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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

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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, $V = 1876.1$ Å³, $Z = 4$, $D_x = 1.656$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.293$ mm⁻¹, $F(000) = 976$, $T = 298$ 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, *P2₁/c*, $a = 8.695$ (2), $b = 15.456$ (7), $c = 8.993$ (2) Å, $\beta = 90.46$ (2)°, $V = 1208.4$ Å³, $Z = 2$, $D_x = 1.561$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.022$ mm⁻¹, $F(000) = 600$, $T = 298$ 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 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

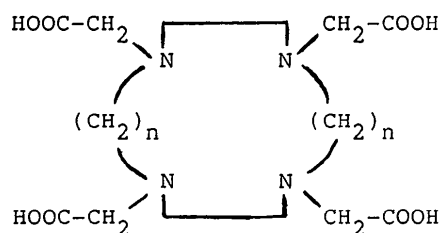


Fig. 1. The structure of dotaH_4 ($n = 2$) and tetaH_4 ($n = 3$).

Table 1. Fractional atomic coordinates and U_{eq} values ($\text{\AA}^2 \times 10^{-2}$) for (1)

	$U_{eq} = (1/3)\sum_i U_{ii}$			U_{eq}
	x	y	z	
Zn	0.2500	0.2500	0.3613 (1)	2.88
O(1)	0.1584 (3)	0.3254 (2)	0.2512 (2)	3.99
O(2)	0.0001 (4)	0.4318 (2)	0.2241 (2)	4.54
C(1)	0.0804 (5)	0.3887 (3)	0.2803 (3)	3.41
C(2)	0.0902 (5)	0.4158 (3)	0.3915 (4)	3.76
N(2)	0.1575 (4)	0.3498 (2)	0.4588 (2)	3.56
C(3)	0.2759 (5)	0.3875 (3)	0.5206 (3)	3.85
C(4)	0.4084 (6)	0.4005 (3)	0.4575 (4)	4.21
C(5)	0.5387 (5)	0.2597 (3)	0.4588 (4)	4.04
C(6)	0.0504 (6)	0.3041 (3)	0.5219 (3)	4.00
N(1)	0.4510 (4)	0.3214 (2)	0.3997 (3)	3.28
C(7)	0.5214 (6)	0.3444 (3)	0.3041 (4)	3.99
C(8)	0.6690 (5)	0.3840 (3)	0.3121 (4)	4.14
O(3)	0.7259 (3)	0.4036 (2)	0.3907 (3)	4.87
O(4)	0.7273 (4)	0.3937 (37)	0.2206 (3)	5.73

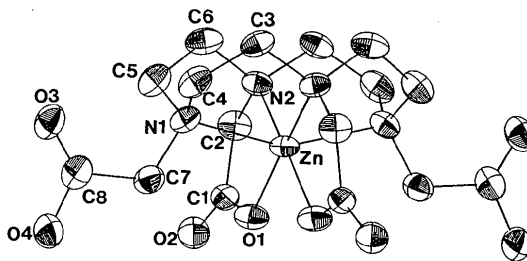
Table 2. Fractional atomic coordinates and U_{eq} values ($\text{\AA}^2 \times 10^{-2}$) for (2)

	$U_{eq} = (1/3)\sum_i U_{ii}$			U_{eq}
	x	y	z	
Zn	0.5000	0.0	0.0	1.93
N(1)	0.3324 (2)	0.0184 (1)	0.1654 (2)	2.23
C(1)	0.1930 (2)	-0.0237 (2)	0.1015 (3)	2.86
C(2)	0.2304 (3)	-0.1105 (2)	0.0306 (3)	2.89
N(2)	0.3377 (2)	-0.0994 (1)	-0.0960 (2)	2.35
C(3)	0.4317 (3)	-0.1785 (1)	-0.1239 (3)	2.83
C(4)	0.4419 (3)	0.1664 (2)	0.2381 (3)	3.05
C(5)	0.3030 (3)	0.1122 (1)	0.1935 (3)	2.79
C(6)	0.3812 (3)	-0.0266 (1)	0.3039 (2)	2.60
C(7)	0.5210 (2)	-0.0853 (1)	0.2863 (2)	2.27
O(1)	0.5789 (2)	-0.0929 (1)	0.1576 (2)	2.45
O(2)	0.5713 (2)	-0.1201 (1)	0.4007 (2)	3.49
C(8)	0.2543 (3)	-0.0706 (2)	-0.2301 (3)	2.75
C(9)	0.1379 (3)	-0.1320 (2)	-0.3009 (3)	3.24
O(3)	0.0811 (2)	-0.0958 (1)	-0.4212 (2)	5.76
O(4)	0.1017 (2)	0.2017 (1)	-0.2549 (2)	5.23
OW(1)	-0.1373 (2)	-0.1874 (1)	-0.5440 (4)	3.99
OW(2)	0.1311 (2)	0.1679 (1)	0.8646 (2)	4.12

