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Crystal Structure of $Li(H_2O)_3[GaEdta]$

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Abstract—The ethylenediaminetetraacetate complex $Li(H_2O)_3[Ga(Edta)]$ was synthesized and its crystal structure composed of octahedral $(Ga(Edta)^-$ anions connected to the $Li(H_2O)_3^+$ ion through the oxygen atom was studied. Five of the six hydrogen atoms of water molecules are involved in weak hydrogen bonds with the oxygen atoms of four $Ga(Edta)^-$ complexes, the complex anion is hydrogen-bonded to five water molecules. In addition, shortened contacts C(221)–H(22*A*)···O(112) between the $Ga(Edta)^-$ anions were found. As a result, the molecular packing in the crystal is determined by the three-dimensional lace of hydrogen bonds. The results are compared with published data for the lithium salts of Bi(III), Sb(III), Fe(III), Ni(II), and Hg(II) ethylenediaminetetraacetates.

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Metal complexes with ethylenediaminetetraacetic acid (H_4Edta) are used in analytical chemistry, chelatotherapy, for the preparation of metal nanoparticles and other high-technology oxide and chalcogenide materials. Heterometallic complexes are used as precursors for the preparation of mixed oxides with useful properties [1].

The structures of compounds containing the $Ga(Edta)^-$ complex anion were studied less comprehensively than $M^{III}(Edta)^-$ (M = Bi, Sb, Fe). For the latter compounds, lithium salts were obtained and their structures were solved by X-ray diffraction. The Cambridge Crystallographic Data Centre (CCDC) [2] contains X-ray diffraction data for nine compounds containing Li^+ and $Edta^{4-}$ ions. The lithium polyhedron in these compounds is a distorted tetrahedron and its hydrated forms exist as both separate ions and bridging fragments. One may also expect other structural forms of lithium hydration environment in complexes of triply charged metals with $Edta^{4-}$.

The purpose of this work was to prepare the lithium salt of gallium(III) ethylenediaminetetraacetate $Li(H_2O)_3[Ga(Edta)]$ (**I**) and to determine its crystal structure.

EXPERIMENTAL

Synthesis. $[Ga(Edta)(H_2O)]$ synthesized by a reported procedure [3] and reagent grade Li_2CO_3 were used. The colorless crystals of **I** were prepared by reaction of these reactants at 1 : 1 molar ratio in an aqueous solution followed by slow evaporation of the solvent for several days.

X-Ray diffraction analysis was carried out on a SMART APEX II (Bruker) diffractometer with a two-coordinate CCD detector with a 0.32-mm crystal fragment. The absorption corrections were applied using the SADABS program [4]. The structural model was found by the direct method and refined in the anisotropic approximation for nonhydrogen atoms (SHELXTL) [5]. The hydrogen atoms were located from the difference electron density syntheses and refined with attachment to the corresponding atoms with free refinement of thermal parameters. Finally, the maximum and minimum difference electron density values were 0.39 and –0.29 e Å^{-3}.

X-Ray experiment details and structure refinement parameters are summarized in Table 1. The crystal data are deposited with the CCDC (no. 714374); http:/www.ccdc.cam.ac.uk(data_request/cif).

RESULTS AND DISCUSSION

Apart from the octahedral molecular complex anions $Ga(Edta)^-$ and lithium ions, the crystal unit cell contains three independent water molecules, which form, together with one oxygen of the $Ga(Edta)^-$ anion, the tetrahedral environment of the lithium ion (Fig. 1). In this compound, $Edta^{4-}$ is a hexadentate ligand (O,O',O'',O''', N, N'). The interatomic distances are as follows: C–C, 1.517–1.530 Å (aver. 1.523(2) Å); C–N, 1.476–1.489 Å (aver 1.485(2) Å). If oxygen atoms are parts of the GaN_2O_4 octahedron, the C–O distances for them are in the range of 1.288–1.300 Å (aver. 1.296(2) A). The other C–O bond lengths (1.217–1.232 Å, aver. 1.223(2) Å) are consistent with their predominantly double bond nature. The Ga–O bond length is

Table 1. X-Ray experiment details and structure refinement parameters for $Li(H_2O)_3[Ga(Edta)]$

Parameter	Value
Molecular formula	$C_{10}H_{18}GaLiN_2O_{11}$
M	418.92
System, space group	Monoclinic, $P2_1/n$
a, Å	8.578(1)
b, Å	10.084(2)
c, Å	17.520(3)
β, deg	95.171(2)
V, Å^3	1509.2(7)
Z	4
ρ(calcd.), g/cm^3	1.844
μ, cm^{-1}	0.189
Radiation (λ, Å)	MoK_α (0.71073)
θ_{min}–θ_{max}, deg	2.33–28.5
Scan mode	φ/ω scan mode
The number of reflections measured/independent	13953/3821
The number of reflections ($I > 2\sigma(I)$)	3464
R_{int}/R_σ	0.019/0.017
The number of refined parameters	262
R_1 for $I > 2\sigma(I)$ (for all)	0.021/0.025
wR_2	0.059
GOOF	1.03

1.942(1)–1.969(1) Å. The OGaO bond angles are 86.13(4)°–112.73(4)°. The Ga–N bond lengths are 2.098(1) and 2.095(1) Å. The geometric parameters of structure **I** almost coincide with those obtained for other compounds containing the $Ga(Edta)^-$ anion, for example, $[Ga(Edta)(H_2O)]$, $K[Ga(Edta)] \cdot 2H_2O$, and $NH_4[Ga(Edta)] \cdot 2H_2O$ [2].

