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# (Acetato-*O*)(*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*,*N'*,*N''*,*N'''*)zinc(II) Perchlorate Monohydrate

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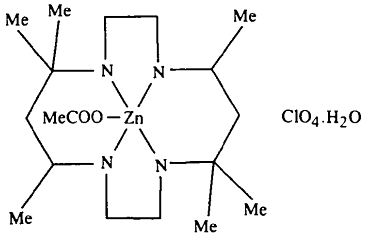
## Abstract

The crystal structure of the title compound, $[Zn(C_2H_3O_2)(C_{16}H_{36}N_4)]ClO_4.H_2O$, has been determined. The coordination about the $Zn^{2+}$ atom is distorted square pyramidal, with the four N atoms of the macrocycle in the basal positions and the coordinating O atom of the acetate group along the axial axis. The Zn—O and average Zn—N bond lengths are 1.997 (3) and 2.128 (3) Å, respectively.

## Comment

The macrocyclic ligand, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, exists as two isomers, teta (*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and tetb (*rat*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) (Curtis, 1964). The coordination behaviour of macrocyclic tetraamine ligands with $Cu^{2+}$ and $Ni^{2+}$ has been widely studied both chemically and crystallographically. The structures of the binuclear $Cu^{2+}$ complex with tetb (Bauer, Robinson & Margerum, 1973), and the mononuclear $Cu^{2+}$ and $Ni^{2+}$ complexes with teta (Clay, Murray-Rust & Murray-Rust, 1979) and tetb (Lu, Wu & Chung, 1986; Shen, Lee, Lu, Liang & Chung, 1983; Curtis, Swann & Waters, 1973) have been determined. We report here the structure of $[Zn(teta)(CH_3COO)]ClO_4.H_2O$, (I), which is part of a long-term research study of non-linear optical properties.



(I)

An *ORTEP*II (Johnson, 1976) plot of the cation of (I) with the atomic numbering scheme is shown in Fig. 1. The $Zn^{2+}$ atom is coordinated in a buckled square pyramid, with the four N atoms of the macrocyclic ligand in the basal positions and the coordinating O atom of the $CH_3COO^-$ ligand axial. The four N atoms of the macrocyclic ligand form a square plane [the mean deviation is 0.0142 (10) Å], with the $Zn^{2+}$ atom lying 0.4048 (10) Å out of this plane towards the acetate group. The perchlorate anion and $H_2O$ molecule are not coordinated to the metal ion. No crystal field stabilization energy is operative upon complexation of the $d^{10}$ metal ion and thus there is no particular preference for geometry in zinc(II) complexes. The resultant geometry of zinc(II) complexes must therefore be dictated solely by steric factors. The bulky methyl groups and protons in the macrocyclic ligand hinder the axial position opposite the acetate group and thus bonding of a sixth ligand in this position is difficult. The average Zn—N bond length is 2.128 (3) Å, longer than that found in $[Zn(1,4,8,11\text{-tetraazacyclotetradecane})(NCS)_2]$ [2.104 (11) Å; Ito, Kato & Ito, 1984] and shorter than that in $[Zn(1,4,8,11\text{-tetramethyl-1,4,8,11-tetraazacyclotetradecane})Cl]^-$ [2.197 (9) Å; Alcock, Herron & Moore, 1978]. The Zn—O bond length is 1.997 (3) Å, which is shorter than that found in (1,4,8,11-tetraazacyclotetradecane-*N*,*N'*,*N''*,*N'''*-dihydrogentetraacetato)zinc tetrahydrate [2.127 (1) Å; Riesen, Zehnder & Kaden, 1991].

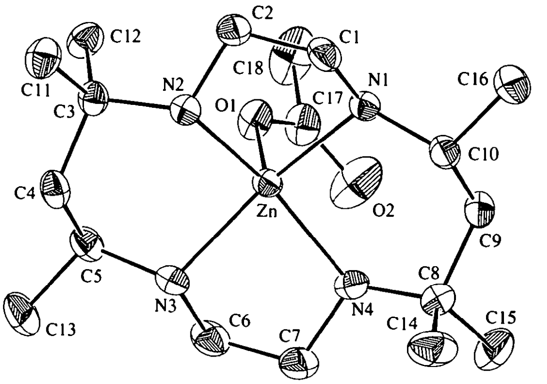


Fig. 1. The structure of the cation of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

As shown in Fig. 1, the complex is characterized by the fact that both five-membered chelate rings are in stable twist conformations and both six-membered chelate rings are in chair conformations. All bond angles and distances are normal.

