Harms, K. (1995). *XCAD4. Program for the Lp Correction of Enraf–Nonius Four-Circle Diffractometer Data.* University of Marburg, Germany.

Hay, B. P. & Rustad, J. R. (1994). *J. Am. Chem. Soc.* **116**, 6316–6326.

Izatt, R. M., Haymore, B. L., Bradshaw, J. S. & Christensen, J. J. (1975). *Inorg. Chem.* **14**, 3132–3133.

Mercer, M. & Truter, M. R. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2215–2220.

Moyer, B. A. & Bonnesen, P. V. (1997). *Supramolecular Chemistry of Anions*, edited by A. Bianchi, K. Bowman-James & E. García-España, pp. 1–44. New York: Wiley–VCH.

Pedersen, C. J. & Frensdorff, H. K. (1972). *Angew. Chem. Int. Ed. Engl.* **11**, 16–25.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1995). *SHELXTL.* Version 5.03/IRIX. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (1998). *PLATON. A Multi-Purpose Crystallographic Tool.* University of Utrecht, The Netherlands.

Steiner, T. (1996). *Cryst. Rev.* **6**, 1–57.

Weller, F., Borgholte, H., Stenger, H., Vogler, S. & Dehnicke, K. (1989). *Z. Naturforsch. Teil B*, **44**, 1524–1530.

Racemic Phase of Diaquabis(5-oxoprolinato)zinc(II)†

A. M. Loireau-Lozach,[a] R. Céolin,[a] X. Solans[b] and M. Font-Bardia[b]

[a]*Laboratoire de Chimie Physique, Faculté de Pharmacie, Université Paris V, F-75270 Paris, France, and* [b]*Departamento de Cristalografía, Mineralogía y Depósitos Minerales, Universidad de Barcelona, Marti i Franqués s/n, E-08028 Barcelona, Spain. E-mail: xavier@natura.geo.ub.es*

Abstract

The title compound, diaquabis(5-oxopyrrolidine-2-carboxylato-O^2)zinc(II), [Zn(C$_5$H$_6$NO$_3$)$_2$(H$_2$O)$_2$], consists of a two-dimensional net of molecules parallel to the ($\bar{1}$01) plane linked by hydrogen bonds, with every Zn^{2+} ion displaying a distorted tetrahedral coordination. The main difference between the two 5-oxoprolinate ligands is in the conformation of the five-membered ring, with one having an envelope form and the other a planar twisted form.

Comment

The structures of 5-oxoproline in the racemic form and L-form (Pattabhi & Venkatesan, 1974; Taira & Watson,

† This work is dedicated to the memory of Professor N. Rodier.

1977; van Zoeren *et al.*, 1978), and the structure of L-diaquabis(5-oxoprolinato)zinc(II) (Rodier *et al.*, 1990) have been reported previously. In this paper, the racemic form, (I), of the Zn derivative is reported.

(I)
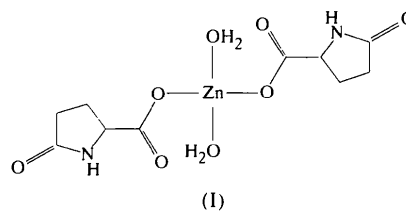
L-Pyroglutamates (also termed 'L-pidolates') are used in human therapeutics as well resorbed vectors of trace elements. Because they are chiral, it has to be ensured that there are no racemates in the solid dosage forms. In order to establish the structural differences between the two forms, an X-ray study was carried out.

There is a non-crystallographic pseudo-twofold axis parallel to the *b* axis, displaced from the origin by $0.63a + 0.37c$ (on the Zn atom). The greatest deviation between pseudo-equivalent sites is 0.34 (2) Å for the N1/N1′ pair of atoms. The structure consists of Zn^{2+} ions tetrahedrally coordinated by two water molecules and two O atoms of two 5-oxoprolinate ligands. The steric hindrance between these two ligands produces an O1—Zn—O1′ bond angle of 132.2 (2)° and a shortening of the O(water)—Zn—O(water) bond angle to 99.4 (2)°. For both ligands, the CC(O)OZn moiety is planar [largest deviation from the mean plane defined by the five atoms is 0.016 (4) Å for O1 and 0.017 (6) Å for Zn in the unprimed and primed ligands, respectively].

