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X-ray Structure of bis(Diacetamide)(nitrato)lithium(I)

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It has been shown that lithium salts may form complexes in which the anion as well as neutral ligands are included in the coordination sphere [1, 2]. However, attempts to determine anion coordination by infrared spectroscopy have not always been conclusive since the coordination may not cause sufficient distortion in the symmetry of the anion to be detectable. Such was the case with $NaClO_4 \cdot 2DA$ (DA = diacetamide), which was shown by X-ray crystallography to contain coordinated perchlorate [3]. Since $LiNO_3 \cdot 2DA$ was part of the same infrared study as $NaClO_4 \cdot 2DA$, and the nitrate was believed to be ionic [4], an X-ray structure analysis was undertaken to determine whether the nitrate was in fact coordinated to the lithium.

Experimental

Crystals of the title compound were obtained by dissolving stoichiometric amounts of anhydrous $LiNO_3$ and diacetamide in methanol and allowing the solvent to evaporate slowly. Oscillation and zero and first layer Weissenberg photographs showed the crystals to be triclinic. Intensity data were measured at room temperature on an Enraf-Nonius CAD-4 automated diffractometer using monochromated Cu Kα radiation and a crystal measuring 0.50 × 0.30 × 0.20 mm. The unit cell parameters were determined by a least-squares fit of the angular settings for 15 reflections and found to be a = 7.126(2), b = 7.804(2), c = 12.345(3) Å, α = 107.91(2), β = 94.57(2), γ = 94.39(2)°. Density determined by flotation (D_o) was 1.37 Mg/m^3 to give $Z = 2$ (D_c = 1.36 Mg/m^3), indicating space group $P\bar{1}$. The ω–2θ scanning mode was used for the data collection with $\theta \leqslant 73°$. The intensities were corrected for Lorentz-polarization effects, but not for absorption [μ(Cu Kα) = 1.03 mm^{-1}]. Of 2539 possible independent reflections, 2349 were accepted as observed on the criterion $I \geqslant 1.5\sigma(I)$.

The structure was solved by direct methods using the program REL [5]. All subsequent calculations were performed with the NRC system [6]. An electron density map calculated from one set of normalized structure factors showed the positions of the non-hydrogen atoms. Isotropic and anisotropic refinement of positional and thermal parameters was carried out. A difference electron density map showed the positions of all the hydrogen atoms. Refinement was then continued on all positional parameters, anisotropic thermal parameters for the non-hydrogen atoms, and isotropic thermal parameters for the hydrogen atoms. The function minimized was $\Sigma w(|F_o| - k|F_c|)^2$, where $w = 1/\sigma^2(F)$ and was obtained from counting statistics for the observed reflections, while unobserved reflections were weighted zero. In the final cycle R = 0.075 for w = 1.0 and R_w = 0.078. The atomic coordinates are given in Table I. The scattering factors for the non-hydrogen atoms

