Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Oxygen *versus* nitrogen interactions in lithium dinitramidate dihydrate and pyridinium dinitramidate

Thomas M. Klapötke,* Burkhard Krumm and Matthias Scherr

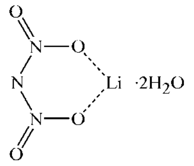
Department of Chemistry and Biochemistry, Ludwig-Maximilian University,
Butenandtstrasse 5–13, D-81377 Munich, Germany
Correspondence e-mail: tmk@cup.uni-muenchen.de

Received 18 October 2007
Accepted 29 October 2007
Online 14 December 2007

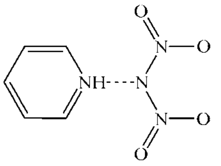
The title compounds, diaquadinitramidatolithium(I), [Li(N_3O_4)(H_2O)$_2$], (I), and pyridinium dinitramidate, $C_5H_6N^+\cdot N_3O_4^-$, (II), differ significantly in their cation–anion contacts. The Li^+ atom of (I) is coordinated by two O atoms of the dinitramide anion in a chelate and by four additional water molecules, with the Li and central N atom of the anion on a twofold rotation axis. The pyridinium cation of (II) exhibits a contact with the dinitramide anion *via* an intermolecular N—H$\cdots$N hydrogen bridge. These interactions are compared with those found in reported anhydrous lithium dinitramide and ammonium dinitramide salts.

Comment

The potential coordination modes (Trammell *et al.*, 1996) of dinitramide include monodentate coordination to the central N atom of the dinitramide skeleton, monodentate coordination to one O atom of the nitro groups, and bidentate coordination to two O atoms of the terminal nitro groups. We report here the molecular structures of the dinitramide salts (I) and (II), and compare (I) with its anhydrous homologue and (II) with ammonium dinitramide in terms of cation–anion contacts.



(I)



(II)

Compound (I) exhibits a distorted octahedral Li^+ cation with a chelate-type coordination by two O atoms of the dinitramide anion and four additional water molecules (Fig. 1). Analogous to what was observed in the anhydrous compound, Li(N_3O_4) (Gilardi *et al.*, 1997), the Li^+ atom is located on a twofold rotation axis which also bisects the dinitramide anion. To the best of our knowledge, these two cases present the only examples of imposed C_2 symmetry in a dinitramide. In all other cases, the dinitramide anion has C_1 symmetry, except for 3,3-dinitroazetidinium, where a crystallographically imposed mirror plane passes through the dinitramide anion (Gilardi & Butcher, 1998).

The Li—O distances to the water molecules are 1.960 (4) (Li1—O3) and 2.490 (3) Å [Li1—O3^{ii}; symmetry code: (ii) $-x$, $1-y$, $1-z$], whereas the distance between the Li^+ atom and the O atom of the dinitramide group is 2.054 (4) Å. In Li(N_3O_4) (Gilardi *et al.*, 1997), the five Li—O distances range from 2.028 (5) to 2.200 (2) Å and are exclusively contacts to O atoms of the dinitramide group. Thus, the entire packing in Li(N_3O_4) is based on Li—O(dinitramide) bonding. By contrast, the presence of coordinated water in (I) allows for the formation of an approximately linear water–dinitramide O—H$\cdots$O hydrogen bond which generates by translation a *C*(5) chain (Etter *et al.*, 1990; Bernstein *et al.*, 1995) running along the [100] direction (Fig. 1).

The dinitramide group in (I) is nearly planar, with a twist angle of 2.0°. This is a measure of the degree by which the nitro group has rotated out of the NNN plane (Pinkerton & Ritchie, 2003; Gilardi, *et al.* 1997) and is significantly smaller

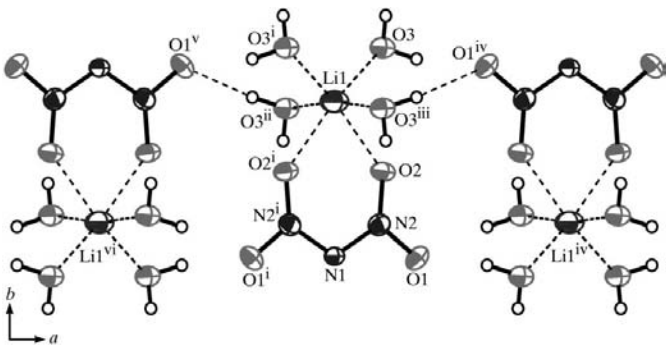


Figure 1
A view of the *C*(5) motif chain in compound (I) running along the *a* axis. Hydrogen bonds and intermolecular Li$\cdots$O contacts are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x, y, \frac{3}{2}-z$; (ii) $-x, 1-y, 1-z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, 2-z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (vi) $-\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.]

