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Aluminium Cupferronate, $[Al(C_6H_5N_2O_2)_3]$

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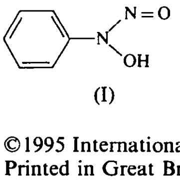
Abstract

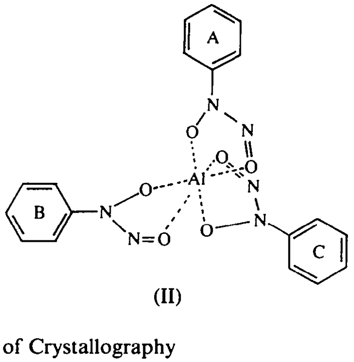
The Al ion in tris(*N*-nitroso-*N*-phenylhydroxylaminato)-aluminium(III), $[Al(C_6H_5N_2O_2)_3]$, has distorted octahedral coordination defined by six O atoms from three chelate ligands [Al—O = 1.875 (4)–1.894 (4) Å]. In each ligand the phenyl ring nearly coincides with the plane of the nitrosohydroxylaminato group.

Comment

N-Nitroso compounds, such as dimethylnitrosoamine and *N*-nitrosourea are known carcinogens (Nishimura *et al.*, 1985; Ishii, Tatsuta, Baba, Uehara & Nakaizumi, 1994). In order to clarify the cytotoxicity of *N*-nitroso compounds, it is important to accumulate precise structural data concerning the interaction modes of *N*-nitroso compounds with biomaterials. Accordingly, the crystal structure of the Al^{III} complex of deprotonated cupferron, (I), tris(*N*-nitrosophenylhydroxylaminato)aluminium(III), (II), has been determined. The structures of the related complexes iron cupferronate (van der Helm, Merritt & Degeilh, 1965) and (*N*-nitrosophenylhydroxylamininato-*O*,*O*′)bis(triphenylphosphine)copper(I) (Charlambous, Haines, Harris, Hendrick & Taylor, 1984) have been reported.



(I)



(II)

The molecular structure is illustrated in Fig. 1. The three cupferronato ligands *A*, *B* and *C* are asymmetrically attached to the Al^{3+} ion. In each ligand, the phenyl ring is nearly coplanar with the plane of the nitrosohydroxylaminato group, although the N—N—C—C torsion angles [N(2*A*)—N(1*A*)—C(1*A*)—C(6*A*) = 2.1 (8), N(2*B*)—N(1*B*)—C(1*B*)—C(6*B*) = −9.0 (9), N(2*C*)—N(1*C*)—C(1*C*)—C(6*C*) = −16 (1)°] show some variation. The Al^{3+} ion has distorted octahedral coordination defined by six O atoms from three ligands with similar O atoms meridional [O(1*A*)—Al(1)—O(1*C*) = 168.1 (2), O(1*B*)—Al(1)—O(2*A*) = 167.6 (2), O(2*B*)—Al(1)—O(2*C*) = 166.0 (2)°]. Although distances and angles within the phenyl rings are unexceptional, physically unreasonable displacement parameters of some phenyl C atoms (Fig. 1 and Table 1) and the high final *R* value are consistent with some positional disorder of the phenyl rings.

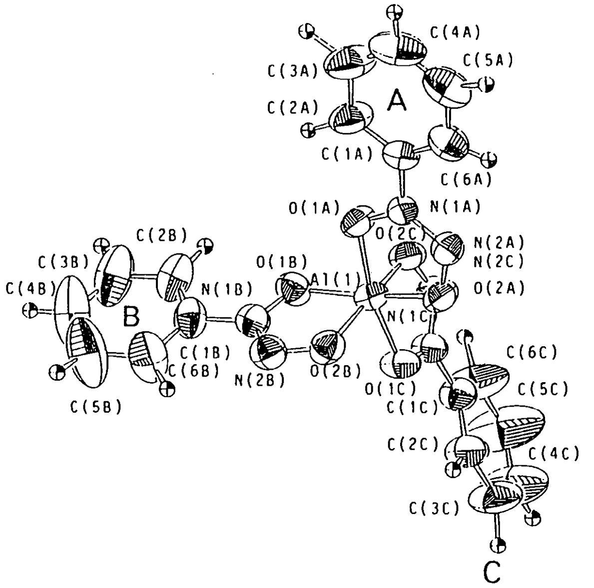


Fig. 1. *ORTEP*II (Johnson, 1976) view of (II) showing the atom-labelling scheme. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Crystals were obtained by slow evaporation at room temperature of solutions in 50% ethanol. The density D_m was measured by flotation in C_6H_6–CCl_4.