The main difference between the two ligands is in the conformation of the five-membered ring, which has an envelope form with the C5′ atom out of the plane defined by the remaining four atoms in the primed ligand, and a planar twisted form on the C2—C5 bond in the unprimed ligand. This produces a widening of C3—C4—C5 [106.4 (5)°], which is 104.3 (4)° in the primed ligand and 104.3 (1)° in the L-derivative (Rodier *et al.*, 1990), and C5—C2—N1 [104.4 (5)°], which is 102.6 (5)° in the primed ligand and 102.9 (1)° in the L-derivative.

The structure consists of layers of molecules parallel to the ($\bar{1}$01) plane linked by hydrogen bonds. Different layers are displaced along the *c* axis and the molecules are twisted around the *b* axis with respect to the position of the L-derivative. This explains the similarity of the *b* axes of the two structures [5.893 (13) and 5.888 (3) Å]. The stress produced by the hydrogen-bond interactions produces a shortening of the Zn—O1′—C1′ angle [112.9 (4)° *versus* 114.1 (4)° for the unprimed ligand and 115.0 (6)° for the L-derivative] and the O2—C1—C2—N1 torsion angle [5.7 (8)° for the primed ligand, 9.9 (8)° for the unprimed ligand and −11.7 (2)° for the L-derivative].
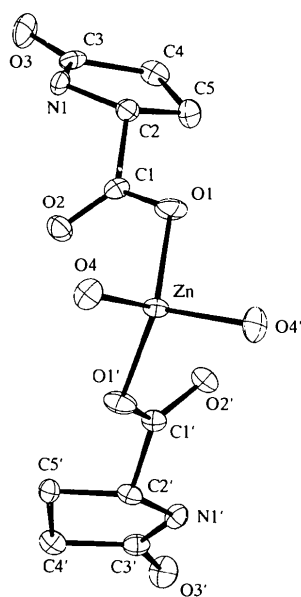
Fig. 1. Plot of the title molecule with 50% probability displacement ellipsoids showing the numbering scheme.

Experimental

Crystals of (I) were prepared by the slow evaporation at room temperature of an aqueous solution of DL-pyroglutamic acid and ZnO in a 2:1 molar ratio.

Crystal data

$[Zn(C_5H_6NO_3)_2(H_2O)_2]$	Mo $K\alpha$ radiation
$M_r = 357.62$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 22.943$ (4) Å	$\theta = 12-25°$
$b = 5.893$ (13) Å	$\mu = 1.810$ mm^{-1}
$c = 20.541$ (5) Å	$T = 293$ (2) K
$\beta = 90.49$ (3)°	Prismatic
$V = 2777$ (6) Å^3	$0.2 \times 0.1 \times 0.1$ mm
$Z = 8$	Colourless
$D_x = 1.711$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.025$
diffractometer	$\theta_{max} = 25.97°$
ω–2θ scans	$h = -26 \rightarrow 26$
Absorption correction: none	$k = -2 \rightarrow 6$
2522 measured reflections	$l = 0 \rightarrow 24$
2418 independent reflections	3 standard reflections
1696 reflections with	frequency: 120 min
$I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.014$
$R[F^2 > 2\sigma(F^2)] = 0.059$	$\Delta\rho_{max} = 0.478$ e Å^{-3}
$wR(F^2) = 0.181$	$\Delta\rho_{min} = -0.581$ e Å^{-3}
$S = 1.041$	Extinction correction: none

2379 reflections
209 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1071P)^2 + 1.2864P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

