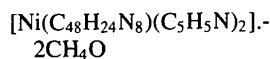## Experimental

The title compound was prepared in quantitative yield by adding 1000 equivalents of pyridine to a 1.4×10^{-4} M solution of [Ni(tpp)(CN)$_4$] (Callot, 1974) in dichloromethane at room temperature. After evaporation of the solvent, the solid was washed with hexane and dried under vacuum, resulting in dark-blue crystalline material. Single crystals suitable for X-ray analysis were obtained by slow diffusion of methanol into a solution of [Ni(tpp)(CN)$_4$] in dichloromethane/pyridine (10:1). ^{1}H NMR (CDCl$_3$, δ, p.p.m.): 49.1 (broad, H$_\beta$), 9.1–7.5 (broad, H$_{phenyl}$). UV–visible (CH$_2$Cl$_2$, λ, nm): 446, 467 (Soret band), 695.

Crystal data

[Ni(C$_{48}$H$_{24}$N$_8$)(C$_5$H$_5$N)$_2$].2CH$_4$O	Mo $K\alpha$ radiation
$M_r = 993.78$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 9.349\,(2)$ Å	$\theta = 18\text{–}20°$
$b = 11.853\,(3)$ Å	$\mu = 0.423$ mm^{-1}
$c = 13.548\,(4)$ Å	$T = 294$ K
$\alpha = 77.92\,(2)°$	Parallelepipedic
$\beta = 69.70\,(2)°$	$0.40 \times 0.35 \times 0.20$ mm
$\gamma = 68.38\,(2)°$	Dark blue
$V = 1303.3\,(6)$ Å^3	
$Z = 1$	
$D_x = 1.27$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius MACH3 diffractometer	3797 reflections with $I > 3\sigma(I)$
$\theta/2\theta$ scans	$R_{int} = 0.016$
Absorption correction:	$\theta_{max} = 25°$
ψ scans (North, Phillips & Mathews, 1968)	$h = -10 \rightarrow 11$
	$k = 0 \rightarrow 14$
$T_{min} = 0.903$, $T_{max} = 0.919$	$l = -15 \rightarrow 16$
4808 measured reflections	3 standard reflections
4564 independent reflections	frequency: 60 min
	intensity decay: none

Refinement

Refinement on F	$w = 4F_o^2/[\sigma^2(F_o^2) + 0.08F_o^4]$
$R = 0.049$	$(\Delta/\sigma)_{max} = 0.005$
$wR = 0.074$	$\Delta\rho_{max} = 0.111$ e Å^{-3}
$S = 1.651$	$\Delta\rho_{min} = -0.120$ e Å^{-3}
3797 reflections	Extinction correction: none
331 parameters	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
H atoms included but not refined	

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

Ni—N1	2.030 (2)	C7—C11	1.434 (3)
Ni—N2	2.079 (2)	C8—C12	1.428 (3)
Ni—N5	2.240 (2)	C11—N3	1.139 (3)
C2—C3	1.343 (3)	C12—N4	1.146 (3)
C7—C8	1.374 (4)		
C1—N1—C4	106.8 (2)	C7—C11—N3	173.6 (3)
C6—N2—C9	108.7 (2)	C8—C12—N4	173.6 (3)

No H atoms could be located for the methanol solvent.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIF IN* in *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1059). Services for accessing these data are described at the back of the journal.

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Zinc(II) Acetate Dihydrate

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Abstract

The Zn atom in bis(acetato-O,O')diaquazinc(II), [Zn(CH$_3$COO)$_2$(H$_2$O)$_2$], adopts a distorted octahedral structure coordinated by two water O atoms and four acetate O atoms.

Comment

The structure of the title complex, (I), is important for models of Zn soaps and Zn ionomers. Van Niekerk, Schoening & Talbot (1953) reported the crystal structure using two-dimensional intensity data. However, an EXAFS study (Vlaic, Williams, Jérome, Tant & Wilkes, 1988) revealed that the structure is somewhat incorrect. We report here the rerefined structure of (I) using three-dimensional intensity data with an R factor of 0.060.