The Li atom is coordinated by three oxygen atoms of water molecules. The $Li(H_2O)_3^+$ ion is connected to the O(212) atom of one of the four carbonyl groups of $Edta^{4-}$. The length of the C(212)–O(212) double bond (1.232(2) Å) differs from the other three bond lengths by only 0.01 Å, whereas the Li–O(212) bond is 0.062–0.102 Å longer than the three bonds of Li ion with water molecules. Apparently, this bond is mainly due to the ion–dipole interaction. The O(212)C(212)O(21) bond angle of the carboxyl group is ~0.8° smaller than the corresponding angles in the three carboxyl groups not bound to Li. The Li polyhedron is a distorted tetrahedron. The Li–O(212) bond length (1.998 Å) is comparable with these distances in *catena*–$Li[Fe(Edta)(H_2O)] \cdot 2H_2O$ (**II**) (1.910 and 2.003 Å), $Li(H_2O)_4[Bi_2Li(Edta)_2(Tu)_4(H_2O)_2] \cdot 5H_2O$ (**III**, Tu is thiourea) (1.916 and 1.942 Å), *catena*–$Li(H_2O)_2[Bi(Edta)] \cdot 2H_2O$ (**IV**) (1.920 and 1.940 Å), $Li[Ni)(HEdta)(H_2O)] \cdot H_2O$ (**V**) (1.904, 1.913, 2.011 Å), and *catena*-$Li[Sb(Edta)(H_2O)] \cdot H_2O$ (1.913, 1.928, 1.957, and 1.972 Å) [2]. Three shorterLi–O(*w*) bonds in **I** correspond to a greater contribution of the covalent component.

The hydrated Li^+ ion was found in complexes **I–V** and $Li_4[Hg(Edta)]_2 \cdot 8H_2O$ (**VI**). In complex **III**, lithium is contained not only in an isolated tetrahedral $Li(H_2O)_4^+$ ion but also in the $[Bi_2Li(Edta)_2(Tu)_4(H_2O)_2]^-$ dimeric anion as a bridging $Li(H_2O)_2^+$, fragment connecting two $[[Bi(Edta)(Tu)_2]^-]$ anions through two O atoms of different $Edta^-$ ions. The same bridging ion binds the $[Bi(Edta)]^-$ anion in structures **II** and **IV**. In structure **V**, the lithium atom is bound only to one water molecule, its tetrahedral coordination being completed by three oxygen atoms of thee $[Ni(HEdta)]^-$ complexes. The same type of hydration environment as in compound **I** was found for Li atom only in structure **VI** in which three Li–O(*w*) bonds (1.955–1.979 Å) are longer than in **I**. Conversely, the Li–O bond in **VI** (1.968 Å) is shorter than Li–O(212) in **I** (1.998 Å). This difference is beyond the limits of experimental errors and can be attributed to different chemical natures of gallium(III) and mercury(II) atoms.

In structure **I**, five of the six hydrogen atoms of water molecules are involved in weak hydrogen bonds with the oxygen atoms of four $GaEdta^-$ complexes (Fig. 2,

Table 2. Geometric parameters of hydrogen bonds in the structure $Li(H_2O)_3[Ga(Edta)]$

D–H···A contact*	distance, Å			DHA angle, deg
	D–H	H···A	D···A	
O(*w*1)–H(*w*1*A*)···O(1)1[a]	0.84(3)	2.01(3)	2.838(2)	170(2)
O(*w*1)–H(*w*1*B*)···O(122)[b]	0.82(3)	1.95(3)	2.772(2)	174(3)
O(*w*2)–H(*w*2*A*)···O(22)[c]	0.83(3)	2.00(3)	2.835(2)	175(3)
O(*w*2)–H(*w*2*B*)···O(112)[d]	0.74(3)	2.20(3)	2.838(2)	144(3)
O(*w*3)–H(*w*3*A*)···O(222)[c]	0.81(3)	2.38(2)	3.123(3)	153(2)
C(221)–H(22*A*)···O(112)[d]	0.97	2.39(3)	3.350(2)	171(3)

* Symmetry operations for A atoms: [a] $1 - x, -y, 1 - z$; [b] $x - 1/2, 1/2 - y, z + 1/2$; [c] $1/2 - x, y - 1/2, 1/2 - z$; [d] $x - 1, y, z$.

