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A Phenoxo-Bridged Digallium(III) Complex with a Ligand Derived from 2,6-Bis{[N,N'-bis(carboxymethyl)amino]-methyl}-4-methylphenol

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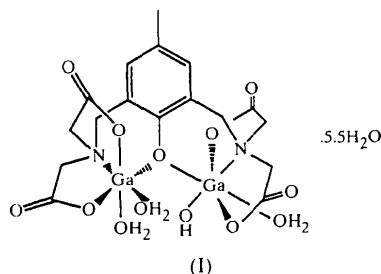
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Abstract

The title complex, triqua-1 κ^2 O,2 κ O-hydroxo-2 κ O- μ -{N,N'-(2-hydroxylato-5-methyl-*m*-phenylenedimethylene- κ^2 O:O)}bis[N-(carboxylatomethyl- κ O)glycinato- κ^2 N,O](5-)}-digallium(III) 5.5-hydrate, [Ga₂(OH)-(C₁₇H₁₇N₂O₉)(H₂O)₃].5.5H₂O, contains two octahedrally-coordinated Ga^{III} atoms. A hydroxyl group in the coordination sphere of one Ga atom corresponds to a water molecule in the second. The hydrogen-bond network includes an intramolecular hydrogen bond.

Comment

There is currently considerable interest in the design of polydentate chelating ligands that form stable complexes with group 13 metal ions (Al, In, Ga) (Caravan & Orvig, 1997). Several studies (Francesconi *et al.*, 1991; Lowe *et al.*, 1996) have suggested the use of gallium and indium radionuclides in radiopharmaceuticals for nuclear medicinal applications (Green & Welch, 1989). In order to extend the knowledge of the chemistry of such compounds and to obtain new metal complexes with greater stability, we prepared the title complex, triqua-1 κ^2 O,2 κ O-hydroxo-2 κ O- μ -{N,N'-(2-hydroxylato-5-methyl-*m*-phenylenedimethylene- κ^2 O:O)}bis[N-(carboxylatomethyl- κ O)glycinato- κ^2 N,O](5-)}-digallium(III) 5.5-hydrate, (I), and describe here its solid-state characterization.



During the preparation of the title complex, the pH of the solution was sufficiently high to lead to deprotonation of the four carboxylic acid functions; furthermore, the presence of Ga³⁺ ions ensures the deprotonation of the phenolic group. Thus, the ligand has a resulting charge of 5- and the neutrality of the complex is achieved by the presence of one hydroxyl group (rather than water) in the coordination sphere of one Ga atom.

The structure of the complex centres on the two Ga³⁺ cations, both of which have octahedral coordination. However, the two coordination spheres are different in two respects. Firstly, the Ga1 sphere contains two carboxylate O atoms (O1 and O3), a tertiary N atom, two water molecules (O11 and O12) and a phenolic O atom (O13), whereas the coordination sphere of the Ga2 atom differs in that one of the water molecules is replaced by a hydroxyl group (O10), induced by the addition of NaOH. Secondly, the relative arrangements of the ligands are different. The two carboxylate O atoms coordinated to Ga1 are in *cis* positions, but are *trans* for Ga2.

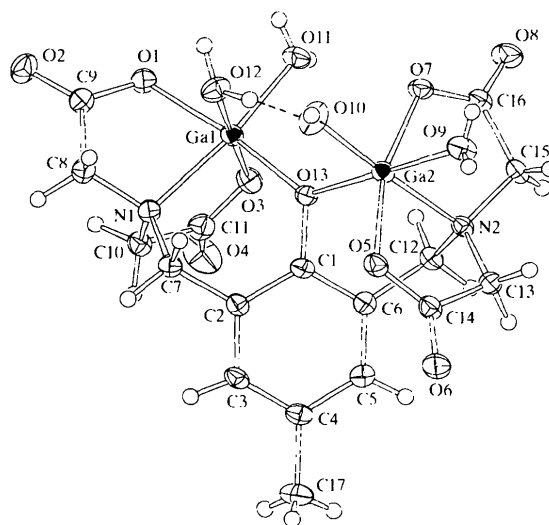


Fig. 1. ORTEP drawing (Johnson, 1976) of the title molecule with 35% probability displacement ellipsoids. The intramolecular hydrogen bond is represented by dashed lines. For clarity, non-ligand water has been omitted.