(I)
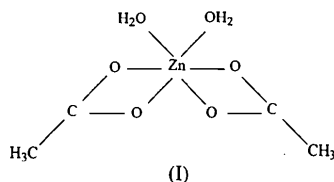
It can be seen from Fig. 1 that the title complex takes a six-coordinate structure and that the coordination geometry around the Zn^{II} ion is approximately octahedral. The Zn atom is coordinated by the two O atoms of the water molecules and four O atoms of the acetate ligands. Van Niekerk, Schoening & Talbot (1953) reported bond lengths for Zn—OH₂ of 2.14 Å and for Zn— O(carboxylate) of 2.17 and 2.18 Å. We found Zn—OH₂ to be 1.987 (4) Å and Zn—O(carboxylate) 2.179 (4) and 2.189 (5) Å. Similar six-coordinate structures were also observed for the corresponding Zn^{II} complexes of several diaquabis(carboxylato)zinc(II) compounds (Smith, O'Reilly, Kennard, Stadnicka & Oleksyn, 1981; Mak, Yip, Smith, O'Reilly & Kennard, 1984; Chan et al., 1987; O'Reilly, Smith, Kennard & Mak, 1987; Smith, Lynch, Mak, Yip & Kennard, 1993). Their averaged Zn—OH₂ distance is 1.996 (3) Å and Zn—O(carboxylate) distances are 2.112 (3) and 2.296 (2) Å. While our result for Zn—OH₂ [1.987 (4) Å] is consistent with their results, the Zn—O distances are slightly different.

The C—O lengths are 1.256 (7) and 1.260 (7) Å, which are comparable with those found by Van

Niekerk, Schoening & Talbot (1953) (1.30 and 1.38 Å). The present results are consistent with those found in both diaquabis(p-chlorophenoxyacetato)zinc(II) [1.260 (3) and 1.266 (3) Å; Smith, O'Reilly, Kennard, Stadnicka & Oleksyn, 1981] and diaquabis[(phenylthio)-acetato]zinc(II) [1.245 (6) and 1.256 (6) Å; Mak, Yip, Smith, O'Reily & Kennard, 1984].

An EXAFS study found that the averaged Zn— O(carboxylate) length increases with increasing coordination number (Pan, Knapp & Cooper, 1984). This is confirmed here: the averaged Zn—O length in four coordination is 1.957 (2) Å (Clegg, Little & Straughan, 1986), in five coordination is 2.016 (2) Å (Montgomery & Lingafelter, 1963) and in six coordination is 2.188 (4) Å (present work). Intermolecular hydrogen bonds are observed between O1···O2(−x, y − 1, ½ − z) [2.675 (6) Å] along the b axis and O1···O3(−x, −y, −z) [2.711 (6) Å] along the c axis as found previously by Van Niekerk, Schoening & Talbot (1953).

Experimental

The title compound was prepared as the dihydrate by recrystallization from an aqueous solution.

Crystal data

[Zn(C₂H₃O₂)₂(H₂O)₂]	Cu $K\alpha$ radiation
$M_r = 219.50$	$\lambda = 1.5418$ Å
Monoclinic	Cell parameters from 24
$C2/c$	reflections
$a = 14.394\,(3)$ Å	$\theta = 76.07$–$79.92°$
$b = 5.330\,(2)$ Å	$\mu = 4.097$ mm⁻¹
$c = 10.962\,(3)$ Å	$T = 292\,(1)$ K
$\beta = 99.88\,(2)°$	Plate
$V = 828.4\,(4)$ Å³	$0.75 \times 0.30 \times 0.25$ mm
$Z = 4$	Colorless
$D_x = 1.760$ Mg m⁻³	
D_m not measured	

Data collection

Rigaku AFC-5R diffractometer	738 independent reflections
$\omega/2\theta$ scans	$R_{int} = 0.062$
Absorption correction:	$\theta_{max} = 62.84°$
empirical via ψ scan	$h = 0 \rightarrow 16$
(North, Phillips &	$k = 0 \rightarrow 6$
Mathews, 1968)	$l = -12 \rightarrow 13$
$T_{min} = 0.295$, $T_{max} = 0.359$	3 standard reflections
764 measured reflections	every 150 reflections
	intensity decay: −0.54%

