (300–180 cm^{-1}) and as CsCl-disks. The ESR powder spectra were recorded on a Varian E-3 spectrometer at a frequency of 9.5 GHz at ambient temperature. The

TABLE I. Experimental Data for the X-ray Diffraction Study on 1 and 2

	$C_{12}H_8CuN_{10}S_2$ (1)	$C_{10}H_8Cl_2CuN_8$ (2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	11.669(2)	9.546(1)
b (Å)	8.808(2)	8.958(1)
c (Å)	7.951(2)	8.082(1)
β (°)	102.52(2)	107.32(1)
V (Å^3)	797.8(3)	659.8(1)
Z	2	2
$F(000)$	422	374
D_{calc} (g cm^{-3})	1.748	1.886
Molecular weight	419.93	374.68
Crystal dimensions (mm)	0.35 × 0.50 × 0.52	0.06 × 0.22 × 0.28
Linear absorption (cm^{-1})	16.41	62.05
Diffractometer	Siemens AED	Siemens AED
Scan type	$\theta/2\theta$	$\theta/2\theta$
Scan speed	3–12° θ/min	3–12° θ/min
Scan width	$[(\theta - 0.55)-(\theta + 0.55 + 0.346 \text{ tg } \theta)]$	
Radiation	Nb-filtered Mo Kα (λ = 0.7107 Å)	Ni-filtered Cu Kα (λ = 1.5418 Å)
2θ range (°)	6–52	6–140
Reflections measured	$\pm h,k,l$	$\pm h,k,l$
Standard reflections	1 measured after every 50 reflections	
Unique total data	1709	1241
Unique observed data $[I \geqslant 2\sigma(I)]$	890	1181
No. variables	131	113
R	0.048	0.053
R_w	0.059	0.069

magnetic susceptibility data were obtained in the temperature range of 4–80 K on a PAR magnetometer model 150A with the vibrating sample technique and with $CoHg(NCS)_4$ as a reference compound.

X-ray Crystallography

A flattened olive green crystal of **1** and a prismatic clear blue crystal of **2** were selected for the X-ray analyses and mounted on the diffractometers. Crystals data and data collection parameters for both compounds are given in Table I. The unit cell parameters were refined by least-squares procedures applied to θ values of 23 reflections for **1** (with θ in the range 11–15°) and 19 reflections for **2** (with θ in the range 24–34°) chosen from diverse regions of the reciprocal space. Data of both compounds were collected at room temperature, the individual reflection profiles having been analyzed following Lehmann and Larsen [10]. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and correction for absorption [11] was applied only to **2** (maximum and minimum transmission factors 1.3696 and 0.6906 respectively). Only the observed reflections were used in the structure solution and refinement of both compounds.

Structure Solution and Refinement

Both structures were solved by Patterson and Fourier methods and the refinements were carried out by full-matrix least-squares using the SHELX system of computer programs [12]. First isotropic and then anisotropic thermal parameters were used for all the non-hydrogen atoms. All the four hydrogen atoms of **1** and **2** were clearly localized from a difference synthesis and refined isotropically. The function minimized during the refinement was $\Sigma w|\Delta F|^2$. Weighting schemes used in the last cycles were $w = 1.0000/[\sigma^2(F_o) + 0.005F_o]$ for **1** and $w = 1.2043/[\sigma^2(F_o) + 0.0019F_o]$ for **2**, with $\sigma(F_o)$ from counting statistics. The final R and R_w values were 0.048 and 0.059 for **1** and 0.053 and 0.069 for **2** ($R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$). Final difference maps were featureless. Scattering factors used were taken from the tabulations of ref. 13 with the exception of those of the hydrogen atoms, which were taken from ref. 14. Corrections for the real and imaginary components of anomalous dispersion were made for the Cu, S and Cl atoms [13]. Final atomic coordinates for the non hydrogen atoms of **1** and **2** are listed in Tables II and III respectively. See also 'Supplementary Material'. All calculations were carried out on the CYBER76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna) with the financial support of the University of Parma.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) (with e.s.d.s in parentheses) for the Non-hydrogen Atoms in the Compound $Cu(tp)_2(NCS)_2$

