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Diamminebis(5,5-diphenylhydantoinato)-zinc(II) Hemihydrate

ALEKSANDER W. ROSZAK AND PAUL MILNE

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

DONALD F. WEAVER

Departments of Chemistry and of Medicine (Neurology), Queen's University, Kingston, Ontario, Canada K7L 3N6

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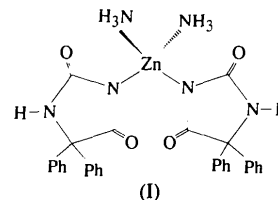
Abstract

In the title compound, diamminebis(5,5-diphenyl-2,4-imidazolidinedionato-*N*³)zinc(II) hemihydrate, $[\text{Zn}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)_2(\text{NH}_3)_2] \cdot \frac{1}{2}\text{H}_2\text{O}$, the zinc(II) ion coordinates with two deprotonated hydantoin and two ammine ligands in a 4-*N* tetrahedral arrangement. The complex has *C*_s symmetry with the Zn cation and the two ammonia N atoms located in the symmetry plane. Geometric changes in the hydantoin ring compared with free phenytoin show the effect of the Zn coordination. The arrangement of phenyl rings in this complex is different from those in free phenytoin and the analogous copper and nickel complexes.

Comment

Despite its widespread use in the treatment of epilepsy, phenytoin (5,5-diphenylimidazolidine-2,4-dione) produces some rather undesirable and poorly understood toxicological effects. Adverse manifestations such as gingival hyperplasia (gum overgrowth) and hirsutism (excess facial hair) are not uncommon. Zn^{II} chelation producing connective tissue changes through an alteration in metallo-enzyme function has been implicated as a source of these toxicities (Hurd, Wilder, Perchalski & McDowell, 1991). The mode of

phenytoin–Zn^{II} complexation, however, was not known. The crystal structure of diamminebis(5,5-diphenylhydantoinato)copper(II) (Shimizu & Uno, 1980*b*) reveals square-planar coordination, with the N3 atom of the N3-deprotonated hydantoin ligand (using the numbering scheme of the present structure) in the Cu^{II} coordination sphere. Similar N3 coordination is observed in the crystal structure of the octahedrally coordinated diamminediaquabis(5,5-diphenylhydantoinato)nickel(II) complex (Shimizu & Uno, 1980*a*). A different interaction is observed in the platinum(II) complex of the related compound 1-methylhydantoin, where N3-deprotonated hydantoin bridges two metal ions through atoms N3 and O4 (Laurent, Lepage & Dahan, 1982). As part of an investigation of the Zn^{II}–phenytoin interaction, the title compound diamminebis(5,5-diphenylhydantoinato)zinc(II) hemihydrate, (I), $\frac{1}{2}\text{H}_2\text{O}$, was synthesized and structurally examined to establish its coordination geometry and mode of bonding.



Complex (I) has tetrahedral 4-*N* Zn coordination with the Zn ion and the ammonia N7 and N8 atoms sitting on a mirror plane perpendicular to the crystallographic *y* axis. The interaction of phenytoin with zinc parallels Cu and Ni complexation. All of these complexes have a deprotonated N3 atom in the coordination sphere of the transition metal. The Zn–N distances are equal but the tetrahedral geometry is distorted due to the large size of the phenytoin ligand, the N3–Zn–N3ⁱ angle [N3ⁱ is the mirror image of N3; symmetry code: (i) $x, \frac{3}{2} - y, z$] being about 10° greater than the ideal value. The hydantoin ring is not symmetrically oriented with respect to the Zn–N3 bond and the two ammonia ligands have O2···O2ⁱ and O4···O4ⁱ distances of 5.177 (4) and 3.155 (4) Å, respectively. The N7···O4 and N8···O2 distances are similar [3.273 (3) and 3.218 (3) Å, respectively], but due to the symmetrically constrained positions of the ammonia H atoms, only the second contact can be considered a weak intramolecular hydrogen bond (see Table 3). The dihedral angle between the hydantoin ring and the mirror plane of the complex is 57.2 (1)°, and the angle between the two hydantoin rings is 114.4 (1)°.

