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catena-Poly[diaquabis(nicotinamide-N^1)-copper(II)-μ-sulfato-O:O']

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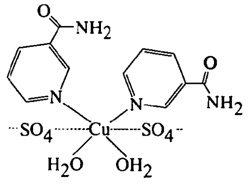
Abstract

The sulfate anion acts as a bridging ligand between the copper(II) ions in the linear polymeric chain of the title compound, $[Cu(SO_4)(C_6H_6N_2O)_2(H_2O)_2]_n$. Distorted octahedral coordination about the copper(II) ion is achieved by two ring N atoms of the nicotinamide groups, in a *cis* conformation [Cu—N 2.016 (3) and 2.018 (3) Å], by two water molecules [Cu—O*W* 1.986 (3) and 1.989 (3) Å], and by two O atoms of two sulfate ligands [Cu—O 2.418 (3) and 2.421 (3) Å].

Comment

During work on coordination compounds of copper carboxylates with the biologically important nicotinamide ligand (*e.g.* Leban, Šegedin & Gruber, 1996), pale-blue crystals of $[Cu(SO_4)(nia)_2(H_2O)_2]_n$ (where nia is nicotinamide, $C_6H_6N_2O$), (I), were accidentally isolated.



(I)

Only a few structures of polymeric diaquacopper(II) complexes with sulfate bridges were found in a survey of the Cambridge Structural Database (Allen & Kennard, 1993): *catena*-(μ-sulfato)-diaqua-(ethylenediamine)-copper(II), AENCUS (Healy *et al.*, 1978) and AENCUS01 (Manríquez *et al.*, 1996); *catena*-(μ-sulfato)-diaqua-(oxamide oxime)-copper(II), CUJDAM (Endres *et al.*, 1984); *catena*-(μ-sulfato)-diaqua-(1,10-phenanthroline-*N*,*N'*)-copper(II), CORHAS (Healy, Patrick & White, 1984); *catena*-[bis(μ-sulfato)-tetraaqua-(μ-2,2'bipyrimidine)-dicopper(II) trihydrate], YOZPOS (De Munno *et al.*, 1995). Additionally, the structure of *catena*-(μ-sulfato)-diaqua-(2,2'-bipyridine)-copper(II) (Tedenac & Philippot, 1975) has been reported.

A fragment of the polymeric chain structure of the title compound, (I), with the atomic numbering is depicted in Fig. 1. Selected bond distances and angles are given in Table 1 and details of the hydrogen bonding are presented in Table 2.

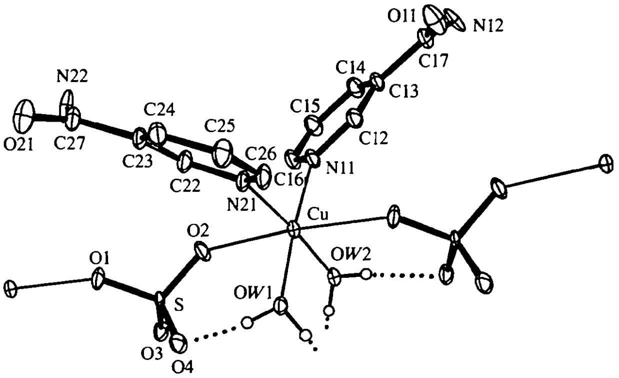


Fig. 1. *ORTEP*II (Johnson, 1971) view of a portion of the chain $[Cu(SO_4)(nia)_2(H_2O)_2]_n$ with the atomic numbering. Anisotropic displacement ellipsoids are drawn at the 30% probability level. H atoms of water molecules are of arbitrary size. Other H atoms have been omitted for clarity.

Distorted octahedral coordination about the Cu^{II} atom is composed of two pyridine N atoms of the nicotinamide groups, in a *cis* orientation [Cu—N 2.016 (3) and 2.018 (3) Å], and two O atoms of water molecules [Cu—O*W* 1.986 (3) and 1.989 (3) Å]; it is completed by two O atoms of two sulfate groups, in the apical positions and at longer distances [Cu—O2 2.418 (3) and Cu—O1 (x, $1+y$, z) 2.421 (3) Å]. An interesting feature of the structure is an array of infinite chains of alternating –O–Cu$(H_2O)_2$(nia)$_2$–O– octahedra and SO_4^{2-} tetrahedra in the **b** direction (Fig. 1). The chains are held together by hydrogen bonds (O—H···O) between the water molecules and the uncoordinated O atoms of the sulfate groups in a neighbouring chain.

The pyridine parts of the two nicotinamide moieties are planar to within 0.016 (3) and 0.017 (3) Å; the dihedral angles between the amide group and the pyridine plane of each of these nicotinamide ligands are 20.9 (3) and 21.7 (3)°. The H atoms of the amide groups are also involved in the hydrogen bonding (N—H···O). Details are given in Table 2.