Table 3. Interatomic distances (\AA) and angles ($^\circ$) for (1) and (2)

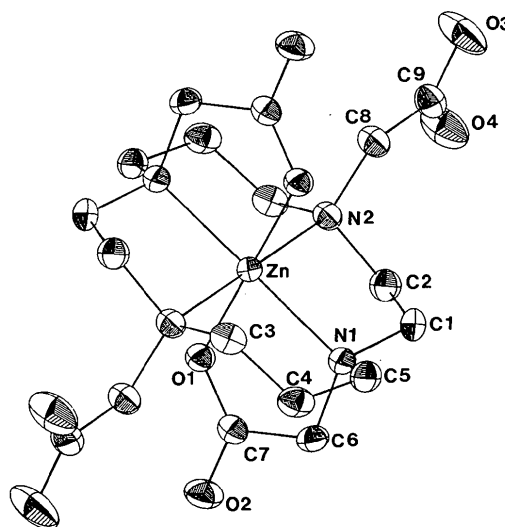
(1)		(2)	
Zn—N(1)	2.232 (3)	Zn—N(1)	2.110 (2)
Zn—N(2)	2.171 (3)	Zn—N(2)	2.253 (2)
Zn—O(1)	2.037 (3)	Zn—O(1)	2.127 (1)
O(1)—C(1)	1.270 (5)	O(1)—C(7)	1.271 (2)
O(2)—C(1)	1.242 (5)	O(2)—C(7)	1.238 (2)
C(1)—C(2)	1.520 (6)	C(7)—C(6)	1.526 (3)
C(2)—N(2)	1.481 (5)	C(6)—N(1)	1.485 (3)
C(3)—N(2)	1.488 (5)	C(1)—N(1)	1.488 (3)
C(3)—C(4)	1.504 (7)	C(1)—C(2)	1.522 (3)
C(4)—N(1)	1.482 (6)	C(2)—N(2)	1.487 (3)
C(5)—N(1)	1.471 (5)	C(3)—N(2)	1.493 (3)
C(5)—C(6)	1.527 (3)	C(3)—C(4)	1.522 (3)
		C(4)—C(5)	1.520 (3)
C(6)—N(2)	1.475 (6)	C(5)—N(1)	1.495 (3)
C(7)—N(1)	1.458 (6)	C(8)—N(2)	1.471 (3)
C(7)—C(8)	1.511 (6)	C(8)—C(9)	1.522 (3)
C(8)—O(3)	1.198 (5)	C(9)—O(4)	1.198 (3)
C(8)—O(4)	1.327 (6)	C(9)—O(3)	1.311 (3)

	(1)	(2)
O(1)—Zn—N(1)	103.7 (1)	80.9 (1)
O(1)—Zn—N(2)	81.5 (1)	89.6 (1)
N(1)—Zn—N(2)	81.9 (1)	85.9 (1)
N(1)—Zn—N(1)'	153.9 (1)	180.0
O(1)—Zn—O(1)'	89.7 (1)	180.0
N(2)—Zn—N(2)'	107.8 (1)	180.0

Fig. 2. ORTEP (Johnson, 1971) plot of Zn(dotaH₂) with atom-numbering scheme.

thermal parameters for all non-H atoms and isotropic parameters for H atoms in observed positions were refined to $R = 0.048$ and 0.029 using 1620 [$I > 2\sigma(I)$] and 2267 [$I > 2\sigma(I)$] reflections in a full-matrix refinement on F with 184 and 236 parameters for (1) and (2), respectively. $R = 0.047$ for (1) and $R = 0.037$ for (2) using unit weights. The largest positive peaks on the ΔF map were 0.68 and 0.40 e \AA^{-3} , the largest negative peaks -0.36 and -0.29 e \AA^{-3} for (1) and (2), respectively. Scattering factors for C, H, N and O are given in *SHELXS86* (Sheldrick, 1986), and those for Zn²⁺ are from Cromer & Mann (1968). Atomic parameters are given in Tables 1 and 2,* selected bond lengths and angles in Table 3, and the numbering schemes are shown in Figs. 2 and 3.

* Lists of structure factors, anisotropic thermal parameters and interatomic parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53512 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 3. ORTEP (Johnson, 1971) plot of Zn(tetaH₂) with atom-numbering scheme.

