

CRYSTAL AND MOLECULAR STRUCTURE OF LITHIUM BENZOHYDROXAMATE–BENZOHYDROXAMIC ACID (1 : 1) ADDUCT

Roman RERICHA^a, Ivana CISAROVA^b and Jaroslav PODLAHA^{b,*}

^a *Institute of Chemical Process Fundamentals,*

Academy of Sciences of the Czech Republic, 165 02 Prague 6-Suchbát, Czech Republic

^b *Department of Inorganic Chemistry,*

Charles University, 128 40 Prague 2, Czech Republic

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The crystal structure of the title compound was determined by single crystal X-ray diffraction. It consists of molecules of benzohydroxamic acid, its *O*-deprotonated anions and lithium cations in the 1 : 1 : 1 molar ratio. Although the molecular geometry of the anion is very similar to that of the acid, these units can be unambiguously distinguished since the short hydrogen bond between the OH group of the acid and the *N*-bonded oxygen atom of the anion is remarkably asymmetric. This bond, together with the lithium cations (being surrounded by five oxygens), links the units into chains running in the crystallographic *ab* plane. The coordination polyhedron around Li represents a rare example of an almost undistorted LiO₅ square pyramidal arrangement.

Key word: Benzohydroxamic acid, adduct with lithium benzohydroxamate.

Despite the importance of hydroxamic acids in biological processes, their structure is often poorly characterized. Some of the problems delineated in an early review¹ have been clarified in recent papers²⁻⁴. Little is known, however, about the solid state structures of simple hydroxamate salts in which deprotonation site(s) of the anion should, in principle, depend on the charge, size and hard-soft character of the counteranion. We describe here the synthesis and crystal structure of the acid salt of benzohydroxamic acid with Li⁺ as the representative of small univalent cations of remarkably hard character.

EXPERIMENTAL

Synthesis

A boiling aqueous suspension of Li₂CO₃ was filtered into 0.1 M benzohydroxamic acid in 10% (v/v) aqueous methanol (10 ml). The resulting solution (total volume 18 ml) was partly evaporated by boil-

* The author to whom correspondence should be addressed.

ing to 15 ml and left to crystallize by slow evaporation at room temperature. Colourless needles up to several mm in length suitable for X-ray diffraction were obtained.

Single-Crystal X-Ray Diffraction – Crystal and Measurement Data

$C_{14}H_{13}LiN_2O_4$, m.w. 190.64, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 5.1956(6)$, $b = 12.4431(6)$, $c = 20.192(1)$ Å, $V = 1\,305.4(2)$ Å³, $Z = 4$, $D_c = 1.426$ g cm⁻³, $F(000) = 584$. A colourless prismatic crystal of the dimensions $0.18 \times 0.21 \times 0.57$ mm was measured at 293(2) K on a CAD4 diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Absorption was neglected ($\mu = 0.104$ mm⁻¹). The cell parameters were determined from 25 reflections in the

TABLE I
Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement parameters (Å² · 10³). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O1	5158(2)	-1025(1)	-761(1)	37(1)
O2	1033(2)	-366(1)	-135(1)	36(1)
N1	5283(3)	-203(1)	-300(1)	33(1)
C1	3259(3)	1004(1)	466(1)	29(1)
C2	5177(3)	1782(1)	449(1)	38(1)
C3	5182(4)	2601(2)	910(1)	45(1)
C4	3298(4)	2642(2)	1393(1)	49(1)
C5	1395(4)	1877(2)	1408(1)	52(1)
C6	1367(3)	1064(2)	944(1)	41(1)
C7	3108(3)	97(1)	-11(1)	28(1)
Li	3174(5)	1955(2)	4600(1)	31(1)
O11	1797(2)	2538(1)	5453(1)	28(1)
O12	-2267(2)	1885(1)	6136(1)	36(1)
N11	2018(3)	1895(1)	6010(1)	27(1)
C11	349(3)	931(1)	6934(1)	27(1)
C12	-1420(4)	142(2)	7085(1)	41(1)
C13	-1075(4)	-513(2)	7632(1)	54(1)
C14	1034(4)	-376(2)	8031(1)	51(1)
C15	2768(4)	427(2)	7897(1)	46(1)
C16	2457(3)	1075(2)	7348(1)	38(1)
C17	-72(3)	1609(1)	6333(1)	26(1)
HO1	6494(49)	-1578(19)	-616(11)	66(7)
HN1	6712(40)	30(16)	-206(9)	39(5)
HN11	3561(39)	1742(14)	6131(8)	32(5)

TABLE II

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses. Symmetry code: (i), $0.5 - x, -y, z - 0.5$; (ii), $x - 0.5, y - 0.5, 1 - z$; (iii), $x + 0.5, y - 0.5, 1 - z$; (iv), $0.5 - x, -y, z + 0.5$; (v), $1 - x, y - 0.5, 0.5 - z$; (vi), $x + 1, y, 0.5 - z$