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

Zn—O1	1.931 (4)	N1—C3	1.322 (8)
Zn—O1'	1.931 (4)	N1—C2	1.439 (7)
Zn—O4	1.978 (5)	N1'—C3'	1.309 (7)
Zn—O4'	1.984 (5)	N1'—C2'	1.447 (7)
O1—Zn—O1'	132.2 (2)	N1—C2—C5	104.3 (5)
O1—Zn—O4	102.4 (2)	C1—C2—C5	109.8 (5)
O1'—Zn—O4	108.9 (2)	C3—C4—C5	106.4 (5)
O1—Zn—O4'	106.5 (2)	C1'—O1'—Zn	112.9 (4)
O1'—Zn—O4'	103.0 (2)	N1'—C2'—C1'	114.4 (5)
O4—Zn—O4'	99.4 (2)	N1'—C2'—C5'	102.7 (5)
C1—O1—Zn	114.1 (4)	C1'—C2'—C5'	111.8 (5)
N1—C2—C1	113.9 (5)	C3'—C4'—C5'	104.3 (4)

Table 2. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O2'	1.00 (3)	1.99 (4)	2.981 (9)	169 (6)
N1'—H1'N···O2'^{iii}	0.99 (3)	2.00 (2)	2.981 (9)	171 (6)
O4—H71···O3'^{ii}	0.99 (4)	1.63 (3)	2.609 (8)	167 (6)
O4'—H71'···O3'^{iii}	1.00 (4)	1.62 (4)	2.604 (8)	169 (4)
O4—H72···O2'^{iv}	0.99 (3)	1.74 (3)	2.729 (8)	171 (6)
O4'—H72'···O2'^{i}	1.00 (3)	1.77 (3)	2.754 (9)	170 (5)

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

Refinement was on F^2 for all reflections except for 49 with negative F^2 flagged by the user for potential systematic errors. The position of the H atoms was located from a difference synthesis. The coordinates of the H atoms of water and those attached to nitrogen were refined with the O—H and N—H lengths constrained to 1 Å, while the H atoms linked to C atoms were refined using a riding model. An overall isotropic displacement parameter was refined for all H atoms.

Data collection: *CAD-4/PC* (Kretschmar, 1996). Cell refinement: *CAD-4/PC*. Data reduction: *CFEO* (Solans, 1978). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP3.2* (Brueggemann & Schmid, 1990). Software used to prepare material for publication: *PLATON* (Spek, 1990).

References

Brueggemann, R. & Schmid, G. (1990). PC version of *ORTEP3.2*. University of Ulm, Germany.

Kretschmar, M. (1996). *CAD-4/PC*. Version 2.0. PC version of *CAD-4 Software* Version 5.0. University of Tübingen, Germany.

Pattabhi, V. & Venkatesan, K. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 1085–1089.

Rodier, N., Ceolin, R., Plat, M. & Zumbihl, H. (1990). *Acta Cryst.* C46, 324–326.

Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Solans, X. (1978). *CFEO. Program for Crystal Data Reduction*. University of Barcelona, Spain.

Spek, A. L. (1990). *Acta Cryst.* A46, C-34.
Taira, Z. & Watson, W. H. (1977). *Acta Cryst.* B33, 3823–3827.
Zoeren, E. van, Oonk, H. A. J. & Kroon, J. (1978). *Acta Cryst.* B34, 1898–1900.

An Oxomolybdenum(V) Cluster, [Mo8O16(OCH3)8(C5H5N)4]

Barbara Modec,[a] Jurij V. Brenčič,[a] Rok Rotar,[a] Ljubo Golič[a] and Keith Prout[b]

[a]*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, 1000 Ljubljana, Slovenia, and* [b]*Chemical Crystallography Laboratory, Oxford University, 9 Parks Road, Oxford OX1 3PD, England. E-mail: barbara.modec@uni-lj.si*

Abstract

The structure of octa-μ-methoxo-octa-μ-oxo-octaoxo-tetrapyridineoctamolybdenum(V), [Mo8O16(CH3O)8(C5H5N)4], consists of discrete puckered cyclic molecules, made up of eight Mo atoms which are linked together by pairs of oxo bridges and pairs of bridging methoxo groups. It may also be regarded as a linkage of four [Mo2O4]$^{2+}$ units, whose two Mo centres differ in that one is coordinated by a pyridine ligand. Short Mo—Mo distances [2.570(1) Å] alternate with longer Mo···Mo contacts [3.435(1) Å].