TABLE I. Fractional Coordinates and their e.s.d.s

Atom	*x*	*y*	*z*
Li	0.2418(7)	0.8914(8)	0.2093(4)
C(1)	−0.0739(4)	0.7189(4)	0.0250(3)
C(2)	0.2751(4)	0.6367(5)	−0.0153(3)
C(3)	0.2081(4)	0.8314(4)	−0.0444(2)
C(4)	0.2783(5)	0.8583(5)	−0.1492(3)
C(5)	0.5352(4)	0.7396(4)	0.3219(3)
C(6)	0.7183(5)	0.6591(6)	0.3274(4)
C(7)	0.2661(4)	0.8231(4)	0.4332(2)
C(8)	0.1920(5)	0.8125(5)	0.5407(3)
N(1)	0.0240(3)	0.7561(4)	−0.0574(2)
N(2)	0.4436(3)	0.7670(3)	0.4182(2)
O(1)	−0.0054(3)	0.7506(3)	0.1229(2)
O(2)	0.3066(3)	0.8744(3)	0.0463(2)
O(3)	0.4736(3)	0.7795(3)	0.2394(2)
O(4)	0.1788(3)	0.8788(3)	0.3649(2)
N(3)	0.2467(4)	1.3009(4)	0.3208(2)
O(5)	0.2318(6)	1.1576(4)	0.2412(3)
O(6)	0.1377(5)	1.4092(4)	0.3061(3)
O(7)	0.3576(6)	1.3427(6)	0.4049(4)
H(1)	−0.037(5)	0.735(5)	−0.117(3)
H(2)	0.480(5)	0.728(5)	0.462(3)
H(2,1)	−0.329(7)	0.711(7)	−0.042(4)
H(2,2)	−0.267(8)	0.515(8)	−0.062(5)
H(2,3)	−0.347(9)	0.622(9)	0.048(6)
H(4,1)	0.340(10)	0.976(9)	−0.124(6)
H(4,2)	0.272(6)	0.754(6)	−0.198(4)
H(4,3)	0.177(8)	0.908(8)	−0.189(5)
H(6,1)	0.691(7)	0.557(6)	0.351(4)
H(6,2)	0.746(12)	0.583(12)	0.256(7)
H(6,3)	0.802(11)	0.739(11)	0.360(6)
H(8,1)	0.157(6)	0.687(6)	0.527(4)
H(8.2)	0.104(7)	0.907(6)	0.562(4)
H(8,3)	0.275(8)	0.845(7)	0.592(4)

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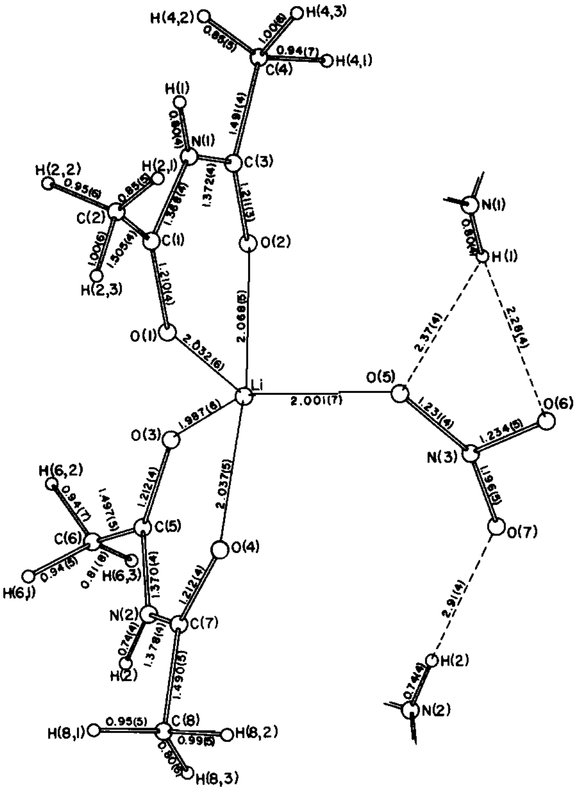

Fig. 1. Structure of $LiNO_3 \cdot 2DA$ with interatomic distances (A).

are from International Tables for X-ray Crystallography [7], and that for hydrogen is from Stewart *et al.* [8].

Results and Discussion

The structure of $LiNO_3 \cdot 2DA$ is shown in Fig. 1. The Li atom is 5-coordinate, bonded by the four oxygens of the diacetamide molecules and by one oxygen of the nitrate. The Li–O distances fall within the ranges of those found in other lithium complexes [9–11]. The coordination sphere is a slightly distorted trigonal bipyramid, similar to those of other 5-coordinate lithium structures [10, 11]. There is distortion of the nitrate group symmetry from D_{3h} to C_{2v} via a shortening of the N(3)–O(7) bond that is observable in the infrared spectrum. However, this is caused by hydrogen bonding to a diacetamide nitrogen rather than by coordination to the lithium. The original infrared interpretation [4] is consistent with this finding since it was based on peak assignments for the diacetamide as well as for the nitrate. Infrared spectroscopy alone could not prove coordination of the nitrate since if coordination did cause distortion of the N(3)–O(5) bond, the resulting symmetry would still be C_{2v} [12]. The Li–O(5) is not sufficiently strong to cause significant distortion of the N–O bond as the N(3)–O(5) and N(3)–O(6) distances are similar. Hydrogen bonding exists between the nitrate group and the diacetamide nitrogens as shown in Fig. 2, resulting in the formation of infinite chains parallel to 001. Bond distances (Fig. 1) and angles are in good agreement with standard values. Angles involving the lithium atom are given in Table II.