Refinement

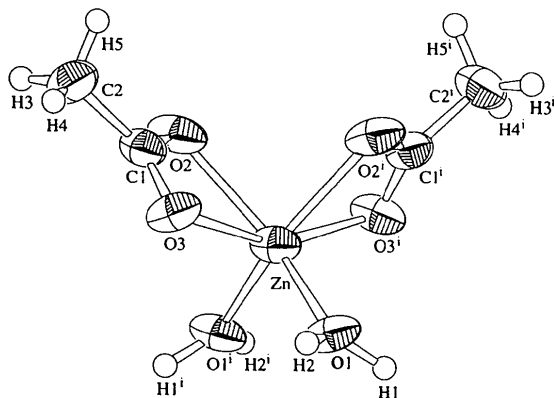|	
Refinement on F	$\Delta\rho_{max} = 0.67$ e Å⁻³
$R = 0.060$	$\Delta\rho_{min} = -0.53$ e Å⁻³
$wR = 0.118$	Extinction correction:
$S = 2.280$	Zachariasen type 2
659 reflections	Gaussian isotropic
51 parameters	(Zachariasen, 1968)
H atoms not refined	Extinction coefficient: none

Fig. 1. The molecular structure of the title complex showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary size. [Symmetry code: (i) −x, y, ½ − z.]

$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.0240$

Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

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

	x	y	z	U_{eq}
Zn	0	0.1304 (1)	1/4	0.0478 (5)
O1	−0.0828 (4)	−0.1128 (7)	0.1453 (4)	0.051 (1)
O2	0.1043 (3)	0.4319 (9)	0.2606 (3)	0.055 (1)
O3	0.0695 (3)	0.2158 (9)	0.0933 (3)	0.052 (1)
C1	0.1147 (4)	0.3940 (10)	0.1503 (6)	0.043 (2)
C2	0.1733 (5)	0.570 (1)	0.0880 (6)	0.054 (2)

Table 2. *Selected geometric parameters ($\mathring{A}$, °)*

Zn—O1	1.987 (4)	O2—C1	1.260 (7)
Zn—O2	2.189 (5)	O3—C1	1.256 (7)
Zn—O3	2.179 (4)	C1—C2	1.503 (8)
O1—Zn—O1^i	98.6 (3)	O2—Zn—O3	59.0 (1)
O1—Zn—O2	147.9 (2)	O3—Zn—O3^i	155.9 (3)
O1—Zn—O2^i	96.3 (2)	Zn—O2—C1	91.4 (4)
O1—Zn—O3	89.5 (2)	Zn—O3—C1	92.0 (3)
O1—Zn—O3^i	106.3 (2)	O2—C1—O3	117.5 (5)
O2—Zn—O2^i	85.5 (2)	O2—C1—C2	120.3 (6)
O2—Zn—O3^i	102.0 (2)	O3—C1—C2	122.0 (5)

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

H atoms were fixed at ideal positions with common isotropic displacement parameters ($U_{iso} = 0.0657 \, \mathring{A}^2$).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b). Program(s) used to solve structure: *PATTY* in *DIRDIF92* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1020). Services for accessing these data are described at the back of the journal.

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{Tris[N-(salicylidene)-2-aminoethyl]amine}-tin(IV) Iodide Acetonitrile Solvate†

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Abstract

The crystal structure of the title compound, $[Sn(C_{27}H_{27}-N_4O_3)]I.0.5CH_3CN$, involves two almost identical complex cations in the asymmetric unit. These cations contain Sn atoms in a pseudo-octahedral environment with facial coordination of the azomethine N and the phenolate O atoms. The average Sn—O and Sn—N bond lengths are 2.048 (4) and 2.192 (5) $\mathring{A}$, respectively, while the apical N atom in the ligand is considered to be non-bonded at an average distance of 2.687 (5) $\mathring{A}$ from the Sn atom.

Comment

The crystal structure of the potentially heptadentate N_4O_3 Schiff base ligand derived from three moles of salicylaldehyde and tris(2-aminoethyl)amine (tren), known as $(sal)_3$tren $[H_3L^1$, (1)], has been reported (Gunduz *et al.*,1985). Metal complexes of the type $[M(L^1)]$ formed from the reaction of H_3L^1 with tripositive metal ions (M^{3+}) have been found to be either six coordinate with the apical N atom uncoordinated when M^{3+} is Co^{III} (Elerman, Kabak, Svoboda & Geselle, 1994) and Mn^{III} (Drew, Harding, McKee, Morgan & Nelson, 1995; Chandra & Chakravorty, 1991), or seven coordinate with all four N atoms bonded when M^{3+} is Bi^{III} (Bharadwaj, Lee, Mandal, Skelton & White,

† Alternative name: {2,2',2''-[nitrilotris(ethylenenitrilomethylidyne-κN)]triphenolato-$\kappa^3 O$}tin(IV) iodide 0.5-acetonitrile solvate.