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Transition metal complexes with pyrazole-based ligands. XXII.[1] Di-μ-thiocyanato-bis[(3,5-dimethyl-1*H*-pyrazole-1-carboxamidine-κ^2N,N')(thiocyanato-κN)copper(II)] and a redetermination of bis(3,5-dimethyl-1*H*-pyrazole-1-carboxamidine-κ^2N,N')bis(nitrato-κO)copper(II)

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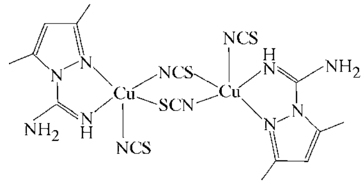
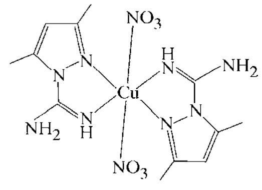
The title Cu^{II} complex, $[Cu_2(NCS)_4(C_6H_{10}N_4)_2]$, represents the first crystal structure of a polynuclear transition metal complex with the 3,5-dimethyl-1*H*-pyrazole-1-carboxamidine ligand (H*L*). It is compared with previously reported crystal structures of metal complexes with the same H*L* ligand. The molecule contains an eight-membered binuclear $Cu_2(NCS)_2$ ring, which is centrosymmetric and in a chair conformation. The Cu atom has a distorted square-pyramidal geometry with a very elongated Cu—S bond of 2.993 (2) Å. The crystal structure redetermination of the bis(3,5-dimethyl-1*H*-pyrazole-1-carboxamidine-κ^2N,N')bis(nitrato-κO)copper(II) complex, $[Cu(NO_3)_2(C_6H_{10}N_4)_2]$, and analysis of its hydrogen bonds confirm the significance of the NO_3 groups in the formation of a three-dimensional hydrogen-bonding network. Both complexes are centrosymmetric, the inversion centre being located at the mid-point of the Cu$\cdots$Cu line in (I) and the Cu atom being located at the inversion centre in (II).

Comment

Metal complexes with pyrazole-derived ligands have been the subject of research interest because of their interesting coordination chemistry and potential applications (Trofimenko, 1986, 1993; Mukherjee, 2000, and references therein). Pyrazole-based compounds find uses in the chemistry of antipyretics, antirheumatics, herbicides and fungicides (Goslar *et al.*, 1988; Ding *et al.*, 1994). Copper complexes containing pyrazole-based ligands are of particular interest in bioinorganic chemistry, since they can be used as models for the active sites in copper proteins, such as haemocyanin and tyrosinase (Karlin & Tyeklar, 1993). Furthermore, polynuclear transition metal complexes (such as the Cu complex presented in this work) are used in the important research area of molecular magnetism (Kahn, 1993).



(I)



(II)

We have synthesized and characterized a number of transition metal complexes containing pyrazole-based ligands (Jaćimović *et al.*, 1999, 2003, 2004; Mészáros Szécsényi, Leovac, Jaćimović, Češljević, Kovács & Pokol, 2001; Mészáros Szécsényi, Leovac, Jaćimović, Češljević, Kovács, Pokol & Gal, 2001; Mészáros Szécsényi *et al.*, 2003; Tomić *et al.*, 2000; Radosavljević Evans, Howard, Howard *et al.*, 2004; Radosavljević Evans, Howard, Mészáros Szécsényi *et al.*, 2004), with the aim of investigating the influence of the pyrazole ring substituents on the formation and properties of the complexes. The crystal structure of the pyrazole-derived ligand H*L*·HNO_3 (H*L* is 3,5-dimethyl-1*H*-pyrazole-1-carboxamidine) was reported by Khudoyarov *et al.* (1995). In this paper, we present the synthesis and molecular and crystal structures of the novel copper complex, $[Cu(NCS)_2(HL)]_2$, (I), containing this ligand.

Besides the uncoordinated H*L*·HNO_3 ligand, three additional crystal structures of metal complexes containing the same ligand have been reported to date. The crystal structure

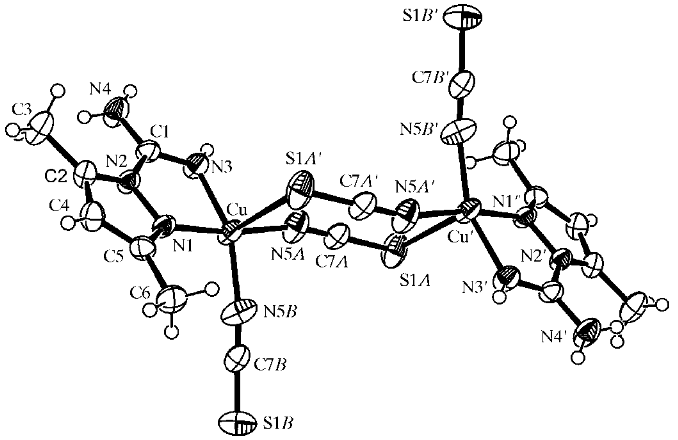


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Each asymmetric unit consists of half a molecule. Primed atoms are at the symmetry position $(1 - x, 2 - y, 2 - z)$.