Acid		Anion	
Atoms	Bond lengths	Atoms	Bond lengths
C1–C2	1.390(2)	C11–C12	1.378(2)
C1–C6	1.379(2)	C11–C16	1.390(2)
C1–C7	1.486(2)	C11–C17	1.494(2)
C2–C3	1.381(2)	C12–C13	1.385(3)
C3–C4	1.382(3)	C13–C14	1.371(3)
C4–C5	1.373(3)	C14–C15	1.372(3)
C5–C6	1.379(3)	C15–C16	1.381(2)
C7–O2	1.248(2)	C17–O12	1.256(2)
C7–N1	1.325(2)	C17–N11	1.316(2)
O1–N1	1.384(2)	O11–N11	1.385(2)
N1–HN1	0.82(2)	N11–HN11	0.86(2)
O1–HO1	1.02(2)		
Atoms	Bond angles	Atoms	Bond angles
C2–C1–C6	119.4(2)	C12–C11–C16	119.0(2)
C2–C1–C7	123.36(14)	C12–C11–C17	118.90(14)
C6–C1–C7	117.2(2)	C16–C11–C17	122.1(2)
C1–C2–C3	120.6(2)	C11–C12–C13	120.6(2)
C4–C3–C2	120.1(2)	C14–C13–C12	119.9(2)
C5–C4–C3	120.0(2)	C13–C14–C15	120.0(2)
C4–C5–C6	120.0(2)	C14–C15–C16	120.4(2)
C5–C6–C1	120.5(2)	C15–C16–C11	120.0(2)
O2–C7–N1	121.19(14)	O12–C17–N11	121.22(13)
O2–C7–C1	121.76(14)	O12–C17–C11	123.03(14)
N1–C7–C1	117.05(14)	N11–C17–C11	115.74(14)
N1–O1–Li ⁱ	101.69(11)	N11–O11–Li ⁱⁱ	107.83(11)
		N11–O11–Li	117.36(11)
		Li ⁱⁱ –O11–Li	114.02(10)
C7–O2–Li ⁱ	108.55(12)	C17–O12–Li ⁱⁱ	108.41(12)
C7–N1–O1	117.65(14)	C17–N11–O11	119.33(13)
C7–N1–HN1	125(1)	C17–N11–HN11	125(1)
O1–N1–HN1	117(1)	O11–N11–HN11	116(1)

TABLE II
(Continued)

Atoms	Bond lengths	Atoms	Bond angles
Li-environment			
Li-O11	2.001(3)	O11 ⁱⁱⁱ -Li-O11	105.68(13)
Li-O11 ⁱⁱⁱ	1.988(3)	O11 ⁱⁱⁱ -Li-O12 ⁱⁱⁱ	81.14(10)
Li-O12 ⁱⁱⁱ	2.084(3)	O11-Li-O12 ⁱⁱⁱ	108.89(13)
Li-O2 ^{iv}	2.089(3)	O11 ⁱⁱⁱ -Li-O2 ^{iv}	97.33(12)
Li-O1 ^{iv}	2.206(3)	O11-Li-O2 ^{iv}	101.15(12)
		O12 ⁱⁱⁱ -Li-O2 ^{iv}	149.2(2)
		O11 ⁱⁱⁱ -Li-O1 ^{iv}	153.1(2)
		O11-Li1-O1 ^{iv}	101.16(12)
		O12 ⁱⁱⁱ -Li-O1 ^{iv}	92.36(11)
		O2 ^{iv} -Li-O1 ^{iv}	75.08(10)
Hydrogen bonding			
O1...O11 ^v	2.467(2)	O1-HO1...O11 ^{vi}	173(2)
HO1...O11 ^v	1.45(2)		

15–19° θ -range. The intensities of reflections were measured by the θ –2 θ scan between h \langle –6,6 \rangle , k \langle 0,15 \rangle , l \langle 0,24 \rangle , $\theta_{\max} = 26^\circ$. Three standard reflections monitored every 1 h showed an intensity variation of 2%. Of 2 742 measured reflections, 2 565 were unique ($R_{\text{int}} = 0.015$) and 2 182 were regarded as “observed” according to the $I \geq 2\sigma(I)$ criterion.

Data Treatment

The structure was solved by direct methods⁵ (SHELXS86) and refined⁶ by SHELXL93 using a full-matrix least-squares procedure based on F^2 . Phenyl hydrogens were fixed in calculated positions and assigned the isotropic displacement parameters of their bonding carbons multiplied by 1.2; the *N*- and *O*-bonded hydrogen atoms, clearly visible on the difference map, were refined isotropically. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2 |F_o^2| + (0.0376P)^2 + 0.15P]$, $P = (F_o^2 + 2F_c^2)/3$. Convergence for 202 parameters was achieved at $R = 0.0291$, $R_w = 0.0713$, GOF = 1.048, $(\Delta/\sigma)_{\max} = \pm 0.001$ for non-H atoms. The final difference electron density map was featureless with extremum values of 0.12; $-0.24 \text{ e } \text{\AA}^{-3}$.

