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Diaquabis(2-quinolinecarboxylato-*N*,*O*)-manganese(II)

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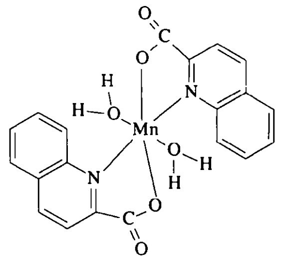
Abstract

The title compound, $[Mn(C_{10}H_6NO_2)_2(H_2O)_2]$, contains a six-coordinate Mn atom at a center of symmetry. The Mn atom displays distorted octahedral coordination. 2-Quinolinecarboxylate anions lie in a *trans* position with respect to one another, forming the equatorial plane, and the water ligands occupy the axial positions. In the equatorial plane, the Mn–ligand distances and the bite angle of the ligand are Mn—O 2.131 (2), Mn—N 2.315 (2) Å and O—Mn—N 74.85 (7)°. In the axial direction, Mn—OH_2 2.185 (2) and O—Mn—N 91.10 (8)°. Molecules are linked by a three-dimensional O—H···O hydrogen-bonding network involving water molecules and carboxylate groups.

Comment

2-Quinolinecarboxylic acid (quinaldinic acid), (I), is one of the final products of tryptophan metabolism and is derived from kynurenic acid (Martin, Mayes & Rodwell, 1983). It inhibits dopamine β-hydroxylase (EC 1.14.17.1), which is a multi-subunit enzyme containing two Cu atoms per subunit (Townes, Titone & Rosenberg, 1990).

2-Quinolinecarboxylic acid is also known to be a potent chelator of copper and other transition metal ions (Martell & Smith, 1974). Accordingly, we have carried out the structure analysis of the chelate compounds of 2-quinolinecarboxylic acid and biologically important metal ions in order to clarify the binding scheme of this metabolite to metal ions. In the present study, the crystal structure of the Mn^{II} complex of 2-quinolinecarboxylic acid, (II), has been determined.



(II)

The structure of the precursor of 2-quinolinecarboxylic acid, kynurenic acid, has been reported (Okabe, Miura & Shimosaki, 1996), and recently the structure of (II) has been reported as the water and ethanol solvate (Haendler, 1996). The molecular structure of (II) with the atom-labeling scheme is shown in Fig. 1. The Mn^{II} atom is coordinated octahedrally by two *trans* quinoline N atoms [Mn1—N1 2.315 (2) Å], by two *trans*-O atoms of the carboxylate groups in position 2 of (I) [Mn1—O2 2.131 (2) Å] and by two *trans*-O atoms of the water molecules [Mn1—O3 2.185 (2) Å]. These Mn^{II}–ligand distances are similar to those values in the water/ethanol solvate [Mn—N 2.324 (3), Mn—O 2.125 (2) and Mn—OH_2 2.209 (3) Å; Haendler, 1996]. The carboxyl group is present in an ionized form and is almost parallel to the quinoline ring plane [O2—C1—C2—N1 −15.4 (3)°]. These conformational features are also observed in the solvated complex (Haendler, 1996). The molecular packing of the crystal

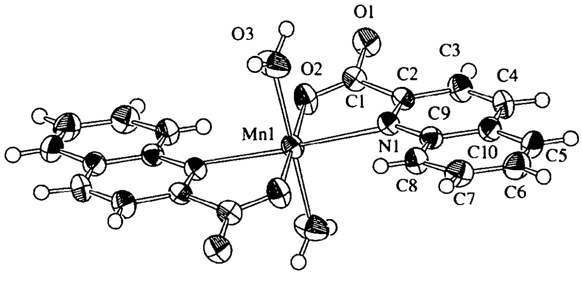


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

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structure is shown in Fig. 2. The crystal structure is stabilized by stacking interaction between quinoline rings and a three-dimensional hydrogen-bonding network between water molecules and carboxylate groups of the neighboring complex: O3—H31···O1^{i} 2.753 (3) Å and O3—H32···O1^{ii} 2.845 (3) Å [symmetry codes: (i) x, y, $-1+z$; (ii) x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$].

