

O(W1) and O(W2). Both O(W1) and O(W2) are hydrogen bonded to O(1) and O(3) of the neighboring molecules, so the cobaloxime complexes are connected along the *b* axis. In (II), one of the H atoms of the amino group of *A* is hydrogen bonded to the O(2*A*) atom of a neighboring molecule, and the two H atoms of the amino group of *B* are hydrogen bonded to O(1*A*) and O(1*B*) atoms of neighboring molecules. Except for this hydrogen bonding there are no short contacts between the molecules in both crystals.

The reaction cavities for the 2-cyanoethyl groups of (I) and (II) were drawn (Ohashi, Uchida, Sasada & Ohgo, 1983) and the volumes of the cavities were calculated to be 12.24 Å<sup>3</sup> for (I) and 13.31 Å<sup>3</sup> for *A* and 16.69 Å<sup>3</sup> for *B* of (II), respectively. The average value for (II) is 14.99 Å<sup>3</sup>. The rates of isomerization were obtained from the change of IR spectra of the C≡N stretching mode, assuming first-order kinetics in the early stages (Sekine, 1989). The rate constants for (I) and (II) are  $1.2 \times 10^{-4}$  and  $1.5 \times 10^{-4} \text{ s}^{-1}$ , respectively. The relation between the reaction cavity and the isomerization rate holds good for the present crystals, as observed in the crystals of 3-ethylpyridine and 4-ethylpyridine complexes (Sekine, Ohashi, Shimizu & Hori, 1991), although the conformations of 2-cyanoethyl groups in 3-ethylpyridine and 4-ethylpyridine complexes are parallel to the cobaloxime plane, whereas those in (I) and (III) take perpendicular conformations. This may indicate that

the  $\beta$ - $\alpha$  (2 $\rightarrow$ 1) photoisomerization is controlled by the crystalline lattice in the early stages in spite of the different conformation of the reactive group.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. We thank Professor Y. Ohgo and Dr S. Baba for their valuable discussion, and Miss E. Shimizu for assistance with the crystal structure determination.

#### References

- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- OHASHI, Y. (1988). *Acc. Chem. Res.* **21**, 268–274.
- OHASHI, Y., UCHIDA, A., SASADA, Y. & OHGO, Y. (1983). *Acta Cryst.* **B39**, 54–61.
- OHGO, Y. & TAKEUCHI, S. (1985). *J. Chem. Soc. Chem. Commun.* pp. 21–23.
- OHGO, Y., TAKEUCHI, S., NATORI, Y., YOSHIMURA, J., OHASHI, Y. & SASADA, Y. (1981). *Bull. Chem. Soc. Jpn.* **54**, 3095–3099.
- SEKINE, A. (1989). Masters thesis, Ochanomizu Univ., Japan.
- SEKINE, A., OHASHI, Y., SHIMIZU, E. & HORI, K. (1991). *Acta Cryst.* **C47**, 53–56.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- UCHIDA, A. (1985). Doctorate thesis, Tokyo Institute of Technology, Japan.
- UCHIDA, A., DANNNO, M., SASADA, Y. & OHASHI, Y. (1987). *Acta Cryst.* **B43**, 528–532.

*Acta Cryst.* (1991). **C47**, 528–531

## Structure of Zinc(II) (*RS*)-1-Isopropyl Citrate Tetrahydrate

BY SUMIKO TSUJI, TADASHI SHIBATA AND YOSHIO ITO

*Osaka Branch, National Institute of Hygienic Sciences, 1-1-43 Hoenzaka, Chuo-ku, Osaka 540, Japan*

AND SATOSHI FUJII AND KEN-ICHI TOMITA

*Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565, Japan*

(Received 7 June 1990; accepted 14 August 1990)