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[1] Part XXI: Mészáros Szécsényi, Leovac, Kovacs, Pokol & Jaćimović (2005).

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of $[Ni(HL)_2(H_2O)_2](NO_3)_2$ was originally determined at 298 K (Podder *et al.*, 1989), but has been redetermined at 120 K and published recently, together with the isostructural Co^{II} complex, $[Co(HL)_2(H_2O)_2](NO_3)_2$ (Jaćimović *et al.*, 2004). The Cu^{II} complex of composition $[Cu(NO_3)_2(HL)_2]$, (II), has also been characterized previously by X-ray analysis (Podder *et al.*, 1986), but that crystal structure was published with the wrong number of H atoms and without a precise description of the hydrogen-bonding interactions (specifically, the $N4H_2$ group was determined as an NH group, with only one H atom; *cf.* Fig. 2). For this reason, we have performed a new X-ray analysis of (II) with crystallographically more relevant results, and this is also presented in this article.

In all three complexes cited above from the literature, as well as in $[Cu(NCS)_2(HL)]_2$ presented in this work (Fig. 1), the H*L* ligand is bonded to the metal atom as a bidentate chelate ligand, with the difference that the three previously published complexes are bis(bidentate)–M^{II} mononuclear complexes, while the present complex, (I), is binuclear, with one H*L* ligand per metal atom. Furthermore, all three previously published complexes have the transition metal atom in an octahedral geometry, while the Cu atom in (I) is coordinated by five atoms.

Complex (I) is centrosymmetric, with an inversion centre located at the mid-point of the $Cu\cdots Cu^{i}$ line [symmetry code: (i) $1 - x, 2 - y, 2 - z$]. The coordination geometry of Cu^{II} is significantly deformed. According to the value of 0.27 calculated for the geometrical parameter $\tau = (\beta - \alpha)/60$ (Addison *et al.*, 1984), where $\alpha = N3—Cu—N5B$ and $\beta = N1—Cu—N5A$, the structure is about 27% distorted from ideal square-pyramidal geometry. The Cu—S bond formed through the NCS ligand is very elongated (Table 1). Searching for crystal structures of pentacoordinated Cu complexes with two equivalent NCS bridging ligands, we found 30 examples with $Cu\cdots S$ bond lengths ranging from 2.41 to 3.23 Å (Cambridge Structural Database; Allen *et al.*, 1991). Compound (I) contains an eight-membered binuclear $Cu_2(NCS)_2$ ring, which is centrosymmetric and in a chair conformation. The two NCS ligands are practically coplanar, forming the base of the chair conformation. The Cu atom is displaced from this $(NCS)_2N_2$ plane by about 0.60 Å. A very similar form of eight-membered $Cu_2(NCS)_2$ ring is identified in the additional 16 crystal structures mentioned above. This ring is centrosymmetric in all complexes, but the position of the Cu atom relative to the $(NCS)_2N_2$ plane is different and consequently the $Cu\cdots Cu$ distance varies. In complex (I), the $Cu\cdots Cu$ distance is 5.744 (2) Å. However, the shortest $Cu\cdots Cu$ distance [4.480 (2) Å] in the structure is outside the ring, *i.e.* it involves a neighbouring molecule in the symmetry position ($-x, 2 - y, 2 - z$).

Bond distances within the 3,5-dimethyl-1*H*-pyrazole-1-carboxamidine ligand are very similar for all four metal complexes, as well as the corresponding bonds in the uncoordinated $HL\cdot HNO_3$. Within the pyrazole ring in all the crystal structures, the longest and shortest bonds are always C4—C5 and N1—C5, respectively. When H*L* is bonded to the metal atom, the C1—N3 bond is significantly shorter then the C1—N4 bond in all complexes. It is interesting to analyze the metal–H*L* bonds, which show remarkable differences. The *M*—N1 and *M*—N3 bond lengths in $[Ni(HL)_2(H_2O)_2](NO_3)_2$ and $[Co(HL)_2(H_2O)_2](NO_3)_2$ are nearly the same, while in $[Cu(NO_3)_2(HL)_2]$ the *M*—N1 bond is about 0.08 Å longer (Table 3). It is worth mentioning again that all three complexes are bis(bidentate)–M^{II} mononuclear complexes with octahedral coordination geometry. In the binuclear Cu^{II} complex presented in this work, the *M*—N1 bond is almost 0.04 Å longer than the *M*—N3 bond (Table 1).