There is an intermolecular O3—H···O2($-x$, $-\frac{1}{2}+y$, $-z$) hydrogen bond of 2.707 (6) Å between the $H_2O$ molecule and the acetate group in the crystal lattice. The non-centrosymmetric $P2_1$ space group makes the title compound a potential non-linear optical material.

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## Experimental

The 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ligand was prepared according to the procedure of Hay, Lawrance & Curtis (1975). The ligand (285 mg, 1 mmol) and zinc acetate trihydrate (237 mg, 1 mmol) were dissolved in ethanol (20 ml) and the mixture stirred and heated for 1 h. $NaClO_4$ (123 mg, 1 mmol) dissolved in ethanol (5 ml) was then added and the resulting solution was allowed to stand at room temperature for a few days whereupon crystals suitable for X-ray structure analysis were formed (found: C 41.06, H 7.86, N 10.23%; calculated for $C_{18}H_{41}ClN_4O_7Zn$: C 41.07, H 7.85, N 10.64%).

### *Crystal data*

$[Zn(C_2H_3O_2)(C_{16}H_{36}N_4)]$-$ClO_4.H_2O$
$M_r = 526.38$
Monoclinic
$P2_1$
$a = 8.683\ (3)$ Å
$b = 16.309\ (5)$ Å
$c = 9.216\ (4)$ Å
$\beta = 99.25\ (3)°$
$V = 1288\ (1)$ Å$^3$
$Z = 2$
$D_x = 1.36$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.97$–$17.92°$
$\mu = 1.119$ mm$^{-1}$
$T = 296$ K
Rectangular
0.60 × 0.40 × 0.36 mm
Colorless

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* $\psi$ scans (*TEXSAN*; Molecular Structure Corporation, 1987)
$T_{min} = 0.9558$, $T_{max} = 1.000$
2810 measured reflections
2737 independent reflections

2631 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.034$
$\theta_{max} = 26°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 20$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 200 reflections intensity decay: 5.8%

