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Bis(2-aminomethylpyridine-*N*,*N*′)bis(nitrato-*O*)copper(II)

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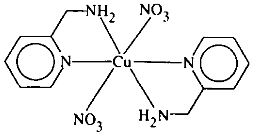
Abstract

In the title compound, $[Cu(NO_3)_2(C_6H_8N_2)_2]$, the copper(II) ion, which lies on a centre of symmetry, is coordinated by four N atoms of two 2-aminomethylpyridine ligands and two O atoms of two nitrate ions in an elongated octahedral geometry.

Comment

In the course of our investigations on models of superoxide dismutase (SOD) (Tainer, Getzoff, Beem, Richardson & Richardson, 1982), the tetradentate ligand 1,5-bis(2-pyridyl)-2,4-diazapentane was synthesized in good yield by a Mannich reaction. Reaction of this ligand with $[Cu(H_2O)_3(NO_3)_2]$ in ethanol unintentionally resulted in the title compound, (I). Apparently, the ligand had decomposed in its original components through a reverse Mannich reaction, which is not uncommon under these circumstances (Heany, 1991).



(I)

The copper(II) ion in bis(nitrato-*O*)bis(2-aminomethylpyridine-*N*,*N*′)copper(II) is coordinated by an O atom from each of the two nitrate ions and the four N atoms of the two ligands in an elongated octahedron. The Cu—N distances of 1.9984 (14) (amine N atom) and 2.0191 (15) Å (pyridine N atom) can be considered as normal, while the Cu—O distance of 2.5428 (14) Å is longer than the normal value of 2.0 Å (see, for example, Neenan, Driessen, Haasnoot & Reedijk, 1996) as a result of the Jahn–Teller effect. The coordination angles around the Cu^{II} ion (Table 2) are mostly very close to the regular octahedral angles, with the exception of the N(amine)—Cu—N(pyridine) angle of 81.99 (6)°, which is due to strain in the five-membered ring imposed by the three-bond ligand bite. Since O22 and O23 lie more than 3.4 Å from the Cu^{II} centre, the nitrate is clearly monodentate.

The amine H atoms are hydrogen bonded to the nitrate anions, forming a two-dimensional network in the *bc* plane, with H181 forming a bifurcated hydrogen bond, intramolecular to O22 and intermolecular to O21, and H182 forming an intermolecular hydrogen bond to O22. The O23 atom is not involved in the hydrogen-bonding network; its bond to the central N atom is significantly shorter than the other N—O bonds of the nitrate anion.

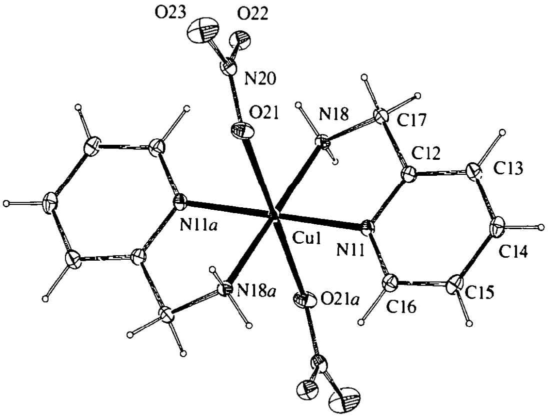


Fig. 1. A view of the title compound showing the atom-labelling scheme. Ellipsoids are drawn at the 30% probability level. Labels with suffix *a* denote atoms generated by symmetry operation $-x, -y, -z$.

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Three structures of the present aminomethylpyridine ligand with copper(I) halides have been reported previously (Healy, Kildea, Skelton & White, 1988), while only the structure of one copper(II) compound with this ligand is found in the literature (O'Connor, Eduok, Owens, Stevens & Klein, 1986), namely $[\mathrm{Cu}L_2(\mathrm{ClO_4})_2]$, which shows a similar elongated octahedral coordination mode around the Cu atom as the present structure. A cadmium complex of the same ligand has been reported by Rodesiler, Charles, Griffith, Lewinski & Amma (1986); this also shows an elongated coordination mode, although it is less pronounced than in the title copper complex.