**Abstract.** *catena*-Poly{diaquazinc- $\mu$ -[1-isopropyl citrato(2-)- $\kappa$ O, $\kappa$ O', $\kappa$ O'': $\kappa$ O''']}, [Zn(C<sub>9</sub>H<sub>12</sub>O<sub>7</sub>)(H<sub>2</sub>O)<sub>2</sub>].2H<sub>2</sub>O, *M*<sub>r</sub> = 369.62, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.934 (4), *b* = 29.692 (3), *c* = 8.941 (4) Å,  $\beta$  = 144.73 (2)°, *V* = 1522.7 (7) Å<sup>3</sup>, *Z* = 4, *D*<sub>m</sub> = 1.610 (3), *D*<sub>x</sub> = 1.612 Mg m<sup>-3</sup>,  $\lambda$ (Cu *K* $\alpha$ ) = 1.54178 Å,  $\mu$  = 2.741 mm<sup>-1</sup>, *F*(000) = 768, *T* = 283 K, final *R* = 0.0346 for 2089 observed reflections. Each 1-isopropyl citrate chelates to a diaquazinc ion in a tridentate manner through the end carboxyl, the

central carboxyl and the hydroxyl O atoms and bridges another diaquazinc ion with its end carboxyl O atom. This leads to extended chelated strips with bridged Zn atoms. Other water molecules are hydrogen bonded to the aqua ligands or 1-isopropyl citrates of the chelated strips. The strips are packed through van der Waals bonds.

**Introduction.** Isopropyl citrate, which is more oil soluble than citric acid, has been developed as a

synergistic antioxidant (Joint FAO/WHO Expert Committee on Food Additives, 1978). Isopropyl citrate is a mixture of citric acid and 1-isopropyl, 2-isopropyl, 1,2-isopropyl, 1,3-isopropyl and triisopropyl citrate (Tsuji, Tonogai, Ito & Harada, 1985) and the purification and chemical structure of its components have been studied (Tsuji, Tonogai, Ito & Fukuoka, 1986). While citric acid chelates various metals and this structural chemistry is clarified by X-ray determination of crystal structures (Nordman, Weldon & Patterson, 1960; Glusker, van der Helm, Love, Dornberg, Minkin, Johnson & Patterson, 1965; Johnson, 1965; Carrell & Glusker, 1973; Strouse, Layten & Strouse, 1977; Swanson, Ilsley & Stanislawski, 1983). However, the chelation of 1-isopropyl citrate, the stable component of isopropyl citrate, has not been studied. The present study was undertaken to clarify the structural chemistry of the chelated 1-isopropyl citrate ion.

**Experimental.** (*RS*)-1-Isopropyl dihydrogen citrate was prepared according to the procedure described in our previous paper (Tsuji, Tonogai, Ito & Fukuoka, 1986). Zinc (*RS*)-1-isopropyl citrate was obtained from a mixture of zinc acetate (Ishizu Pharmaceutical Co.) in 90% methanol and 1-isopropyl dihydrogen citrate in methanol, and crystallized from dilute acetic acid solution; density by flotation in a mixture of carbon tetrachloride and ethylene bromide; crystal dimensions  $0.3 \times 0.2 \times 0.2$  mm, Rigaku automatic four-circle diffractometer (AFC-5R-300),  $\omega$ - $2\theta$  scanning technique ( $2\theta_{\max} = 126^\circ$ ), graphite-monochromatized  $\text{Cu K}\alpha$  radiation, unit-cell dimensions by least-squares procedure based on  $2\theta$  values ( $46 < 2\theta < 60^\circ$ ) of 48 reflections, intensity fluctuation ( $< 2.6\%$ ) monitored periodically by four reflections ( $\bar{2}51$ ,  $0,16,1$ ,  $404$ ,  $504$ ); 2089 unique reflections ( $-11 \leq h \leq 6$ ,  $0 \leq k \leq 34$ ,  $0 \leq l \leq 10$ ); Lorentz and polarization corrections, but not absorption; structure solved by *SHELX86* (Sheldrick, 1986) and refined by block-diagonal least squares with anisotropic temperature factors for all non-H atoms; all H atoms located from a difference Fourier map and refined with isotropic temperature factors fixed at the  $B_{\text{eq}}$  values of the non-H atoms to which they are attached;  $R = 0.0346$  ( $wR = 0.0547$ ,  $S = 1.46$ ) for 2089 observed reflections ( $F_o \neq 0$ ) and 271 variables; function minimized:  $\sum w(|F_o| - k|F_c|)^2$ , where  $w = 1/[\sigma^2(F_o) - 0.0188|F_o| + 0.0014 \times |F_o|^2]$  and  $k$  is the scale factor; highest and lowest residuals in final difference Fourier map:  $0.44$  and  $-0.40 \text{ e } \text{\AA}^{-3}$ ;  $(\Delta/\sigma)_{\max} = 0.58$  for non-H atoms; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 72–75); program system *UNICS* (1979) on the ACOS 930 computer of the Protein Engineering