No significant hydrogen bonds or intermolecular interactions exist in the crystal packing of (I), except for two weak $N—H\cdots S$ hydrogen bonds, the details of which are given in Table 2. The hydrogen-bonding network of (II) is much more interesting. Two axially coordinated NO_3 groups with elongated Cu—O bonds (Fig. 2) play a dominant role in the formation of a three-dimensional network of hydrogen bonds.

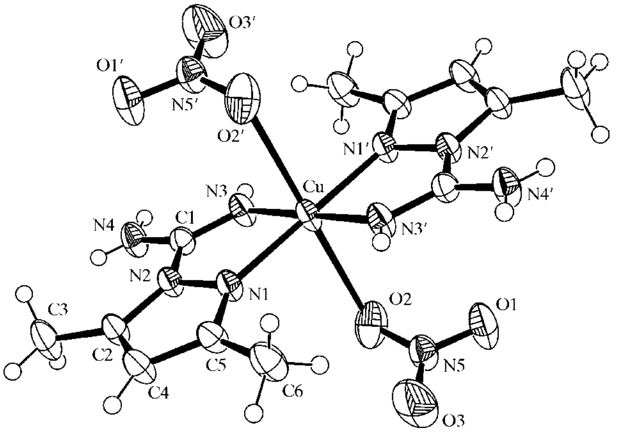

Figure 2
The molecular structure of (II), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Each asymmetric unit consists of half a molecule. Primed atoms are at the symmetry position ($-x, -y, -z$).

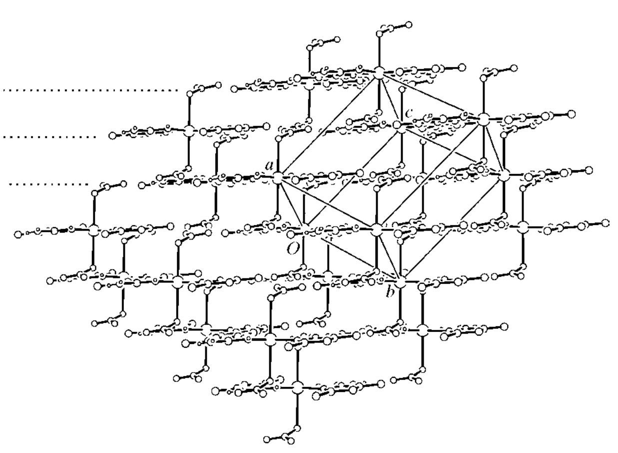

Figure 3
A view of the packing in (II), showing parallel layers interconnected by Cu—O2 bonds.

Only three hydrogen bonds are listed in Table 4, but since the molecule of (II) is centrosymmetric (with the Cu atom located on an inversion centre), each molecule is hydrogen bonded to eight neighbouring molecules (four from the same layer and 2 + 2 from two neighbouring layers). Thus, the crystal packing consists of parallel layers (Fig. 3) which are composed of equatorial coordination planes created by H*L* pyrazole ligands, with NO_3 groups bonded to Cu atoms in neighbouring layers. In this way, the layers are interconnected by Cu—O2 bonds, while the equatorial coordination planes within the layers are interconnected by NO_3 groups. This interesting role of NO_3 in the formation of the hydrogen-bonding network has also been reported by us for a previous Cu^{II} complex (Leovac *et al.*, 2002).

Experimental

A methanol solution of the nitrate salt of 3,5-dimethyl-1*H*-pyrazole-1-carboxamidine ($HL\cdot HNO_3$) and the Cu^{II} salt $[Cu(OAc)_2\cdot H_2O]$ in a molar ratio of 2:1, in the presence of NH_4SCN, gave dark-green crystals of complex (I), formula $[Cu(NCS)_2(HL)]_2$. Elemental analysis found (calculated): C 30.78 (30.22), N 26.73 (26.44), H 2.99% (3.18%). The molar conductivity of the complex in dimethylformamide is 45.7 S cm^2 mol^{-1}. The effective magnetic moment μ_{eff} = 1.90 μ_B. Complex (II) was prepared according to the previously published procedure of Podder *et al.* (1986).