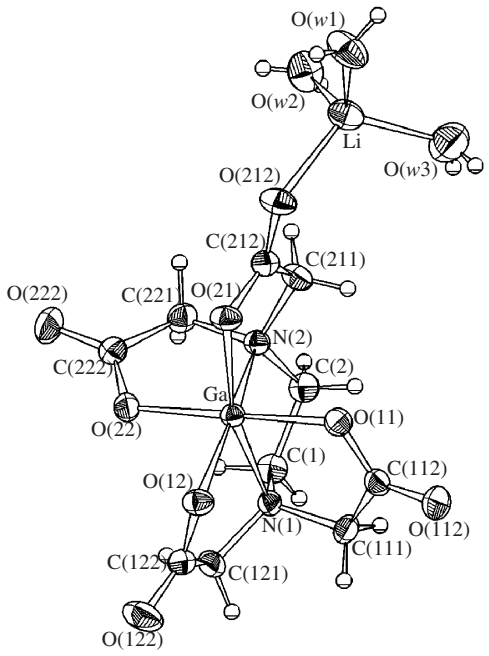

Fig. 1. Structure of the complex $Li(H_2O)_3[Ga(Edta)]$. Bond lengths (Å): Li–O(212), 1.998(3); Li–O(*w*1) 1.896(3); Li–O(*w*2), 1.908(3); Li–O(*w*3), 1.936(3); углы (град): O(212)LiO(*w*1) 103.2(1), O(212)LiO(*w*2) 108.8(1), O(212)LiO(*w*3) 116.2(2), O(*w*1)LiO(*w*2) 116.4(2), O(*w*1)LiO(*w*3) 111.3(2), O(*w*2)Li(O(*w*3) 101.6(2).

Table 2). Each complex is hydrogen-bonded to five water molecules (Fig. 3). In addition, there are shortened contacts C(221)–H(22*A*)···O(112) between the $GaEdta^-$ and two neighboring ions (Table 2). The molecules in the crystal are combined into chains along the

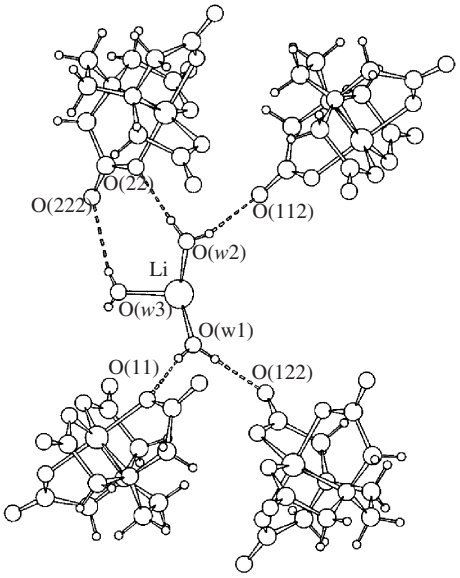

Fig. 2. Hydrogen bond distribution around the $Li(O(w))_3$ group.

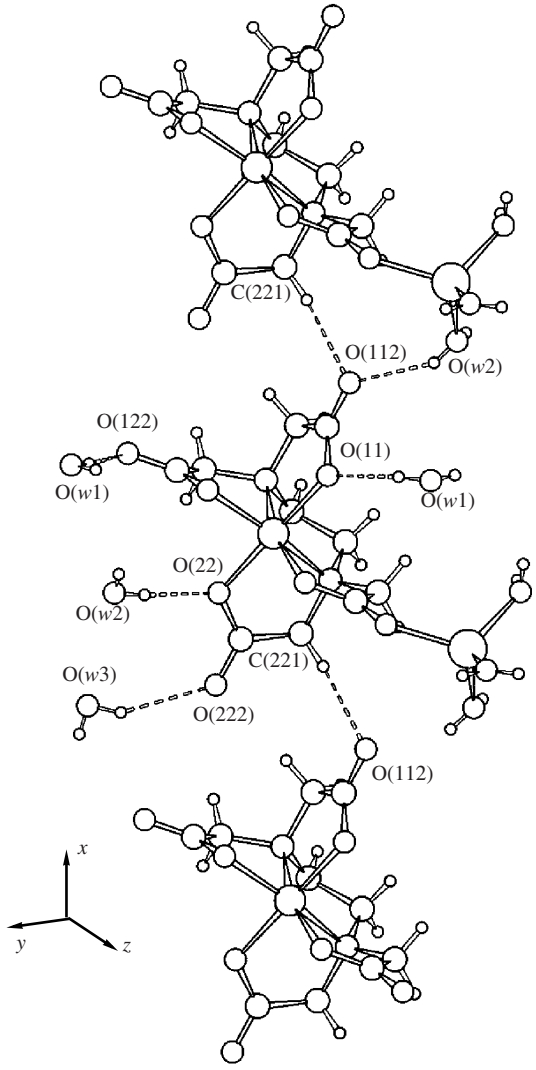

Fig. 3. Hydrogen bonds of the $Ga(Edta)^-$ molecular ions with neighbors.

z axis with axial line coordinates (0.5, 0, *z*) and (0, 0.5, *z*) where hydrogen-bonded pairs of molecules are the units of the chain. As a result, the molecular packing in the crystal is determined by the three-dimensional lace of hydrogen bonds.

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