Research Center, Institute for Protein Research, Osaka University.

**Discussion.** Final positional and thermal parameters are listed in Table 1.\* Bond distances and angles are shown in Table 2. The molecular conformation with the atomic numbering for diaquazinc (*S*)-1-isopropyl citrate is given in Fig. 1.

The Zn atom is coordinated to six O atoms and there are no shared edges. The 1-isopropyl citrate ion is chelated to the Zn atom as a tridentate ligand with the hydroxyl O(5) atom and two carboxyl O atoms, O(3) from the central carboxyl group and O(7) from the end carboxyl group, ligated. This is a similar arrangement to that found in triionized citrate complexes of magnesium (Johnson, 1965), manganese(II) (Carrell & Glusker, 1973), iron(II) (Strouse, Layten & Strouse, 1977) and zinc(II) (Swanson, Ilsley & Stanislawski, 1983). But the remaining three ligands of the isopropyl citrate complex are different from those of the citrate complexes above. The remaining three O atoms of the octahedron are two water O atoms, O(1*W*) and O(2*W*), and the carboxyl O(6) atom of another isopropyl citrate ion ( $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ).

The shortest edge distance of the octahedron is  $2.622(4) \text{ \AA}$  between the hydroxyl O(5) atom and the central carboxyl O(3) atom. The longest distance is  $3.201(5) \text{ \AA}$  between the end carboxyl O(6) atom and the water O(2*W*) atom.

The four atoms O(3), O(7), O(1*W*), O(2*W*) are planar, the maximum deviation from the best plane being  $0.049(5) \text{ \AA}$ . The Zn atom deviates from this plane by  $0.104(2) \text{ \AA}$  toward the O(6) ligand. The angles ligand–Zn–ligand in this plane are nearly  $90^\circ$ .

The associated Zn–O(5) and Zn–O(7) distances of  $2.157(3)$  and  $2.138(3) \text{ \AA}$  are the longest of this type in these structures. These Zn–ligand bonds may be weaker than other Zn–ligand ones because of the hydroxyl O(5) and acid O(7) atoms.

The five C atoms of the backbone, C(6), C(3), C(2), C(1) and C(4), lie nearly on a plane with a maximum deviation of  $0.102(7) \text{ \AA}$ . This *trans*-zigzag coplanarity is common to the citrate chelates of  $\text{Zn}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$  and  $\text{Mg}^{\text{II}}$ . The torsion angle defined by the atoms O(3), C(5), C(2), O(5) is  $26.3(5)^\circ$ .

