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

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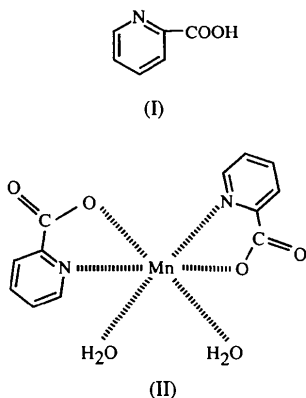
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Abstract

In the title compound, [Mn(C₆H₄NO₂)₂(H₂O)₂], the Mn^{II} atom has a distorted octahedral coordination geometry defined by two N atoms of the pyridine rings, two O atoms of the carboxylate groups and two O atoms of the water molecules; all of the corresponding pairs of the ligand atoms lie in *cis* positions. The carboxylate group is nearly coplanar with the pyridine ring. The crystal structure is stabilized by intermolecular O—H...O hydrogen bonds involving all water H atoms and the carboxylate groups.

Comment

2-Pyridinecarboxylic acid, (I) (also called picolinic acid), is a well known terminal tryptophan metabolite (Mahler & Cordes, 1971) and its crystal structure has been determined (Takusagawa & Shimada, 1973). The association of picolinic acid with divalent cations such as Fe^{II} may induce growth inhibition by withholding them from the cell (Fernandez-Pol, 1977). The anion of (I) has been used as a valuable chelating ligand. The crystal structures of its Ni^{II} and Zn^{II} complexes (Takenaka *et al.*, 1970) and Cu^{II} complex (Faure *et al.*, 1973) have been determined. Kinetic studies of Co^{II}, Cu^{II} and Ni^{II} in solution have also been reported (Das & Dash, 1993).



its chelate-forming properties. Accordingly, the structure of the manganese(II) complex of picolinic acid, (II), has been determined (Fig. 1). The Mn atom is coordinated octahedrally by N atoms of the two pyridine rings [Mn(1)—N(1) 2.272 (2) and Mn(1)—N(2) 2.284 (2) Å], two O atoms of the carboxylate groups [Mn(1)—O(2) 2.142 (2) and Mn(1)—O(4) 2.156 (2) Å] and two O atoms of the water molecules [Mn(1)—O(5) 2.162 (2) and Mn(1)—O(6) 2.148 (2) Å]. As shown in Table 1, the coordinate angles around the Mn atom are considerably distorted from the ideal octahedral values of 90/180°. The main distortions are those of the chelate rings with narrow O—Mn—N angles: O(2)—Mn(1)—N(1) 74.61 (7) and O(4)—Mn(1)—N(2) 73.00 (7)°. These values are much smaller than those observed in other related metal complexes [O—Ni—N 81 and O—Zn—N 80° (Takenaka *et al.*, 1970), and O—Cu—N 83.6 (1)° (Faure *et al.*, 1973)], which, however, have a different ligand arrangement (see below). The two 2-pyridinecarboxylato ligands lie roughly perpendicular to one another, a typical torsion angle being O(2)—Mn(1)—O(4)—C(13) 98.5 (2)°, and all corresponding pairs of ligand atoms lie in *cis* positions. The carboxyl group is ionized and nearly coplanar with the pyridine ring plane; O(2)—C(7)—C(2)—N(1) −3.7 (3) and O(4)—C(13)—C(8)—N(2) 0.7 (4)°

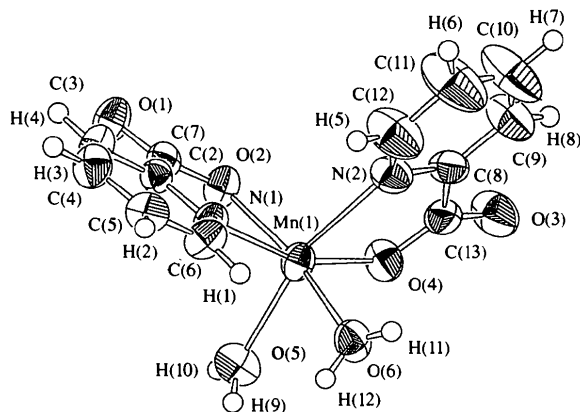


Fig. 1. ORTEP (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability.

In the crystal packing (Fig. 2), the complex molecules are connected into layers running diagonally across the cell by hydrogen bonds between the carboxylate O(1), O(3) and O(4) atoms, and the water O(5) and O(6) atoms as shown in Table 2.

The crystal structure determined in this study is markedly different from those of the Ni^{II} and Zn^{II} complexes (Takenaka *et al.*, 1970) and the Cu^{II} complex (Faure *et al.*, 1973), in all of which the two 2-pyridinecarboxylato ligands lie in the equatorial plane and all of the corresponding pairs of ligand atoms lie not in *cis* but in *trans* positions in the octahedral coordination.