### *Refinement*

Refinement on $F$
$R = 0.034$
$wR = 0.044$
$S = 1.47$
2631 reflections
279 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.18$
$\Delta\rho_{max} = 0.47$ e Å$^{-3}$
$\Delta\rho_{min} = -0.52$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Zn | 0.26875 (4) | 0.0059 | 0.10998 (3) | 2.83 (1) |
| O1 | 0.2082 (4) | 0.0857 (2) | 0.2555 (3) | 4.2 (1) |
| O2 | −0.0098 (6) | 0.1342 (3) | 0.1322 (6) | 8.1 (2) |
| N1 | 0.3896 (4) | 0.0859 (2) | −0.0155 (3) | 3.2 (1) |
| N2 | 0.4989 (4) | −0.0285 (2) | 0.2083 (3) | 3.1 (1) |
| N3 | 0.1805 (4) | −0.1053 (2) | 0.1829 (4) | 3.3 (1) |
| N4 | 0.0603 (3) | 0.0040 (3) | −0.0465 (3) | 3.5 (1) |
| C1 | 0.5574 (5) | 0.0675 (3) | 0.0230 (5) | 4.1 (2) |
| C2 | 0.5946 (5) | 0.0432 (3) | 0.1842 (5) | 4.2 (2) |
| C3 | 0.5251 (4) | −0.0633 (3) | 0.3605 (4) | 3.4 (1) |
| C4 | 0.4139 (5) | −0.1361 (3) | 0.3635 (4) | 3.9 (2) |
| C5 | 0.2368 (5) | −0.1215 (3) | 0.3405 (5) | 3.9 (2) |
| C6 | 0.0075 (6) | −0.0932 (3) | 0.1427 (6) | 4.7 (2) |
| C7 | −0.0279 (5) | −0.0706 (3) | −0.0166 (6) | 5.2 (2) |
| C8 | 0.0516 (5) | 0.0273 (3) | −0.2033 (4) | 4.1 (2) |
| C9 | 0.1580 (6) | 0.1027 (3) | −0.2096 (4) | 4.3 (2) |
| C10 | 0.3343 (5) | 0.0898 (3) | −0.1776 (4) | 3.7 (1) |
| C11 | 0.6922 (2) | −0.0973 (4) | 0.3993 (5) | 4.8 (2) |
| C12 | 0.4975 (5) | 0.0020 (4) | 0.4723 (4) | 4.3 (1) |
| C13 | 0.1553 (8) | −0.1951 (4) | 0.3974 (7) | 6.2 (3) |
| C14 | 0.1005 (8) | −0.0421 (4) | −0.2934 (6) | 6.4 (3) |
| C15 | −0.1177 (7) | 0.0544 (4) | −0.2643 (6) | 6.4 (3) |
| C16 | 0.4177 (7) | 0.1594 (4) | −0.2456 (6) | 5.6 (2) |
| C17 | 0.0975 (6) | 0.1363 (3) | 0.2364 (5) | 4.3 (2) |
| C18 | 0.099 (1) | 0.2027 (5) | 0.3499 (7) | 8.1 (4) |
| O3 | 0.2076 (5) | −0.2500 (3) | 0.0001 (5) | 7.1 (2) |
| Cl | 0.4398 (2) | 0.31848 (8) | 0.1371 (1) | 5.09 (5) |
| O4 | 0.5291 (9) | 0.2532 (4) | 0.1933 (8) | 10.9 (4) |
| O5 | 0.3772 (8) | 0.3661 (4) | 0.2359 (6) | 10.4 (3) |
| O6 | 0.527 (2) | 0.3617 (6) | 0.055 (1) | 18.1 (8) |
| O7 | 0.326 (1) | 0.2924 (9) | 0.029 (1) | 20.7 (8) |

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

| | | | |
|---|---|---|---|
| Zn—O1 | 1.997 (3) | Zn—N2 | 2.132 (3) |
| Zn—N3 | 2.123 (3) | O1—C17 | 1.256 (5) |
| Zn—N4 | 2.125 (3) | O2—C17 | 1.226 (6) |
| Zn—N1 | 2.131 (3) | | |
| O1—Zn—N3 | 101.3 (1) | N3—Zn—N1 | 158.7 (1) |
| O1—Zn—N4 | 100.3 (1) | N3—Zn—N2 | 90.1 (1) |
| O1—Zn—N1 | 99.9 (1) | N4—Zn—N1 | 94.6 (1) |
| O1—Zn—N2 | 102.4 (1) | N4—Zn—N2 | 157.2 (1) |
| N3—Zn—N4 | 83.7 (2) | N1—Zn—N2 | 83.2 (1) |

The title structure was solved by direct methods and refined by full-matrix least squares. All H atoms were located in difference Fourier maps. All calculations were carried out on a MicroVAX 3100 computer.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1987). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: KH1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Alcock, N. W., Herron, N. & Moore, P. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1282–1288.
Bauer, R. A., Robinson, W. R. & Margerum, D. W. (1973). *J. Chem. Soc. Chem. Commun.* pp. 289–290.
Clay, R., Murray-Rust, P. & Murray-Rust, J. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1135–1139.
Curtis, N. F. (1964). *J. Chem. Soc.* pp. 2644–2650.

Curtis, N. F., Swann, D. A. & Waters, T. N. (1973). *J. Chem. Soc. Dalton Trans.* pp. 1963–1974.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Department of Chemistry, University of Glasgow, Scotland.
Hay, R. W., Lawrance, A. G. & Curtis, N. F. (1975). *J. Chem. Soc. Perkin Trans.* 1, pp. 591–593.
Ito, T., Kato, M. & Ito, H. (1984). *Bull. Chem. Soc. Jpn*, **57**, 2634–2640.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lu, T.-H., Wu, D.-T. & Chung, C.-S. (1986). *J. Chem. Soc. Dalton Trans.* pp. 1999–2001.
Molecular Structure Corporation (1987). *TEXSAN. TEXRAY Structure Analysis Package*. Version 2.1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Riesen, A., Zehnder, M. & Kaden, T. A. (1991). *Acta Cryst.* C**47**, 531–533.
Shen, H.-R., Lee, T.-J., Lu, T.-H., Liang, B.-F. & Chung, C.-S. (1983). *Proc. Natl Sci. Counc. B Rep. China*, **7**, 113–115.

