# Di-μ-aqua-bis[aqua(5-carboxylato-1H-1,2,3-triazole-4-carboxylic acid-κ²N³,O⁴)lithium]

## Wojciech Starosta and Janusz Leciejewicz*

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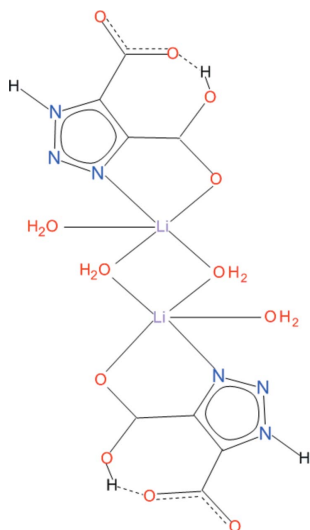Correspondence e-mail: j.leciejewicz@ichtj.waw.pl

The crystal structure of the title compound, $[Li_2(C_4H_2N_3O_4)_2(H_2O)_4]$, contains centrosymmetric dinuclear molecules in which two Li$^I$ ions are bridged by two water O atoms. The metal ion is coordinated by one *N,O*-bidentate ligand and three water O atoms (one of them is symmetry generated), with one of the bridging water O atoms in the apical position of a distorted square pyramid. The carboxylate group that participates in coordination to the metal ion remains protonated; the other is deprotonated and coordination inactive. An intramolecular O—H⋯O hydrogen bond between carboxylate groups is observed. In the crystal, dimers are linked by O—H⋯O, O—H⋯N and N—H⋯O hydrogen bonds, generating a three-dimensional network.

## Related literature

For the structures of Co and Ni complexes with the 1,2,3-trizole-4,5-dicarboxylate ligand, see: Tong *et al.* (2011).

## Experimental

### Crystal data

| | |
|---|---|
| $[Li_2(C_4H_2N_3O_4)_2(H_2O)_4]$ | $\gamma = 85.16\,(3)°$ |
| $M_r = 398.12$ | $V = 376.12\,(13)$ Å$^3$ |
| Triclinic, $P\bar{1}$ | $Z = 1$ |
| $a = 5.1264\,(10)$ Å | Mo $K\alpha$ radiation |
| $b = 8.0350\,(16)$ Å | $\mu = 0.16$ mm$^{-1}$ |
| $c = 10.040\,(2)$ Å | $T = 293$ K |
| $\alpha = 68.60\,(3)°$ | $0.45 \times 0.26 \times 0.22$ mm |
| $\beta = 77.64\,(3)°$ | |

### Data collection

| | |
|---|---|
| Kuma KM-4 four-circle diffractometer | 2185 independent reflections |
| Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008) | 1695 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.110$ |
| $T_{min} = 0.951$, $T_{max} = 0.966$ | 3 standard reflections every 200 reflections |
| 2414 measured reflections | intensity decay: 3.7% |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.057$ | 151 parameters |
| $wR(F^2) = 0.151$ | All H-atom parameters refined |
| $S = 1.04$ | $\Delta\rho_{max} = 0.62$ e Å$^{-3}$ |
| 2185 reflections | $\Delta\rho_{min} = -0.43$ e Å$^{-3}$ |

**Table 1**
Selected bond lengths (Å).

| Li1—O1 | 2.156 (3) | Li1—O6 | 1.916 (3) |
|---|---|---|---|
| Li1—O5 | 2.089 (3) | Li1—N3 | 2.234 (3) |
| Li1—O5$^i$ | 2.029 (3) | | |

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O5—H52⋯O1$^{ii}$ | 0.86 (2) | 1.93 (2) | 2.7873 (16) | 172 (2) |
| O6—H61⋯N2$^{iii}$ | 0.84 (4) | 2.30 (4) | 3.0545 (19) | 150 (4) |
| O5—H51⋯O3$^{iv}$ | 0.90 (2) | 1.98 (3) | 2.8834 (16) | 174 (2) |
| O6—H62⋯O4$^v$ | 0.91 (5) | 1.83 (5) | 2.7343 (16) | 176 (4) |
| N1—H1⋯O4$^{vi}$ | 0.86 (2) | 1.92 (2) | 2.7522 (17) | 162 (2) |
| O2—H2⋯O3 | 0.93 (5) | 1.63 (5) | 2.5380 (16) | 167 (4) |

Symmetry codes: (ii) $x + 1, y, z$; (iii) $-x + 2, -y, -z + 1$; (iv) $-x + 1, -y + 1, -z$; (v) $x, y, z + 1$; (vi) $-x + 2, -y, -z$.

