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Bis(cyanamidonitrato-κN)[tris(3,5-dimethylpyrazole)copper(II)]

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The title compound, $[Cu(CN_3O_2)_2(C_5H_8N_2)_3]$, is the first example of a pentacoordinated 3*d*-central atom involving the cyanamidonitrate ligand. The crystal structure is formed by neutral molecues stabilized by a three-dimensional network consisting of one intramolecular and three intermolecular hydrogen bonds. The Cu atom is pentacoordinated by three N-donor atoms from 3,5-dimethylpyrazole neutral ligands and two N-donor atoms from cyanamidonitrate anions.

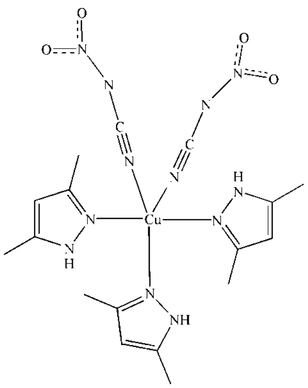
Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.003 Å
R factor = 0.044
wR factor = 0.121
Data-to-parameter ratio = 25.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Non-linear pseudohalides such as dicyanamide, $(N(CN)_2)^-$, tricyanomethanide, $(C(CN)_3)^-$, nitrosodicyanomethanide, $(ONC(CN)_2)^-$ and cyanamidonitrate (can), $[O_2NN(CN)]^-$, exhibit a rich variety of bonding modes for coordination in 3*d*-complexes (Kohout *et al.*, 2000; Hvastijová *et al.*, 1998; Potočňák at al., 2001, 2002). Redistribution of electron density due to coordination in some circumstances leads to activation for nucleophilic addition reactions (Kožíšek *et al.*, 2002). The bond distances for central atom—N(nitrile) donor atom in the equatorial plane of octahedral cyanamidonitrate complexes of 3*d*-transition metals are in the range 2.027–2.167 Å {2.0273 (5) Å in $[Cu(imidazole)_2(cyanamidonitrate)_2]$ (Kožíšek *et al.*, 2002), 2.076 (3) and 2.096 (3) Å in $[Ni(pyrazole)_4(can)_2]$ (Hvastijová *et al.*, 2001), 2.100 (3) Å in $[Ni(1\text{-}methylimidazole)_4(can)_2]$ (Hvastijová *et al.*, 2000), 2.167 (2) and 2.164 (2) Å in $[Co(imidazole)_4(can)_2]$ (Hvastijová *et al.*, 2000), and 2.146 (1) and 2.136 (1) Å in $[Co(pyrazole)_4(can)_2]$ (Hvastijová *et al.*, 2003)}, in contrast to higher values in the axial position {2.600 (3) Å in $[Cu(1\text{-}methylimidazole)_4(can)_2]$ (Kohout *et al.*, 1999) and 2.683 (3) Å in $[Cu(5\text{-}methylimidazole)_4(can)_2]$ (Kohout *et al.*, 1999)}.



(I)

In the title complex, (I), the Cu atom is pentacoordinated with a CuN_5 chromophore. The coordination polyhedron is a