The SO_4^{2-} tetrahedron is slightly distorted. The S—O distances involving the coordinated O atoms, O1 and O2, are smaller [1.467 (3) and 1.465 (3) Å, respectively] than those involving the uncoordinated O atoms, O3 and O4 [1.484 (3) and 1.482 (3) Å, respectively]. The elongation could be attributed to the rather strong, nearly linear, intramolecular hydrogen bonds involving the water molecules. The O—S—O angles range from 108.23 (16) (O3—S—O4) to 111.46 (16)° (O1—S—O2).

Experimental

$CuSO_4.5H_2O$ and nicotinamide (from commercial sources) were used without further purification. The title compound was prepared by dissolving 5.0 g (20 mmol) of finely ground $CuSO_4.5H_2O$ in 150 ml of H_2O and acidifying with a few drops of 20% H_2SO_4. This solution was thoroughly mixed with a solution of 10.0 g (82 mmol) of nicotinamide in 90 ml of H_2O. The mixture was left at room temperature for 3 d. Pale-blue crystals were filtered off, washed with several portions of absolute ethanol, and dried in air and over KOH under reduced pressure. Average yield: 70%. Thermogravimetric (TG) analysis: found Cu 13.7, C 32.5, H 3.32, N 12.9, H_2O 8.3%; $[Cu(SO_4)(nia)_2(H_2O)_2]$ requires Cu 14.4, C 32.8, H 3.67, N 12.7, H_2O 8.2%. The crystals were sealed in glass capillaries.

Crystal data

$[Cu(SO_4)(C_6H_6N_2O)_2(H_2O)_2]$
$M_r = 439.89$
Monoclinic
$P2_1/c$
$a = 11.019 (2)$ Å
$b = 6.844 (2)$ Å
$c = 21.424 (3)$ Å
$\beta = 93.80 (1)°$
$V = 1612.1 (6)$ Å^3
$Z = 4$
$D_x = 1.812$ Mg m^{-3}
$D_m = 1.80 (5)$ Mg m^{-3}
D_m measured by flotation in CCl_4/bromoform

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–12°$
$\mu = 1.538$ mm^{-1}
$T = 293 (2)$ K
Needle
1.00 × 0.10 × 0.08 mm
Pale blue

Data collection

Nonius CAD-4 diffractometer
Variable $\theta/2\theta$ scans
Absorption correction: by integration
$T_{min} = 0.726$, $T_{max} = 0.899$
6205 measured reflections
3178 independent reflections
2170 reflections with $I > 2\sigma(I)$

$R_{int} = 0.025$
$\theta_{max} = 26°$
$h = -13 \rightarrow 13$
$k = -8 \rightarrow 0$
$l = -26 \rightarrow 26$
3 standard reflections every 300 reflections intensity decay: 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.143$
$S = 1.012$
3178 reflections
247 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1043P)^2]$

$(\Delta/\sigma)_{max} = 0.100$
$\Delta\rho_{max} = 2.072$ e Å^{-3}
$\Delta\rho_{min} = -0.925$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—OW2	1.986 (3)	Cu—O1^i	2.421 (3)
Cu—OW1	1.989 (3)	S—O2	1.465 (3)
Cu—N11	2.016 (3)	S—O1	1.467 (3)
Cu—N21	2.018 (3)	S—O4	1.482 (3)
Cu—O2	2.418 (3)	S—O3	1.484 (3)
OW2—Cu—OW1	90.26 (11)	OW1—Cu—O1^i	87.43 (10)
OW2—Cu—N11	86.84 (13)	N11—Cu—O1^i	89.25 (12)
OW1—Cu—N11	175.64 (12)	N21—Cu—O1^i	94.83 (11)
OW2—Cu—N21	175.36 (12)	O2—Cu—O1^i	174.57 (9)
OW1—Cu—N21	87.19 (12)	O2—S—O1	111.46 (16)
N11—Cu—N21	95.92 (14)	O2—S—O4	109.39 (16)
OW2—Cu—O2	87.13 (10)	O1—S—O4	109.24 (17)
OW1—Cu—O2	88.86 (10)	O2—S—O3	108.95 (17)
N11—Cu—O2	94.24 (11)	O1—S—O3	109.51 (16)
N21—Cu—O2	88.95 (12)	O4—S—O3	108.23 (16)
OW2—Cu—O1^i	88.92 (10)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
OW1—H1···O3^i	0.84 (4)	1.87 (4)	2.697 (4)	169 (4)
OW1—H2···O4	0.85 (3)	1.76 (3)	2.609 (4)	170 (4)
OW2—H3···O4^i	0.78 (4)	1.89 (4)	2.671 (4)	175 (4)
OW2—H4···O3^{ii}	0.73 (3)	1.90 (3)	2.623 (4)	169 (5)
N12—H121···O21^{iii}	0.86	2.05	2.901 (5)	170
N12—H122···OW2^{iv}	0.86	2.29	3.080 (5)	154
N22—H221···O11^v	0.86	2.12	2.979 (5)	173
N22—H222···O11^{vi}	0.86	2.09	2.900 (5)	156

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x, 1+y, z$; (iii) $2-x, \frac{3}{2}+y, \frac{1}{2}-z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $2-x, y-\frac{3}{2}, \frac{1}{2}-z$; (vi) $x, y-1, z$.

