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The Crystal Structure of Lithium 2-Carbamoylphenoxyacetate

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An extension of the current program of investigation of the nature of the divalent metal complexes of phenoxyalkanoic acids to include the Group 1A metal ions has to date provided only one new structure, potassium 2,4-dichlorophenoxyacetate hemihydrate [1]. This complex is 8-coordinate with an irregular stereochemistry having K–O distances ranging from 2.69–3.11 Å. Elsewhere, the structure of sodium phenoxyacetate hemihydrate was shown to have an irregular MO_8 coordination with Na–O distances ranging from 2.30–2.61 Å [2]. It is also possible with these salts to obtain adducted acid species in the crystal lattice, first observed in the analogous thio series with potassium (phenylthio)-acetate–(phenylthio)acetic acid [3]. In this complex, both species are involved in coordination to K. Because of the more regular coordination observed for lithium salts of carboxylic acids, the Li salt of 2-carbamoyl-phenoxyacetic acid, [Li(SA)] was prepared and its structure determined by X-ray diffraction, to obtain the complex stereochemistry and to verify the possible participation of the acid amide group of the SA ligand in coordination with the metal. Previous examples of metal complexes with the ligand SA, $[Cu(SA)_2(H_2O)_2]$ and $[Ni(SA)_2(H_2O)_4]$ [4], show no coordination involving the amide group. However, the latter group was involved in both inter and intramolecular hydrogen bonding interactions in both complexes.

Experimental

Preparation

The title compound was prepared by reacting an aqueous ethanolic solution of 2-carbamoylphenoxyacetic acid (SAH) with excess lithium carbonate at 80–90 °C on a steam bath. Crystals were obtained as colourless needles by partial room temperature evaporation of the filtrate.

Crystal Data

$C_9H_8LiNO_4$, $M_r = 201.1$, orthorhombic, $a = 4.965(2)$, $b = 11.660(5)$, $c = 15.060(7)$ Å, $V = 871.9(6)$ Å^3, $Z = 4$, $D_c = 1.532$ g cm^{-3}, $D_m = 1.554$ g cm^{-3}, $F(000) = 416$, $\lambda = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 1.12$ cm^{-1}, space group $P2_12_12_1(D_2{}^4$, No. 19).

X-ray Data Collection, Structure Solution and Refinement

Data were collected on a Nicolet R3m four-circle diffractometer using monochromated Mo Kα radiation. 705 unique reflections were collected from one crystal (0.26 × 0.20 × 0.08 mm) up to $2\theta_{\max} = 45°$. Of these, 607 with $I > 2.5\sigma(I)$ were considered observed and were used in structure analysis. Data were processed using the learnt profile fitting procedure of Diamond [5] and used without corrections for absorption or extinction. The structure was solved by the non-centrosymmetric tangent refinement direct methods of SHELX-76 [6] and refined by full-matrix least-squares to a final $R\{=\Sigma||F_o - F_c||/\Sigma||F_o||\}$ of 0.051. Unit weights were used. Hydrogen atoms were located in a difference-Fourier synthesis and included in the refinement at fixed positions with their isotropic U values set invariant at 0.05 Å^2. Neutral atom scattering factors were used [7] with corrections for the effects of anomalous dispersion [7]. Final atomic parameters and equivalent isotropic thermal parameters [defined as $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$] are listed in Table I while bond distances and angles are given in Table II. Lists of anisotropic thermal parameters together with observed and calculated structure factors and hydrogen atom coordinates are available from the authors.

Discussion

The structure of Li(SA) consists of lithium ions coordinated to 2-carbamoylphenoxyacetate ligands to form a three-dimensional polymeric network (Figs. 1, 2). The four-coordination about Li is distorted tetrahedral [angle range, 103.3–122.8(5)°; Li–O range, 1.913–1.985(10) Å], comprising an oxygen from the 2-carbamoyl group and three from the carboxyl groups of different SA ligands. Two are from O(11) ($1 - x$, $-\frac{1}{2} + y$, $-\frac{1}{2} - z$; $1\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$) the other O(10) ($\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$). These Li–O distances are considered normal for lithium carboxylates, where tetrahedral stereochemistry predominates (Table III). Only in one example, lithium ammonium citrate monohydrate [22] is octahedral