The two gallium coordinations are regular and the Ga—O and Ga—N distances (Table 1) are comparable with those found in similar compounds, [Ga₃(μ_3 -O)(μ -O₂CC₆H₅)₆(4-Mepy)₃]⁺[GaCl₄(4-Mepy)]⁻, where 4-Mepy is 4-methylpyridine (Andras *et al.*, 1992), and [Ga₂C₁₄H₃₅N₆O₄]³⁺·3I⁻·H₂O (Wiegardt *et al.*, 1986). In the title compound, the two Ga—O distances of the Ga—O—Ga bridge [1.999 (1) and 2.078 (1) Å] are among the longest, whereas the shortest [1.857 (2) Å], as

expected, is that to the hydroxyl group. [For the compound prepared by Andras *et al.* (1992), the only previous example to exhibit such a bridge, the bridging Ga—O distances were, however, the shortest of the gallium coordination.] The Ga1···Ga2 distance of 3.7260 (4) Å is the same (3.726 Å) as the observed Cu—Cu bond length in the copper complex of the same ligand (Holtz *et al.*, 1994).

The H atoms of the water molecules and that of the OH⁻ group form an intricate hydrogen-bond network (Table 2), resulting in the three-dimensional cohesion of the structure. The O12 water molecule is involved in an intramolecular hydrogen bond, with the OH⁻ group as acceptor. It must be noted that the H atoms of two water molecules, O18 and O19, could not be located because of the high displacement parameters of the O atoms. One of these O atoms, O19, is statistically disordered across a centre of symmetry.

Experimental

The title compound was prepared according to a procedure first reported by Schwarzenbach *et al.* (1952) and later modified by Murch *et al.* (1987). Addition of 1 equivalent of Ga(NO₃)₃.9H₂O to an aqueous solution (0.1 M) of the sodium salt of the ligand lowered the pH to 2. The pH was raised to 8–9 (with 1 M NaOH solution) and a further equivalent of Ga(NO₃)₃.9H₂O was added to the reaction mixture, which, upon standing for several days, yielded colourless crystals suitable for X-ray structure determination.

Crystal data

[Ga ₂ (OH)(C ₁₇ H ₁₇ N ₂ O ₉)(H ₂ O) ₃].5.5H ₂ O	Mo K α radiation
$M_r = 702.902$	$\lambda = 0.7107$ Å
Triclinic	Cell parameters from 23 reflections
$P\bar{1}$	$\theta = 10.1\text{--}13.3^\circ$
$a = 10.108$ (2) Å	$\mu = 2.194$ mm ⁻¹
$b = 10.925$ (2) Å	$T = 293$ K
$c = 13.061$ (6) Å	Prism with diamond-shaped cross-section
$\alpha = 100.05$ (2) $^\circ$	$0.52 \times 0.30 \times 0.30$ mm
$\beta = 107.65$ (3) $^\circ$	Colourless
$\gamma = 90.24$ (2) $^\circ$	
$V = 1350.8$ (7) Å ³	
$Z = 2$	
$D_x = 1.728$ Mg m ⁻³	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	5990 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.017$
Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)	$\theta_{\text{max}} = 29.96^\circ$
$T_{\text{min}} = 0.358$, $T_{\text{max}} = 0.518$	$h = 0 \rightarrow 14$
8155 measured reflections	$k = -15 \rightarrow 15$
7835 independent reflections	$l = -18 \rightarrow 17$
	2 standard reflections frequency: 120 min intensity decay: none