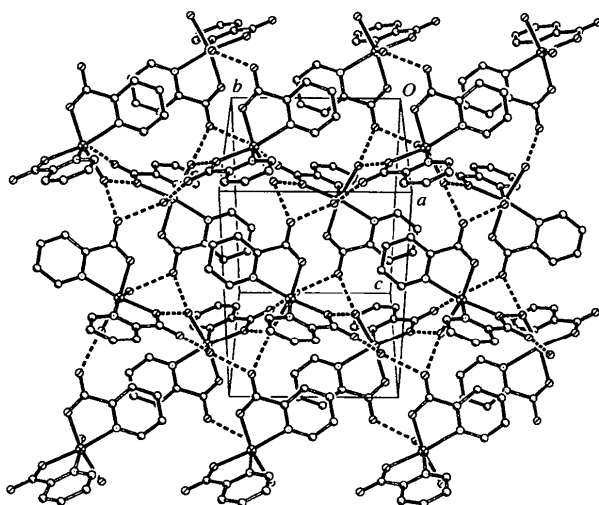


Fig. 2. Packing diagram of the title compound showing one hydrogen-bonded layer; hydrogen bonds are indicated as dashed bonds.

Experimental

A single colorless crystal was obtained by slow evaporation of a 70% methanol solution of a 2:1 molar ratio mixture of 2-pyridinecarboxylic acid and $[\text{Mn}(\text{CH}_3\text{COO})_2] \cdot 4\text{H}_2\text{O}$ at room temperature.

Crystal data

$[\text{Mn}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2]$
 $M_r = 335.17$
 Monoclinic
 $P2_1/n$
 $a = 11.708(2) \text{ \AA}$
 $b = 8.991(2) \text{ \AA}$
 $c = 14.994(2) \text{ \AA}$
 $\beta = 106.46(1)^\circ$
 $V = 1513.6(4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.471 \text{ Mg m}^{-3}$
 D_m not determined

Data collection

Rigaku AFC-5R diffractometer
 ω - 2θ scans
 Absorption correction:
 ψ scans (North *et al.*, 1968)
 $T_{\min} = 0.703$, $T_{\max} = 0.772$
 3876 measured reflections
 3703 independent reflections

Refinement

Refinement on F
 $R = 0.036$
 $wR = 0.046$
 $S = 1.76$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 21.05$ – 23.00°
 $\mu = 0.862 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Prism
 $0.40 \times 0.30 \times 0.30 \text{ mm}$
 Colorless

2601 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = 0 \rightarrow 15$
 $k = 0 \rightarrow 10$
 $l = -19 \rightarrow 18$
 3 standard reflections every 150 reflections
 intensity decay: 0.50%

$(\Delta/\sigma)_{\text{max}} = 0.02$
 $\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
 Extinction correction: none

2601 reflections
 238 parameters
 All H atoms refined
 $w = 4F_o^2/\sigma^2(F_o^2)$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Mn(1)—O(2)	2.142 (2)	Mn(1)—O(6)	2.148 (2)
Mn(1)—O(4)	2.156 (2)	Mn(1)—N(1)	2.272 (2)
Mn(1)—O(5)	2.162 (2)	Mn(1)—N(2)	2.284 (2)
O(2)—Mn(1)—O(4)	93.59 (7)	O(5)—Mn(1)—N(2)	164.02 (8)
O(2)—Mn(1)—O(5)	92.50 (8)	O(6)—Mn(1)—N(1)	93.46 (8)
O(2)—Mn(1)—O(6)	167.11 (7)	O(6)—Mn(1)—N(2)	86.55 (8)
O(2)—Mn(1)—N(1)	74.61 (7)	N(1)—Mn(1)—N(2)	94.51 (8)
O(2)—Mn(1)—N(2)	99.04 (8)	Mn(1)—O(2)—C(7)	119.4 (2)
O(4)—Mn(1)—O(5)	95.40 (7)	Mn(1)—O(4)—C(13)	121.1 (2)
O(4)—Mn(1)—O(6)	99.16 (8)	Mn(1)—N(1)—C(2)	112.8 (1)
O(4)—Mn(1)—N(1)	161.53 (7)	Mn(1)—N(1)—C(6)	129.1 (2)
O(4)—Mn(1)—N(2)	73.00 (7)	Mn(1)—N(2)—C(8)	114.3 (2)
O(5)—Mn(1)—O(6)	84.48 (9)	Mn(1)—N(2)—C(12)	128.0 (2)
O(5)—Mn(1)—N(1)	99.20 (8)		

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O(5)—H(9) \cdots O(3 ⁱ)	0.81 (3)	1.90 (3)	2.701 (3)	170.8 (3)
O(5)—H(10) \cdots O(1 ⁱⁱ)	0.84 (3)	1.89 (4)	2.705 (3)	163.1 (3)
O(6)—H(11) \cdots O(1 ⁱⁱⁱ)	0.79 (3)	1.96 (3)	2.721 (3)	163.4 (3)
O(6)—H(12) \cdots O(4 ⁱ)	0.85 (4)	1.82 (4)	2.669 (3)	173.3 (3)

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

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: *SHELXS86* (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1229). Services for accessing these data are described at the back of the journal.