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7130).

# metal-organic compounds

## References

Kuma (1996). *KM-4 Software*. Kuma Diffraction Ltd, Wrocław, Poland.

Kuma (2001). *DATAPROC*. Kuma Diffraction Ltd, Wrocław, Poland.

Oxford Diffraction (2008). *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, England.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Tong, X.-L., Xin, J.-H., Guo, V.-H. & Zhu, X.-P. (2011). *J. Coord. Chem.* **64**, 2984–2994.

# supporting information

# Di-*μ*-aqua-bis[aqua(5-carboxylato-1*H*-1,2,3-triazole-4-carboxylic acid-*κ²N³,O⁴*)lithium]

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### S1. Comment

The triclinic unit cell of the title compound comprises two $Li(C_4H_2N_3O_4)(H_2O)_2$ molecules related by an inversion centre to form a dimeric moiety in which two $Li^I$ ions are bridged by an aqua O atom donated by each molecule {Fig.1}. The coordination of the $Li^I$ ion is distorted square-pyramidal: carboxylate O1, hetero-ring N1, aquua O6 and O5$^{(i)}$ atoms constitute its base [r.m.s. 0.0798 (2) Å], the Li1 ion is 0.1995 (2) Å out of it, the aqua O5$^{(i)}$ is at the apex. Li—O and Li—N bond distances are usual (Table 2). The ligand triazole ring is almost planar [r.m.s. 0.0006 (1) Å]. The carboxylate C6/O1/O2 and C7/O3/O4 groups make with it dihedral angles of 2.0 (1)° and 5.5 (1)°, respectively. The Fourier map indicates clearly that the O2 atom is protonated and acts as a donor in a fairly short intra-molecular hydrogen bond of 2.538 (2) Å to the O3 atom as an acceptor. The C7/O3/O4 carboxylic group remains deprotonated and coordination inactive. The bond distances and bond angles within the triazole ring do not differ from those reported in the structures of other complexes, for example, with Co and Ni (Tong *et al.*, 2011). The dimers form molecular sheets (Fig. 2) in which they interact *via* an extensive hydrogen bond network; coordinated water molecules are as donors a hetero-ring N atom and carboxylate O atoms as acceptors (Table 3).

### S2. Experimental

1 mmol of 1,2,3-triazole-4,5-dicarboxylic acid and *ca*2 mmol s of lithium hydroxide dissolved in 50 ml of hot, doubly distilled water were boiled under reflux with stirring for ten hours and then left to crystallize at room temperature. Colourless blocks deposited after a week among polycrystalline material. After extraction, the crystals were washed with cold ethanol and dried in the air.

### S3. Refinement

H atoms belonging to water molecules, the carboxylate group and hetero-ring N atom were located in a difference map and refined isotropically.
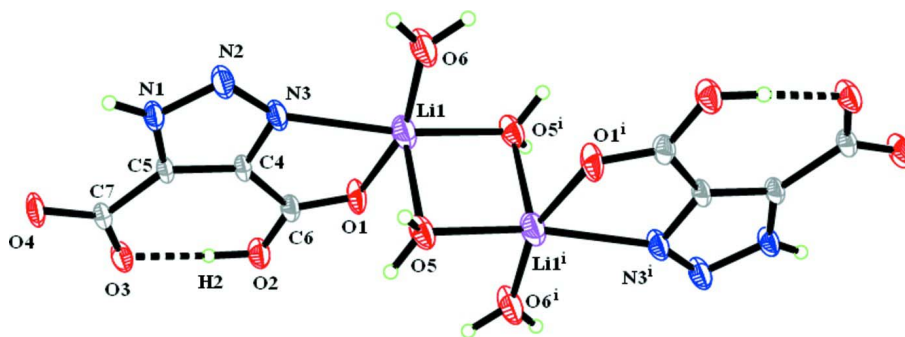
**Figure 1**