Discussion. In $\text{Zn}(\text{dotaH}_2)$ (Fig. 2) the metal ion is surrounded by the four nitrogens of the macrocycle and by two carboxylate oxygens, so that a distorted *cis*-octahedral geometry results. The two nitrogens $\text{N}(2)$ and $\text{N}(2)'$ (*trans* to each other in the macrocycle) and the two oxygens $\text{O}(1)$ and $\text{O}(1)'$ stemming from the acetate groups attached at $\text{N}(2)$ and $\text{N}(2)'$ form a plane in which the metal ion is also situated. The other two nitrogens $\text{N}(1)$ and $\text{N}(1)'$ are axially coordinated and complete the octahedron. The macrocycle is folded along the $\text{N}(1)$ – $\text{N}(1)'$ axis and assumes the *cis*-I configuration (Bosnich, Poon & Tobe, 1965). The Zn^{2+} is situated on the C_2 axis which bisects the $\text{O}(1)$ – Zn – $\text{O}(1)'$ angle. The other two carboxylates are protonated and not involved in coordination. They form hydrogen bonds $\text{O}(4)$ – $\text{H}(13)\cdots\text{O}(2)$ to a second molecule, the $\text{O}(4)$ – $\text{O}(2)$ distance being 2.62 (8) Å and the O – H – O angle 162 (5)°. The Zn – N and Zn – O bonds are somewhat longer than those of the corresponding Ni^{2+} complex (Riesen, Zehnder & Kaden, 1986), but the angles are similar. The $\text{N}(1)$ – M – $\text{N}(1)'$ angle is 153.9° for $M = \text{Zn}^{2+}$, compared to 153.9 and 158.6° for Ni^{2+} and Cu^{2+} , respectively, and is distinctly smaller than that expected for the octahedron (180°). This is due to the strain inherent in the 12-membered macrocycle, which does not allow the nitrogens to occupy the ideal position.

The structure of $\text{Zn}(\text{tetaH}_2)\cdot 4\text{H}_2\text{O}$, shown in Fig. 3, indicates that the metal ion in a *trans*-octahedral arrangement of the four amino nitrogens of the macrocycle and two carboxylate oxygens. Since the Zn^{2+} sits on an inversion centre it is in the plane defined by the four nitrogens with Zn – N bond

lengths of 2.110 and 2.253 Å. The Zn – O bonds are 2.127 Å long, so that the octahedron is somewhat elongated along the $\text{N}(2)$ – Zn – $\text{N}(2)$ axis. This is in contrast to the geometry found for the $\text{Cu}(\text{teta})^{2-}$ species (Riesen, Zehnder & Kaden, 1988), which is elongated along the O – Cu – O axis. The angles around the Zn^{2+} are close to 90°, the $\text{O}(1)$ – Zn – $\text{N}(1)$ angle being the smallest at 80.9°. The macrocycle is in the *trans*-III configuration according to the nomenclature of Bosnich, Poon & Tobe (1965). The two carboxylates not involved in coordination are protonated and form hydrogen bonds, from $\text{O}(3)$ – $\text{H}(15)$ to $\text{OW}(1)'$, which itself forms hydrogen bonds to $\text{O}(2)$ and $\text{OW}(2)'$. This last water is also hydrogen bonded to $\text{O}(1)$. The O – O distances range from 2.61 to 2.78 Å with O – H – O angles from 161 to 177°.

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Structure of a Monocyclopentadienyl Niobium(III) Phosphine Adduct

BY ABDENASSER ZAKI AND LILIANE G. HUBERT-PFALZGRAF*

Laboratoire de Chimie Moléculaire, Associé au CNRS, Université de Nice, Parc Valrose, 06034 Nice, France

AND LOIC TOUPET

Laboratoire de Cristallographie, Associé au CNRS, Campus de Beaulieu, 35042 Rennes, France

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Abstract. Dichloro(η^5 -cyclopentadienyl)tris(trimethylphosphine)niobium(III), $[\text{NbCl}_2(\text{C}_5\text{H}_5)-$

$\{\text{P}(\text{CH}_3)_3\}_3]$, $M_r = 457.15$, monoclinic, $P2_1/n$, $a = 18.900$ (9), $b = 12.696$ (7), $c = 18.820$ (8) Å, $\beta = 113.11$ (4)°, $V = 4153$ Å³, $Z = 8$, $D_x = 1.462$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 10.3$ cm⁻¹, $F(000) =$

* To whom correspondence should be addressed.