Atom	*x/a*	*y/b*	*z/c*
Cu	0	0	0
S	3999(2)	−1013(3)	1505(4)
N	1587(5)	−702(7)	886(7)
N3	2360(5)	2508(6)	−214(8)
N5	1478(4)	4269(6)	1391(6)
N7	474(5)	4413(6)	1976(7)
N9	511(4)	2175(6)	619(6)
C	2590(7)	−828(7)	1145(9)
C1	3286(6)	4844(9)	877(10)
C2	3231(6)	3485(9)	−30(10)
C4	1482(5)	2917(7)	545(8)
C6	2382(6)	5235(8)	1591(9)
C8	−72(6)	3114(8)	1467(8)

TABLE III. Fractional Atomic Coordinates ($\times 10^4$) (with e.s.d.s in parentheses) for the Non-hydrogen Atoms in the Compound $Cu(tp)_2Cl_2$

Atom	*x/a*	*y/b*	*z/c*
Cu	0	0	0
Cl	2361(1)	820(1)	424(2)
N3	−2882(4)	2585(4)	−2114(6)
N5	−1801(4)	4239(4)	218(5)
N7	−560(4)	4344(4)	1615(5)
N9	−627(4)	2128(4)	213(5)
C1	−3997(6)	4937(5)	−1728(8)
C2	−3926(5)	3597(6)	−2621(8)
C4	−1821(5)	2913(4)	−636(6)
C6	−2886(5)	5265(5)	−279(8)
C8	83(5)	3037(5)	1533(6)

Results and Discussion

Description of the Molecular Structures

In both compounds (Figs. 1 and 2) Cu atoms, lying on a centre of symmetry, are in a square planar arrangement determined by two nitrogen atoms (*trans*) from tp ligands coordinating through non-hydrazinic triazole nitrogen atom and two donor atoms (*trans*) from the anions (nitrogen atoms from thiocyanate groups in **1**). Tables IV and V list the relevant bond distances and bond angles for **1** and **2** respectively. In **1** Cu–N(tp ligand) = 2.035(5) and Cu–N(thiocyanate group) = 1.935(6) Å; in **2** Cu–N(tp ligand) = 2.021(4) and Cu–Cl = 2.297(1) Å. The Cu–N(thiocyanate group) bond distance in **1** clearly reveals the nature of the equatorial bond [8]. Cu atoms also form in both compounds two longer contacts (2.633(6) Å in **1** and 2.692(4) Å in **2**) involving, in the axial positions, the hydrazinic

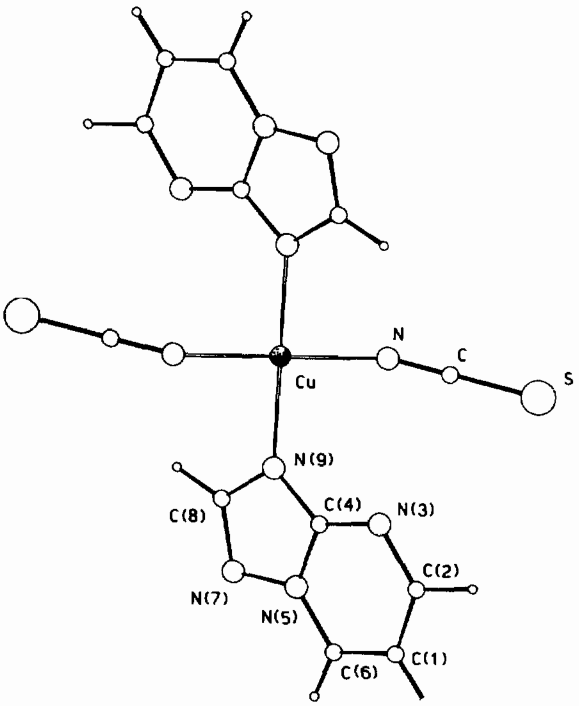

Fig. 1. Perspective view of the complex **1** with the atomic numbering scheme.