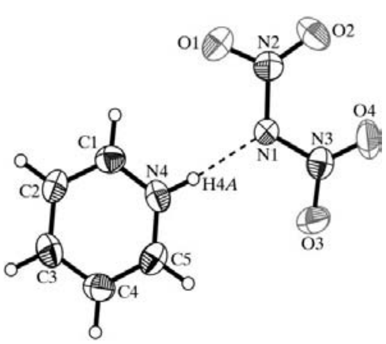


Figure 2
A view of the molecular structure of (II), showing the atom-labelling scheme and the hydrogen bond (dashed line) between the cation and anion. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

DOI: 10.1107/S0108270107054212

than the twist angle of 15.8° in $Li(N_3O_4)$ (Gilardi *et al.*, 1997). The dinitramide group has a bend angle of 1.3°, representing the pyramidalization of the nitro N atoms (expected values are 0° for ideal *sp*^{2} and 54.8° for ideal *sp*^{3} conformations), and this value is slightly smaller than the bend angle of 4.6° found in $Li(N_3O_4)$.

The O···O chelate distance in (I) [2.576 (2) Å] is comparable with that reported for $Li(N_3O_4)$ [2.593 Å], while the pseudo-torsion angle between the two closest N—O bonds in different nitro groups in the molecule is smaller in (I) [4.4° *versus* 29.6° in $Li(N_3O_4)$].

The structure of (I) exhibits bifurcated hydrogen bonding involving water atom H2. This gives rise to a two-dimensional network in the (001) plane.

In contrast with the dinitramide coordination in (I), compound (II) exhibits an intermolecular secondary contact to the central N atom of the dinitramide group *via* an N—H···N hydrogen bond (Fig. 2). The dinitramide anion has C_1 symmetry, with N—N and N—O distances comparable with those in compound (I) and other dinitramide anions (Gilardi *et al.*, 1997; Christe *et al.*, 1996).

The twist and bend angles of the dinitramide group tend, as also observed in (I), to a relatively planar conformation (twist angles = 4.8 and 5.9°; bend angles = 1.5 and 0.4°) and are significantly different from those in ammonium dinitramide (twist angles = 25.6 and 20.8°; bend angles = 5.1 and 5.3°; Gilardi *et al.*, 1997).

The O···O distance in (II) is slightly smaller than that in the ammonium salt [2.532 (4) *versus* 2.591 Å, respectively] and the pseudo-torsion angle is considerably smaller [9.6 *versus* 37.9°, respectively].

Atom N4 in the cation of (II) acts as hydrogen-bond donor to atom N1 in the anion, giving rise to an approximately linear N—H···N interaction. Since no further hydrogen bonds are present, the structure of (II) consists of isolated cation–anion pairs with no significant interactions between them. This is in contrast with ammonium dinitramide, where extensive hydrogen bonding involving all four ammonium H atoms furnishes a multidimensional hydrogen-bond architecture (Gilardi *et al.*, 1997). The hydrogen bonds are directed tetrahedrally involving exclusively the O atoms of the dinitramide group as hydrogen-bond acceptors, with H···O distances in the range 2.153–2.230 Å.

The packing motif in (II) consists of layers lying parallel to the *bc* plane with different orientations of the cation–anion pairs and a distance of 3.7 Å between those layers along the *a* axis. Weak C—H···O contacts give rise to a two-dimensional net which lies in the $(10\bar{3})$ plane.

Experimental

Compound (I) was obtained as a by-product in the preparation of a dinitramide salt. A mixture of trimethyltelluronium chloride (1.11 mmol) and $[Ag(py)_2](N_3O_4)$ (py is pyridine; 1.22 mmol) was dissolved in water (15 ml) and stirred at ambient temperature for 1 h. The resulting precipitate (AgCl) was removed by filtration and all volatile materials of the remaining solution were removed *in vacuo*. Colourless crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in acetone. The presence of lithium in the structure arises from impurities in the starting material $[Me_3Te]Cl$ that result from its preparation *via* the reaction of $TeCl_4$ with MeLi, and was proved by ^{7}Li NMR spectroscopy (δ = −0.99 p.p.m.). Compound (II) was obtained as a by-product in the attempted preparation of an organodinitramide with the help of $[Ag(py)_2](N_3O_4)$ as a dinitramide transfer reagent (Ang *et al.*, 2002). Single crystals were grown by slow evaporation of a dichloromethane solution.