The geometry of the hydantoin ring is similar, within experimental error, to that found in the analogous Cu and Ni complexes (Shimizu & Uno, 1980*a,b*), but shows some differences in bond angles when compared to the free phenytoin of the first determination

(Camerman & Camerman, 1971). When compared to free phenytoin of the latest more accurate determination (Chattopadhyay, Palmer & Lisgarten, 1993), significant differences can be observed, namely, an increase in the N1—C2 and C4—C5 bond lengths and concerted changes in all endocyclic bond angles, which can be rationalized by the effect of coordination to the Zn atom. The N3 atom is being pulled out of the hydantoin ring so that the C2—N3—C4 angle decreases from 112.2(2)° in free phenytoin to 109.0(2)° in the Zn complex; the adjacent angles at atoms C2 and C4 increase by about 2.6° and the angles at N1 and C5 decrease slightly. The same effect can be seen by comparing the endocyclic distances N3...N1 and N3...C5 in the two compounds; they are 2.194 and 2.326 Å, respectively, in the free phenytoin and 2.248(3) and 2.374(3) Å in the Zn complex, an increase of about 0.050 Å. Consistent with these changes, the bonds N1—C2 and C4—C5 increase by about 0.02 and 0.01 Å, respectively.

Another significant difference occurs in the arrangement of the phenyl rings with respect to the hydantoin ring. In free phenytoin, one of the phenyl rings almost eclipses the N1—C5 bond and the second eclipses the C4—C5 bond [torsion angles N1—C5—C_{Ph1}—C_{Ph1} and C4—C5—C_{Ph2}—C_{Ph2} are 2.3 and -1.9°, respectively, according to Camerman & Camerman (1971), and 1.5 and -3.6° in the paper by Chattopadhyay, Palmer & Lisgarten (1993)]. Such arrangements result in a dihedral angle of about 90° between the phenyl rings. A similar situation is observed in the Cu complex with corresponding torsion angles of 7.9 and -4.2°, and in the Ni complex the arrangement is somewhat distorted with angles of -21.4 and 16.9°; the phenyl—phenyl angle is still close to 90° in both these complexes. In the Zn complex, the phenyl-ring bond C61—C66 is relatively close to the eclipsing position with a torsion angle N1—C5—C61—C66 of 17.3(4)°, but the other phenyl-ring bond, C51—C56, forms a torsion angle of -68.9(3)° [C4—C5—C51—C56] with the C4—C5 bond resulting in a dihedral angle of 63.4(2)° between the two phenyl rings. This different arrangement of phenyl rings in the Zn complex is probably due to the tetrahedral coordination and reflection symmetry of the molecule which place the C51—C56 phenyl ring in close proximity to its mirror counterpart; the shortest C...C distance observed between these rings (C55...C55ⁱ) is 3.589(9) Å. It should be noted that this arrangement of phenyl rings does not fall into one of the potential energy minima allowed for free phenytoin calculated by Chattopadhyay, Palmer & Lisgarten (1993).

The packing of molecules in the crystal is determined by hydrogen bonding between the N1 amino function and the carbonyl O2 atom, and by several other hydrogen bonds between the ammonia ligands and the carbonyl O2 and O4 functions (Table 3 provides details of the hydrogen bonding). Formally, a half molecule of the solvent water sits on the mirror plane of the com-

plex and is disordered over two positions, OW1 and OW2, 0.77(5) Å apart and each with 0.25 occupancy. OW1 and OW2 form hydrogen bonds to the hydantoin O atoms O2 and O2ⁱ on both sides of the mirror plane.

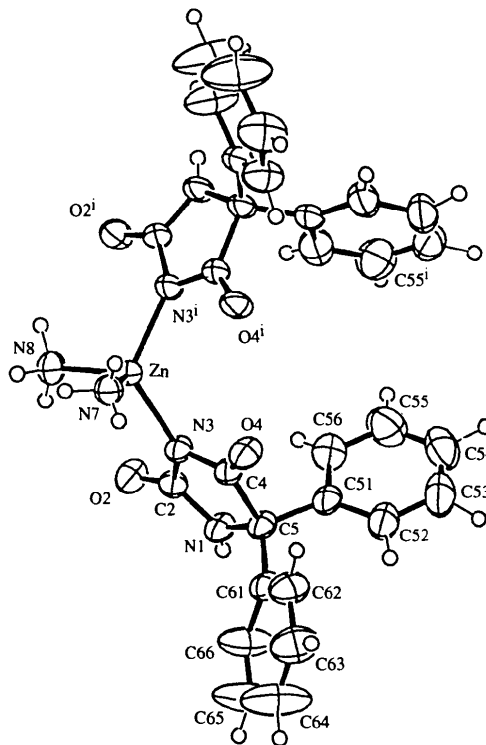


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are drawn as unlabeled spheres of arbitrary size.