The O atoms, O(3*W*) and O(4*W*), of two of the water molecules are associated with the terminal carboxyl O(6) atom and the neighboring aqua ligands O(1*W*), O(2*W*) and the esterified carboxyl O(2) atom through hydrogen bonds. There are inter-

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53487 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and temperature factors

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
Zn	0.40782 (6)	0.29500 (1)	0.26672 (7)	2.25 (3)
C(1)	0.5585 (6)	0.4184 (1)	0.1684 (6)	2.2 (2)
C(2)	0.5355 (5)	0.3682 (1)	0.1776 (5)	1.6 (2)
C(3)	0.5032 (6)	0.3430 (1)	0.0011 (6)	2.0 (2)
C(4)	0.6436 (6)	0.4454 (1)	0.3778 (7)	2.6 (3)
C(5)	0.7627 (5)	0.3507 (1)	0.4596 (6)	1.9 (2)
C(6)	0.4655 (5)	0.2922 (1)	-0.0246 (6)	1.7 (2)
C(7)	0.8115 (8)	0.5165 (1)	0.5979 (7)	3.7 (3)
C(8)	1.0615 (8)	0.5059 (2)	0.8428 (8)	5.0 (4)
C(9)	0.7690 (10)	0.5637 (1)	0.4979 (10)	6.3 (5)
O(1)	0.7077 (5)	0.4864 (1)	0.3904 (5)	3.2 (2)
O(2)	0.6593 (6)	0.4326 (1)	0.5177 (6)	4.1 (3)
O(3)	0.7385 (4)	0.3192 (1)	0.5318 (4)	2.3 (2)
O(4)	0.9506 (4)	0.3675 (1)	0.5912 (4)	2.9 (2)
O(5)	0.3462 (3)	0.3595 (1)	0.1070 (4)	1.7 (1)
O(6)	0.5044 (4)	0.2709 (1)	-0.1105 (4)	2.1 (2)
O(7)	0.3960 (4)	0.2734 (1)	0.0280 (4)	2.5 (2)
O(1 <i>W</i> )	0.0646 (4)	0.2795 (1)	-0.0170 (4)	2.6 (2)
O(2 <i>W</i> )	0.4180 (5)	0.3201 (1)	0.4949 (5)	3.2 (2)
O(3 <i>W</i> )	0.9326 (5)	0.2921 (1)	0.1503 (6)	4.5 (3)
O(4 <i>W</i> )	0.2295 (7)	0.6216 (1)	0.1210 (7)	5.8 (4)

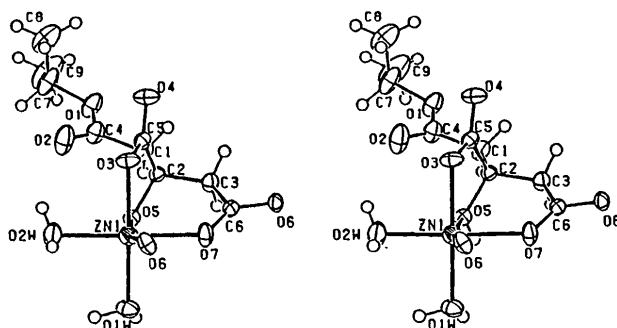
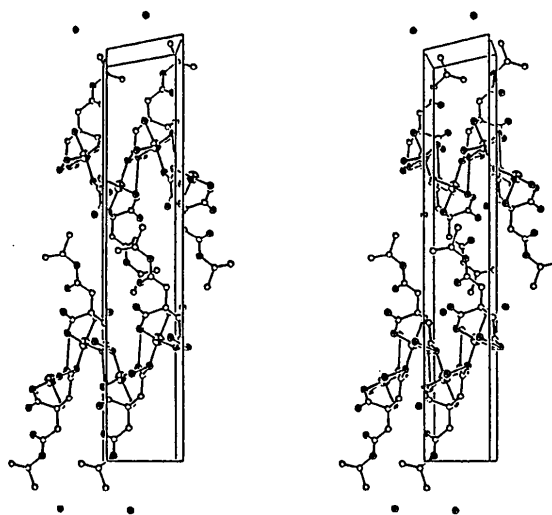
Table 2. Bond distances (Å) and angles (°)