A dimeric molecule of the title complex with 50% probability displacement ellipsoids. Symmetry code: (i): $-x + 1$, $-y + 1$, $-z + 1$.
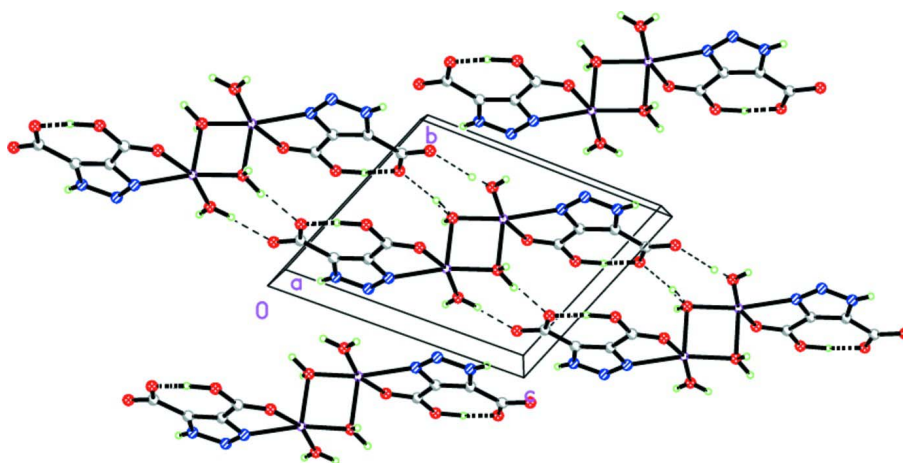


**Figure 2**

The packing of the dimers with hydrogen bonds shown as dashed lines.

**Di-μ-aqua-bis[aqua(5-carboxylato-1H-1,2,3-triazole-4-carboxylic acid-κ²N³,O⁴)lithium]**

*Crystal data*

| | |
|---|---|
| $[Li_2(C_4H_2N_3O_4)_2(H_2O)_4]$ | $Z = 1$ |
| $M_r = 398.12$ | $F(000) = 204$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.758$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 5.1264\ (10)$ Å | Cell parameters from 25 reflections |
| $b = 8.0350\ (16)$ Å | $\theta = 6–15°$ |
| $c = 10.040\ (2)$ Å | $\mu = 0.16$ mm$^{-1}$ |
| $\alpha = 68.60\ (3)°$ | $T = 293$ K |
| $\beta = 77.64\ (3)°$ | Blocks, colourless |
| $\gamma = 85.16\ (3)°$ | $0.45 \times 0.26 \times 0.22$ mm |
| $V = 376.12\ (13)$ Å$^3$ | |

*Data collection*

| | |
|---|---|
| Kuma KM-4 four-circle diffractometer | profile data from $\omega/2\theta$ scan |
| Radiation source: fine-focus sealed tube | Absorption correction: analytical |
| Graphite monochromator | (*CrysAlis RED*; Oxford Diffraction, 2008) |
| | $T_{min} = 0.951$, $T_{max} = 0.966$ |

2414 measured reflections

2185 independent reflections

1695 reflections with $I > 2\sigma(I)$

$R_{int} = 0.110$

$\theta_{max} = 30.1°$, $\theta_{min} = 2.2°$

$h = 0 \rightarrow 7$

$k = -11 \rightarrow 11$

$l = -13 \rightarrow 13$

3 standard reflections every 200 reflections

intensity decay: 3.7%

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.151$

$S = 1.04$

2185 reflections

151 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.121P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.62$ e Å$^{-3}$

$\Delta\rho_{min} = -0.43$ e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)*