The final atom coordinates are in Table I and bond lengths and angles in Table II. The tables of the observed and calculated structure factors and of the anisotropic displacement parameters, as well as the standard CIF files produced by SHELXL93, can be obtained upon request.

DESCRIPTION OF STRUCTURE

The symmetrically independent part of the structure (Fig. 1) consists of one lithium cation, one benzohydroxamate anion and one molecule of benzohydroxamic acid. As expected for the hard lithium cation, the deprotonated site of the anion is the *N*-bonded oxygen atom. Although the anion and the acid are metrically very similar (see Fig. 2 for their superposition), they can be easily distinguished since the locations of the critical hydrogen atom HO1 (and of HN1 and HN11, too) are unambiguous. The geometry of the "organic" part is unexceptional and the bond distances lie within the ranges tabulated for similar fragments⁷. Both the planarity of the C(O)N(H)O fragments (within ± 0.009 Å) and the involved bond distances and angles indicate a high degree of electron delocalization. Moreover, the formally single bond linking the phenyl and hydroxamate groups is shortened significantly. The hydroxamate fragments differ a little in the amount of twist around this bond: the dihedral angle between the mean planes of hydroxamate and phenyl groups is $24.35(10)^\circ$ for the anion and $35.42(8)^\circ$ for the acid. It appears, however, that this is the consequence of hydrogen bonding rather than an indication of different electronic distribution within the anion and the acid.

From the viewpoint of coordination chemistry, the behavior of the anion and of the acid as ligands towards lithium is totally different. While the acid acts as a bidentate O,O'-chelating donor, the anion is terdentate: O,O'-chelating to one lithium cation and simultaneously O-bridging through the deprotonated oxygen atom O11 to the second, symmetry-related lithium cation. This bonding mode is satisfied through a chain of LiO₅ polyhedra linked by one common vertex (Fig. 3). The chain runs parallel to the crystallographic *ab*-plane and is further stabilized by a short hydrogen bond between

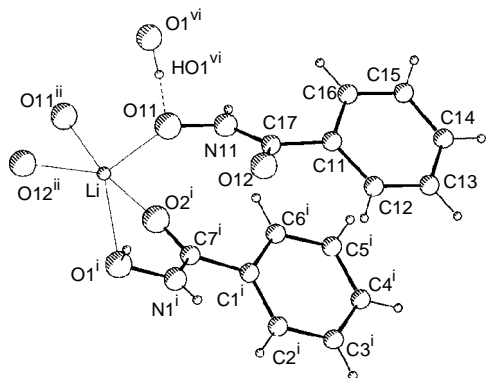


FIG. 1

View of symmetrically independent part of the structure with atom labelling; lithium environment completed by intermolecular contacts; H-bond involving O11 shown as dotted line. For symmetry code, see Table II

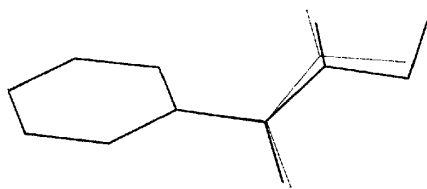


FIG. 2

Superposition of hydroxamic acid (thick lines) and hydroxamate anion; phenyl ring taken as reference

the OH group of the acid and the deprotonated oxygen atom of the anion. In contrast to many similar cases of polymeric acid salts of this type (see ref.⁸ for a recent example and for discussion of this phenomenon), this hydrogen bond is markedly asymmetric, thus excluding any possibility of "averaging" the acid and the anion. Five oxygen atoms are located around lithium at the distances of 1.988–2.206 Å in a spatial arrangement which is uncommon for lithium cation. The polyhedron approximates closely to tetragonal pyramid having one O11 atom of the anion at the axial site and the second, symmetry-related O11 atom at the equatorial site; the remaining equatorial positions are occupied by the O12 atom of the anion and the O1, O2 atoms of the chelated acid. In general, LiO_5 polyhedra are infrequent and only 25 such fragments could be retrieved from Cambridge Structural Database⁹. The analysis of their shape according to the method of Muetterties and Guggenberger¹⁰ (which is capable to characterize the distortion of bond angles quantitatively) suffered from vast differences of Li–O bond lengths in most of the polyhedra, as might be expected for a non-transition element. To take these differences into account, the data were parametrized as follows. In the scatterogram depicted in Fig. 4, the y -axis is defined as $\Delta = [\sum|(d_m - d_i)|]/5$, i.e., as the average difference between the mean Li–O distance, and the individual five distances; the x -axis is $\alpha = \delta_3 - \delta_2$ and describes the Berry pseudorotation which interconverts the two idealized pentacoordinated polyhedra, trigonal bipyramid and tetragonal pyramid. The