Experimental

Single crystals of the title compound were obtained by slow evaporation, at a constant temperature of 323 K, of aqueous ammonia containing phenytoin and [Zn(NO₃)₂].6H₂O. Elemental analysis revealed the presence of a half molecule of water per molecule of complex in the crystal structure.

Crystal data

[Zn(C₁₅H₁₁N₂O₂)₂(NH₃)₂]. $\frac{1}{2}$ H₂O

M_r = 610.96

Orthorhombic

Pnma

a = 10.345(1) Å

b = 17.316(2) Å

c = 15.940(2) Å

V = 2855.4(6) Å³

Z = 4

D_x = 1.421 Mg m⁻³

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 16–21°

μ = 0.909 mm⁻¹

T = 293(2) K

Prism

0.62 × 0.40 × 0.17 mm

Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer	$\theta_{\max} = 26.96^\circ$
$\omega/2\theta$ scans	$h = 0 \rightarrow 13$
Absorption correction: none	$k = 0 \rightarrow 22$
3938 measured reflections	$l = 0 \rightarrow 20$
3214 independent reflections	3 standard reflections
2458 observed reflections [$I > 2\sigma(I)$]	frequency: 60 min
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.001$
$R(F) = 0.0423$	$\Delta\rho_{\max} = 0.833 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.1373$	$\Delta\rho_{\min} = -0.588 \text{ e } \text{\AA}^{-3}$
$S = 1.092$	Atomic scattering factors
3214 reflections	from <i>International Tables for Crystallography</i> (1992),
202 parameters	Vol. C, Tables 4.2.6.8 and 6.1.1.4)
$w = 1/[\sigma^2(F_o^2) + (0.0905P)^2 + 0.4658P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Zn	0.48397 (4)	3/4	0.67046 (2)	0.0322 (2)
N1	0.6263 (2)	0.54062 (12)	0.57262 (14)	0.0435 (5)
C2	0.5351 (2)	0.59686 (14)	0.5769 (2)	0.0376 (5)
O2	0.4374 (2)	0.60052 (11)	0.53269 (12)	0.0504 (5)
N3	0.5688 (2)	0.65029 (11)	0.63819 (13)	0.0362 (4)
C4	0.6790 (2)	0.62708 (13)	0.67563 (14)	0.0374 (5)
O4	0.7333 (2)	0.65891 (11)	0.73411 (12)	0.0496 (5)
C5	0.7299 (2)	0.55281 (13)	0.6320 (2)	0.0391 (5)
C51	0.8569 (2)	0.57523 (14)	0.5865 (2)	0.0445 (6)
C52	0.9784 (3)	0.5513 (2)	0.6119 (2)	0.0578 (7)
C53	1.0875 (3)	0.5760 (2)	0.5704 (3)	0.0748 (10)
C54	1.0790 (4)	0.6233 (2)	0.5032 (3)	0.0759 (11)
C55	0.9613 (4)	0.6464 (3)	0.4775 (3)	0.0847 (12)
C56	0.8495 (4)	0.6233 (2)	0.5183 (2)	0.0680 (9)
C61	0.7460 (3)	0.48645 (15)	0.6937 (2)	0.0459 (6)
C62	0.8150 (3)	0.4951 (2)	0.7679 (2)	0.0618 (8)
C63	0.8340 (5)	0.4336 (2)	0.8214 (2)	0.0804 (11)
C64	0.7839 (7)	0.3634 (3)	0.8027 (3)	0.123 (2)
C65	0.7106 (8)	0.3549 (2)	0.7308 (4)	0.145 (3)
C66	0.6914 (5)	0.4156 (2)	0.6763 (2)	0.0842 (13)
N7	0.4731 (3)	3/4	0.7963 (2)	0.0405 (6)
N8	0.3077 (3)	3/4	0.6181 (2)	0.0439 (7)
OW1	0.494 (3)	3/4	0.436 (2)	0.105 (12)
OW2	0.420 (3)	3/4	0.435 (2)	0.116 (14)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Zn—N3	2.004 (2)	C2—N3	1.390 (3)
Zn—N7	2.010 (3)	N3—C4	1.348 (3)
Zn—N8	2.006 (3)	C4—O4	1.220 (3)
N1—C2	1.358 (3)	C4—C5	1.554 (3)
N1—C5	1.445 (3)	C5—C51	1.550 (4)
C2—O2	1.233 (3)	C5—C61	1.522 (4)
N3 ⁱ —Zn—N3	118.99 (12)	O4—C4—C5	124.1 (2)
N7—Zn—N3	106.31 (7)	N3—C4—C5	109.6 (2)
N3—Zn—N8	106.94 (7)	N1—C5—C4	99.4 (2)
N7—Zn—N8	111.38 (12)	N1—C5—C51	111.1 (2)
C2—N1—C5	112.2 (2)	N1—C5—C61	113.2 (2)
O2—C2—N1	125.3 (2)	C4—C5—C51	106.8 (2)
O2—C2—N3	125.0 (2)	C4—C5—C61	111.9 (2)
N1—C2—N3	109.7 (2)	C51—C5—C61	113.5 (2)
C4—N3—C2	109.0 (2)	C5—C51—C52	123.9 (3)
C4—N3—Zn	120.89 (15)	C5—C51—C56	118.4 (2)