|  | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
| --- | --- | --- | --- | --- |
| O1 | 0.21219 (19) | 0.40701 (15) | 0.33815 (11) | 0.0281 (2) |
| N3 | 0.6270 (2) | 0.17626 (16) | 0.33674 (12) | 0.0254 (3) |
| C5 | 0.6283 (2) | 0.17546 (15) | 0.11571 (12) | 0.0194 (2) |
| C4 | 0.5041 (2) | 0.24296 (16) | 0.22126 (12) | 0.0195 (3) |
| N1 | 0.8213 (2) | 0.07012 (16) | 0.17492 (12) | 0.0245 (3) |
| C6 | 0.2768 (2) | 0.36533 (16) | 0.22992 (13) | 0.0205 (3) |
| N2 | 0.8203 (2) | 0.07056 (17) | 0.30842 (13) | 0.0295 (3) |
| O3 | 0.38723 (19) | 0.29832 (14) | −0.07107 (10) | 0.0269 (2) |
| O4 | 0.7499 (2) | 0.13549 (15) | −0.10818 (11) | 0.0301 (3) |
| O5 | 0.71001 (19) | 0.56809 (15) | 0.36456 (11) | 0.0280 (2) |
| O6 | 0.7261 (3) | 0.19431 (19) | 0.60872 (13) | 0.0419 (3) |
| Li1 | 0.4924 (5) | 0.3334 (4) | 0.4828 (3) | 0.0317 (5) |
| H52 | 0.871 (4) | 0.527 (3) | 0.358 (2) | 0.032 (5)* |
| H51 | 0.682 (4) | 0.618 (3) | 0.272 (3) | 0.042 (6)* |
| O2 | 0.15267 (19) | 0.42563 (14) | 0.12078 (11) | 0.0266 (2) |
| C7 | 0.5863 (2) | 0.20502 (16) | −0.03313 (12) | 0.0207 (3) |
| H61 | 0.848 (8) | 0.120 (5) | 0.600 (4) | 0.094 (12)* |
| H62 | 0.735 (8) | 0.181 (6) | 0.701 (5) | 0.117 (14)* |
| H2 | 0.214 (8) | 0.380 (6) | 0.047 (5) | 0.099 (12)* |
| H1 | 0.944 (4) | 0.012 (3) | 0.136 (2) | 0.036 (5)* |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0267 (4) | 0.0409 (6) | 0.0228 (5) | 0.0088 (4) | −0.0017 (3) | −0.0222 (4) |
| N3 | 0.0307 (5) | 0.0320 (6) | 0.0160 (5) | 0.0076 (4) | −0.0041 (4) | −0.0134 (4) |
| C5 | 0.0236 (5) | 0.0229 (5) | 0.0130 (5) | 0.0028 (4) | −0.0005 (4) | −0.0104 (4) |
| C4 | 0.0236 (5) | 0.0232 (5) | 0.0131 (5) | 0.0020 (4) | 0.0000 (4) | −0.0106 (4) |
| N1 | 0.0300 (5) | 0.0298 (5) | 0.0163 (5) | 0.0098 (4) | −0.0044 (4) | −0.0135 (4) |
| C6 | 0.0205 (5) | 0.0248 (6) | 0.0170 (5) | 0.0014 (4) | 0.0014 (4) | −0.0117 (4) |
| N2 | 0.0367 (6) | 0.0372 (6) | 0.0188 (5) | 0.0135 (5) | −0.0091 (4) | −0.0159 (5) |
| O3 | 0.0302 (5) | 0.0359 (5) | 0.0171 (4) | 0.0086 (4) | −0.0051 (3) | −0.0138 (4) |
| O4 | 0.0360 (5) | 0.0401 (6) | 0.0175 (4) | 0.0134 (4) | −0.0031 (4) | −0.0184 (4) |
| O5 | 0.0258 (5) | 0.0406 (6) | 0.0181 (4) | 0.0071 (4) | −0.0011 (3) | −0.0144 (4) |
| O6 | 0.0534 (7) | 0.0546 (7) | 0.0232 (5) | 0.0265 (5) | −0.0144 (5) | −0.0224 (5) |
| Li1 | 0.0375 (12) | 0.0382 (13) | 0.0210 (11) | 0.0030 (10) | −0.0014 (9) | −0.0158 (10) |
| O2 | 0.0275 (4) | 0.0341 (5) | 0.0215 (5) | 0.0086 (3) | −0.0050 (3) | −0.0155 (4) |
| C7 | 0.0259 (5) | 0.0241 (5) | 0.0132 (5) | 0.0016 (4) | −0.0006 (4) | −0.0102 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Li1—O1 | 2.156 (3) | N1—N2 | 1.3405 (15) |
| Li1—O5 | 2.089 (3) | N1—H1 | 0.86 (2) |
| Li1—O5$^i$ | 2.029 (3) | C6—O2 | 1.3035 (16) |
| Li1—O6 | 1.916 (3) | O3—C7 | 1.2559 (16) |
| Li1—N3 | 2.234 (3) | O4—C7 | 1.2415 (15) |
| O1—C6 | 1.2229 (15) | O5—Li1$^i$ | 2.029 (3) |
| N3—N2 | 1.3029 (16) | O5—H52 | 0.86 (2) |
| N3—C4 | 1.3529 (16) | O5—H51 | 0.90 (2) |
| C5—N1 | 1.3386 (17) | O6—H61 | 0.84 (4) |
| C5—C4 | 1.3765 (16) | O6—H62 | 0.91 (5) |
| C5—C7 | 1.4852 (16) | Li1—Li1$^i$ | 2.831 (5) |
| C4—C6 | 1.4692 (17) | O2—H2 | 0.93 (5) |
| | | | |
| C6—O1—Li1 | 115.52 (11) | Li1—O6—H61 | 133 (3) |
| N2—N3—C4 | 108.64 (11) | Li1—O6—H62 | 132 (3) |
| N2—N3—Li1 | 140.62 (11) | H61—O6—H62 | 95 (4) |
| C4—N3—Li1 | 108.55 (11) | O6—Li1—O5$^i$ | 92.37 (11) |
| N1—C5—C4 | 103.63 (11) | O6—Li1—O5 | 102.05 (13) |
| N1—C5—C7 | 123.52 (11) | O5$^i$—Li1—O5 | 93.17 (11) |
| C4—C5—C7 | 132.82 (11) | O6—Li1—O1 | 161.54 (16) |
| N3—C4—C5 | 108.86 (11) | O5$^i$—Li1—O1 | 98.57 (11) |
| N3—C4—C6 | 118.02 (11) | O5—Li1—O1 | 92.20 (12) |
| C5—C4—C6 | 133.12 (12) | O6—Li1—N3 | 89.77 (11) |
| C5—N1—N2 | 111.56 (11) | O5$^i$—Li1—N3 | 165.21 (15) |
| C5—N1—H1 | 128.6 (14) | O5—Li1—N3 | 100.70 (11) |
| N2—N1—H1 | 119.7 (14) | O1—Li1—N3 | 75.95 (9) |
| O1—C6—O2 | 122.70 (12) | O6—Li1—Li1$^i$ | 100.59 (15) |
| O1—C6—C4 | 119.06 (12) | O5$^i$—Li1—Li1$^i$ | 47.47 (8) |