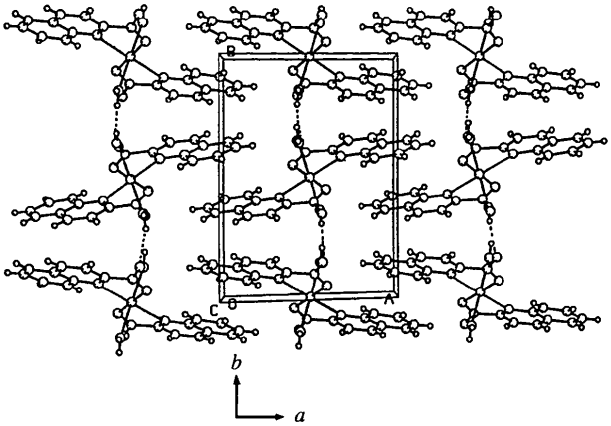

Fig. 2. Packing diagram of the title compound as viewed down the c axis.

Experimental

The light-yellow plate crystal was obtained by the slow evaporation of an aqueous solution of a mixture of 2-quinolinecarboxylic acid and [Mn(CH_3CO_2)$_2$].4H_2O in the molar ratio of 4:1 at room temperature.

Crystal data

[Mn($C_{10}H_6NO_2$)$_2$(H_2O)$_2$]
M_r = 435.30
Monoclinic
$P2_1/c$
a = 10.028 (6) Å
b = 13.118 (7) Å
c = 7.321 (5) Å
β = 107.33 (4)°
V = 919.3 (9) Å^3
Z = 2
D_x = 1.572 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 24 reflections
θ = 18.25–23.40°
μ = 0.729 mm^{-1}
T = 296 K
Plate
0.40 × 0.40 × 0.15 mm
Light yellow

Data collection

Rigaku AFC-6S diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.582, T_{max} = 0.896
2333 measured reflections
2215 independent reflections

1666 reflections with $I > 3\sigma(I)$
R_{int} = 0.019
θ_{max} = 27.5°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 16$
$l = -9 \rightarrow 9$
4 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F
R = 0.035
wR = 0.043
S = 1.670
1666 reflections
165 parameters
H atoms refined isotropically
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mn1	1/2	0	1/2	2.31 (2)
O1	0.5718 (2)	0.1537 (1)	1.0170 (2)	3.06 (6)
O2	0.5952 (2)	0.0525 (1)	0.7845 (2)	3.14 (6)
O3	0.5607 (2)	0.1411 (2)	0.3876 (3)	4.2 (1)
N1	0.3241 (2)	0.0838 (1)	0.5851 (2)	2.11 (6)
C1	0.5241 (2)	0.1045 (2)	0.8652 (3)	2.32 (8)
C2	0.3680 (2)	0.1120 (2)	0.7674 (3)	2.26 (8)
C3	0.2794 (3)	0.1503 (2)	0.8672 (3)	2.85 (9)
C4	0.1403 (3)	0.1597 (2)	0.7737 (3)	2.88 (9)
C5	−0.0529 (3)	0.1461 (2)	0.4710 (4)	3.1 (1)
C6	−0.0959 (3)	0.1244 (2)	0.2809 (4)	3.4 (1)
C7	−0.0002 (3)	0.0890 (2)	0.1905 (3)	3.2 (1)
C8	0.1371 (3)	0.0736 (2)	0.2892 (3)	2.70 (8)
C9	0.1849 (2)	0.0967 (2)	0.4867 (3)	2.24 (7)
C10	0.0893 (2)	0.1341 (2)	0.5788 (3)	2.54 (8)

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

Mn1—O2	2.131 (2)	C3—C4	1.364 (4)
Mn1—O3	2.185 (2)	C4—C10	1.406 (3)
Mn1—N1	2.315 (2)	C5—C6	1.359 (4)
O1—C1	1.250 (3)	C5—C10	1.418 (4)
O2—C1	1.254 (3)	C6—C7	1.397 (4)
N1—C2	1.327 (3)	C7—C8	1.366 (3)
N1—C9	1.378 (3)	C8—C9	1.414 (3)
C1—C2	1.518 (3)	C9—C10	1.414 (3)
C2—C3	1.401 (3)		
O2—Mn1—O3	90.01 (8)	C2—C3—C4	118.9 (2)
O2—Mn1—O3^{i}	89.99 (8)	C3—C4—C10	119.8 (2)
O2—Mn1—N1	74.85 (8)	C6—C5—C10	120.4 (2)
O3—Mn1—N1	91.10 (8)	C5—C6—C7	120.1 (2)
O2—Mn1—N1^{i}	105.15 (8)	C6—C7—C8	121.7 (2)
Mn1—O2—C1	119.0 (1)	C7—C8—C9	119.4 (2)
C2—N1—C9	118.2 (2)	N1—C9—C8	119.4 (2)
O1—C1—O2	125.3 (2)	N1—C9—C10	121.2 (2)
O1—C1—C2	117.0 (2)	C8—C9—C10	119.4 (2)
O2—C1—C2	117.7 (2)	C4—C10—C5	122.7 (2)
N1—C2—C1	116.2 (2)	C4—C10—C9	118.3 (2)
N1—C2—C3	123.6 (2)	C5—C10—C9	119.0 (2)
C1—C2—C3	120.1 (2)		