Refinement

Refinement on F	$\Delta\rho_{\text{max}} = 0.65$ e Å ⁻³
$R = 0.035$	$\Delta\rho_{\text{min}} = -0.41$ e Å ⁻³
$wR = 0.053$	Extinction correction: Zachariassen (1967, 1968)
$S = 1.310$	Extinction coefficient: $1.4(2) \times 10^{-6}$
5990 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
394 parameters	
Only H-atom U 's refined	
$w = 1/[\sigma^2(F_o) + 0.00063 F_o ^2]$	
$(\Delta/\sigma)_{\text{max}} = 0.068$	

Table 1. Selected bond distances (Å)

Ga1—O1	2.051 (2)	Ga2—O5	1.946 (1)
Ga1—O3	1.939 (2)	Ga2—O7	1.991 (1)
Ga1—O11	1.972 (2)	Ga2—O9	2.029 (2)
Ga1—O12	1.920 (2)	Ga2—O10	1.857 (2)
Ga1—O13	1.999 (1)	Ga2—O13	2.078 (1)
Ga1—N1	2.077 (2)	Ga2—N2	2.116 (2)

Table 2. Hydrogen-bonding geometry (Å, $^\circ$)

D—H···A	D—H	H···A	D···A	D—H···A
O9—H93···O2 ⁱ	0.76	1.92	2.672 (2)	169.7
O9—H94···O14 ⁱⁱ	0.74	1.88	2.615 (2)	174.0
O10—H103···O17 ⁱⁱⁱ	0.87	2.04	2.900 (3)	169.2
O11—H113···O16 ^{iv}	0.89	1.87	2.742 (3)	167.4
O11—H114···O7 ^v	0.91	1.88	2.782 (2)	172.0
O12—H123···O10	0.91	1.53	2.433 (2)	174.2
O12—H124···O8 ^{vi}	0.90	1.80	2.680 (2)	163.8
O14—H14 ^{vii} ···O1	0.96	1.81	2.753 (2)	164.9
O14—H14 ^{viii} ···O16 ^{ix}	0.86	1.94	2.796 (3)	174.2
O15—H15 ^x ···O6 ^x	1.00	2.02	3.008 (4)	170.0
O15—H15 ^{xi} ···O4	0.92	1.93	2.831 (3)	164.2
O16—H16 ^{xii} ···O17	0.90	2.05	2.801 (3)	139.9
O16—H16 ^{xiii} ···O15 ^{xiv}	0.94	1.95	2.869 (4)	166.8
O17—H17 ^{xv} ···O8	1.09	1.87	2.936 (3)	164.1
O17—H17 ^{xvi} ···O19 ^{xvii}	1.11	1.67	2.61 (1)	138.4
O17—H17 ^{xviii} ···O19 ^{xviii}	1.11	1.81	2.88 (1)	159.3

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x, -y, -z$; (iii) $1 + x, y, z$; (iv) $-1 - x, -y, -z$; (v) $-x, -y, 1 - z$; (vi) $x - 1, y - 1, z - 1$.

H atoms were located from Fourier difference syntheses and then refined using a riding model. The presence of a hydroxyl group was thus unambiguously established. A peak of 1.87 e Å⁻³ near a symmetry centre was attributed to water molecule O19; its high U value may indicate partial occupation, but the ideal occupation of 0.5 was assumed for calculating the composition and related parameters.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1260). Services for accessing these data are described at the back of the journal. An ellipsoid plot showing the solvate water molecules has also been deposited.

