O14—Ti1—O22	86.21 (13)	O34—Ti2—O42	86.23 (11)
O14—Ti1—O24	164.05 (13)	O34—Ti2—O44	163.44 (12)
O22—Ti1—O24	82.90 (13)	O42—Ti2—O44	83.03 (11)

The compound crystallized in the monoclinic system; space group $P2_1/c$ was determined from the systematic absences. The crystal did not diffract well (only 32% of the data were classified as 'observed' at the 2σ level) presumably because the molecules take part in no significant intermolecular interactions.

Four of the eight independent *tert*-butyl groups showed clear evidence of rotational disorder and this was allowed for using the *DFIX* options in *SHELXL*93 (Sheldrick, 1993) with suitable distance and occupancy constraints. For all *tert*-butyl groups, free variables were refined for the C—C(methyl) [1.502 (1) Å], methyl···methyl [2.447 (1) Å] and C(sp^2)···C(methyl) [2.474 (1) Å] distances to ensure approximate tetrahedral geometry.

Examination of the structure with *PLATON* (Spek, 1994*a*) showed that there were no solvent accessible voids in the crystal lattice.

Data collection: Enraf–Nonius (1992) *CAD*-4 *PC Software*. Cell refinement: Enraf–Nonius (1992) *SET*4 and *CELDIM*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*94 (Patterson heavy-atom method). Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93. Molecular graphics: *NRCVAX*94, *PLUTON* (Spek, 1994*b*) and *ORTEP*II (Johnson, 1976) as implemented in *PLATON*. Software used to prepare material for publication: *NRCVAX*94 and *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1297). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetramethylammonium Lithium Zinc Cyanide, $[N(CH_3)_4]LiZn(CN)_4$

XIANHUI BU, THURMAN E. GIER AND GALEN D. STUCKY

Department of Chemistry, University of California, Santa Barbara, CA 93106, USA

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Abstract

The title crystal has a diamond-type framework structure with Zn^{2+} and Li^+ ions on tetrahedral atom sites and $(CN)^-$ anions as bridging 'rods' between them. The charge-balancing $[N(CH_3)_4]^+$ cations are located in half of the adamantane cages.

Comment

This work is part of our efforts to synthesize diamond-type structures with variable adamantane cage sizes. The X-ray powder diffraction study of the $[N(C_2H_5)_4]^+$ templated sample shows that it has the same cubic diamond-type structure as $[N(CH_3)_4]LiZn(CN)_4$ with a sightly expanded cage (3% volume increase per cell). The cubic structure (possibly the diamond-type framework) is lost when other organic templates, such as $[N(C_3H_7)_4]^+$, are used.

In diamond-type frameworks, the number of the adamantane cages is the same as the number of tetrahedral atom sites. Thus, in the title compound, only half of the adamantane cages are occupied. The crystal structure of $[N(CH_3)_4]CuZn(CN)_4$ has been reported previously (Hoskins & Robson, 1991). By replacing Cu^+ with Li^+, we were able to distinguish two different tetrahedral atom sites and prove that $N(CH_3)_4^+$ cations are located in the more negative cages formed with six Li^+ ions and four Zn^{2+} ions, avoiding cages with four Li^+ ions and six Zn^{2+} ions.

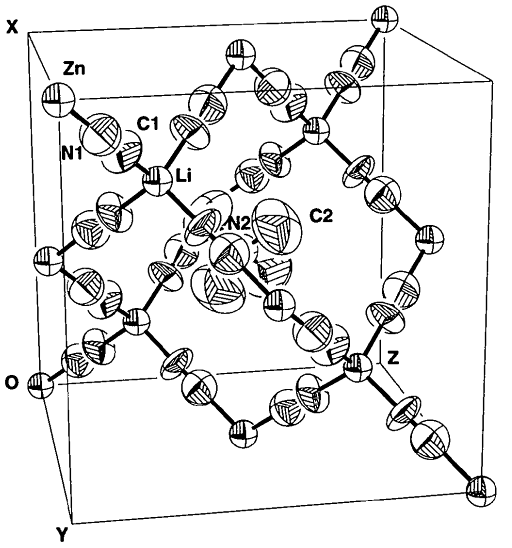

Fig. 1. The atomic labelling diagram showing the tetramethylammonium ion located in the cavity of the adamantane cage. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