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TABLE I. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2; ×10^3) for Li(SA)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}^{a}	Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}^{a}
Li	1570(21)	3399(10)	142(7)	31(5)	C(5)	4495(19)	8649(6)	−1643(4)	45(4)
C(1)	6351(13)	6770(5)	−1868(4)	29(3)	C(6)	6381(14)	7932(5)	−2060(4)	34(4)
C(2)	4613(12)	6315(5)	−1240(4)	25(3)	O(7)	8123(9)	6006(3)	−2256(3)	32(2)
C(21)	4472(15)	5081(6)	−951(4)	31(3)	C(8)	9834(13)	6403(6)	−2953(4)	27(3)
O(21)	2403(10)	4687(4)	−637(3)	46(3)	C(9)	8412(13)	6703(5)	−3821(4)	23(3)
N(21)	6642(11)	4451(5)	−1034(4)	41(3)	O(10)	5950(8)	6495(4)	−3901(3)	30(3)
C(3)	2729(15)	7047(5)	−830(4)	35(4)	O(11)	9895(8)	7141(4)	−4406(3)	30(2)
C(4)	2737(15)	8215(6)	−1027(4)	41(4)					

$^a[U_{eq} = U_{11}U_{22}U_{33})^{1/3}]$.

TABLE II. Bond Distances (Å) and Angles (°) for Li(SA)

(a) Distances					
Li–O(21)	1.950(11)	C(1)–O(7)	1.382(7)	C(4)–C(5)	1.371(10)
Li–O(10)^a	1.913(10)	C(2)–C(3)	1.409(9)	C(5)–C(6)	1.403(10)
Li–O(11)^b	1.977(11)	C(2)–C(21)	1.505(9)	O(7)–C(8)	1.427(7)
Li–O(11)^c	1.985(10)	C(21)–O(21)	1.221(9)	C(8)–C(9)	1.526(8)
C(1)–C(2)	1.386(8)	C(21)–N(21)	1.310(9)	C(9)–O(10)	1.252(8)
C(1)–C(6)	1.385(9)	C(3)–C(4)	1.394(9)	C(9)–O(11)	1.257(7)
(b) Angles					
O(21)–Li–O(10)^a	122.8(5)	C(6)–C(1)–C(2)	121.6(6)	C(3)–C(4)–C(5)	120.4(6)
O(21)–Li–O(11)^b	108.2(5)	C(2)–C(1)–O(7)	116.0(5)	C(4)–C(5)–C(6)	120.5(6)
O(21)–Li–O(11)^c	105.2(5)	C(6)–C(1)–O(7)	122.4(5)	C(5)–C(5)–C(1)	118.8(6)
O(10)^a–Li–O(11)^b	103.3(5)	C(1)–C(2)–C(3)	118.7(6)	C(1)–O(7)–C(8)	118.7(5)
O(10)^a–Li–O(11)^c	109.9(5)	C(1)–C(2)–C(21)	126.3(6)	O(7)–C(8)–C(9)	115.4(5)
O(11)^b–Li–O(11)^c	106.4(5)	C(3)–C(2)–C(21)	114.9(5)	C(8)–C(9)–O(10)	119.3(5)
Li–O(21)–C(21)	134.5(5)	C(2)–C(21)–O(21)	120.7(6)	C(8)–C(9)–O(11)	115.0(5)
Li–O(10)^a–C(9)^a	134.3(5)	C(2)–C(21)–N(21)	118.1(6)	O(10)–C(9)–O(11)	125.7(6)
Li–O(11)^b–C(9)^b	118.6(5)	O(21)–C(21)–N(21)	121.2(6)		
Li–O(11)^c–C(9)^c	129.0(5)	C(2)–C(3)–C(4)	119.8(6)		

$^a(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$. $^b(1 - x, -\frac{1}{2} + y, -\frac{1}{2} - z)$. $^c(1\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$.

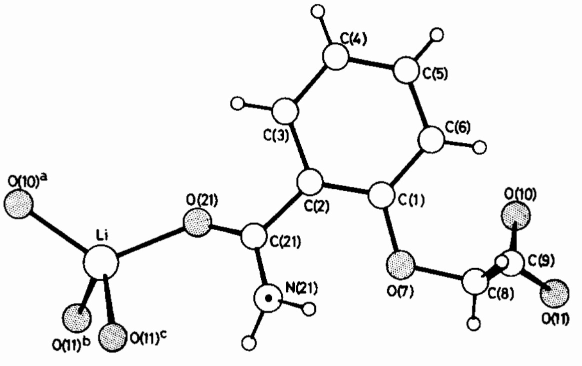

Fig. 1. Molecular configuration and atom labeling scheme for Li(SA).