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Bis(acetonitrile-*N*)diaquatrichloro-erbium(III) Acetonitrile Solvate

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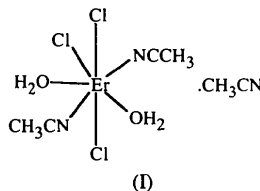
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Abstract

The metal atom in the title compound, [ErCl₃(MeCN)₂(H₂O)₂].MeCN, is seven-coordinate and has a distorted pentagonal-bipyramidal geometry, with two of the chlorines in the axial positions.

Comment

Thionyl chloride dehydration of MCl₃.6H₂O in the presence of tetrahydrofuran (thf) invariably leads to the formation of the solvates MCl₃(thf)_x. However, there are examples where incomplete removal of water is observed. Typically, we have previously isolated the 'mixed' solvates [ThCl₄(thf)₃(H₂O)] (Spry *et al.*, 1997) and [YCl₃(H₂O)₂(MeCN)₂] (Willey *et al.*, 1996). In this report, we describe [ErCl₃(MeCN)₂(H₂O)₂].MeCN, (I), as obtained from the reaction of ErCl₃.6H₂O/SOCl₂/MeCN.



The [ErCl₃(MeCN)₂(H₂O)₂] complex in (I) is represented in Fig. 1. The Er—Cl bond distances range

from 2.6132 (9) to 2.6443 (9) Å, with a mean value of 2.6255 (9) Å. These values compare well with the mean Er—Cl bond distances of 2.590 (2) Å in ErCl₃(triethylene glycol) (Rodgers, Voss & Etzenhouser, 1988) and 2.632 (3) Å in [ErCl₂(12-crown-4)(H₂O)₂]Cl (Rodgers, Rollins & Benning, 1988). The Er—N bond distances of 2.436 (3) and 2.455 (3) Å [mean 2.446 (3) Å] are slightly longer than those found in [ErFe(CN)₆].4H₂O [mean 2.420 (5) Å] (Dommann *et al.*, 1990), but shorter than those in [ErCl(H₂O)₄(terpy)]Cl₂, terpy is terpyridyl (Keppert *et al.*, 1994). Similarly, the Er—O(H₂O) distances of 2.318 (3) and 2.369 (3) Å [mean 2.344 (3) Å] are slightly shorter than those present in [ErCl(H₂O)₄(terpy)]Cl₂ [mean 2.353 (7) Å], but are significantly longer than those found in [ErCl₂(12-crown-4)(H₂O)₂]Cl [mean 3.311 (5) Å].

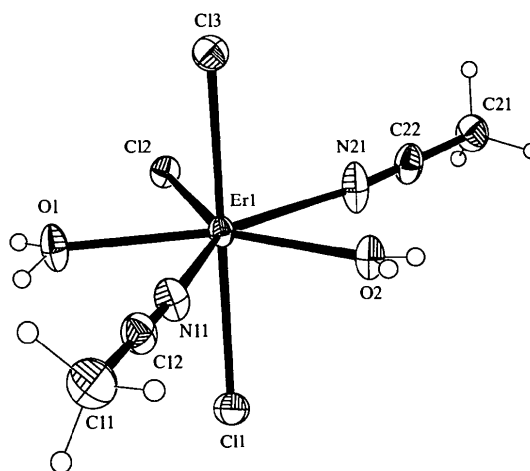


Fig. 1. View of the title complex showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

For the seven-coordinate Er^{III} centre, the metal geometry approximates to distorted pentagonal bipyramidal. The atoms in the equatorial (eq) plane have an r.m.s. deviation from the least-squares plane of only 0.018 Å. The axial (ax) Cl atoms have a Cl—Er—Cl angle of 170.55 (3)°. This non-linearity may be due to the Cl_{ax}—Cl_{eq} repulsions, with a consequent bending of the Cl_{ax}—Er—Cl_{eq} angles to 95.18 (3) and 93.82 (3)°. The equatorial inter-ligand angles are also slightly distorted from the ideal (72°), with the largest angles unsurprisingly involving the single equatorial Cl atom, Cl₂—Er—N₂₁ 72.85 (8) and Cl₂—Er—O₁ 76.38 (7)°. Similar variations are observed in the seven-coordinate ErCl₃(triethylene glycol), viz Cl_{ax}—Er—Cl_{ax} 169.82 (7), and Cl_{eq}—Er—O_{glycol} 80.2 (1) and 79.5 (1)°.

Experimental

The title compound was obtained from the ErCl₃.6H₂O/SOCl₂/MeCN system following heating at reflux for 24 h.