TABLE IV. Bond Distances (Å) and Angles (°) in Cu(tp)$_2$-(NCS)$_2$ (**1**)

(i) In the coordination sphere of Cu			
Cu–N	1.935(6)	Cu–N(7^{i})	2.633(6)
Cu–N(9)	2.035(5)		
N(9)–Cu–N	90.3(2)	N(7^{i})–Cu–N	88.8(2)
N(9)–Cu–N(7^{i})	94.2(2)		
(ii) In the anion			
N–C	1.149(9)	C–S	1.615(8)
N–C–S	179.8(6)	Cu–N–C	162.5(6)
(iii) In the organic ligand			
C(1)–C(2)	1.392(11)	C(6)–C(1)	1.347(11)
C(2)–N(3)	1.315(9)	C(4)–N(9)	1.320(8)
N(3)–C(4)	1.346(9)	N(9)–C(8)	1.342(9)
C(4)–N(5)	1.368(8)	C(8)–N(7)	1.329(9)
N(5)–C(6)	1.338(8)	N(7)–N(5)	1.357(8)
C(6)–C(1)–C(2)	119.1(7)	C(4)–N(5)–N(7)	110.2(5)
C(1)–C(2)–N(3)	124.6(7)	N(5)–N(7)–C(8)	102.0(5)
C(2)–N(3)–C(4)	114.8(6)	N(7)–C(8)–N(9)	114.9(6)
N(3)–C(4)–N(5)	122.5(5)	C(8)–N(9)–C(4)	104.5(5)
C(4)–N(5)–C(6)	121.7(5)	Cu–N(9)–C(4)	131.6(4)
N(5)–C(6)–C(1)	117.2(6)	Cu–N(9)–C(8)	123.2(4)
N(5)–C(4)–N(9)	108.3(5)		

[i] Asymmetric units: $-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$.

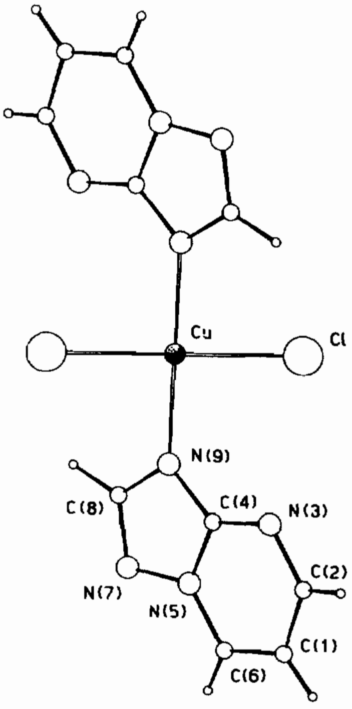

Fig. 2. Perspective view of the complex **2** with the atomic numbering scheme.

TABLE V. Bond Distances (Å) and Angles (°) in Cu(tp)$_2$-Cl$_2$ (**2**)

(i) In the coordination sphere of Cu			
Cu–Cl	2.297(1)	Cu–N(7^{i})	2.692(4)
Cu–N(9)	2.021(4)		
N(9)–Cu–Cl	95.4(1)	N(7^{i})–Cu–Cl	91.7(1)
N(9)–Cu–N(7^{i})	89.3(1)		
(ii) In the organic ligand			
C(1)–C(2)	1.413(8)	C(6)–C(1)	1.358(7)
C(2)–N(3)	1.319(6)	C(4)–N(9)	1.341(5)
N(3)–C(4)	1.349(5)	N(9)–C(8)	1.353(6)
C(4)–N(5)	1.371(5)	C(8)–N(7)	1.333(6)
N(5)–C(6)	1.353(6)	N(7)–N(5)	1.375(5)
C(6)–C(1)–C(2)	118.7(5)	C(4)–N(5)–N(7)	110.6(3)
C(1)–C(2)–N(3)	124.9(5)	N(5)–N(7)–C(8)	101.3(4)
C(2)–N(3)–C(4)	115.1(4)	N(7)–C(8)–N(9)	116.0(4)
N(3)–C(4)–N(5)	121.9(4)	C(8)–N(9)–C(4)	103.8(4)
C(4)–N(5)–C(6)	123.0(4)	Cu–N(9)–C(4)	132.8(3)
N(5)–C(6)–C(1)	116.2(4)	Cu–N(9)–C(8)	103.8(4)
N(5)–C(4)–N(9)	108.3(4)		

[i] Asymmetric units: $-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$.