C2—N3—Zn	130.1 (2)	C5—C61—C62	121.7 (2)
O4—C4—N3	126.4 (2)	C5—C61—C66	119.8 (3)
N1—C2—N3—Zn	175.2 (2)	N1—C5—C51—C52	-143.3 (3)
O2—C2—N3—Zn	-4.3 (4)	N1—C5—C51—C56	38.5 (3)
N3 ⁱ —Zn—N3—C2	-106.6 (2)	C4—C5—C51—C52	109.3 (3)
N3 ⁱ —Zn—N3—C4	70.7 (2)	C4—C5—C51—C56	-68.9 (3)
N7—Zn—N3—C2	133.7 (2)	C61—C5—C51—C52	-14.5 (3)
N7—Zn—N3—C4	-49.1 (2)	C61—C5—C51—C56	167.3 (2)
N8—Zn—N3—C2	14.6 (2)	O4—C4—C5—C61	57.6 (3)
N8—Zn—N3—C4	-168.2 (2)	N3—C4—C5—C61	-123.2 (2)
Zn—N3—C4—O4	5.0 (4)	N1—C5—C61—C62	-162.7 (3)
Zn—N3—C4—C5	-174.1 (2)	N1—C5—C61—C66	17.3 (4)
C2—N1—C5—C51	-110.1 (2)	C4—C5—C61—C62	-51.5 (3)
C2—N1—C5—C61	120.9 (2)	C4—C5—C61—C66	128.6 (3)
O4—C4—C5—C51	-67.1 (3)	C51—C5—C61—C62	69.5 (3)
N3—C4—C5—C51	112.0 (2)	C51—C5—C61—C66	-110.4 (3)

Symmetry code: (i) $x, \frac{3}{2} - y, z$.Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)H atoms of the ammonia atoms N7 and N8 are denoted with *A* for atoms in the mirror plane and *B* for out-of-mirror-plane atoms.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O2 ⁱ	0.86	2.20	3.037 (3)	164
N7—H7A...O4 ⁱⁱ	0.89	2.38	2.980 (3)	125
N8—H8B...O2	0.89	2.50	3.218 (3)	138
N8—H8A...O4 ⁱⁱ	0.89	2.34	2.938 (3)	125
OW1...O2 ⁱⁱⁱ			3.074 (16)	
OW2...O2 ⁱⁱⁱ			3.029 (16)	

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (iii) $x, \frac{3}{2} - y, z$.

All H atoms of the title molecule, except two bonded to atoms C64 and C65, which showed some degree of disorder, were located in the difference Fourier map but idealized calculated positions were used in the refinement. The distances used in calculations were 0.86, 0.89 and 0.93 \AA for the amide H atom, ammonia H atoms and aromatic H atoms, respectively. For the H atoms of the N7 and N8 ammonia groups tetrahedral geometry was used and the eclipsed orientations were chosen following the features of the difference Fourier map. In the refinement, all H atoms were riding on the non-H atoms to which they are attached with U_{iso} values fixed at 120% of the U_{eq} values of these non-H atoms. H atoms of the disordered water molecule were not located.