A 1.0 *M* solution of $Li_2Zn(CN)_4$ was prepared from appropriate quantities of LiOH, ZnO and acetone cyanohydrin, with stirring and warming to remove excess acetone. Addition of a 25% solution of tetramethylammonium hydroxide (such that TMA^+/Zn^{2+} = 1/1) gave a clear colorless solution which on slow evaporation yielded masses of small equiaxial crystals suitable for the structure determination.

Crystal data

$(C_4H_{12}N)[LiZn(CN)_4]$
$M_r = 250.53$
Cubic
$F\bar{4}3m$
$a = 11.7739\,(13)$ Å
$V = 1632.15\,(18)$ Å^3
$Z = 4$
$D_x = 1.020$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 26 reflections
$\theta = 7.5–15.0°$
$\mu = 1.52$ mm^{-1}
$T = 293$ K
Tetrahedral
0.33 × 0.33 × 0.33 mm
Colourless, transparent

Data collection

Huber four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.552$, $T_{max} = 0.641$
316 measured reflections
79 independent reflections

79 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.042$
$\theta_{max} = 22.4°$
$h = 1 \rightarrow 12$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 7$
3 standard reflections monitored every 97 reflections
intensity decay: 2.1%

Refinement

Refinement on *F*
$R = 0.031$
$wR = 0.033$
$S = 3.05$
79 reflections
15 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Extinction correction: Larson (1970)
Extinction coefficient: 1.2 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)
Absolute configuration: Flack (1983) parameter = 0.558 (190)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn1	0	0	0	0.0782 (5)
Li1	1/4	1/4	1/4	0.076 (4)
C1	0.1549 (5)	x	x	0.123 (3)
N1	0.1013 (7)	x	x	0.132 (3)
C2	0.5765 (11)	x	x	0.260 (8)
N2	1/2	1/2	1/2	0.100 (2)

Table 2. *Selected geometric parameters (Å, °)*

Zn1—N1	2.065 (14)	C1—N1	1.094 (18)
Li1—C1	1.939 (11)	C2—N2	1.561 (22)
N1—Zn1—N1a^i	109.47	Zn1—N1—C1	180.0
C1—Li1—C1^{ii}	109.47	C2—N2—C2^{iii}	109.47
Li1—C1—N1	180.0		

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

The structure was solved by the heavy-atom method followed by difference Fourier maps. Anisotropic displacement parameters were used for all non-H atoms. H atoms were not included because of the large thermal motion of the methyl groups.

Data collection: *UCLA* (Strouse, 1991). Cell refinement: *UCLA*. Data reduction: *UCLA*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX LSTSQ* (Gabe, Le Page, Charland, Lee & White, 1989). Molecular graphics: *NRCVAX*, *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Di-μ-aqua-bis[bis(nitrato-*O*,*O′*)dioxouranium(VI)] Bis(2-dimethylaminoethanol)

REIJO HÄMÄLÄINEN, URHO TURPEINEN AND ILPO MUTIKAINEN

Department of Chemistry, PO Box 55, A. I. Virtasen aukio, Fin-00014, University of Helsinki, Finland

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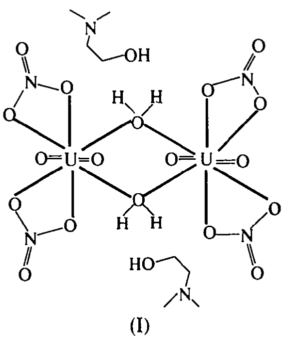
Abstract

Each linear uranyl group in the title compound, $[(UO_2)_2(NO_3)_4(H_2O)_2].2C_4H_{11}NO$, is perpendicular to the equatorial plane formed by six O atoms, of which two belong to the bridging water molecules and four to the bidentate nitrate groups. The coordination polyhedron has a slightly distorted hexagonal bipyramidal arrangement. The non-coordinated 2-dimethylaminoethanol molecules are hydrogen bonded to the bridging water molecules with an O···O distance of 2.77 (3) Å.