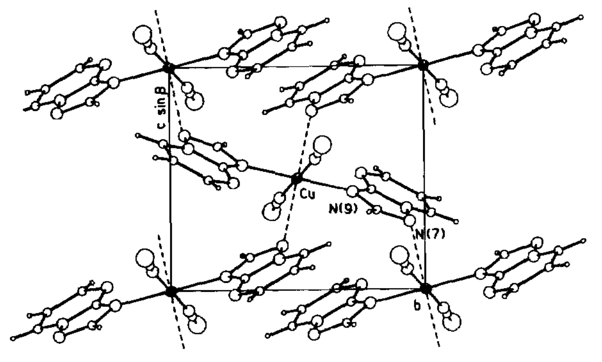

Fig. 3. Projection of the structure of 1 along *a* showing the pseudo layer.

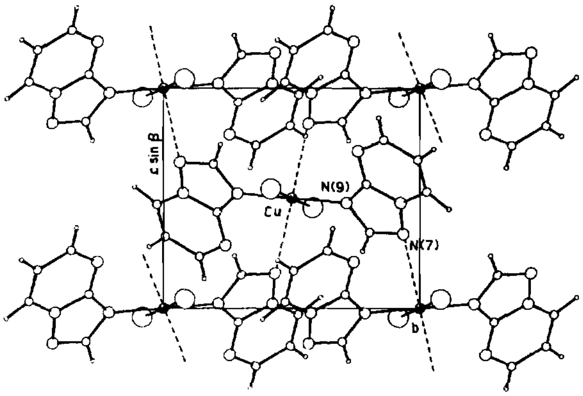

Fig. 4. Projection of the structure of 2 along *a* showing the pseudo layer.

non-bridgehead triazole nitrogen atom from tp molecules of adjacent complexes, so the coordination can be described as slightly distorted octahedral (Figs. 3 and 4). When compared to the M–N(tp ligand) distances found in the previously reported tp compounds [4], where tp acts as a bridge through both non-bridgehead triazole nitrogen atoms, these last Cu–N distances are significantly longer. However, taking into account that the coordination of the hydrazinic triazole nitrogen atom of tp ligands has occurred in the previous tp compounds via the equatorial positions of the metal ions (this being reflected in differences in metal–ligand distances and suggesting a pseudo linkage isomerism for the thiocyanate metal complexes with tp) the compounds 1 and 2 can best be classified as pseudo two-dimensional systems with semi-coordination. The distance Cu···Cu in the layers is 8.905 Å in 1 and 8.406 Å in 2; the N–Cu···N grid is almost planar in both compounds (94.2(2)° for 1 and 95.4(1)° for 2). The tp molecules are nearly planar in both compounds (the dihedral angle between the mean planes through planar pyrimidine and triazole rings being 2.0(2)° in 1 and 2.5(1)° in 2).

The molecular structure of 1 differs only slightly from that of 2. In the layers, parallel in both compounds to (100), the pseudo-bridging tp molecules are tilted with respect to the corresponding coordination equatorial plane by 44.5(2)° in 1 and 46.9(1)° in 2. In both compounds the geometry of two inter and intra-molecular contacts the triazole –CH group of each tp molecule forms in the layer with anions coordinated atoms [C(8)···N = 3.115(9), H(8)···N = 2.77(7) Å, C(8)–H(8)–N = 103(5)°, C(8)···N(–*x*, ½ + *y*, ½ – *z*) = 3.202(10), H(8)···N(–*x*, ½ + *y*, ½ – *z*) = 2.67(8) Å, C(8)–H(8)–N(–*x*, ½ + *y*, ½ – *z*) = 117(5)° in compound 1; C(8)···Cl = 3.261(5), H(8)···Cl = 2.86(5) Å, C(8)–H(8)–Cl = 103.(3)°, C(8)···Cl(*x*, ½ – *y*, ½ + *z*) = 3.405(4), H(8)···Cl(*x*, ½ – *y*, ½ + *z*) = 2.69(4) Å, C(8)–H(8)–Cl(*x*, ½ – *y*, ½ + *z*) = 125(3)° in compound 2] suggests bifurcated interactions stabilizing the configuration of the complexes and contributing to their connection in the layer. In earlier studied metal compounds with tp dimethyl derivative ligand [15] or imidazole ligand [16], C–H···N and C–H···Cl interactions are found (involving an activated C–H group of the same type of that of the present compound) stabilizing the configuration of the corresponding complexes and playing a significant role in determining the packing, respectively.