Crystal data

$[Al(C_6H_5N_2O_2)_3]$
$M_r = 438.33$
Monoclinic
$P2_1/n$
$a = 11.119\ (6)$ Å
$b = 16.062\ (3)$ Å
$c = 12.027\ (4)$ Å
$\beta = 100.72\ (3)°$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.15–11.75°$
$\mu = 0.137\ mm^{-1}$
$T = 296$ K
Plate

$V = 2110\,(1)$ Å^3
$Z = 4$
$D_x = 1.379$ Mg m^{-3}
$D_m = 1.394\,(1)$ Mg m^{-3}

0.3 × 0.3 × 0.2 mm
Colorless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5282 measured reflections
5035 independent reflections
1987 observed reflections $[I > 1.5\sigma(I)]$
$R_{\rm int} = 0.046$

$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 18$
$l = -15 \rightarrow 14$
3 standard reflections monitored every 150 reflections
frequency: 55 min
intensity decay: 0.92%

Refinement

Refinement on F
$R = 0.076$
$wR = 0.067$
$S = 1.65$
1987 reflections
280 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\max} = 0.016$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ 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)

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

	x	y	z	$B_{\rm eq}$
Al(1)	0.0428 (2)	0.2251 (1)	0.4621 (1)	4.17 (8)
O(1A)	0.0427 (4)	0.3263 (2)	0.5408 (3)	4.6 (2)
O(1B)	−0.1257 (3)	0.2355 (2)	0.4067 (3)	4.7 (2)
O(1C)	0.0749 (4)	0.1311 (2)	0.3789 (3)	4.9 (2)
O(2A)	0.2034 (3)	0.2236 (2)	0.5468 (3)	4.9 (2)
O(2B)	−0.0167 (4)	0.1549 (2)	0.5656 (3)	5.0 (2)
O(2C)	0.0791 (3)	0.2783 (2)	0.3318 (3)	4.8 (2)
N(1A)	0.1492 (4)	0.3404 (3)	0.6063 (4)	3.9 (2)
N(1B)	−0.1886 (5)	0.1928 (3)	0.4688 (4)	4.5 (2)
N(1C)	0.1055 (4)	0.1524 (3)	0.2830 (4)	4.4 (2)
N(2A)	0.2368 (4)	0.2876 (3)	0.6120 (4)	4.5 (2)
N(2B)	−0.1361 (5)	0.1488 (3)	0.5529 (4)	5.2 (3)
N(2C)	0.1087 (4)	0.2297 (3)	0.2540 (4)	4.7 (2)
C(1A)	0.1661 (6)	0.4165 (4)	0.6713 (5)	4.3 (3)
C(1B)	−0.3205 (6)	0.1972 (5)	0.4398 (6)	5.5 (3)
C(1C)	0.1393 (6)	0.0887 (4)	0.2114 (5)	4.9 (3)
C(2A)	0.0670 (7)	0.4681 (4)	0.6649 (6)	6.3 (4)
C(2B)	−0.3717 (6)	0.2532 (5)	0.3600 (5)	6.2 (4)
C(2C)	0.1680 (6)	0.0118 (4)	0.2585 (6)	6.2 (4)
C(3A)	0.084 (1)	0.5429 (5)	0.7254 (8)	8.5 (5)
C(3B)	−0.4984 (8)	0.2564 (7)	0.3326 (6)	9.0 (5)
C(3C)	0.2050 (8)	−0.0500 (4)	0.1930 (7)	8.6 (5)
C(4A)	0.196 (1)	0.5597 (5)	0.7899 (8)	8.7 (5)
C(4B)	−0.5663 (8)	0.2067 (9)	0.3867 (9)	11.5 (7)
C(4C)	0.210 (1)	−0.0352 (6)	0.0836 (9)	12.3 (7)
C(5A)	0.2934 (8)	0.5064 (6)	0.7957 (6)	7.4 (4)
C(5B)	−0.516 (1)	0.1519 (8)	0.4657 (8)	11.3 (7)
C(5C)	0.181 (1)	0.0416 (7)	0.0386 (8)	15.0 (8)
C(6A)	0.2775 (6)	0.4325 (4)	0.7356 (5)	5.5 (3)
C(6B)	−0.3890 (8)	0.1449 (6)	0.4930 (7)	8.5 (5)
C(6C)	0.146 (1)	0.1049 (5)	0.1041 (6)	9.9 (5)