Comment

Most uranium complexes have been found to be di-, tetra- or polynuclear. For example, uranyl acetate dihydrate has a dimeric structure with both bridging and terminal acetate groups (Howatson, Grew & Morosin, 1975) while the recently prepared uranium complex including both acetate and 2-dimethylaminoethanol units is a tetramer (Turpeinen, Hämäläinen, Mutikainen & Orama, 1995). In the present dimeric uranyl compound, (I), the amino alcohol molecules act as secondary ligands since they are only hydrogen bonded to the bridging water molecules.



(I)

Two neutral $UO_2(NO_3)_2$ units are bridged by two water O atoms. The bridging angle U(1)—O(2)—U(1*a*) is 112.1 (6)°. The bridging U—O(water) distances are typically about 0.2 Å shorter than the terminal U—O(nitrate) distances, as observed in related compounds (Cragg, Bott & Atwood, 1988; Åberg, 1969). The U···U distance [3.931 (4) Å] and other geometric parameters of the dimer unit are similar to those of related structures (Perry, Ruben, Templeton & Zalkin, 1980; Perrin, 1976; Dalley, Mueller & Simonsen, 1971; Taylor & Mueller, 1965).

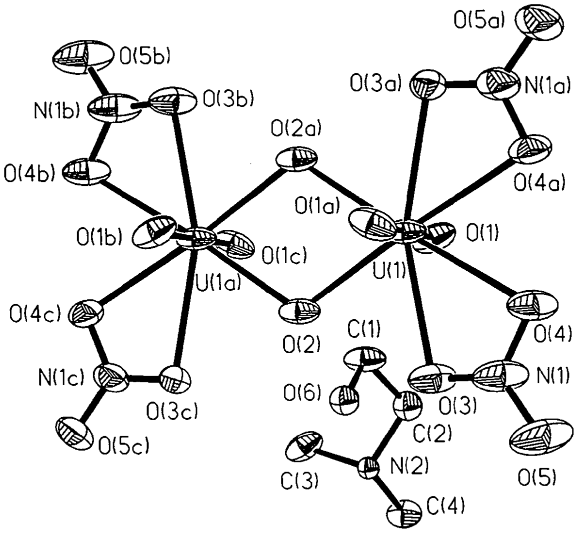


Fig. 1. View of the dinuclear complex and organic molecule with 30% probability ellipsoids. Only one of the two possible positions for each of C(2), C(3) and N(2) is shown.

Experimental

The title compound was prepared by slow evaporation a 1:1 molar ratio of uranyl nitrate hexahydrate and 2-dimethylaminoethanol in methanol solution at room temperature.

Crystal data

$[U_2O_4(NO_3)_4(H_2O)_2]$.-
$2C_4H_{11}NO$
$M_r = 1002.38$
Monoclinic
$C2/m$
$a = 12.799$ (5) Å
$b = 12.969$ (9) Å
$c = 7.885$ (4) Å
$\beta = 99.01$ (4)°
$V = 1293$ (1) Å^3
$Z = 2$
$D_x = 2.575$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 18 reflections
$\theta = 7–14°$
$\mu = 12.61$ mm^{-1}
$T = 293$ K
Cubiform
0.2 × 0.2 × 0.15 mm
Yellow

Data collection

Nicolet *P*3*F* diffractometer
ω scans

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 27°$