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Doxylaminium Tetrachlorozincate(II) and Doxylaminium Tetrachlorocobaltate(II)

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Abstract

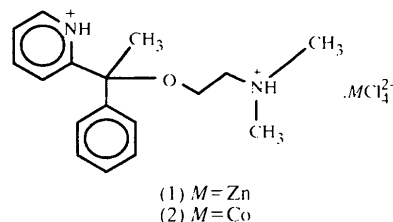
Doxylamine is an anti-allergic ether effective on H₁-type receptors. The crystal structures of dihydro cationic salts of doxylamine {2-[1-(dimethylammonioethoxy)-1-phenylethyl]pyridinium} with the anions tetrachlorozincate(II), (C₁₇H₂₄N₂O)[ZnCl₄], and tetrachlorocobaltate(II), (C₁₇H₂₄N₂O)[CoCl₄], are isomorphous. The molecular dimensions in both structures are normal, and the anions and cations are hydrogen bonded, resulting in chain structures. The ZnCl₄²⁻ and CoCl₄²⁻ anions exhibit normal tetrahedral geometries.

Comment

Doxylamine, 2-[1-(dimethylaminoethoxy)-1-phenylethyl]pyridine, C₁₇H₂₂N₂O, is a chiral tertiary aminoalkyl ether which exhibits an antihistaminic action on the H₁ receptor site (Casy, 1991). The crystal structures of a number of compounds belonging to this class of ethers that possess anti-allergic activities have been

reported, *e.g.* diphenhydramine hydrochloride (Glaser & Maartmann-Moe, 1990), diphenhydramine thiourea complex (Wiedenfeld & Knoch, 1987), carbinoxamine maleate (Bertolasi *et al.*, 1980) and clemastine hydrogen fumarate (Parvez & Wendling, 1991). Glaser *et al.* (1992) have reported the crystal structure of orphenadrine hydrochloride, a skeletal muscle relaxant, which is also closely related to these compounds.

Our interest in the conformations of antihistamines effective on H₁ receptors has led to the preparation of dihydro cationic salts of doxylamine in order to investigate the influence of tetrachlorozinc(II) and tetrachlorocobalt(II) ions on the conformation of doxylamine. In this paper, we report the crystal structures of doxylaminium tetrachlorozincate(II), (1), and doxylaminium tetrachlorocobaltate(II), (2). The crystal structures of dihydro cationic salts of several antihistamines, *e.g.* clemizole.CuCl₄²⁻ and clemizole.CoCl₄²⁻ (Parvez & Sabir, 1997*a*), chlorpyramine.CuCl₄²⁻ (Parvez & Sabir, 1997*b*), and triprolidine.CuCl₄²⁻ (Parvez & Sabir, 1997*c*), have been reported recently by our laboratory.



Compounds (1) and (2) are isomorphous. An *ORTEPII* (Johnson, 1976) drawing of compound (1) is shown in Fig. 1. The molecular dimensions in the cations of both compounds are normal with the following respective mean bond distances: C_{sp³}—C_{sp³} 1.517 (14) and 1.52 (2), C_{sp³}—C_{sp²} 1.522 (4) and 1.527 (12), O—C_{sp³} 1.432 (5) and 1.438 (15), N—C_{sp³} 1.478 (9) and 1.484 (7), N—C_{sp²} 1.337 (4) and 1.350 (7), C—C_{pyridyl} 1.372 (6) and 1.375 (11), and C—C_{aromatic} 1.378 (11) and 1.382 (13) Å.

The ethereal O atom in each of (1) and (2) is not only hydrogen bonded to the ammonium H atom, but is also hydrogen bonded to the pyridinium H atom, *i.e.* both lone pairs of electrons of the ethereal O atom of the antihistamine in each of (1) and (2) are oriented towards H atoms bonded to N atoms. The N···O separations for these intramolecular interactions in the two structures lie between 2.513 (6) and 2.748 (7) Å. The N—H groups are also hydrogen bonded to the Cl atoms of two MCl₄²⁻ anions [$M = \text{Zn}$ in (1) and Co in (2)], with N···Cl separations in the range 3.211 (6)–3.265 (5) Å, thus forming hydrogen-bonded structures extending along the *a* axis, as observed in the structure of clemizole.CoCl₄²⁻ (Parvez & Sabir, 1997*a*). Similar bifurcated hydrogen bonding has been reported for the dihydro cation of the antihistamine chlorpyramine