Data collection: Enraf-Nonius CAD-4 system software. Cell refinement: Enraf-Nonius CAD-4 system software. Data reduction: *Xtal3.0* (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992). Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Complex Between Uranyl Trifluoromethanesulfonate Hydrate and Benzo-15-crown-5

PIERRE THUÉRY, MARTINE NIERLICH, NELLY KELLER,
MONIQUE LANCE AND JULIEN-DANIEL VIGNER

CEA, DSM/DRECAM/SCM, CE Saclay, Bâtiment 125,
91191 Gif-sur-Yvette, France

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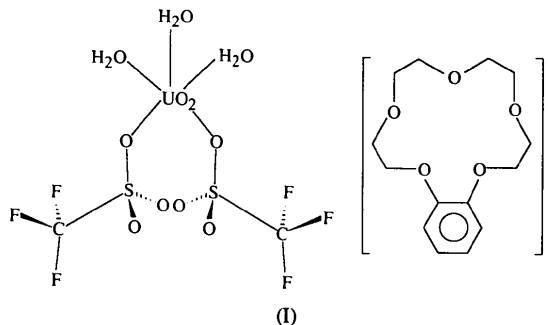
Abstract

In triaquadioxobis(trifluoromethanesulfonato)uranium(VI)–benzo-15-crown-5 (1/2), $[\text{UO}_2(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_3] \cdot 2\text{C}_{14}\text{H}_{20}\text{O}_5$, the uranyl ion is in a pentagonal pseudoplanar equatorial environment, consisting of two O atoms from two trifluoromethanesulfonate (triflate) ions and three from water molecules. The coordination of CF_3SO_3^- is particularly notable owing to the poor coordinating character of this ion. Two molecules of benzo-15-crown-5 are hydrogen bonded to the water molecules (one water molecule bridging) without any direct interaction with the uranyl moiety.

Comment

The inclusion of the uranyl ion into the cavity of crown ethers and azacrowns can only be achieved in a poorly coordinating medium (solvent and counterion); in other conditions, complexes in which the macrocycles are only hydrogen bonded to the uranyl coordination-sphere atoms are obtained (Thuéry, Keller, Lance, Vigner & Nierlich, 1995, and references therein). Several examples have been given of such hydrogen-bonded out-of-cavity complexes in which the coordination to water molecules or counterions such as nitrate or chlorine prevents inclusion. Furthermore, an 18-crown-6-type cavity size has been shown to be a prerequisite for uranyl inclusion (Deshayes, Keller, Lance, Navaza, Nierlich & Vigner, 1994); in particular, no

uranyl inclusion is observed with 15-crown-5 or benzo-15-crown-5, even in a poorly coordinating medium. In this paper we report the structure of the out-of-cavity complex $[\text{UO}_2(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_3] \cdot 2\text{C}_{14}\text{H}_{20}\text{O}_5$, (I). *ORTEPII* (Johnson, 1976) drawings of the asymmetric unit and of the crystal packing are shown in Figs. 1 and 2.



The U atom is located on a site without any local symmetry. The linear uranyl ion (with normal geometrical features) is surrounded in its equatorial plane by five donor O atoms, one from each CF_3SO_3^- counterion and three from the water molecules. The U—O(water) distances [2.383 (9), 2.42 (1) and 2.424 (9) Å] are comparable to those found in pentaqua uranyl complexes (Alcock & Esperás, 1977; Deshayes, Keller, Lance, Nierlich & Vigner, 1994). The U—O(triflate) distances [2.38 (1) and 2.392 (9) Å] are in agreement with those determined by EXAFS spectrometry in $[\text{UO}_2(\text{CF}_3\text{SO}_3)_2(\text{CH}_3\text{CN})_3]$ [2.400 (1) in the solid state, 2.36 (1) Å in solution] and in out-of-cavity complexes with various crown ethers (ranging between 2.30 and 2.39 Å) (Deshayes, Keller, Lance, Nierlich & Vigner, 1994). The five O-atom donors are in a plane with a maximum deviation of ± 0.06 (1) Å, the U atom being 0.013 (1) Å from this mean plane.

Two crystallographically independent crown ethers are present in the asymmetric unit. Each of them displays short intermolecular contacts (between 2.66 and 2.86 Å) with two water molecules, which suggests the formation of hydrogen bonds. One of the water molecules is possibly bonded to both crown ethers. One of the two crown ethers (corresponding to O atoms O17–O21) adopts the conformation $g^-g^+g^-g^-$ for the O—C—C—O torsion angles (except the one corresponding to the aromatic cycle) with two C—O—C—C torsion angles in a *gauche* rather than *anti* conformation [-74 (2) and -76 (2)^o]. The other crown ether (corresponding to O atoms O12–O16) adopts a more distorted conformation, with one O—C—C—O torsion angle of 10 (4)^o and one C—O—C—C of 66 (2)^o. For both crown ethers, the dihedral angle between the aromatic ring and the mean plane defined by the five O atoms is rather high [65.3 (4) and 76.6 (4)^o, respectively].