The space group $P2_1/c$ was deduced from the systematic absences. All H atoms were found in the difference electron-density map. H atoms (besides those of the water molecules) were placed at calculated positions with isotropic displacement parameters taken from those of the attached heavy atoms and multiplied by 1.2 (or by 1.5 for amide H atoms). H atoms of water molecules were refined with restraints imposed on the O—H and H···H distances, and the angle H—O—H. $\Delta\rho_{max}$ and $\Delta\rho_{min}$ of 2.07 and −0.92 e Å^3 were found at distances of 0.96 and 0.84 Å, respectively, from the Cu atom. Calculations were performed on standard PC (486/16 MB).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1971) and *PLUTON* (Spek, 1991). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1322). Services for accessing these data are described at the back of the journal.

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A Cyano-Bridged Ionic Pair Complex: $[FeNd_2(CN)_6(C_{10}H_8N_2)_4(H_2O)_8][Fe(CN)_6].8H_2O$

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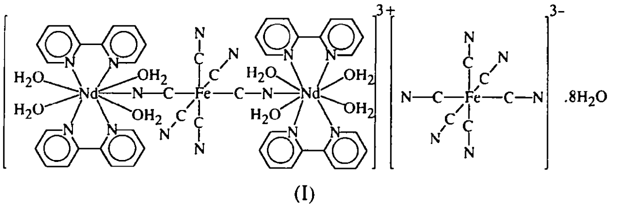
Abstract

The title compound, octaaqua-$2\kappa^4O,3\kappa^4O$-tetrakis(2,2′-bipyridyl)-$2\kappa^4N,N';3\kappa^4N,N'$-di-$\mu$-cyano-$1\kappa C:2\kappa N;$-$1\kappa C:3\kappa N$-tetracyano-$1\kappa^4C$-irondineodymium hexacyanoferrate octahydrate, is an ion-pair complex composed of an octahedral hexacyanoferrate(III) anion, a centrosymmetric cyano-linked [NdFeNd] trinuclear cation and eight solvate water molecules.

Comment

Two kinds of cyano-bridged bimetallic compounds, namely Prussian Blue-like phases and molecular species, have been reported. The former are three-dimensional-network solids and the latter are normally one- or two-dimensional compounds (Kahn, 1995). A few well characterized cyano-bridged molecular compounds have been reported recently (Mullica, Hayward & Sappenfield, 1996; Fu *et al.*, 1997). In the course of our work on 4*f*–3*d* heterometallic compounds, we obtained the title compound, (I), in which an isolated [NdFeNd] trinuclear cation is associated with an octahedral hexacyanoferrate(III) anion.



(I)

In the $[FeNd_2(CN)_6(dipy)_4(H_2O)_8]^{3+}$ (dipy is 2,2′-bipyridyl) trinuclear cation, six CN groups form an octahedral array around the Fe1 atom, which lies on a centre of symmetry. The average length of the Fe1—C distances is 1.937 (4) Å. Each Nd atom is nine-coordinate; the four N atoms of two dipy ligands [Nd—N 2.641 (3)–2.717 (3) Å], one N atom of the cyano group [Nd—N 2.550 (3) Å] and four O atoms of four water molecules [Nd—O 2.436 (3)–2.539 (3) Å] form an approximate tricapped trigonal prism. The three square faces of the prism are defined by the sets of atoms (O1*W*, O2*W*, O4*W*, N1), (O4*W*, N1, N4, N5) and (O1*W*, O2*W*, N4, N5), and the deviation of these atoms from the respective square faces is not larger than 0.08 Å. The three capping species are N2, N3 and O3*W*. The Fe1 atom is connected to two Nd atoms through two bridging cyano groups to form the centrosymmetric trinuclear cation. The bridging C—N bond length is 1.148 (4) Å, which is in the range of reported C—N distances (1.13–1.15 Å) of cyano bridges (Mullica, Hayward & Sappenfield, 1996; Fu *et al.*, 1997). The angles N5—C21—Fe1 and C21—N5—Nd1 are 173.9 (3) and 168.8 (3)°, respectively, deviating slightly from linearity. The distance between Fe1 and Nd1 is 5.583 (2) Å.

The $[Fe(CN)_6]^{3-}$ anion is octahedral with Fe2 lying on a centre of symmetry and with Fe2—C bond lengths in the range 1.936 (4)–1.949 (4) Å. The anion is connected to the trinuclear cation by O4*W*—H4*A*···N10 and O3*W*—H3*A*···N9 hydrogen bonds with O4*W*···N10 and O3*W*···N9 distances 2.912 (5) and 3.078 (5) Å, respectively. Compared with other bimetallic cyanide compounds, the most interesting feature of the structure is the discrete [NdFeNd] trinuclear unit, which is not the same as in the three-dimensional cubic Prussian Blue or other molecular cyanides.