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

All H atoms were located from difference Fourier maps and included in the refinement calculations isotropically.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1028). Services for accessing these data are described at the back of the journal.

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Tetrakis(μ-benzoato-*O*:*O*′)bis(urea)-1κ*O*,2κ*O*-dicopper(II)

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Abstract

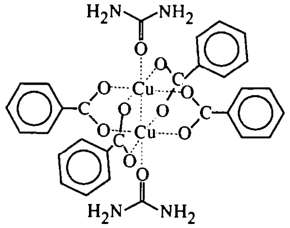
The adduct of tetra-μ-benzoato-dicopper(II) with urea, $[Cu(C_7H_5O_2)_2(CH_4N_2O)]_2$, is dinuclear. Each Cu atom is displaced by 0.195 (3) Å from the plane of the four benzoato O atoms to which it is bonded. The Cu···Cu distance is 2.633 (2) Å. The average Cu—O(benzoate) distance is 1.964 (3) Å and the Cu—O(urea) bond length is 2.156 (6) Å.

Comment

Carboxylic acid complexes of copper(II) are of special chemical and biological interest and accordingly have been extensively studied. Their preparation, structural, magnetic and spectral properties have frequently been described (see Melnik, 1982; Kato & Muto, 1988; Valko, Bilton, Morris & Melnik, 1993; Sundberg, Uggla & Melnik, 1996, and references therein). Our interest in copper(II) carboxylates evolves from their biological activity (Bergant, Petrič, Pohleven, Reberšek & Šegedin, 1994; Grgurevič, Petrič, Pohleven & Šegedin, 1996). Different pharmacological effects have been established for solvated mononuclear and dinuclear complexes (Sorensen, 1983) and fungicidal and insecticidal action is to be anticipated.

Several dinuclear tetrabenzoatocopper(II) complexes of general formula $Cu_2(benz)_4.2L$ (benz = $C_6H_5COO^-$; L = axially bonded neutral ligand) have been structurally characterized. The axial ligands L were: methanol, CH_3OH (DAYJIW); dimethylsulfoxide, $(CH_3)_2SO$ (COCYUO); pyridine, C_5H_5N (BZPRCV, BZPRCV01); quinoline, C_9H_7N (TBZOQC); triphenylphosphine oxide, $(C_6H_5)_3PO$ (PILBIV); benzoic acid, C_6H_5COOH (KUBHOE); β-picoline, C_6H_7N (KUBHUK); 4-methylquinoline, $C_{10}H_9N$ (KUBJAS); 7-methylquinoline, $C_{10}H_9N$ (KUBJIA); 4,7-dichloroquinoline, $C_9H_5Cl_2N$ (KUBJOG); caffeine, $C_8H_{10}N_4O_2$ (KUBJUM) (from the Cambridge Structural Database, October 1995 release, with refcodes in parentheses; Allen & Kennard, 1993). Additionally, the dimeric copper(II) benzoate with *N*,*N*-diethylnicotinamide has been described recently (Hökelek, Necefoğlu & Balci, 1995).

In this paper, we report the structure determination of a dinuclear copper(II) benzoate complex with two urea molecules [urea = $CO(NH_2)_2$, CH_4N_2O] acting as axial ligands (Fig. 1), $Cu_2(benz)_4.2(urea)$, (I).



(I)

The structure analysis confirmed the expected dimeric form. Four bidentate benzoate anions form bridges between Cu atoms which have a 4+1 environment. The coordination sphere around each Cu atom is made up of four O atoms of benzoate groups in the basal plane, the apical position being occupied by the urea O atom. The average Cu—O(basal) distance is 1.964 (3) Å, which is a typical value in dimeric copper carboxylates complexes. The Cu atom is shifted by 0.195 (3) Å out of the plane of the four O atoms towards the axial ligand.

As suggested by Kawata *et al.* (1992), $\varphi_{\rm rot}$ (the dihedral angle between the phenyl and carboxyl planes