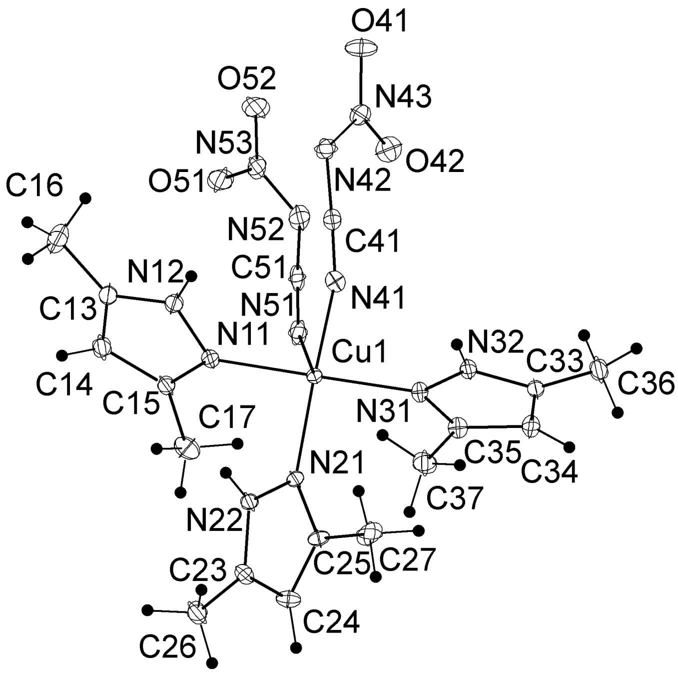


Figure 1
The atom-numbering scheme for (I), with displacement ellipsoids shown at the 30% probability level.

quasi-tetragonal pyramid. The basal plane is formed by three N-donor atoms from 3,5-dimethylpyrazole ligands and one N-donor atom from a canamidonitrate anion (Table 1). In the apical position, there is an N-donor atom from the other cyanamidonitrate anion [Cu1—N51 2.244 (2) Å]. As the electron configuration of Cu^{II} is d^9, the coordination bonds in the equatorial/basal plane for both octahedral and quasi-tetragonal pyramidal coordination are considered as an overlap between non-fully populated $d_{x^2-y^2}$ orbital and lone electron pairs of the N-donor atoms. On the other hand, the two axial or one apical position may be explained as an interaction between the non-fully populated d_{z^2} orbital and lone electron pairs of the N-donor atom.

Thus, the bond distance for the apical position in the case of the pentacoordinated compound [2.442 (2) Å] lies between the two border limits for hexacoordinated equatorial and axial bonds [2.027–2.167 and 2.683 (3) Å, respectively]. The Cu atom is 0.196 (1) Å above the mean plane defined by atoms N11, N21, N31 and N41. Comparison of the interatomic distances for (can) bonded in the equatorial position [Cu1—N41 2.008 (2) Å and N41—C41 1.154 (2) Å] with corresponding bonds in [Ni(1-methylimidazole)$_4$(can)$_2$] (Hvastijová *et al.*, 2000) [Ni–N 2.100 (3) Å and N—C 1.107 (4) Å] and in [Cu(imidazole)$_2$(can)$_2$] (Kožíšek *et al.*, 2002) [Cu—N 2.0273 (5) Å and N—C 1.1607 (6) Å] is in good agreement with the hypothesis of weakening the triple bond in the nitrile group by formation of a strong coordination bond [Cu1—N41 2.008 (2) Å and N41—C41 1.154 (2) Å]. On the other hand, comparison of the interatomic distances for apically bonded (can) [Cu1—N51 2.244 (2) Å and N51—C51 1.164 (2) Å] with axial bonds in the octahedral complexes [Cu(1-methylimidazole)$_4$(can)$_2$] [Cu—N 2.600 (3) Å and N—C 1.133 (4) Å] and [Cu(5-methylimidazole)$_4$(can)$_2$] [Cu—N 2.683 (3) Å and N—C 1.148 (4) Å] (Kohout *et al.*, 1999) does not follow this trend. This is caused by the fact that the d_{z^2} orbital in the pentacoordinated Cu^{2+} cation cannot be considered identical to the hexacoordinated one due to different local symmetry. The electronic structure of the title complex, (I), could be elucidated only by charge–density studies.

The crystal structure of (I) is stabilized by a three-dimensional network of hydrogen bonds consisting of one intramolecular and three intermolecular hydrogen bonds (Table 2). The hydrogen-bonding pattern based on the methodology of Bernstein *et al.* (1995) and Grell *et al.* (1999) can be described as follows: N12—H12···O51 is an intramolecular bond, $S_1^1(9)$; N22—H22···O52 forms, on the first-level graph set, an $R_2^2(18)$ ring, as does N32—H32···O41, again $R_2^2(18)$. On the second-level graph set, the N22—H22···O52 and N42—H42···O42 hydrogen bonds form a $C_2^2(18)$ chain. The fourth, C24—H2···O42, is a weak intermolecular interaction.