Experimental

1,5-Bis(2-pyridyl)-2,4-diazapentane was obtained in 90% yield by a Mannich reaction between aminomethylpyridine and formaldehyde, and the absence of starting materials was demonstrated spectroscopically. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.25 (*s*, 2H, CH_2), 3.57 (*s*, 4H, CH_2), 6.79 (*t*, 1H, py-H), 7.14 (*d*, 1H, py-H), 7.29 (*t*, 1H, py-H), 8.16 (*d*, 1H, py-H). A solution of this product (118 mg, 0.517 mmol) in ethanol (10 ml) was added to a solution of $[\mathrm{Cu(H_2O)_3(NO_3)_2}]$ (122 mg, 0.505 mmol) in 7 ml ethanol. The solution was stirred vigorously and filtered. Blue crystals of the title compound appeared after three months at room temperature.

Crystal data

$[\mathrm{Cu(NO_3)_2(C_6H_8N_2)_2}]$
M_r = 403.84
Monoclinic
$P2_1/c$
a = 8.5236 (8) Å
b = 8.9284 (7) Å
c = 9.9279 (8) Å
β = 98.955 (7)°
V = 746.32 (11) Å^3
Z = 2
D_x = 1.797 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10.05–14.16°
μ = 1.51 mm^{-1}
T = 150 K
Plate
0.8 × 0.5 × 0.2 mm
Blue

Data collection

Enraf–Nonius CAD-4T diffractometer with rotating anode
ω scans
Absorption correction: semi-empirical, ψ scan from 3 reflections (*PLATON*; Spek, 1990)
T_{min} = 0.532, T_{max} = 0.739
1956 measured reflections
1703 independent reflections

1557 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 27.49°
$h = -11 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = -8 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R(F)$ = 0.028
$wR(F^2)$ = 0.078
S = 1.032
1703 reflections
139 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.523P]$
where $P = [\max(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.86 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu1	0	0	0	0.0137 (1)
O21	−0.08381 (18)	0.25920 (15)	0.06761 (13)	0.0254 (4)
O22	−0.15355 (17)	0.32767 (15)	−0.14263 (12)	0.0233 (4)
O23	−0.2108 (3)	0.4663 (2)	0.02078 (18)	0.0435 (6)
N11	0.22927 (17)	0.05190 (17)	0.06774 (14)	0.0148 (4)
N18	0.05793 (18)	0.07128 (17)	−0.17664 (14)	0.0159 (4)
N20	−0.14954 (18)	0.35212 (17)	−0.01802 (15)	0.0180 (4)
C12	0.2931 (2)	0.14261 (19)	−0.01695 (17)	0.0165 (5)
C13	0.4469 (2)	0.1972 (2)	0.01613 (19)	0.0211 (5)
C14	0.5380 (2)	0.1535 (2)	0.1366 (2)	0.0216 (5)
C15	0.4736 (2)	0.0567 (2)	0.22222 (18)	0.0202 (5)
C16	0.3191 (2)	0.00927 (19)	0.18505 (19)	0.0180 (5)
C17	0.1886 (2)	0.1805 (2)	−0.14808 (18)	0.0187 (5)

Table 2. *Selected geometric parameters (Å, °)*

Cu1—O21	2.5428 (14)	O21—N20	1.256 (2)
Cu1—N11	2.0191 (15)	O22—N20	1.2514 (19)
Cu1—N18	1.9984 (14)	O23—N20	1.234 (3)
O21—Cu1—N11	90.02 (6)	Cu1—N11—C12	113.30 (11)
O21—Cu1—N18	93.43 (5)	Cu1—N11—C16	127.90 (12)
N11—Cu1—N18	81.99 (6)	Cu1—N18—C17	108.93 (10)
Cu1—O21—N20	122.46 (10)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N18—H181···O22	0.87 (2)	2.47 (3)	2.965 (2)	116.5 (17)
N18—H181···O21^{i}	0.87 (2)	2.27 (2)	3.040 (2)	146 (2)
N18—H182···O22^{ii}	0.88 (2)	2.14 (2)	3.012 (2)	170 (2)