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

Al(1)—O(1A)	1.882 (4)	C(1A)—C(2A)	1.370 (8)
Al(1)—O(1B)	1.875 (4)	C(1A)—C(6A)	1.358 (8)
Al(1)—O(1C)	1.881 (4)	C(1B)—C(2B)	1.361 (8)
Al(1)—O(2A)	1.885 (4)	C(1B)—C(6B)	1.369 (9)
Al(1)—O(2B)	1.888 (4)	C(1C)—C(2C)	1.371 (8)
Al(1)—O(2C)	1.894 (4)	C(1C)—C(6C)	1.331 (8)
O(1A)—N(1A)	1.314 (5)	C(2A)—C(3A)	1.399 (9)
O(1B)—N(1B)	1.308 (5)	C(2B)—C(3B)	1.387 (9)
O(1C)—N(1C)	1.308 (5)	C(2C)—C(3C)	1.377 (8)
O(2A)—N(2A)	1.304 (5)	C(3A)—C(4A)	1.37 (1)
O(2B)—N(2B)	1.312 (6)	C(3B)—C(4B)	1.35 (1)
O(2C)—N(2C)	1.307 (5)	C(3C)—C(4C)	1.35 (1)
N(1A)—N(2A)	1.285 (5)	C(4A)—C(5A)	1.37 (1)
N(1A)—C(1A)	1.444 (6)	C(4B)—C(5B)	1.34 (1)
N(1B)—N(2B)	1.282 (6)	C(4C)—C(5C)	1.36 (1)
N(1B)—C(1B)	1.445 (7)	C(5A)—C(6A)	1.384 (9)
N(1C)—N(2C)	1.291 (6)	C(5B)—C(6B)	1.39 (1)
N(1C)—C(1C)	1.432 (7)	C(5C)—C(6C)	1.38 (1)
O(1A)—Al(1)—O(1B)	90.4 (2)	O(1A)—Al(1)—O(1C)	168.1 (2)
O(1A)—Al(1)—O(2A)	80.1 (2)	O(1A)—Al(1)—O(2B)	98.7 (2)
O(1A)—Al(1)—O(2C)	92.6 (2)	O(1B)—Al(1)—O(1C)	99.1 (2)
O(1B)—Al(1)—O(2A)	167.6 (2)	O(1B)—Al(1)—O(2B)	80.7 (2)
O(1B)—Al(1)—O(2C)	91.1 (2)	O(1C)—Al(1)—O(2A)	91.3 (2)
O(1C)—Al(1)—O(2B)	89.8 (2)	O(1C)—Al(1)—O(2C)	80.3 (2)
O(2A)—Al(1)—O(2B)	92.8 (2)	O(2A)—Al(1)—O(2C)	97.3 (2)
O(2B)—Al(1)—O(2C)	166.0 (2)	Al(1)—O(1A)—N(1A)	111.5 (3)
Al(1)—O(1B)—N(1B)	110.8 (3)	Al(1)—O(1C)—N(1C)	111.5 (3)
Al(1)—O(2A)—N(2A)	116.8 (3)	Al(1)—O(2B)—N(2B)	116.0 (3)
Al(1)—O(2C)—N(2C)	116.3 (3)	O(1A)—N(1A)—N(2A)	120.5 (5)
O(1A)—N(1A)—C(1A)	118.9 (4)	N(2A)—N(1A)—C(1A)	120.6 (5)
O(1B)—N(1B)—N(2B)	121.8 (5)	O(1B)—N(1B)—C(1B)	117.5 (5)
N(2B)—N(1B)—C(1B)	120.7 (6)	O(1C)—N(1C)—N(2C)	120.9 (5)
O(1C)—N(1C)—C(1C)	119.0 (5)	N(2C)—N(1C)—C(1C)	120.1 (5)
O(2A)—N(2A)—N(1A)	111.1 (4)	O(2B)—N(2B)—N(1B)	110.7 (5)
O(2C)—N(2C)—N(1C)	111.0 (4)	N(1A)—C(1A)—C(2A)	117.4 (6)
N(1A)—C(1A)—C(6A)	118.8 (6)	C(2A)—C(1A)—C(6A)	123.8 (6)
N(1B)—C(1B)—C(2B)	118.4 (7)	N(1B)—C(1B)—C(6B)	119.0 (7)
C(2B)—C(1B)—C(6B)	122.6 (7)	N(1C)—C(1C)—C(2C)	117.5 (5)
N(1C)—C(1C)—C(6C)	120.8 (6)	C(2C)—C(1C)—C(6C)	121.7 (6)
C(1A)—C(2A)—C(3A)	117.3 (7)	C(1B)—C(2B)—C(3B)	117.7 (7)
C(1C)—C(2C)—C(3C)	119.0 (6)	C(2A)—C(3A)—C(4A)	119.2 (8)
C(2B)—C(3B)—C(4B)	120.0 (8)	C(2C)—C(3C)—C(4C)	120.2 (7)
C(3A)—C(4A)—C(5A)	122.2 (8)	C(3B)—C(4B)—C(5B)	122.3 (9)
C(3C)—C(4C)—C(5C)	119.7 (8)	C(4A)—C(5A)—C(6A)	119.1 (8)
C(4B)—C(5B)—C(6B)	119.5 (9)	C(4C)—C(5C)—C(6C)	120.7 (8)
C(1A)—C(6A)—C(5A)	118.3 (7)	C(1B)—C(6B)—C(5B)	117.9 (8)
C(1C)—C(6C)—C(5C)	118.7 (7)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Structure solution: *SHELXS*86 (Sheldrick, 1985); *DIRDIF* (Beurskens, 1984). Structure refinement: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1149). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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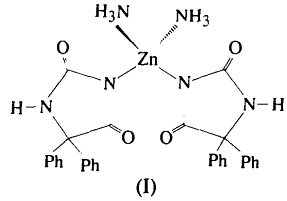
Abstract

In the title compound, diamminebis(5,5-diphenyl-2,4-imidazolidinedionato-N^3)zinc(II) hemihydrate, $[Zn(C_{15}H_{11}N_2O_2)_2(NH_3)_2].\frac{1}{2}H_2O$, 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).$\frac{1}{2}H_2O$, was synthesized and structurally examined to establish its coordination geometry and mode of bonding.



(I)

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—N3^{i} angle [N3^{i} 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···O2^{i} and O4···O4^{i} 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