X-Ray Crystal Structure of Lithium Azide Monohydrate, and Net Atomic Charges as Obtained by the Extended L-Shell Method

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Summary The structure of LiN_3,H_2O has been determined from single-crystal X-ray diffractometer data and charges on the atoms obtained by least-squares refinement on the occupancy of the atomic valence shells.

SMALL colourless needles of LiN_3,H_2O were grown from an aqueous solution prepared by the exchange of a lithium-saturated resin with sodium azide. The hexagonal crystals belong to space group $P6_3/mcm$, $Z = 6$, $a = b = 9{\cdot}259$ (12) Å, $c = 5{\cdot}594(11)$ Å. Data were collected on a Picker 4-circle diffractometer with graphite monochromatized Mo-K_α radiation. Full-matrix least-squares refinement including anisotropic temperature parameters and isotropic extinction gives an R_F of 0·042 for 216 uniquely observed reflections (23 parameters).

The lithium atoms occupy two different octahedral sites, one surrounded by the oxygens of six water molecules; the other by the terminal nitrogens of each of six azide ions. The (001) projection (Figure) clearly shows the lithium co-ordination, which is similar to that found[1] in $LiClO_4$,$3H_2O$, though the Li–O distance of 2·170(3) Å is slightly longer than the corresponding distances in the perchlorate (2·112 and 2·150 Å).[2] The present structure appears to be the first instance of 6-fold nitrogen co-ordination about lithium. The Li–N distance of 2·226(3) Å is longer than the Li–N distances of 2·10, 2·07, 1·94, and 2·06 Å in four-co-ordinate lithium compounds previously reported for benzyl-lithium triethylenediamine,[3] $LiX,2(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)$ (X = Cl, Br),[4] $Li(NH_3)_4$[5] and LiCN[6] respectively. The N–N distance is 1·174(2) Å which compares well with values ranging from 1·157 to 1·193 Å[7] reported recently for other symmetric azides.

Hydrogen-bonds are found between the water molecules and the terminal atoms of the azide groups. The N · · · · H distance of 2·148 Å is shorter than the sum of the van der Waals radii, 2·9 Å, and is even shorter (by perhaps 0·1 Å), if the well known apparent shortening of *X*-ray O–H bond-lengths is taken into account.

Net charges on the atoms in the crystal were obtained by

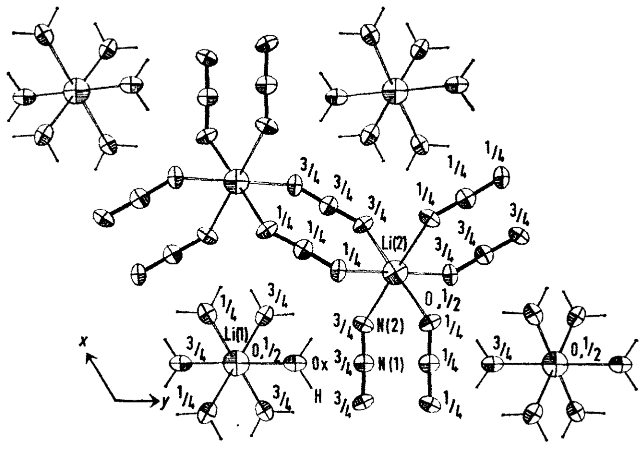

FIGURE. *Lithium azide monohydrate*, (001) *projection. Numbers indicate height along* c *axis.*

the extended L-shell projection method, in which the electron occupancy of a spherical valence-shell is refined simultaneously with the other structural parameters.[8] Optimized Slater type orbitals (STO)[9] ($\zeta_{\mathrm{Li}} = 0{\cdot}75$; $\zeta_{\mathrm{N}} = 1{\cdot}95$ a.u.$^{-1}$) were used for the calculation of valence shell scattering, while the core electrons were represented by an isolated-atom Hartree-Fock basis set. The results (Table) indicate that the Li atoms are practically neutral, though the standard deviations in the Li charges are large as a result of the diffuseness of the Li valence electron. The positive charges which the Li would have according to the ionic formula are distributed over the co-ordinated water molecules or serve to neutralize part of the azide-ion negative charge. As a result the water molecules are more positive than found with the extended L-shell method for a number of crystalline hydrates in which water is not co-ordinated to a metal atom.[8] The central atom of the azide group is more positive than the terminal atoms, in qualitative (but not quantitative) agreement with results of INDO calculations on N_3^- (see Table). INDO calculations on a Li atom surrounded by three azide groupings also confirm the approximate neutrality of the lithium for this type of basis functions. Calculated charges agree somewhat better with the experimental results when a larger fragment of the crystal is included in the calculation.

TABLE

Experimental and calculated net atomic charges (proton units)[a]

	expt.	calc. N_3^-	calc. LiN_3	calc. $[Li(N_3)_3]^{2-}$
Li (1)[b]	− 0·21 (40)			
O	+ 0·20 (11)			
H	+ 0·05 (9)			
Li (2)	− 0·55 (45)		+ 0·50	+ 0·15
N (1)	+ 0·19 (9)	+ 0·36	+ 0·36	+ 0·34
N (2)	− 0·02 (9)	− 0·67	− 0·52	− 0·49
N (3)	as N (2)	− 0·67	−0·34	− 0·56

[a] Experimental net atomic charges are the differences between the number of valence electrons in the neutral atom and the occupancy of a spherical valence shell defined by optimized Slater-type orbitals[9] and determined by least-squares refinement of the *X*-ray data. Calculated charges are from Mulliken population analysis of INDO calculations (on parts of the crystal) with the same atomic orbitals.

[b] Li (1) is H_2O co-ordinated; Li (2) is co-ordinated by the azide group. N (1) is the central atom of the azide group. Calculations of fragments of the crystal were done at the experimental geometry. N (2) is co-ordinated to Li (2) in the second and third calculation.

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