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Poly[methylammonium tri-μ_2-formato-κ^6O:O'-zinc(II)]

Chun-Xiang Wang,* Xiao-Mei Zhou and Wen-Yuan Shi

School of Materials and Chemical Engineering,
Jiangxi University of Science and Technology,
Ganzhou 341000, People's Republic of China

Correspondence e-mail: jxwchx@yahoo.com.cn

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The structure of the polymeric title compound, $\{(CH_6N)[Zn(CHO_2)_3]\}_n$, consists of a three-dimensional anionic zinc formate network charge-compensated by methylammonium cations. The Zn atom (site symmetry $\overline{1}$) adopts a slightly distorted octahedral geometry arising from O atoms from six different formate anions. One complete formate ion is generated by mirror symmetry, and the C and N atoms of the organic cation lie on a mirror plane.

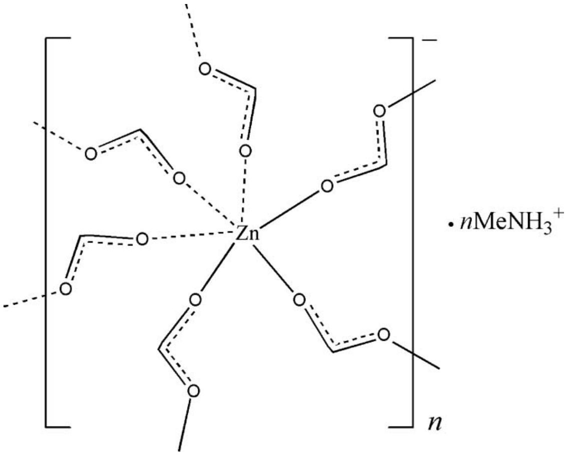
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(N–C) = 0.009 Å
R factor = 0.050
wR factor = 0.115
Data-to-parameter ratio = 15.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Li and coworkers reported the synthesis and properties of a new ligand, 2′-(4,5-diazafluoren-9-ylidene)picolinohydrazide, and its zinc(II) complexes (Li *et al.*, 2006). The initial aim of the present study was the preparation of single crystals of zinc(II) complexes containing the new ligand N,N'-bis(4,5-diazafluoren-9-ylidene)pyridine-2,6-dicarbohydrazide in order to compare with known $[Zn(L)_2(H_2O)_2]\cdot 4H_2O$ complexes (Li *et al.*, 2006). During the synthesis, decomposition of the ligand occurred, to yield the title compound, (I). The mechanism of this decomposition seems to be complicated. The reasons may include the presence of water in the starting complex, the basic nature of pyridine and the acid properties of the remaining part of the ligand. The formation of protonated methylamine is quite common and has been observed in many structures.



(I)

Being isostructural with $[Co(CHO_2)_3]_n.nCH_6N$ (Boča, *et al.*, 2004), complex (I) consists of a three-dimensional network of Zn^{II} ions connected *via* formate (methanediolate) bridges. As depicted in Fig. 1, the central Zn^{II} ion lies on an inversion centre and is coordinated by six carboxyl O atoms from six formate anions to form a slightly distorted octahedron

(Table 1). The mean Zn—O bond distance of 2.108 (2) Å is similar to the mean Co—O distance found in the previously reported isostructural complex.

The two crystallographically independent formate groups (one generated from the asymmetric unit atoms by mirror symmetry) function as bidentate ligands in bridging two metal atoms in an *anti*/*anti* fashion, to result in a three-dimensional anionic framework with protonated methylamine cations in the channels. The closest Zn···Zn distance is 5.842 (1) Å, which is half the length of the diagonal of the *ac* plane. The second-shortest Zn···Zn contact is only slightly longer, at 5.864 (1) Å, which is half the length of the *b* axis.

Two N—H···O hydrogen bonds (Table 2) help to stabilize the crystal structure.

Experimental

An ethanol–dimethylformamide (2:1, *v*/*v*) solution (40 ml) of the ligand *N*,*N*′-bis(4,5-diazafluoren-9-ylidene)pyridine-2,6-dicarbohydrazide (0.5 mmol, 0.15 g) and $Zn(NO_3)_2 \cdot 4H_2O$ (0.25 mmol, 0.26 g) were mixed together, and then five drops of pyridine were added. Red single crystals of (I) suitable for X-ray structure analysis were obtained after two months by slow evaporation of the solvents at room temperature.

Crystal data

$(CH_6N)[Zn(CHO_2)_3]$
$M_r = 232.51$
Orthorhombic, *Pnma*
$a = 8.4127$ (8) Å
$b = 11.727$ (1) Å
$c = 8.1080$ (8) Å
$V = 799.89$ (13) Å^3
$Z = 4$
$D_x = 1.914$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 3.06$ mm^{-1}
$T = 296$ (2) K
Block, red
0.24 × 0.22 × 0.10 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan *SADABS* (Sheldrick, 2003)
$T_{min} = 0.523$, $T_{max} = 0.743$
4334 measured reflections
934 independent reflections
777 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 27.7°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.115$
$S = 1.04$
934 reflections
62 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1236P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.88$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.025 (6)

Table 1
Selected bond lengths (Å).

Zn—O1	2.1065 (16)	Zn—O3^{v}	2.1202 (14)
Zn—O2	2.0948 (14)		

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

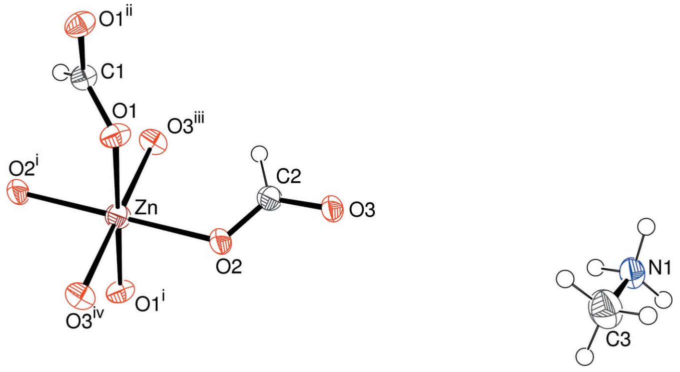


Figure 1
A view of a fragment of (I), showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radius. [Symmetry codes: (i) $-x, 1 - y, -z$; (ii) $x, \frac{3}{2} - y, z$; (iii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, y, z - \frac{1}{2}$.]

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3^{vi}	0.89	2.01	2.889 (4)	170
N1—H1*B*···O1^{vii}	0.89	2.29	3.061 (3)	145

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

C-bound H atoms were positioned geometrically, with C—H = 0.96–0.97 Å, and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}$(methyl C). N-bound H atoms were found in difference maps, relocated in idealized positions with N—H = 0.89 Å, and refined as riding, with $U_{iso}(H) = 1.5U_{eq}(N)$.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2004); software used to prepare material for publication: *SHELXTL*.

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