Spectra and Magnetic Measurements

A comparison of the IR spectra of the compounds reveals only minor differences between the absorptions that may be ascribed to the tp ligands. These small differences are in accordance with the identical coordination mode through the non-hydrazinic triazole nitrogen atom N_3, the usually favoured coordination site in dimethyl derivatives of tp [7, 8, 17, 18]. More important are the differences in the vibrations due to the different anions (Table VI). For compound 1 the ν(CN) absorption occurs at 2102 cm^{-1}, *i.e.* in the 2050–2100 cm^{-1} region, expected for N-bonding non-bridging NCS-anions. No splitting of the relatively sharp ν(CN) was observed, in accordance with a *trans*-coordination. In the ν(CS) region, known to be highly diagnostic for the

TABLE VI. Infrared Spectra of Anion and Copper–Ligand Vibrations for 1 and 2

Compound 1		Compound 2	
Vibration	Wavenumber (cm^{-1})	Vibration	Wavenumber (cm^{-1})
ν(CN)	2102s	ν(CuCl)	294m
ν(CS)	792mw	ν(Cu–N_3)(lig)	252m
δ(NCS)	474m		
ν(Cu–NCS)	333m		
ν(Cu–N_3)(lig)	243s		

NCS bonding mode [19], ν(CS) is observed at 792 cm^{-1}, indicating coordination via nitrogen. The δ(NCS) vibrations are easily assigned to the absorptions around 474 om^{-1}. In the far-infrared region a medium strong absorption at 333 cm^{-1} is observed, tentatively assigned to the Cu–NCS stretching [20]. A strong band at 243 cm^{-1} might be due to the Cu–N$_3$(lig) vibration. In the IR spectrum of 2 the Cu–N$_3$ absorption is noticed at 252 cm^{-1} and the Cu–Cl absorption at 294 cm^{-1}. These values agree very well with those of other CuX$_2$N$_2$ skeletons [21]. The colour of compound **1** (green) is influenced by a low energy charge transfer band (Cu–NCS charge transfer) at 400 nm (25 900 cm^{-1}). For 2 (with a blue colour) a charge transfer band is observed at 330 nm (30 300 cm^{-1}). The lower energy part of the spectra of **1** and **2** shows a fairly broad ligand field band near 700 nm (14 300 cm^{-1}) in accordance with the medium weak ligand field of elongated rhombic distorted octahedral geometry in both compounds [22].

TABLE VII. ESR and Ligand Field Spectra of **1** and **2**

Compound	$g_\perp$	$g_\parallel$	LF + charge transfer (cm^{-1})	
1	2.06	2.26	14300	25900
2	2.07	2.26	14300	30300

The g values of the ESR spectra of both compounds can be found in Table VII. The values for $g_\parallel$ and $g_\perp$ of **1** and **2** differ only slightly, as expected since their structures are quite similar. No splitting of $g_\parallel$ into four lines is observed which is quite common for magnetically undiluted species.

The magnitude of the magnetic exchange was determined by low-temperature magnetic suceptibility measurements. **1** is only weakly antiferromagnetic ($\theta = -2$ K for the range 80–9 K), while **2** showed a weak ferromagnetic interaction ($\theta = +5$ K for 80–26 K). At lower temperature, under the influence perhaps of the Cu–N distances varying with temperature, the θ value however drops to zero. It is clear, that the long intra-layer Cu–Cu distance is reflected here in the magnetic interaction: the behaviour of both compounds differs very little from that of monomeric copper(II) compounds.

Supplementary Material

Atomic coordinates for the hydrogen atoms, thermal parameters and a list of calculated and observed structure factors are available from the authors on request.

Acknowledgements

The authors wish to thank CNR, Rome and the Werkgroep voor Fundamenteel Materialenonderzoek, State University Leiden for support. Mr. R. Prins is thanked for doing the susceptibility measurements.

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