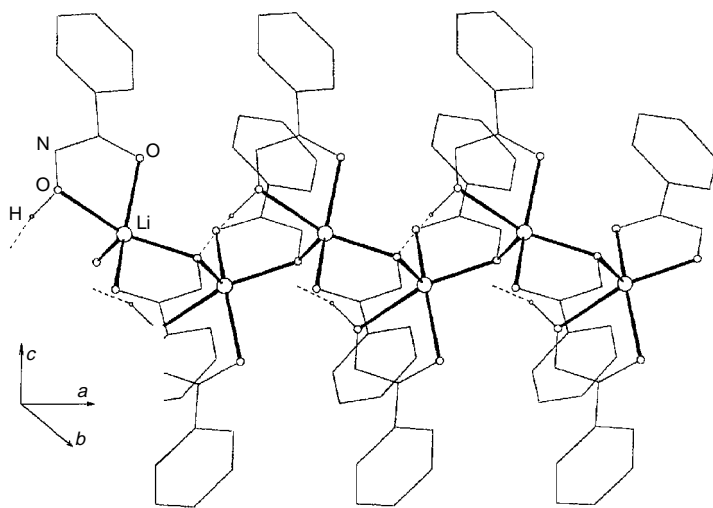


FIG. 3

Fragment of chain of LiO_5 polyhedra showing hydrogen bonds between hydroxamate fragments

δ 's are the second and third lowest dihedral angles between the adjacent polyhedron faces according to Muetterties and Guggenberger's definition. Since the values of δ_2 , δ_3 , α are 53.1, 53.1, 0° for regular trigonal bipyramid but 0, 75.7, 75.7 $^\circ$ for tetragonal pyramid, the horizontal axis of the scatterogram describes the pathway interconverting the idealized forms, and the vertical axis is a qualitative measure of the overall deformation originating from unequal bond lengths. Clearly, most fragments may be described as more or less distorted trigonal bipyramid and only five of them are close to tetragonal pyramid. Within the square pyramidal family, all polyhedra are isolated with Li–Li distances greater than 5 Å. Hence, the present structure appears to be unique with respect to the linking of the square pyramidal LiO_5 polyhedra.

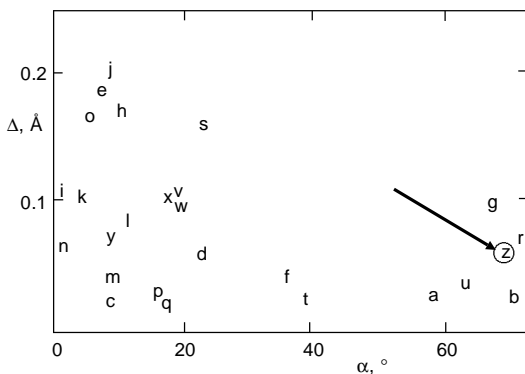


FIG. 4

Scatterogram of geometry of LiO_5 polyhedra (the present structure is marked by arrow). For definition of axes, see text. Compound CODENs and short references from CSD are as follows: a CAW-REX20, *J. Inclusion Phenomena* 12, 341 (1992); b DIVVUZ, *J. Chem. Res.* 388, 4201 (1985); c DIXSIM, *Inorg. Chim. Acta* 111, L39 (1986); d DOLJAP, *Proc. Natl. Acad. Sci.* 82, 7155 (1985); e DOZZAT, *Inorg. Chem.* 25, 1027 (1986); f FADHEX, *Acta Crystallogr.*, C 42, 1329 (1986); g GAVZAE, *Tetrahedron Lett.* 29, 1259 (1988); h, i GAXYUZ, j, k GAXZAG, *Rev. Chim. Miner.* 24, 382 (1987); l GEKFOR, *Polyhedron* 4, 567 (1985); m, n HAGREM, *Acta Chem. Scand.* 47, 663 (1993); o, p, q JAKCIH, *Z. Naturforsch.*, B 44, 444 (1989); r JITREJ, *Acta Crystallogr.*, C 47, 1968 (1991); s KEXDIA, *Can. J. Chem.* 68, 1201 (1990); t KEXXAM, *Can. J. Chem.* 68, 49 (1990); u KOXCUV, *J. Am. Chem. Soc.* 113, 6570 (1991); v PAHXEB, *Z. Naturforsch.*, B 47, 1141 (1992); w SEMWUC, *Acta Crystallogr.*, C 46, 465 (1990); x WEVREU, *Tetrahedron Lett.* 35, 2525 (1994); y YADTIG, *Z. Anorg. Allg. Chem.* 612, 72 (1992)

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