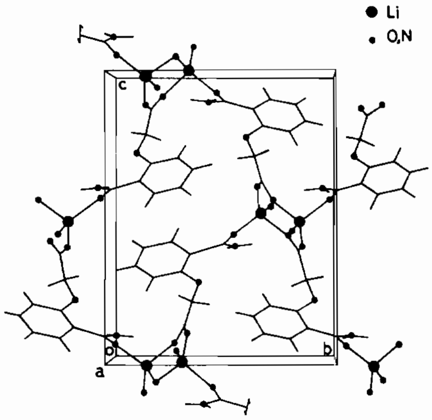

Fig. 2. Packing of Li(SA) in the unit cell.

coordination found. Furthermore, polymers in several variations are formed without exception, irrespective of whether the compound is anhydrous or hydrated. Coordination involving the oxygen of the amide group is unique among the known complexes of 2-carbamoylphenoxyacetic acid [4]. A greater tendency exists for chelation to occur involving the ether oxygen of the phenoxy group.

TABLE III. Comparative Structural Data for Lithium Carboxylates

Compound	Coordination		Li–O range (Å)	Reference
Lithium 2-carbamoylphenoxyacetate	$(LiO_4)_n$	tetrahedral	1.91–1.98	This study
Lithium formate monohydrate	$(LiO_3Ow)_n$	tetrahedral	1.92–1.95	8
Lithium acetate dihydrate	$[LiO_2(Ow)_2]_n$	tetrahedral	1.90–2.04	9
Lithium oxalate	$(LiO_4)_n$	tetrahedral	1.93–2.07	10
Lithium hydrogen oxalate monohydrate	$(LiO_4Ow)_n$	distorted square pyramidal	2.07–2.27	11, 12
Lithium oxalate monoperhydrate	$(LiO_3O_2)_n$	distorted square pyramidal	1.90–2.33	13
Lithium succinate	$(LiO_4)_n$	tetrahedral	1.94–1.96	14
Lithium hydrogen phthalate dihydrate	$(LiO_4)_n$	tetrahedral	1.90–2.00	15
Lithium hydrogen maleate	$(LiO_3Ow)_n$	tetrahedral	1.92–1.95	16
Lithium hydrogen malate	$[LiO_3(OH)]_n$	tetrahedral	1.91–2.00	17
Lithium glycolate	$[LiO_4(OH)]_n$	distorted square pyramidal	1.95–2.36	18
Lithium glycolate monohydrate	$[LiO_4(OH)]_n$	distorted square pyramidal	2.01–2.10	19
Lithium oxydiacetate	$(LiO_5)_n$	trigonal bipyramidal	2.03–2.12	20
Lithium ammonium tartrate	$(LiO_4Ow)_n$	distorted trigonal bipyramidal	1.96–2.20	21
Lithium ammonium citrate monohydrate	$(LiO_6)_n$	octahedral	1.96–2.49	22
Lithium [(edta)Fe^{III}] dehydrate	$[LiO_2(Ow)_2]$	tetrahedral	1.91–2.01	23
Lithium [$(en)_3Cr^{III}$] *d*-tartrate trihydrate	(LiO_3Ow)	tetrahedral	1.94–2.04	24
Lithium [(Hedta)Ni^{II}] dihydrate	(LiO_3Ow)	tetrahedral	1.88–2.05	25

The SA ligand is itself twisted unlike the complexes $[Cu(SA)_2(H_2O)_2]$ and $[Ni(SA)_2(H_2O)_4]$ [4] where the preferred planar conformation is found. Both the oxoacetate side-chain [torsion angles: C(2)–C(1)–O(7)–C(8), (+176°); C(1)–O(7)–C(8)–C(9), (−69°); O(7)–C(8)–C(9)–O(11), (+174°)] and the carbamoyl group [torsion angle C(1)–C(2)–C(21)–N(21), (+26°)] are out of the phenyl plane. Those conformational changes are probably the result of the polymer formation. The N–H···O-(ether) hydrogen bond [2.686(8) Å] in Li(SA) is comparable with the values of 2.63 Å and 2.62 Å for the copper and nickel examples respectively, despite the differences in the conformation of the ligands.

The molecular packing of Li(SA) in the unit cell is almost devoid of any intermolecular hydrogen bonding associations among the polymer chains, only one [N(21)···O(21)′, 2.94 Å] being found.

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