Zn—O(3)	2.052 (3)	O(3)—Zn—O(5)	77.0 (1)
Zn—O(5)	2.157 (3)	O(3)—Zn—O(7)	89.4 (1)
Zn—O(7)	2.138 (3)	O(3)—Zn—O(2 <i>W</i> )	89.5 (1)
Zn—O(1 <i>W</i> )	2.037 (3)	O(3)—Zn—O(6')	96.1 (1)
Zn—O(2 <i>W</i> )	2.095 (4)	O(5)—Zn—O(7)	81.4 (1)
Zn—O(6')	2.058 (3)	O(5)—Zn—O(1 <i>W</i> )	95.4 (1)
C(1)—C(2)	1.520 (6)	O(5)—Zn—O(2 <i>W</i> )	95.2 (1)
C(1)—C(4)	1.510 (7)	O(7)—Zn—O(1 <i>W</i> )	91.0 (1)
C(2)—C(3)	1.525 (6)	O(6')—Zn—O(7)	82.4 (1)
C(2)—C(5)	1.558 (6)	O(6')—Zn—O(1 <i>W</i> )	91.5 (1)
C(2)—O(5)	1.436 (5)	O(6')—Zn—O(2 <i>W</i> )	100.8 (1)
C(3)—C(6)	1.527 (7)	O(1 <i>W</i> )—Zn—O(2 <i>W</i> )	89.7 (1)
C(4)—O(1)	1.334 (6)	C(2)—C(1)—C(4)	114.2 (4)
C(4)—O(2)	1.189 (7)	C(1)—C(2)—C(3)	109.8 (4)
C(5)—O(3)	1.267 (5)	C(1)—C(2)—C(5)	109.4 (3)
C(5)—O(4)	1.238 (5)	C(1)—C(2)—O(5)	110.8 (3)
C(6)—O(6)	1.274 (6)	C(3)—C(2)—O(5)	111.3 (3)
C(6)—O(7)	1.242 (6)	C(5)—C(2)—O(5)	107.3 (3)
C(7)—C(8)	1.478 (9)	C(2)—C(3)—C(6)	117.3 (4)
C(7)—C(9)	1.525 (10)	C(1)—C(4)—O(1)	109.5 (4)
C(7)—O(1)	1.477 (7)	C(1)—C(4)—O(2)	126.4 (5)
O(3 <i>W</i> )H...O(6)	2.780 (6)	O(1)—C(4)—O(2)	124.0 (5)
O(3 <i>W</i> )H...O(1 <i>W</i> <sup>iv</sup> )	2.951 (6)	C(2)—C(5)—O(3)	116.3 (4)
O(3 <i>W</i> )...HO(1 <i>W</i> <sup>iv</sup> )	2.702 (6)	C(2)—C(5)—O(4)	118.1 (4)
O(3 <i>W</i> )...HO(4 <i>W</i> <sup>iv</sup> )	2.945 (7)	O(3)—C(5)—O(4)	125.5 (4)
O(4 <i>W</i> )H...O(2')	2.902 (7)	C(3)—C(6)—O(6)	115.1 (4)
O(4 <i>W</i> )...HO(2 <i>W</i> <sup>iv</sup> )	2.723 (7)	C(3)—C(6)—O(7)	122.1 (4)
O(1 <i>W</i> )H...O(3 <sup>iv</sup> )	2.611 (4)	O(6)—C(6)—O(7)	122.7 (4)
O(2 <i>W</i> )H...O(7)	2.819 (5)	C(8)—C(7)—C(9)	113.0 (5)
O(5)H...O(4 <sup>iv</sup> )	2.679 (4)	C(8)—C(7)—O(1)	109.7 (5)
		C(9)—C(7)—O(1)	104.2 (5)
		C(4)—O(1)—C(7)	117.0 (4)

Symmetry code: (i)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iii)  $x + 1, y, z$ ; (iv)  $-x + 1, -y + 1, -z + 1$ ; (v)  $-x + 1, -y + 1, -z + 1$ ; (vi)  $x - 1, y, z - 1$ .

molecular hydrogen bonds between the aqua ligands O(1*W*), O(2*W*) or hydroxy O(5) and the carboxyl atoms O(3), O(7), O(4) of neighboring isopropyl citrate molecules.