Compound (I)

Crystal data

$[Cu_2(NCS)_4(C_6H_{10}N_4)_2]$
M_r = 635.76
Triclinic, $P\overline{1}$
a = 7.172 (2) Å
b = 8.742 (3) Å
c = 11.360 (3) Å
α = 70.35 (2)°
β = 86.00 (2)°
γ = 67.06 (2)°
V = 616.2 (3) Å^3

Z = 1
D_x = 1.713 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
θ = 12.2–15.6°
μ = 2.10 mm^{-1}
T = 293 (2) K
Prismatic, dark green
0.22 × 0.14 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (*PLATON*; Spek, 2003)
T_{min} = 0.751, T_{max} = 0.825
2906 measured reflections
2685 independent reflections
2096 reflections with $I > 2\sigma(I)$

R_{int} = 0.021
θ_{max} = 27.0°
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

Table 1
Selected geometric parameters (Å, °) for (I).

Cu—S1*A*^{i}	2.993 (2)	N1—C5	1.318 (4)
Cu—N1	1.983 (3)	N2—C2	1.364 (4)
Cu—N3	1.952 (3)	N3—C1	1.281 (4)
Cu—N5*A*	1.939 (3)	N4—C1	1.323 (4)
Cu—N5*B*	1.933 (3)	C2—C4	1.360 (5)
N1—N2	1.382 (3)	C4—C5	1.402 (5)
N5*B*—Cu—N5*A*	91.99 (15)	N5*B*—Cu—N1	95.62 (13)
N5*B*—Cu—N3	154.40 (16)	N5*A*—Cu—N1	170.81 (13)
N5*A*—Cu—N3	95.67 (13)	N3—Cu—N1	79.60 (11)

Symmetry code: (i) $1 - x, 2 - y, 2 - z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.125
S = 1.07
2685 reflections
165 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2 + 0.1077P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H1N4···S1*A*^{ii}	0.86 (4)	2.74 (4)	3.567 (4)	162 (4)
N3—H1N3···S1*B*^{iii}	0.85 (4)	2.63 (4)	3.477 (3)	170 (4)

Symmetry codes: (ii) $x, y - 1, z$; (iii) $-x, 2 - y, 2 - z$.

Compound (II)

Crystal data

$[Cu(NO_3)_2(C_6H_{10}N_4)_2]$
M_r = 463.92
Triclinic, $P\overline{1}$
a = 5.476 (2) Å
b = 9.379 (3) Å
c = 9.529 (3) Å
α = 76.99 (2)°
β = 75.38 (2)°
γ = 86.96 (2)°
V = 461.4 (3) Å^3
Z = 1
D_x = 1.670 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 13.4–17.7°
μ = 1.24 mm^{-1}
T = 293 (2) K
Prismatic, blue
0.16 × 0.14 × 0.14 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
4799 measured reflections
2691 independent reflections
2311 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 30.0°

$h = -7 \rightarrow 7$
$k = -12 \rightarrow 13$
$l = -10 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.05
2691 reflections
147 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.1115P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Cu—N1	2.0221 (14)	N2—C2	1.3725 (19)
Cu—N3	1.9457 (15)	N3—C1	1.293 (2)
Cu—O2	2.6049 (19)	N4—C1	1.322 (2)
N1—N2	1.3781 (17)	C2—C4	1.366 (2)
N1—C5	1.323 (2)	C4—C5	1.408 (2)
N2—C1	1.409 (2)		
N3—Cu—N1	79.27 (6)	N1—Cu—O2	87.18 (6)
N3—Cu—O2	92.11 (6)		

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Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H1N3···O2^{i}	0.81 (3)	2.20 (3)	2.993 (2)	164 (2)
N4—H1N4···O1^{i}	0.89 (3)	2.14 (3)	3.001 (2)	163 (2)
N4—H2N4···O1^{ii}	0.79 (2)	2.28 (2)	2.843 (2)	129 (2)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $x+1, y, z-1$.

A Gaussian-type absorption correction based on the crystal morphology (*PLATON*; Spek, 2003) was applied in the case of complex (I). All H atoms for both crystal structures were easily found in difference Fourier maps, but those attached to C atoms were placed in calculated positions and treated using a riding model, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C), or 1.5$U_{\rm eq}$(C) for methyl H atoms. The positions of the methyl H atoms as defined by the HFIX 137 command (*SHELXL97*; Sheldrick, 1997) were in very good agreement with those found in the difference Fourier maps. H atoms bonded to N atoms were located in difference Fourier maps and refined isotropically. In complex (I), one of the H atoms bonded to N4 was also found in a difference map but its coordinates were fixed during the final stage of refinement to prevent a shortening of the N4—H bond length. However, the $U_{\rm iso}$(H) value of this H atom was refined freely, resulting in a reasonable displacement parameter of 0.075 (17) Å^2.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996) and *ORTEPIII* (Burnett & Johnson, 1996); publication software: *PARST* (Nardelli, 1995) and *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1248). Services for accessing these data are described at the back of the journal.

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