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# Sodium Hydrogen L-Tartrate

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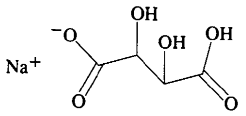
## Abstract

Crystals of sodium hydrogen L-tartrate, $Na^+.C_4H_5O_6^-$, were grown from an aqueous solution at 393 K in a closed vessel. An asymmetric O—H···O hydrogen bond is formed between the hydrogen L-tartrate anions [O···O 2.476 (3) Å]. The H atom involved in the hydrogen bond is disordered. The sodium ion is coordinated by six O atoms, in contrast to the eight atoms about other alkali metal ions in their hydrogen L-tartrates.

## Comment

The crystals of alkali metal hydrogen L-tartrates, $M^+.C_4H_5O_6^-$ ($M^+$ = $K^+$, $Rb^+$, $Cs^+$), belong to space group $P2_12_12_1$ and are isostructural with one another (Buschmann & Luger, 1985; Templeton & Templeton, 1978, 1989). The corresponding sodium salt crystallizes as a monohydrate from an aqueous solution at room temperature (Bott, Sagatys, Lynch, Smith & Kennard, 1993; Kubozono, Hirano, Nagasawa, Maeda & Kashino, 1993). Packing considerations showed that sodium hydrogen L-tartrate, (I), may not crystallize as an anhydrate which is isostructural with the other alkali metal salts under ambient conditions (Kubozono *et al.*, 1993).



(I)

The crystals of sodium hydrogen L-tartrate (Fig. 1) obtained at 393 K belong to space group $P2_1$. The chain of four C atoms in the anion has the usual planar zigzag conformation [C1—C2—C3—C4 177.5 (2)°] and lies nearly on (101). A disordered O—H···O hydrogen bond is formed between the anions related by a **c** translation. This disordering was confirmed by careful examination of both the $\Delta\rho$ maps and the results of the least-squares refinement. Bond distances around the C1 and C4 atoms indicate that C1 has a larger carboxyl character than C4, as is also suggested by the occupancy factor of the disordered H atom. The O···O distance is shorter than those found in the corresponding hydrogen bonds in the monohydrate of (I) [2.533 (3) Å; Kubozono *et al.*, 1993] and in the acid salts of the other alkali metals [2.531 (1), 2.559 (3) and 2.575 (3) Å for K, Rb and Cs, respectively; Buschmann & Luger, 1985; Templeton & Templeton, 1978, 1989]. The OH groups attached to atoms C2 and C3 donate a hydrogen bond to the O6 atom of the ion

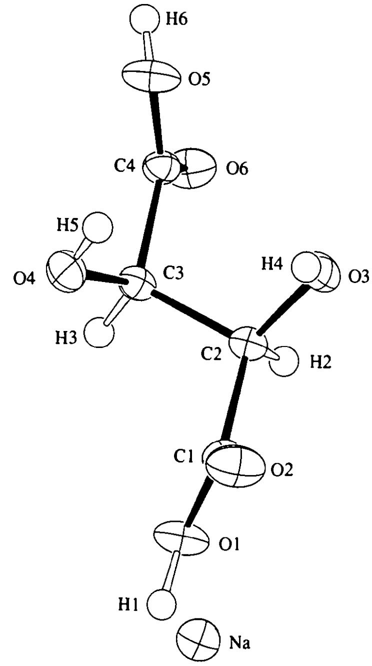


Fig. 1. A displacement ellipsoid plot of (I) with the atomic numbering scheme. Ellipsoids of 50% probability are shown for non-H atoms and H atoms are represented as spheres equivalent to $B$ = 1.0 Å$^2$. Atoms H1 and H6 are disordered, their occupancy factors being 0.58 (2) and 0.42 (2), respectively.

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