Experimental

A solution of 2.0 mmol of $Cu(NO_3)_2$ in 3 ml of water was mixed with a solution of 4.0 mmol of KNO_2NCN in 10 ml of water and with a solution of 4.0 mmol of 3,5-dimethylpyrazole in 10 ml of methanol. From this system, after standing for a few days, blue single crystals of $[Cu(NCNNO_2)_2(3,5\text{-dmpz})_3]$ suitable for X-ray diffraction measurements were isolated.

Crystal data

$[Cu(CN_3O_2)_2(C_5H_8N_2)_3]$
$M_r = 524.02$
Monoclinic, $P2_1/n$
$a = 9.1516$ (1) Å
$b = 21.2660$ (1) Å
$c = 12.9498$ (1) Å
$\beta = 109.154$ (2)°
$V = 2380.74$ (3) Å^3
$Z = 4$

$D_x = 1.462$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.4$–33.0°
$\mu = 0.97$ mm^{-1}
$T = 183$ (2) K
Prism, blue
0.40 × 0.28 × 0.14 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002; Blessing, 1995)
$T_{\min} = 0.698$, $T_{\max} = 0.877$
36079 measured reflections

8955 independent reflections
6968 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 33.0°$
$h = -13 \rightarrow 13$
$k = -31 \rightarrow 31$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.121$
$S = 1.04$
8460 reflections
337 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 1.0978P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.16$ e Å^{-3}
$\Delta\rho_{\min} = -1.13$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Cu1—N21	1.985 (1)	N43—O42	1.235 (2)
Cu1—N31	2.002 (1)	N43—O41	1.246 (2)
Cu1—N41	2.008 (2)	N51—C51	1.164 (2)
Cu1—N11	2.020 (1)	N52—C51	1.333 (2)
Cu1—N51	2.244 (2)	N52—N53	1.353 (2)
N41—C41	1.154 (2)	N53—O51	1.239 (2)
N42—C41	1.327 (2)	N53—O52	1.246 (2)
N42—N43	1.364 (2)		
N21—Cu1—N31	90.73 (6)	N41—Cu1—N51	97.08 (7)
N21—Cu1—N41	162.03 (6)	N11—Cu1—N51	90.46 (6)
N31—Cu1—N41	90.04 (6)	C41—N41—Cu1	149.9 (2)
N21—Cu1—N11	90.35 (6)	C41—N42—N43	109.8 (2)
N31—Cu1—N11	174.79 (6)	C51—N51—Cu1	139.4 (2)
N41—Cu1—N11	87.36 (6)	C51—N52—N53	109.9 (2)
N21—Cu1—N51	100.77 (6)	N41—C41—N42	173.5 (2)
N31—Cu1—N51	94.34 (6)	N51—C51—N52	174.9 (2)
Cu1—N41—C41—N42	132 (1)	Cu1—N51—C51—N52	133 (2)
N43—N42—C41—N41	168 (2)	N53—N52—C51—N51	176 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N12—H12$\cdots$O51	0.880 (2)	2.126 (2)	2.959 (2)	157.5 (1)
N22—H22$\cdots$O52^{i}	0.880 (1)	2.014 (2)	2.844 (2)	156.8 (1)
N32—H32$\cdots$O41^{ii}	0.880 (2)	2.029 (3)	2.885 (2)	163.8 (1)
C24—H24$\cdots$O42^{iii}	0.950 (2)	2.411 (2)	3.246 (2)	146.5 (2)

Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $1 - x, 2 - y, -z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

H atoms were constrained to an ideal geometry using a riding model. Methyl C—H distances were set at 0.98 Å, aromatic C—H distances were set at 0.95 Å, and N—H distances were set at 0.88 Å. H-atom displacement parameters were fixed at 1.2 times the $U_{\rm eq}$ value of the parent C, or N atom. The maximum and minimum electron-density peaks are located 0.82 and 0.75 Å, respectively, from atom Cu1.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXTL*.

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