Comment

The title compound belongs to the family of poly-oxoalkoxymolybdate(V) complexes with various organic ligands. The O-donor groups can serve as terminal, μ- or μ_3-bridging ligands, thereby providing a means for the structure to expand (Khan & Zubieta, 1995). The [Mo2O4]$^{2+}$ structural unit, which is common to all polynuclear oxomolybdenum(V) compounds and which dominates the chemistry of Mo^V, is known to occur in a well known geometry and is usually not affected by the metal environment (Chae *et al.*, 1993). The Mo(μ-O)2Mo ring is severely puckered, thus making possible the close approach (2.5–2.7 Å) of two Mo atoms and the formation of a localized single metal–metal bond, which accounts for the experimentally observed diamagnetism (Cotton & Ilsley, 1982).

Diverse geometries are adopted among oxomolybdenum(V) complexes with pyridine. A single, almost linear, oxo bridge connects two octahedrally coordinated Mo centres in [Mo2O3Cl4py4].CH2Cl2 (py = C5H5N,

pyridine) (El-Essawi *et al.*, 1986). The [Mo2O4]$^{2+}$ core was found in the binuclear complex [Mo2O4-(SN2C4H3)2py2].py (SN2C4H3$^-$ is a thiopyrimidinato anion) (Cotton & Ilsley, 1982). In [Mo4O8(O^{i}Pr)4py4].-2py (O^{i}Pr = C3H7O$^-$, isopropoxide), four octahedra are connected in an edge-sharing manner to form a tetranuclear fragment (Chisholm *et al.*, 1981). In the recently determined structure of a pentanuclear mixed-valence complex, [Mo5O11(OCH3)4py4].CH3OH, two [Mo2O4]$^{2+}$ moieties are fused with a six-valent Mo centre (Modec *et al.*, 1998). We report here on the structure of a related octanuclear complex, [Mo8O16-(OCH3)8py4], (I). It was obtained as a product in the reaction of mononuclear [MoOCl5]$^{2-}$ with pyridine and methanol. The labile chloride ligands undergo a facile substitution reaction, then the formation of larger less soluble aggregates takes place. Factors such as concentration and reaction temperature have a substantial influence on the course of the reaction.

(I)
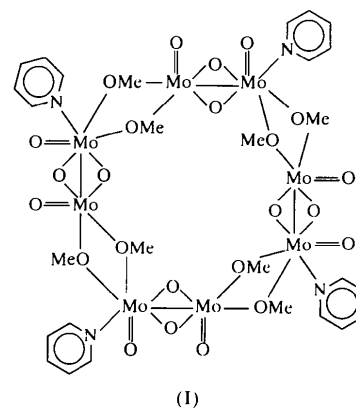
The title compound, illustrated in Fig. 1, is seen to consist of discrete molecules with the [Mo8O16(OCH3)8-py4] stoichiometry. An octanuclear ring is produced by the action of the crystallographic S_4 axis on an [Mo2O4]$^{2+}$ binuclear asymmetric unit, whose two Mo centres are in different coordination environments. Both Mo atoms are ligated by a terminal O atom, a pair of bridging O atoms and a pair of methoxo groups. While Mo2 exhibits a five-coordinate square-pyramidal geometry, Mo1 attains a distorted octahedral coordination by bonding to pyridine. The short bonds between Mo and the terminal multiply-bonded O atom [Mo1—O1 1.682(4) and Mo2—O2 1.664(4) Å] are in a *syn* disposition with respect to the Mo1—O3—Mo2—O4 rhombus. The *trans* influence of the terminal O atom is demonstrated by the square-pyramidal geometry of Mo2, with the vacant site in a *trans* position to the molybdenyl group. The position of Mo2, 0.622(2) Å above the approximate basal plane defined by O3, O4, O5^i and O6^i [symmetry code: (i) $\frac{1}{4} + y$, $\frac{7}{4} - x$, $\frac{3}{4} - z$], is a characteristic feature of Mo^V in a square-pyramidal