| | | | |
|---|---|---|---|
| O2—C6—C4 | 118.23 (11) | O5—Li1—Li1$^i$ | 45.70 (8) |
| N3—N2—N1 | 107.31 (11) | O1—Li1—Li1$^i$ | 97.76 (14) |
| Li1$^i$—O5—Li1 | 86.83 (11) | N3—Li1—Li1$^i$ | 146.10 (17) |
| Li1$^i$—O5—H52 | 126.9 (15) | C6—O2—H2 | 115 (3) |
| Li1—O5—H52 | 101.1 (13) | O4—C7—O3 | 126.12 (12) |
| Li1$^i$—O5—H51 | 118.6 (15) | O4—C7—C5 | 117.29 (12) |
| Li1—O5—H51 | 112.5 (13) | O3—C7—C5 | 116.59 (11) |
| H52—O5—H51 | 107 (2) | | |

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O5—H52···O1$^{ii}$ | 0.86 (2) | 1.93 (2) | 2.7873 (16) | 172 (2) |
| O6—H61···N2$^{iii}$ | 0.84 (4) | 2.30 (4) | 3.0545 (19) | 150 (4) |
| O5—H51···O3$^{iv}$ | 0.90 (2) | 1.98 (3) | 2.8834 (16) | 174 (2) |
| O6—H62···O4$^v$ | 0.91 (5) | 1.83 (5) | 2.7343 (16) | 176 (4) |
| N1—H1···O4$^{vi}$ | 0.86 (2) | 1.92 (2) | 2.7522 (17) | 162 (2) |
| O2—H2···O3 | 0.93 (5) | 1.63 (5) | 2.5380 (16) | 167 (4) |

Symmetry codes: (ii) *x*+1, *y*, *z*; (iii) −*x*+2, −*y*, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*; (v) *x*, *y*, *z*+1; (vi) −*x*+2, −*y*, −*z*.