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catena-Poly[[bis(nitrato)(pyrimidine)-copper(II)]- μ -pyrimidine-*N:N'*]

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The title compound, [Cu(NO₃)₂(C₄H₄N₂)₂]_n, crystallizes as a linear polymeric compound with one pyrimidine ligand bridging between two Cu^{II} atoms and a second pyrimidine ligand coordinated in a monodentate manner. The distorted octahedral geometry around the Cu^{II} atom consists of two pyrimidine N atoms at distances of 2.033 (4) and 2.025 (4) Å, and two nitrate O atoms at distances of 1.987 (3) and 1.973 (3) Å. The apical positions are occupied by an N atom of a bridging pyrimidine ligand [2.291 (4) Å] and a nitrate O atom at a long distance of 2.781 (3) Å. The basal plane is almost planar, with *trans* angles of 176.23 (14) and 165.34 (15)°.

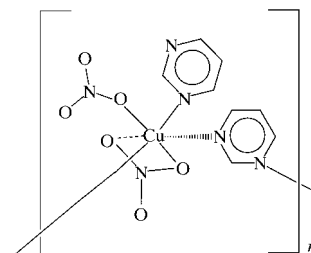
Comment

Low-molecular weight bifunctional heterocyclic *N*-donor molecules have received much interest due to the fact that they can form interesting polymeric structures (van Albada *et al.*, 2000; Batten *et al.*, 1998; Jensen *et al.*, 1999; Manson *et al.*, 1998). With pyrimidine as a ligand and nitrate as an anion, only a few polymeric copper(II) structures have been reported in which the nitrate anion acts as a monodentate anion and the ligand is bridging between the Cu atoms (Blasco *et al.*, 1994; Carlucci *et al.*, 1998; Power *et al.*, 1998).

In the title compound, (I), the Cu^{II} atom is surrounded by two pyrimidine N atoms [Cu1—N11 2.033 (4) Å and Cu1—N21 2.025 (4) Å] and two nitrate O atoms [Cu1—O11 1.987 (3) Å and Cu1—O21 1.973 (3) Å], which form the planar base of the distorted octahedron, with basal angles of 176.23 (14) (O21—Cu1—O11) and 165.34 (15)° (N21—Cu1—N11). The apical positions are occupied by an N atom of a bridging pyrimidine ligand [Cu1—N23ⁱ 2.291 (4) Å; symmetry code: (i) $\frac{1}{2} + x, 1 - y, z$] and a nitrate O atom at a quite long

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semicoordinating distance [Cu1···O22 2.781 (3) Å]. One of the pyrimidine ligands bridges the Cu atoms, forming a polymeric two-dimensional network, while a second pyrimidine ligand acts as a monodentate ligand. This is quite uncommon



(I)

for copper(II) compounds, but not unprecedented. Spectroscopic measurements were performed to verify the structural features. The ligand field spectrum, measured as a solid in the diffuse reflectance mode, shows a broad tail-shaped *d-d* transition band with maxima at 15.4 and 10.3 × 10³ cm⁻¹ which is normal for a tetragonal-type CuN₃O₂(O) chromophore (Amani Komaei *et al.*, 1999; Driessen *et al.*, 1993; van Koningsbruggen *et al.*, 1993). The EPR spectra measured as a polycrystalline powder showed an axial *S* = $\frac{1}{2}$ spectrum with a *g*(perp) of 2.09 and a *g*(par) of 2.28.

Experimental

Copper(II) nitrate (1.2 mmol) and pyrimidine (1.2 mmol) were each dissolved in 10 ml of ethanol. The copper(II) solution was then added slowly to the ligand solution, thereby preventing any precipitation. The solution was filtered to remove any solids and after a few days, blue crystals separated. Satisfactory elemental analyses were obtained. A crystal was mounted on a glass fiber using the oil-drop method (Kottke & Stalke, 1993) and data were collected at 193 K.

Crystal data

[Cu(NO₃)₂(C₄H₄N₂)₂]
M_r = 347.74
Orthorhombic, *Pca*2₁
a = 9.987 (2) Å
b = 8.451 (2) Å
c = 14.233 (3) Å
V = 1201.3 (5) Å³
Z = 4
D_x = 1.923 Mg m⁻³

Mo *K*α radiation
Cell parameters from 25 reflections
θ = 3.5–7.0°
μ = 1.861 mm⁻¹
T = 193 (2) K
Prismatic, blue
0.35 × 0.30 × 0.25 mm

Data collection

Rigaku AFC-7S diffractometer
ω-2*θ* scans
Absorption correction: *ψ* scan (North *et al.*, 1968)
T_{min} = 0.581, *T_{max}* = 0.628
1133 measured reflections
1133 independent reflections
1109 reflections with *I* > 2σ(*I*)

θ_{max} = 25.24°
h = -11 → 0
k = -10 → 0
l = -17 → 0
3 standard reflections every 200 reflections
intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.030
wR (*F*²) = 0.077
S = 1.083
1133 reflections
190 parameters
H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0576*P*)² + 0.5672*P*]
where *P* = (*F_o*² + 2*F_c*²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.54 e Å⁻³
Δρ_{min} = -0.86 e Å⁻³
Absolute structure: Flack (1983)
Flack parameter = 0.07 (2)

Table 1

Selected geometric parameters (Å, °).

Cu1—O21	1.973 (3)	Cu1—N11	2.033 (4)
Cu1—O11	1.987 (3)	Cu1—N23 ⁱ	2.291 (4)
Cu1—N21	2.025 (4)		
O21—Cu1—O11	176.23 (14)	N21—Cu1—N11	165.34 (15)
O21—Cu1—N21	89.88 (14)	O21—Cu1—N23 ⁱ	90.79 (15)
O11—Cu1—N21	91.49 (14)	O11—Cu1—N23 ⁱ	85.50 (14)
O21—Cu1—N11	91.42 (15)	N21—Cu1—N23 ⁱ	100.63 (14)
O11—Cu1—N11	88.14 (15)	N11—Cu1—N23 ⁱ	93.96 (15)

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

H atoms were introduced in calculated positions and refined with fixed geometry (C—H = 0.95 Å) with respect to their carrier atoms.

Data collection and cell refinement: *AFC-7S* software; data reduction: *TEXSAN* (Molecular Structure Corporation, 1993); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

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