A stereoview of the crystal packing in the unit cell is illustrated in Fig. 2. Each isopropyl citrate ligand

Fig. 1. Molecular conformation with atomic numbering of diaqua-zinc (*S*)-1-isopropyl citrate.Fig. 2. Stereoscopic drawing of the molecular packing viewed along the *a* axis. The thin lines indicate hydrogen bonds.

bridges two Zn atoms which are related by a *c*-glide operation. This leads to an infinite fern-like chelated system which extends along the *c* axis and is different from that of the citrate chelates. These chelate systems are packed in the cell with a crystallographic inversion center. The intermolecular hydrogen bonds between water molecules and isopropyl citrates form an infinite three-dimensional network.

## References

- CARRELL, H. L. & GLUSKER, J. P. (1973). *Acta Cryst.* **B29**, 638–640.
- GLUSKER, J. P., VAN DER HELM, D., LOVE, W. E., DORNBERG, M. L., MINKIN, J. A., JOHNSON, C. K. & PATTERSON, A. L. (1965). *Acta Cryst.* **19**, 561–572.
- JOHNSON, C. K. (1965). *Acta Cryst.* **18**, 1004–1017.
- JOINT FAO/WHO EXPERT COMMITTEE ON FOOD ADDITIVES (1978). *FAO Food and Nutrition*, Paper No. 4, p. 221.
- NORDMAN, C. E., WELDON, A. S. & PATTERSON, A. L. (1960). *Acta Cryst.* **13**, 414–417, 418–426.

SHELDRICK, G. M. (1986). *SHELX86*. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.

STROUSE, J., LAYTEN, S. W. & STROUSE, C. E. (1977). *J. Am. Chem. Soc.* **99**, 562–572.

SWANSON, R., ILSLEY, W. H. & STANISLAWSKI, A. G. (1983). *J. Inorg. Biol.* **18**, 187–194.

TSUJI, S., TONOGAI, Y., ITO, Y. & FUKUOKA, M. (1986). *Eisei Kagaku*, **32**, 185–190.

TSUJI, S., TONOGAI, Y., ITO, Y. & HARADA, M. (1985). *J. Food Hyg. Soc. Jpn.* **26**, 357–364.

UNICS (1979). *The Universal Crystallographic Computing System* – Osaka. Library of Programs, Computation Center, Osaka Univ., Japan.

*Acta Cryst.* (1991). **C47**, 531–533

## Structures of Two $Zn^{2+}$ Complexes with Two Tetraaza Macrocyclic Tetraacetates

BY ANDREAS RIESEN, MARGARETA ZEHNDER AND THOMAS A. KADEN

*Institute of Inorganic Chemistry, University of Basel, CH-4056 Basel, Switzerland*

(Received 9 October 1989; accepted 28 August 1990)

**Abstract.** (1,4,7,10-Tetraazacyclododecane-*N,N,N',N''*-dihydrogentetraacetato)zinc,  $[Zn(C_{16}H_{26}N_4O_8)]$  (1),  $M_r = 467.77$ , orthorhombic, *Pccn*,  $a = 9.354$  (4),  $b = 15.294$  (7),  $c = 13.114$  (4) Å,  $V = 1876.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.656$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 1.293$  mm<sup>-1</sup>,  $F(000) = 976$ ,  $T = 298$  K,  $R = 0.048$  for 1620 reflections with  $I \geq 2\sigma(I)$ . (1,4,8,11-Tetraazacyclotetradecane-*N,N',N'',N'''*-dihydrogentetraacetato)zinc tetrahydrate,  $[Zn(C_{18}H_{30}N_4O_8)] \cdot 4H_2O$  (2),  $M_r = 567.89$ , monoclinic, *P2<sub>1</sub>/c*,  $a = 8.695$  (2),  $b = 15.456$  (7),  $c = 8.993$  (2) Å,  $\beta = 90.46$  (2)°,  $V = 1208.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.561$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 1.022$  mm<sup>-1</sup>,  $F(000) = 600$ ,  $T = 298$  K,  $R = 0.029$  for 2267 reflections with  $I \geq 2\sigma(I)$ . In both  $Zn^{2+}$  complexes the metal ion is coordinated by four nitrogens of the macrocycle and two carboxylate oxygens. The other two carboxylate moieties are protonated and are not involved in coordination, but form hydrogen bonds. Due to the ring size of the macrocycle, the geometry around the  $Zn^{2+}$  is, however, different in the two complexes. In (1) the  $Zn^{2+}$  is in a *cis*-octahedral arrangement, whereas in (2) a *trans*-octahedral coordination is observed with the  $Zn^{2+}$  in the plane of the four nitrogens of the macrocycle. The configuration of the macrocycle is *cis*-I and *trans*-III for (1) and (2), respectively.