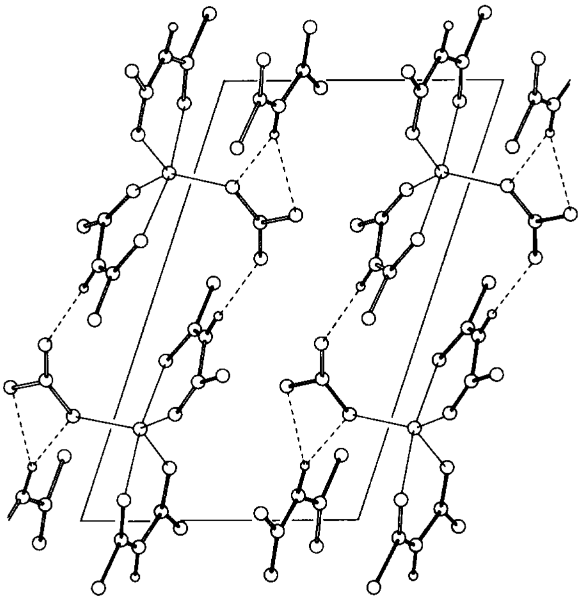

Fig. 2. Unit cell contents. Methyl hydrogens have been omitted for clarity.

TABLE II. Angles (°) and their e.s.d.s for the LiO_5 Group

O(1)–Li–O(3)	124.6(3)
O(3)–Li–O(5)	124.2(3)
O(5)–Li–O(1)	110.7(3)
O(2)–Li–O(1)	82.7(2)
O(2)–Li–O(3)	91.4(2)
O(2)–Li–O(5)	88.6(2)
O(4)–Li–O(1)	94.9(2)
O(4)–Li–O(3)	85.4(2)
O(4)–Li–O(5)	97.5(3)
O(2)–Li–O(4)	173.9(3)

References

1 F. Durant, P. Piret and M. VanMeerssche, *Acta Crystallogr., 22,* 52 (1967).

2 F. Durant, Y. Gobillon, P. Piret and M. VanMeerssche, *Bull. Soc. Chim. Belg., 75,* 52 (1966).

3 P. S. Gentile, J. G. White and D. D. Cavalluzzo, *Inorg. Chim. Acta, 18,* 183 (1976).

4 P. S. Gentile and T. A. Shankoff, *J. Inorg. Nucl. Chem., 27,* 2301 (1965).

5 R. E. Long, *Ph.D. Thesis,* University of California at Los Angeles, 1965.

6 F. R. Ahmed, S. R. Hall, M. E. Pippy and C. P. Huber, *J. Appl. Crystallogr., 6,* 324 (1973).

7 'International Tables for X-ray Crystallography, Vol. III', Kynoch Press, Birmingham, 1962, p. 201–214.

8 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42,* 3175 (1965).

9 P. S. Gentile, J. G. White and D. D. Cavalluzzo, *Inorg. Chim. Acta, 20,* 37 (1976).

10 H. Herbertsson, *Acta Crystallogr., Sect. B:, 32,* 2381 (1976).

11 J. O. Thomas, *Acta Crystallogr., Sect. B:, 28,* 2037 (1972).

12 C. C. Addison, N. Logan, S. C. Wallwork and C. D. Garner, *Chem. Soc. Rev.,* 289 (1971).