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

Data were collected during 6 h of X-ray exposure time. Reflections were measured with scan angle $\Delta\omega = (0.78 + 0.35\tan\theta)°$; horizontal and vertical aperture were $(2.45 + 1.22\tan\theta)$ and 4.00 mm, respectively. All H atoms were located from a difference Fourier map; their coordinates were included as parameters in the refinement and refined with $U_{iso}(\mathrm{H}) = 1.2U_{eq}(\mathrm{C\ or\ N})$.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SET4* (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *DIRDIF96* (Beurskens *et al.*, 1996). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996). Molecular graphics: *PLUTON* (Spek, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1138). Services for accessing these data are described at the back of the journal.

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Bis[(1,4,7,10-tetraazacyclododecane-κ^4N)(thiocyanato-*S*)copper(II)] Diaquatetrakis(isothiocyanato-*N*)calcate(2–) Dihydrate

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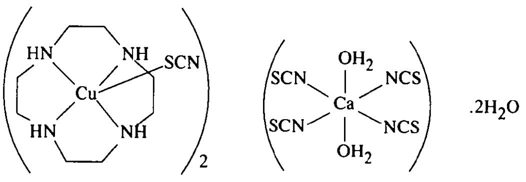
Abstract

The Ca^{II} ion of the title complex, $[Cu(SCN)(C_8H_{20}N_4)]_2$-$[Ca(NCS)_4(H_2O)_2].2H_2O$, is situated at an inversion center. The coordination geometry around the Cu^{II} ion is a symmetrical square pyramid with the tetraamine N atoms equatorial and thiocyanato S atom axial. The four donor N atoms of the macrocyclic ligand form a buckled plane, with the Cu^{II} ion lying 0.553 (1) Å out of this plane towards the thiocyanato group. Hydrogen bonds between the water molecules and thiocyanato groups help stabilize the crystal structure. A water molecule binds the Cu^{II} complex and the Ca^{II} complex together through hydrogen bonds.

Comment

Metal complexes of the thiocyanate ion have been extensively investigated (Burmeister, 1990). One aspect of these compounds which is of interest is the bonding mode of the thiocyanate ligand; either the N or the S atom may be bound to the metal ion. According to Pearson (1963) and Ahrland, Chatt & Davies (1958), S in SCN^- is soft and prefers to coordinate with soft acids (class *b* metals), whereas N in SCN^- is hard and coordinates with hard acids (class *a* metals). The Cu^{II} ion is borderline between hard and soft (Yingst & McDaniel, 1967). Thus, the nature of the other ligands attached to it has a great effect on the coordination behavior of the thiocyanato group (Bennett, Clark & Goodwin, 1967; Wu & Chung, 1986). In order to investigate the influence of the ligand on the Cu^{II} ion, we determined the crystal structure of the title complex, (I).



(I)

The Cu^{II} ion is five coordinate with tetraamine N atoms equatorial and the thiocyanato S atom axial. The distribution of Cu^{II}—N distances, ranging from 2.018 (2) to 2.040 (2) Å, is comparable with the average Cu—N length of 2.03 (3) Å for Cu^{II} macrocyclic complexes (Lu, Chung & Ashida, 1991). All four H atoms of the N—H groups are on the same side of the metal–nitrogen plane. The four donor N atoms of the macrocyclic ligand form a buckled plane, with the Cu^{II} ion lying 0.553 (1) Å above the plane towards the thiocyanato group. The four five-membered rings are in the skew form and the inter-chelate N—Cu—N bond angles are 85.68 (10), 85.39 (9), 85.62 (10) and 86.12 (9)°. The Ca^{II} ion at a special position is six-coordinate with four isothiocyanato N atoms equatorial and two water O atoms axial. Its coordination geometry is octahedral. The Ca—N distances range from 2.386 (3) to 2.436 (3) Å. Hydrogen bonds (Table 2) between coordinated water and the thiocyanato group help stabilize the crystal structure.

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