**Introduction.** The coordination behaviour of macrocyclic tetraacetates with  $Cu^{2+}$  and  $Ni^{2+}$  has been studied chemically and crystallographically (Riesen, Zehnder & Kaden, 1985, 1986, 1988). The structures of the binuclear  $Cu^{2+}$  complexes with dota (dota = 1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetic acid) and teta (teta = 1,4,8,11-tetraazacyclotetradecane-*N,N',N'',N'''*-tetraacetic acid), as well as those of the mononuclear  $Cu^{2+}$  and  $Ni^{2+}$  complexes with dota and that of the mononuclear  $Cu^{2+}$  complex of teta have shown how complicated and many-

fold the geometry around the metal ion can be. In continuation of these studies we have now solved the structures of two  $Zn^{2+}$  complexes, which have the same stoichiometry  $Zn(LH_2)$  ( $L = \text{dota}^{4-}$  or  $\text{teta}^{4-}$ , see Fig. 1), but completely different geometries.

**Experimental.** Crystals of  $Zn(\text{dotaH}_2)$  and  $Zn(\text{tetaH}_2) \cdot 4H_2O$  were prepared as described in the literature (Riesen, Zehnder & Kaden, 1986). An Enraf–Nonius CAD-4 diffractometer controlled by a Digital MicroVAX computer was used for the measurements. The Mo  $K\alpha$  radiation was graphite monochromated. Cell parameters were obtained on a crystal  $0.4 \times 0.3 \times 0.3$  mm for (1) and  $0.3 \times 0.3 \times 0.2$  mm for (2) from the setting angles of 25 strong reflections in the range  $8 \leq \theta \leq 12^\circ$  and  $10 \leq \theta \leq 20^\circ$ , respectively. A total of 2344 and 2738 reflections ( $2 \leq \theta \leq 27^\circ$ ) were measured in the range  $h \leq 11$ ,  $k \leq 19$ ,  $l \leq 16$  and  $-11 \leq h \leq 11$ ,  $k \leq 19$ ,  $l \leq 11$  for (1) and (2), respectively, by the  $\omega/2\theta$  scan technique. No significant variation was observed in the intensities of four standards [ $\bar{4}72$ ,  $\bar{4}16$ ,  $\bar{5}34$ ,  $\bar{5}50$  for (1) and  $\bar{4}10$ , 402, 214,  $\bar{4}11$  for (2)] monitored every 3600 s. The raw data set was corrected for polarization effects. The structures were solved by direct methods using *SHELXS86* (Sheldrick, 1986). All H atoms were located by difference Fourier mapping. Anisotropic

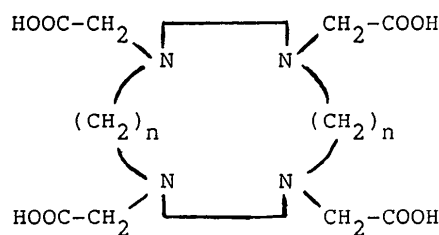


Fig. 1. The structure of  $\text{dotaH}_4$  ( $n = 2$ ) and  $\text{tetaH}_4$  ( $n = 3$ ).