Compound (I)

Crystal data

$[Li(N_3O_4)(H_2O)_2]$
M_r = 148.99
Monoclinic, $C2/c$
a = 12.574 (5) Å
b = 7.679 (5) Å
c = 6.321 (5) Å
β = 114.351 (5)°
V = 556.0 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 200 (2) K
0.13 × 0.10 × 0.02 mm

Data collection

Oxford Xcalibur3 CCD area-detector diffractometer
Absorption correction: multi-scan [*CrysAlis RED* (Oxford Diffraction, 2006), empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
T_{min} = 0.977, T_{max} = 0.999
1464 measured reflections
575 independent reflections
312 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.069
S = 1.00
575 reflections
55 parameters
2 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···O1^{i}	0.89 (3)	1.96 (3)	2.852 (2)	173 (2)
O3—H2···O1^{ii}	0.79 (3)	2.27 (3)	2.998 (3)	154 (2)
O3—H2···N1^{ii}	0.79 (3)	2.61 (3)	3.285 (3)	146 (2)

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, y+1, z$.

Compound (II)

Crystal data

$C_5H_6N^+\cdot N_3O_4^-$
M_r = 186.13
Monoclinic, $P2_1/n$
a = 3.7009 (2) Å
b = 14.4548 (7) Å
c = 14.6214 (8) Å
β = 94.281 (6)°
V = 780.00 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 200 (2) K
0.21 × 0.10 × 0.06 mm

Data collection

Oxford Xcalibur3 CCD area-detector diffractometer
Absorption correction: multi-scan [*CrysAlis RED* (Oxford Diffraction, 2006), empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
T_{min} = 0.982, T_{max} = 0.995
3991 measured reflections
1537 independent reflections
881 reflections with $I > 2\sigma(I)$
R_{int} = 0.047

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.077$
$S = 0.98$
1537 reflections
118 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N4—H4A⋯N1	0.88	1.92	2.794 (2)	171

Water H atoms of (I) were located in a difference Fourier map and refined freely with isotropic displacement parameters. The highest peak and deepest hole in the final difference map are located 0.57 Å from N1 and 0.73 Å from N2, respectively. H atoms in (II) were placed in idealized positions and allowed to ride on their respective parent atoms, with C_{ar}—H = 0.95 Å and N_{ar}—H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$. The highest peak and deepest hole in the final difference map are located 0.72 Å from H2 and 1.24 Å from C1, respectively.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXL97*.

Financial support of this work by the University of Munich (LMU), the Fonds der Chemischen Industrie, the European Research Office (ERO) of the US Army Research Laboratory (ARL) (contract Nos. N 62558-05-C-0027 and 9939-AN-01), the Bundeswehr Research Institute for Materials, Explosives, Fuels and Lubricants (WIWEB) (contract Nos. E/E210/4D004/X5143 and E/E210/7D002/4 F088), and the Deutsche Forschungsgemeinschaft (KL 636/10-1) is gratefully acknowledged. We thank research student Mr Richard Moll for his commitment.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3109). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Ang, H.-G., Fraenk, W., Karaghiosoff, K., Klapötke, T. M., Mayer, P., Nöth, H., Sprott, J. & Warchhold, M. (2002). *Z. Anorg. Allg. Chem.* **628**, 2894–2900.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Brandenburg, K. (1996). *DIAMOND*. University of Bonn, Germany.

Christe, K. O., Wilson, W. W., Petrie, M. A., Michels, H. H., Bottaro, J. C. & Gilardi, R. (1996). *Inorg. Chem.* **35**, 5068–5071.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.

Gilardi, R. D. & Butcher, R. J. (1998). *J. Chem. Crystallogr.* **28**, 163–169.

Gilardi, R. D., Flippen-Anderson, J., George, C. & Butcher, R. J. (1997). *J. Am. Chem. Soc.* **119**, 9411–9416.

Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.31.7. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Pinkerton, A. A. & Ritchie, J. P. (2003). *J. Mol. Struct.* **657**, 57–74.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Trammell, S., Goodson, P. A. & Sullivan, B. P. (1996). *Inorg. Chem.* **35**, 1421–1422.